A comprehensive analytical study of sludge from water reclamation plants in Singapore for advanced thermochemical conversion processes

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2017

Chan, W. P. (2017). A comprehensive analytical study of sludge from water reclamation plants in Singapore for advanced thermochemical conversion processes. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/69581>

<https://doi.org/10.32657/10356/69581>

A COMPREHENSIVE ANALYTICAL STUDY OF
SLUDGE FROM WATER RECLAMATION PLANTS IN
SINGAPORE FOR ADVANCED THERMOCHEMICAL
CONVERSION PROCESSES

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School of Civil and Environmental Engineering

2016

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A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

2016

Acknowledgements

It is a great pleasure to express my sincere appreciation and gratitude to my supervisor Associate Professor, Dr Wang Jing-Yuan, for his guidance and enlightenment throughout my study. His support, both academic and non-academic, is important to the completion of this thesis.

I appreciate the National Research Foundation (NRF) Clean Energy Scholarship and Economic Development Board of Singapore (EDB) for sponsoring my study and scientific exploration. I also appreciate the constructive advice from members of my qualifying examination panel: Assistant Professor Chang Wei-Chung, Associate Professor Law Wing-Keung and Associate Professor Yang Yanhui.

I would also like to thank Dr Zhao Lei, Dr Yin Ke, Dr Apostolos Giannis, Dr Chen Chia-Lung, and Dr Ge Li Ya from Residues & Resource Reclamations Centre (R3C) of Nanyang Environment and Water Research Institute (NEWRI) for their valuable suggestions and willingness to discuss and work with me.

Last but not least, I would like to express my appreciation to all the staffs and researchers in NEWRI-R3C and School of Civil and Environmental Engineering (CEE) of Nanyang Technological University for their assistance during my study.

Table of Contents

Acknowledgements	ii
Summary	vii
List of Tables	ix
List of Figures	xii
List of Abbreviations	xvi
List of Symbols	xviii
List of Equations	xix
1. Introduction	1
1.1. Background	1
1.2. Objectives and Scope	4
1.3. Thesis structure	5
2. Literature review	8
2.1. Waste management of sludge	8
2.1.1. General introduction.....	8
2.2.2. Environmental concerns.....	10
2.2. Thermochemical conversion process	12
2.2.1. General introduction	12
2.2.2. Thermodynamics analysis	14
2.2.3. Kinetics study	15
2.2.4. Experimental research	21
2.2.4.1. Pyrolysis and gasification of sludge.....	21
2.2.4.2. Tar formation and removal.....	22
2.2.4.3. Sequential thermochemical conversion.....	24
2.2.4.4. Impacts of moisture and steam.....	25
2.3. Biomass composition analysis	26
2.3.1. General introduction	26
2.3.2. Categorisation and quantification	28
2.3.3. Thermochemical properties	30
2.4. Research gaps and current issues	31
3. General Materials and Methods.....	35

3.1. Sludge sampling.....	35
3.2. Sample pre-treatment.....	36
3.3. Analytical methods for physical properties.....	37
3.3.1. Heating value analysis.....	37
3.3.2. Proximate analysis.....	37
3.3.3. Heat capacity analysis.....	38
3.4. Analytical methods for chemical properties.....	40
3.4.1. Ultimate analysis.....	40
3.4.2. Functional group analysis.....	40
3.5. Analytical methods for pyrolysis.....	43
3.5.1. Thermal analysis.....	43
3.5.2. Products evolution analysis.....	44
3.6. Statistical analysis.....	45
4. Comprehensive characterisation study of sludge for advanced thermochemical conversion processes	46
4.1. Introduction	46
4.2. Materials and Methods	47
4.2.1. Physical properties	47
4.2.1.1. Physical appearance, pH and density analysis.....	47
4.2.1.2. Heating value analysis	47
4.2.1.3. Proximate analysis	49
4.2.2. Chemical properties	50
4.2.2.1. Ultimate analysis	50
4.2.2.2. Inorganic composition analysis	52
4.3. Results and Discussion	55
4.3.1. Properties on handling and storage	55
4.3.2. Physical properties	57
4.3.2.1. Heating value analysis	57
4.3.2.2. Proximate analysis	63
4.3.2.3. Heat capacity analysis	73
4.3.3. Chemical properties	74
4.3.3.1. Ultimate analysis	74

4.3.3.2. Inorganic composition analysis	81
4.3.3.3. Functional group analysis	90
4.4. Conclusions	94
5. Thermal degradation behaviours and products evolution analysis of sludge by using analytical and experimental pyrolysis study	97
5.1. Introduction	97
5.2. Materials and Methods.....	98
5.2.1. Analytical pyrolysis	98
5.2.2. Experimental pyrolysis	100
5.3. Results and Discussion	101
5.3.1. Multiple heating rates TGA-DTG analysis	101
5.3.2. Kinetics analysis	110
5.3.3. Products evolution analysis	114
5.3.4. Yield distributions analysis.....	118
5.3.5. Energy requirements analysis.....	123
5.3.6. Solid products analysis.....	124
5.3.7. Operating temperature analysis.....	129
5.3.8. FTIR spectra analysis.....	134
5.3.9. Gas composition analysis.....	137
5.4. Conclusions.....	140
6. Biomass composition analysis of sludge.....	143
6.1. Introduction	143
6.2. Materials and Methods	144
6.2.1. Categorisation for biomass composition of sludge.....	144
6.2.2. Extractives analysis.....	145
6.2.3. Proteins content.....	145
6.2.4. Alkaline hydrolysis and acid digestion.....	146
6.2.5. Other organic matters.....	146
6.2.6. Characterisation study on sludge components.....	147
6.3. Results and Discussion	148
6.3.1. Extractives analysis.....	148

6.3.2. Proteins content.....	155
6.3.3. Summary of sludge biomass composition.....	157
6.3.4. Correlation analysis.....	163
6.4. Conclusions.....	167
7. Simulation study on thermochemical properties of sludge by biomass composition analysis and model compounds selection.....	169
7.1. Introduction	169
7.2. Materials and Methods	170
7.2.1. Selection and characterisation of model compounds....	170
7.2.2. Simulation analysis.....	173
7.3. Results and Discussion	175
7.3.1. Characterisation of model compounds.....	175
7.3.2. Simulation analysis.....	179
7.4. Conclusions.....	192
8. Thermal degradation behaviours and products evolution analysis of biomass components, model compounds and synthetic sludge....	193
8.1. Introduction	193
8.2. Materials and Methods	194
8.3. Results and Discussion	195
8.3.1. Model compounds analysis.....	195
8.3.2. Sludge biomass components analysis.....	202
8.3.3. Synthetic sludge analysis.....	210
8.3.4. TGA-DTG analysis and kinetics study.....	221
8.3.5. Products evolution analysis.....	227
8.4. Conclusions.....	234
9. Conclusions and Recommendations	235
References.....	239
Appendix A: Supporting materials for kinetics analysis.....	253

Summary

Rising demand on wastewater treatment caused by population growth, urbanisation and industrialisation was producing increasing amount of sludge residues as by-product. Innovative management strategy and technology for energy and resource recovery were therefore required to properly handle sludge which consisted significant amount of moisture, ash, nitrogen, sulphur, and heavy metals. Mechanical dewatering, thermal drying, agricultural utilisation, landfilling, and incineration were commonly applied for sludge treatment and final disposal but facing issues on low dewatering effectiveness, high energy consumptions, restrictions on agricultural reuse, limitation on landfill availability, low energy recovery efficiency and generation of flue gas with considerable amount of pollutants. Recently, sludge attracted great interests as a potential feedstock for advanced thermochemical conversion processes such as pyrolysis and gasification which were capable to convert cheap heterogeneous waste mixtures into valuable homogenous products such as synthetic gas, pyrolysis oil and char. However, composition and thermal degradation behaviours of sludge were found to be highly complex and distinctive as compared to other traditional feedstock and therefore created significant challenges in engineering design and system optimisation.

To address the need of fundamental research on sludge, a comprehensive analytical study specifically for advanced thermochemical conversion processes was performed. 14 different sludge samples were collected based on type, plant, and batch categorisation from all operating Water Reclamation Plants (WRPs) in Singapore. Existing and proposed characterisation methods were applied and examined by using samples collected. Although no general consensus was achieved on the most efficient conversion method, thermally induced degradations occurred in all thermochemical processes and were considered as primary reactions important to reactor design and process modelling. Therefore comparison study on sludge thermal degradation behaviours and products evolution by using complementary analytical and experimental pyrolysis was carried out. Synthetic sludge study was also performed based on biomass composition analytical procedure and model compounds selection method developed in this study to address issues of

uncertainty in kinetics modelling caused by heterogeneity of sludge and limited understanding on impacts of sludge composition to thermochemical processes.

Qualitative similarities and quantitative variations on thermochemical characteristics and composition of different sludge samples were identified which suggested the presence of waste mixtures with comparable main components but in varying proportions. Oxidation of inorganics (apparent oxidation degree, $O_D = 47.07 \pm 19.59\%$) during ash formation caused deviations on characterisation results of sludge which could be reduced by alternative parameters and comparison bases proposed. Thermal degradation behaviours and products distribution found to be varied according to operating conditions applied and characteristics of sludge. Multiple components in sludge thermally degraded at different but overlapping temperature regions with varying reactivity and products evolution therefore causing variations of apparent activation energy in kinetics analysis and release of volatile compounds depended on temperature and conversion degree. Main components in sludge were satisfactory categorised, quantified and characterised by biomass composition analysis as supported by simulations of sludge properties. Correlations were established between composition and thermochemical characteristics of sludge. Acceptable representation of real waste sample by synthetic sludge was achieved and supported by kinetics and products evolution studies. Discrepancies were identified for further improvement in future work.

List of Tables

Table 2.1	Comparison on pyrolysis studies of sludge.....	33
Table 2.2	Comparison on gasification studies of sludge.....	34
Table 3.1	Heat capacity and specific heat flux for reference materials.....	39
Table 3.2	Linear correlations of heat capacity and specific heat flux.....	39
Table 3.3	Functional groups and suggested compounds of FTIR spectra....	41
Table 3.4	Functional groups and suggested compounds for TGA-FTIR spectra.....	42
Table 4.1	Fusibility of ash residues from sludge.....	54
Table 4.2	Linear correlations of $R_{B/A}$ and $R_{B+P/A}$ with fusion temperatures.	54
Table 4.3	Sample label with pH, bulk and pellet density for sludge.	56
Table 4.4	Heating value and residual energy analysis of sludge.....	60
Table 4.5	HHV of sludge estimated by Calculation 1 and 2.....	62
Table 4.6	Char residues of sludge by multiple heating rate TGA analysis..	63
Table 4.7	Proximate and residues analysis proposed for sludge.....	66
Table 4.8	Distributions of VM, FC and FR.....	67
Table 4.9	Proximate analysis of reference materials.....	67
Table 4.10	Ash contents analysis for sludge.....	71
Table 4.11	Heat capacity analysis of sludge.....	73
Table 4.12	Ultimate analysis of sludge samples.....	76
Table 4.13	Ultimate analysis of ash residues.....	76
Table 4.14	Total carbon and total organic carbon analysis.....	77
Table 4.15	Summary of CHNSO elements and inorganic contents.....	77
Table 4.16	Molecular formula of sludge samples collected.....	79
Table 4.17	Ultimate analysis for model compounds in molar basis.....	79
Table 4.18	Oxygen contents analysis for sludge.....	81
Table 4.19	Combustion released halogens from sludge.....	82
Table 4.20	Major ash forming elements in sludge.....	84
Table 4.21	Minor elements in sludge.....	84
Table 4.22	Trace elements in sludge.....	85
Table 4.23	Summary of inorganic elements in sludge.....	85

Table 4.24	Mass% of major ash forming oxides.....	88
Table 4.25	Relative composition of oxides in ash residues.....	88
Table 4.26	Fusion temperatures calculated for ash residues of sludge.....	89
Table 4.27	Functional groups and suggested compounds for FTIR spectra..	93
Table 5.1	Multiple heating rates TGA-DTG of CsP, CsS and CsY sludge..	106
Table 5.2	Summary of multiple heating rates TGA -DTG of sludge.....	108
Table 5.3	Mean activation energy and temperature-conversion data.....	113
Table 5.4	Peaks identified in TGA-FTIR spectra for CsP, CsS and CsY....	115
Table 5.5	Yield distributions of sludge pyrolysis at 500°C.....	122
Table 5.6	Energy requirements for pyrolysis and heating values of char....	126
Table 5.7	Ultimate analysis of char collected after pyrolysis at 500°C.....	127
Table 5.8	Ultimate analysis in normalised molar basis and residual CHNSO contents in relative% of Char _{500C}	128
Table 5.9	Yield distributions of CsY pyrolysis.....	132
Table 5.10	Heat capacity and HHV data of CsY sludge, char and ash.....	132
Table 5.11	Ultimate analysis in dry basis of Cs-Y sludge and char solids....	133
Table 5.12	Ultimate analysis in normalised molar basis and residual CHNSO contents in relative% of Cs-Y sludge and char solids...	133
Table 5.13	Apparent peaks in FTIR spectra of CsY sludge, char and ash.....	136
Table 5.14	Gas composition analysis of sludge pyrolysis at 500°C.....	138
Table 5.15	Gas composition analysis of CsY sludge pyrolysis.....	138
Table 6.1	Extractives analysis of sludge.....	152
Table 6.2	Heating value analysis for extractives and solvent extracted residues.....	153
Table 6.3	Elemental analysis of solvent extracted residues from sludge....	154
Table 6.4	Proteins contents analysis of sludge.....	156
Table 6.5	Biomass composition analysis for sludge in db.....	159
Table 6.6	Biomass composition analysis for sludge in icf.....	160
Table 7.1	Selected model compounds.....	172
Table 7.2	Heat capacity of reference compounds from literature.....	172
Table 7.3	Estimated mean heat capacity for biomass composition of sludge.....	172

Table 7.4	Thermochemical characteristics of model compounds.....	174
Table 7.5	Elemental contents analysis of model compounds.....	174
Table 7.6	Characterisation of model compounds.....	177
Table 7.7	Heat capacity analysis for sludge simulation.....	180
Table 7.8	Heat capacity estimation compared to measured data.....	181
Table 7.9	Heating value analysis for sludge simulation.....	184
Table 7.10	Comparison of HHV correlations.....	185
Table 7.11	Heat of pyrolysis analysis for sludge simulation.....	186
Table 7.12	Comparison of VM/FC and VM/FR ratios with simulated data..	189
Table 7.13	Distributions analysis of thermal degradation for sludge simulation.....	190
Table 7.14	Elemental contents analysis for sludge simulation.....	191
Table 8.2	TGA-DTG analysis of model compounds.....	197
Table 8.3	Thermal degradation stages of model compounds.....	198
Table 8.4	TGA-DTG analysis of sludge biomass composition.....	205
Table 8.5	Thermal degradation stages of sludge biomass composition.....	206
Table 8.6	Thermochemical characteristics of sludge biomass composition.....	207
Table 8.7	Formation of synthetic sludge for CsY.....	213
Table 8.8	Thermochemical characteristics of CsY and synthetic sludge....	213
Table 8.9	Peaks identification of FTIR spectra for synthetic sludge analysis.....	217
Table 8.10	Thermal analysis of CsY and synthetic sludge.....	219
Table 8.11	TGA-DTG analysis of CsY and synthetic sludge.....	219
Table 8.12	Thermal degradation stages of CsY and synthetic sludge.....	219
Table 8.13	Multiple heating rates TGA-DTG analysis of synthetic sludge...	223
Table 8.14	Thermal degradation stages of synthetic sludge.....	223
Table 8.15	Comparison study for activation energy of CsY and synthetic sludge by Friedman and Ozawa-Flynn-Wall analysis.....	226

List of Figures

Figure 1.1	Locations of WRPs and Pulau Semakau in Singapore.....	1
Figure 1.2	Flowchart to illustrate structure and flow of this thesis.....	7
Figure 3.1	Schematic representation of wastewater treatment system and different types of sludge samples collected from various treatment stages.....	36
Figure 3.2	Linear correlations of C_p and specific heat flux for reference materials.....	39
Figure 4.1	Correlations of bulk and pellet density of sludge with Ash_{950} contents.....	57
Figure 4.2	(a) Residual energy at different moisture contents in percentage and (b) moisture contents at zero residual energy for different lower heating values.....	61
Figure 4.3	Distribution of bias errors for Calculation 1 and 2 on HHV estimation.....	62
Figure 4.4	Correlations of apparent degree of oxidation, O_D with relative mass% of inorganic elements presence in inorganic matters of sludge.....	69
Figure 4.5	Simulations of apparent-to-intrinsic distribution ratio R^*/R at three different conditions of (a) apparent degree of oxidation $OD = 45\%$, (b) $IM = 20$ mass% and (c) $R = 3.50$	72
Figure 4.6	Heat capacity analysis. (a) C_p of sludge at temperature from 343K to 393K and (b) mean values of C_p calculated for different sludge samples.....	74
Figure 4.7	FTIR spectra of (a) sludge samples collected from WRPs in Singapore and (b) ash residues produced from combustion of sludge at 550°C	92
Figure 4.8	Distributions of organics and inorganics in sludge during pyrolysis.....	96
Figure 4.9	Distributions of organics and inorganics in sludge during combustion.....	96

Figure 5.1	Multiple heating rates (a) TGA (b) DTG on temperature and (c) TGA and (d) DTG on time of CsY sludge.....	107
Figure 5.2	Mean data for sludge on (a) TGA (b) DTG in dry basis and (c) TGA (d) DTG in volatile basis.....	109
Figure 5.3	Activation energy of sludge by (a) Friedman and (b) OFW analysis.....	112
Figure 5.4	Comparison of TGA-FTIR spectra for (a) CsP, (b) CsS and (c) CsY in primary degradation region from 250-500°C.....	116
Figure 5.5	Comparison of peaks identified in TGA-FTIR spectra for CsP, CsS and CsY. (a) 3032 cm ⁻¹ (C=C-H), (b) 3016 cm ⁻¹ (CH ₄), (c) 2974 cm ⁻¹ (C-H), (d) 2359 cm ⁻¹ (CO ₂), (e) 2173 cm ⁻¹ (CO), (f) 1541 cm ⁻¹ (H ₂ O), (g) 1176 cm ⁻¹ (C-O), (h) 966 cm ⁻¹ (NH ₃), (i) 951 cm ⁻¹ (C=C) and (j) 712 cm ⁻¹ (HCN).....	117
Figure 5.6	Correlations analysis for (a) solid, (b) liquid and (c) gas yields with mass% of inorganic matters and (d) solid, (e) liquid and (f) gas yields with CHNSO contents in sludge.....	123
Figure 5.7	FTIR spectra of (a) char solids for CsP, CsS, and CsY sludge after pyrolysis at 500°C and (b) comparison of CsY sludge, char solids and ash residues.....	135
Figure 5.8	Gas composition in relative volume% of pyrolysis for (a) 14 different sludge samples at 500°C and (b) CsY from 200°C to 500°C.....	139
Figure 6.1	Categorisation flowchart for biomass composition analysis of sludge.	144
Figure 6.2	FTIR spectra of (a) ethanol and (b) water extractives from sludge.....	151
Figure 6.3	FTIR spectra of (a) EER, (b) EFR, (c) AHR and (d) ADR from sludge.....	161
Figure 6.4	FTIR spectra of CsY sludge with (a) solid residues and (b) extractives.....	162
Figure 6.5	Correlations for biomass composition with (a) HHV and LHV, (b) VM/FR ratio, (c) carbon and (d) nitrogen contents.....	165

Figure 6.6	Correlations for biomass composition with (a) (b) Bulk density in db, (c) solid and (d) liquid yields at 500°C pyrolysis.....	166
Figure 7.1	Heat of pyrolysis for model compounds at different VM or FC mass%.....	176
Figure 7.2	FTIR Spectra of (a) proteins, (b) lipids, (c) carbohydrates and (d) lignocellulosic biomass model compounds.....	178
Figure 7.3	Distribution of bias errors for heat capacity calculation.....	181
Figure 7.4	Distribution of bias errors for organic CHNSO contents calculation.....	189
Figure 8.1	Model compounds analysis. (a) TGA (b) DTG for proteins. (c) TGA (d) DTG for lipids.....	199
Figure 8.2	Model compounds analysis. (a) TGA (b) DTG for carbohydrates. (c) TGA (d) DTG for lignocellulosic biomass.....	200
Figure 8.3	Model compounds analysis. (a) TGA (b) DTG for alkaline treated cellulose. (c) TGA (d) DTG for acid treated lignin.....	201
Figure 8.4	Sludge, EER and EFR analysis. (a) TGA and (b) DTG of CsP. (c) TGA and (d) DTG of CsS. (e) TGA and (f) DTG of CsY calculated in dry sludge basis.....	204
Figure 8.5	CsP, CsS and CsY extractives analysis. (a) TGA (b) DTG of EE. (c) TGA (d) DTG of WE in dry basis.....	208
Figure 8.6	CsP, CsS and CsY residues analysis. (a) TGA (b) DTG of AHR. (c) TGA (d) DTG of ADR in dry basis.....	209
Figure 8.7	(a) TGA (b) DTG of simulation of lipids model compounds and compared to (c) TGA (d) DTG of CsY-EE in icf basis.....	214
Figure 8.8	(a) TGA (b) DTG of simulation of model compounds and compared to (c) TGA (d) DTG of CsY-EFR in icf basis.....	215
Figure 8.9	Comparison analysis in icf basis. (a) TGA (b) DTG of WE, (c) TGA (d) DTG of AHR and (e) TGA (f) DTG of ADR with respective model compounds.....	216
Figure 8.10	FTIR spectra of CsY and synthetic sludge with/without ash residues.....	217

Figure 8.11	CsY and synthetic sludge analysis. (a) TGA (b) DTG in dry basis and (c) TGA (d) DTG in volatile basis.....	220
Figure 8.12	Multiple heating rates analysis of synthetic sludge. (a) TGA (b) DTG on temperature and (c) TGA (d) DTG on time.....	224
Figure 8.13	Multiple heating rates data of CsY. (a) TGA (b) DTG on temperature in °C and (c) TGA and (d) DTG on time in minutes.....	225
Figure 8.14	Mean data and standard deviations for activation energy of CsY and synthetic sludge determined by (a) Friedman and (b) Ozawa-Flynn-Wall analysis.....	227
Figure 8.15	TGA-FTIR spectra for pyrolysis of (a) CsY-EE, (b) asolectin, (c) cholesterol, (d) glyceryl tripalmitate, (e) CsY-WE and (f) sucrose.....	229
Figure 8.16	TGA-FTIR spectra for pyrolysis of (a) CsY-EFR, (b) whey isolates, (c) glycogen, (d) cellulose, (e) xylan and (f) lignin.....	230
Figure 8.17	TGA-FTIR spectra for pyrolysis of (a) CsY and (b) synthetic sludge.....	232
Figure 8.18	Peaks identified on TGA-FTIR spectra of CsY and synthetic sludge pyrolysis. (a) 3032 cm ⁻¹ (C=C-H), (b) 3016 cm ⁻¹ (CH ₄), (c) 2974 cm ⁻¹ (C-H), (d) 2359 cm ⁻¹ (CO ₂), (e) 2173 cm ⁻¹ (CO), (f) 1541 cm ⁻¹ (H ₂ O), (g) 1176 cm ⁻¹ (C-O), (h) 966 cm ⁻¹ (Ammonia), (i) 951 cm ⁻¹ (C=C) and (j) 712 cm ⁻¹ (HCN).....	233

List of Abbreviations

AD	Anaerobic digestion
ADR	Acid digested residues
AHR	Alkaline hydrolysed residues
ATR	Attenuated total reflection
CP	Primary sludge from Changi WRP, Batch 1
CsP	Primary sludge from Changi WRP, Batch 2
CS	Secondary sludge from Changi WRP, Batch 1
CsS	Secondary sludge from Changi WRP, Batch 2
CY	Dried sludge from Changi WRP, Batch 1
CsY	Dried sludge from Changi WRP, Batch 2
daf	Dry ash free basis
db	Dry basis
DN	Dumas nitrogen contents
dsb	Dry sludge basis
DSC	Differential scanning calorimetry
EE	Ethanol extractives
EER	Ethanol extracted residues
EFR	Extractives free residues
EPS	Extracellular polymeric substances
ER	Equivalence ratio
FC	Fixed carbon
FID	Flame ionization detector
FR	Fixed residues
FT	fluid temperature
FTIR	Fourier-transform infrared spectroscopy
HHV	Higher heating value
HT	hemispherical temperature
icf	Total inorganic contents free basis
IDT	Initial deformation temperature
IM	Inorganic matters

imf	Inorganic matters free basis
JD	Dewatered sludge from Jurong WRP, Batch 1
JR	Raw sludge from Jurong WRP, Batch 1
KD	Dewatered sludge from Kranji WRP, Batch 1
KN	Kjedahl nitrogen contents
KR	Raw sludge from Kranji WRP, Batch 1
L/G	Liquid to gas yields ratio
LHV	Lower heating value
MIR	Mid-infrared region
N-to-P	Nitrogen-to-Protein factor
OOM	Other organic matters
PAH	Poly-aromatic hydrocarbon
SD	Standard deviation
ST	Softening temperature
TC	Total carbon
TCD	Thermal conductivity detector
TGA	Thermogravimetric analysis
TI	Total inorganic contents
TIC	Total inorganic carbon
TOC	Total organic carbon
UR	Raw sludge from Ulu Pandan WRP, Batch 1
UsR	Raw sludge from Ulu Pandan WRP, Batch 2
UD	Dewatered sludge from Ulu Pandan WRP, Batch 1
UsD	Dewatered sludge from Ulu Pandan WRP, Batch 2
vb	Volatile basis
VM	Volatile matters
VM _O	Volatile matters released from organics
VM _I	Volatile matters released from inorganics
V/S	Volatile to solid yields ratio
WRP	Water reclamation plant
WE	Water extractives

List of Symbols

α	Conversion degree
A	Pre-exponential factor
Ash ₅₅₀	Ash residues remained after combustion at 550°C
Ash ₉₅₀	Ash residues remained after combustion at 950°C
Char ₅₀₀	Char solids remained after pyrolysis in inert environment at 500°C
Char ₉₅₀	Char solids remained after pyrolysis in inert environment at 950°C
CHNSO _{Inorganic}	CHNSO contents of Ash ₅₅₀
CHNSO _{Organic}	CHNSO contents of organic matters in sludge
CHNSO _{Total}	Total CHNSO contents in sludge
C _p	Heat capacity at constant pressure
E _a	Activation energy
ϵ_{Abs}	Absolute error
ϵ_{Bias}	Bias error
$\Delta H_{\text{pyrolysis}}$	Heat of pyrolysis
mass%	Mass percentage
M _w	Moisture content as received
M _{w,critical}	Critical moisture level at zero residual energy content
O _D	Apparent oxidation degree
O _{deviation}	Difference between O _{Total} and O _{difference}
O _{difference}	Oxygen contents in sludge calculated by difference
O _{oxidation}	Difference between IM and Ash ₉₅₀
O _{Total}	Oxygen contents in sludge determined by direct measurement
Q_{Residual}	Residual energy content
R	Intrinsic distribution ratio, VM/FR
R*	Apparent distribution ratio, VM/FC
R _{B/A}	Base (without phosphate)-to-Acid ratio of inorganic oxides
R _{B+P/A}	Base (with phosphate)-to-Acid ratio of inorganic oxides

List of Equations

Equation 2.1	$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P)$	18
Equation 2.2	$\frac{d}{dT^{-1}} \ln \frac{d\alpha}{dt} = \frac{d}{dT^{-1}} \ln k(T) + \frac{d}{dT^{-1}} \ln f(\alpha) + \frac{d}{dT^{-1}} \ln h(P)$	18
Equation 2.3	$k(T) = A \exp^{-\frac{Ea}{RT}}$	18
Equation 2.4	$\frac{d}{dT^{-1}} \ln k(T) = \frac{d}{dT^{-1}} \left[\ln A + \left(-\frac{Ea}{RT} \right) \right]$	18
Equation 2.5	$\frac{d}{dT^{-1}} \ln \frac{d\alpha}{dt} = -\frac{Ea}{R}$	19
Equation 2.6	$\ln \beta \frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E}{RT}$	19
Equation 2.7	$\ln \beta = \ln \left(\frac{AE}{R} \right) - \ln g(\alpha) - 5.3305 - 1.052 \left(\frac{E}{RT} \right)$	19
Equation 2.8	$g(\alpha) = t_{\alpha} A_{\alpha} \exp^{-E_{\alpha}/RT_0}$	20
Equation 2.9	$g(\alpha) = \frac{A_{\alpha}}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT$	20
Equation 2.10	$t_{\alpha} = [\beta \exp^{-E_{\alpha}/RT_0}]^{-1} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT$	20
Equation 2.11	$\frac{1}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT - \frac{1}{\beta_0} \int_0^{T_{\alpha,0}} \exp^{-\frac{E_{\alpha}}{RT}} dT = 0$	20
Equation 3.1	$LHV = HHV - 2.26 \times (9H/100)$	37
Equation 3.2	$C_s = \left(\frac{\Phi_s - \Phi_0}{\Phi_{ref} - \Phi_0} \times \frac{m_{ref}}{m_s} \right) C_{ref}$	38
Equation 3.3	$C_s \propto \left(\frac{\Phi_s - \Phi_0}{m_s} \right)$	38
Equation 3.4	Mean, $\mu = \frac{\sum x}{n}$	45
Equation 3.5	Standard deviation, $SD = \sqrt{\frac{\sum (x - \mu)^2}{(n-1)}}$	45
Equation 3.6	Relative standard deviation, $RSD\% = \frac{SD}{\mu} \times 100\%$	45
Equation 3.7	Coefficient of determination, $R^2 = \left[\frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}} \right]^2$	45
Equation 3.8	$\mathcal{E}_{Bias} = \text{Data}_{measured} - \text{Data}_{calculated}$	45
Equation 3.9	$\mathcal{E}_{Abs} = \sqrt{(\mathcal{E}_{Bias})^2}$	45
Equation 3.10	$\mathcal{E}_{\%} = \frac{\mathcal{E}_{Abs}}{\text{Data}_{measured}} \times 100\%$	45
Equation 4.1	$Q_{Residual} = Q_o - Q_w$	48

Equation 4.2	$m_{w,critical} = 1 - h_w/(h_o + h_w)$	48
Equation 4.3	HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A	48
Equation 4.4	$\frac{R^*}{R} = \frac{(100-IM)}{100 + [R - R(\frac{O_D}{100} + 1) - (\frac{O_D}{100} + 1)] \times IM}$	50
Equation 4.5	$CHNSO_{Total} \cong CHNSO_{Organic} + CHNSO_{Inorganic}$	51
Equation 4.6	$CHNS_{Total} + O_{Total} + IM + Halogens \cong 100\%$	51
Equation 4.7	$TI \cong IM + Halogens + CHNSO_{Inorganic}$	51
Equation 4.8	$CHNS_{Total} + O_{difference} + Ash_{950} + Halogens \cong 100\%$..	51
Equation 4.9	$IM + O_{oxidation} = Volatile Inorganics + Ash_{950}$	52
Equation 4.10	$IM + O_{oxidation} \cong Ash_{950}$	52
Equation 4.11	$O_{Total} - O_{difference} = O_{deviation}$	52
Equation 4.12	$O_{deviation} \cong Ash_{950}^{OC} - IM \cong O_{oxidation}$	52
Equation 4.13	$R_{B/A} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{Al_2O_3 + SiO_2 + TiO_2}$	54
Equation 4.14	$R_{B+P/A} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5}{Al_2O_3 + SiO_2 + TiO_2}$	54
Equation 5.1	TGA in volatile basis, $M_{vb} = \left[1 - \frac{100 - M_{db}}{100 - Char_{db}}\right] \times 100\%$	99
Equation 5.2	DTG in volatile basis, $R_{vb} = \left[\frac{100}{100 - Char_{db}}\right] \times R_{db}$	99
Equation 5.3	Standard deviation of slope, $SD_m = \sqrt{S_{yx}^s / SS_{xx}}$	99
Equation 7.1	$W_s P_s = \sum_{i=1}^n W_i P_i$	173

1. Introduction

1.1 Background

Sludge was a generic term that referred to a mixture of solid materials and liquid in a semi-solid state. In this study, sludge referred to semi-solid residues generated in wastewater treatment plants as a by-product and commonly known as sewage sludge. In Singapore, domestic (generated from household) and industrial wastewater (after treatment at source) was discharged as a used water mixture into sewer and transferred to four existing Water Reclamation Plants (WRPs) for further treatment as illustrated in Figure 1.1. Based on reported data from Public Utilities Board (PUB) for year 2015, 575 million m³ of used water was treated in Singapore where 55% by Changi WRP, 21% by Ulu Pandan WRP, 12% by Jurong WRP and Kranji WRP respectively. Wastewater treatment process produced water safe for discharge and recoverable as recycled water (NEWater) by application of advanced membrane technology and ultra-violet disinfection. However, significant amount of semi-solid residues were generated as sewage sludge during the process. According to waste statistic from National Environment Agency (NEA) of Singapore, 160,200 tonnes of sludge were generated in year 2012 with 0% recycling rate. Sludge residues generated from WRPs were currently incinerated and ashes remained were then landfilled in Pulau Semakau, the only operating landfill in Singapore.

Figure 1.1 Locations of WRPs and Pulau Semakau in Singapore.

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, urbanisation and industrialisation (Spinosa, 2007). Presence of significant amount of moisture, ash residues, nitrogen, sulphur, toxic organic compounds and heavy metals resulted in sludge considered as a serious waste management concern based on both economical and environmental perspectives (Chen et al., 2002; Nipattummakul et al., 2010). Existing technologies commonly applied for sludge treatment and final disposal were mechanical dewatering, thermal drying, agricultural utilisation, composting, landfilling, land reclamation and incineration (Fytli and Zabaniotou, 2008; Spinosa, 2007). However, mechanical dewatering and thermal drying processes were facing issues on low dewatering effectiveness and high energy consumptions (Jin et al., 2004). Restrictions were also set on agricultural reuse due to the concerns of pathogens, heavy metals and organic pollutants in sludge (Fonts et al., 2012). Land disposal of sludge was costly and facing limitation on the availability of landfill. Furthermore, sludge disposal before removing all the organic contents would lead to potential greenhouse gases emission from microorganism activities (Ning-Yi et al., 2013). While incineration plants were capable to reduce volume of sludge significantly, large amount flue gas generated from incineration needed to be treated with care and incurred high cost because of the pollutants presence which included dioxins (PCDDs), furans (PCDFs), sulphur oxides (SO_x), nitrogen oxides (NO_x), hydrogen chloride (HCl), heavy metals and fly ash (Roy et al., 2011). Innovative waste management and treatment technology therefore required to manage sludge treatment and final disposal issues with economic and environmental friendly consideration and to discover possibilities on resource recovery from sludge.

Recently, feasibility of advanced thermochemical conversion processes to convert municipal solid waste and sludge into oil through pyrolysis and into synthetic gas through gasification as new technologies applied on waste management issues were attracting great attentions and interests (Arena, 2012; Manara and Zabaniotou, 2012). Compared to incineration, advanced thermochemical conversion processes

were capable to convert low value and highly heterogeneous waste and biomass into more uniform and valuable products such as synthetic gas, pyrolysis oil and char instead of heat and to recover carbon and hydrogen resources from waste residues (Wang et al., 2008). Biomass wastes were considered as unique sources of organic carbon when compared to other forms of renewable energy such as solar, wind and nuclear energy. Advanced thermochemical conversion of sludge to produce synthetic products provided an opportunity to utilize carbon and hydrogen resources in biomass for both energy and chemicals production.

Pyrolysis process could convert organic matters in sludge into char solids, combustible gases and fuel liquids. Char solids were demonstrated to be more resistant to lixiviation than initial sludge samples and incinerated ash residues with low surface area therefore suitable for landfilling or used as absorbents for acidic compounds (Arena, 2012; Manara and Zabaniotou, 2012). Gasification process could convert the organic content presence in sludge into synthetic gas which was having a good potential to be utilised as a fuel gas or further synthesized into useful and valuable chemicals such as Fischer-Tropsch liquid hydrocarbon, dimethyl ether (DME) and methanol (Arena, 2012; Huber et al., 2006; Manara and Zabaniotou, 2012). Syngas could also be superheated and combusted in a gas turbine to generate electricity with higher efficiency through Integrated Gasification Combined Cycle (IGCC) instead of direct combustion and generated heat for steam turbine (Gupta et al., 2010; Kolev et al., 2001). Combined heat and power system was suitable for sewage sludge treatment plants where heat for drying and power for operating equipment are both required (Dogru et al., 2002). In addition, gasification utilized only 25-50% of stoichiometric air required for combustion therefore produced lower volume of flue gas and reduced flue gas cleaning cost as compared to incineration. Pyrolysis and gasification of sludge could also reduce the volume of waste, degrade toxic organic compounds, fix heavy metals presence and reduce the need and cost of landfilling (De Andres et al., 2011; Many et al., 2005; Marrero et al., 2004). Furthermore, high temperature reducing environment presence in pyrolysis and gasification reduced the formation of dioxins, furans, SO_x and NO_x (Arena, 2012; Vehlow, 2005). Formation of PCDD/Fs were inhibited because these pollutants were suggested to be formed through de novo synthesis in waste

incineration where the formation required presence of products of incomplete combustion, halogenides, oxidizing atmosphere and metal catalysts at temperature of 200-500°C (Vehlow, 2005). Gasification of sewage sludge was also considered as self-sustaining at steady-state operation where no external heat input would be required (Dogru et al., 2002). However, thermal degradation behaviours of sludge found to be very complex and different from traditional feedstock such as coal, wood and other lignocellulosic biomass (Fytili and Zabaniotou, 2008). Therefore fundamental research on sludge as a feedstock for advanced thermochemical conversion needed for more efficient utilization of sludge and process optimisation.

1.2. Objectives and Scope

Sludge as a complex and heterogeneous wastes mixture with diverse organic and inorganic composition created significant barrier for efficient resource recovery. Characteristics of sludge could also vary significantly because of different sources of wastewater, treatment facilities available and temporal variations on properties of wastewater influent. However, advanced thermochemical conversion processes such as pyrolysis and gasification could convert waste mixtures such as sludge and municipal solid wastes into homogeneous streams of char solids, pyrolysis liquids and synthetic gases for further applications. To address the need of fundamental research on sludge in these systems for optimisation and innovative engineering design, a comprehensive analytical study of sludge collected from WRPs in Singapore with the focus on thermochemical conversion processes was carried out.

Specifically, this study aimed to achieve the following main objectives:

1. To establish a thermochemical characteristics survey of sludge generated in Singapore for energy and resource recovery through thermal processes.
2. To analyse existing methods and propose alternative parameters specifically applicable for characterisation of sludge and calculation bases for comparison study of different sludge samples.
3. To determine impacts of sludge composition on thermochemical characteristics, thermal degradation behaviours and products evolution.

4. To categorise and quantify main organic and inorganic composition presence in sludge for understanding on behaviours of sludge in conversion systems.
5. To develop methodology for the formation of synthetic sludge with known and consistent composition representing real waste sample with complex and heterogeneous components.

Scope of this study was determined based on objectives proposed and also the concept of holistic approach of sludge management. Comparison study was carry out for sludge collected based on type, plant, and batch categorisation by considering existing wastewater and sludge treatment processes. Five different types of sludge generated in different stages included primary, secondary, raw, dewatered and dried sludge were collected in two batches from four operating WRPs in Singapore with total of 14 samples analysed in detail. Thermochemical characteristics, thermal degradation behaviours, products evolution, organic composition, inorganic components and pyrolysis yield distributions were examined. A sequential extraction, isolation and quantification procedure was developed to categorise and quantify biomass composition of sludge with the focus on main components such as lipids, protein, polysaccharides, cellulose, hemicellulose and lignin. Model compounds were selected based on categorisation and findings of sludge biomass composition to form synthetic sludge.

1.3. Thesis structure

Chapter 1 of this thesis introduced the background information on sludge management issues and recent interests in advanced thermochemical conversion processes as a potential waste treatment method. Objectives, scope and structure of thesis were also described in detail. Structure of this thesis was illustrated in Figure 1.2. Chapter 2 reviewed existing literature and provided detailed information on the aspects of waste management, thermochemical conversion processes and biomass composition analysis with the focus on sludge. Literature review established the groundwork of this study and identified the research gaps and current issues on sludge treatment and final disposal. Chapter 3 described materials used and methods

generally applied throughout this thesis. Chapter 4 described the comprehensive characterisation of sludge for advanced thermochemical conversion processes carried out for sludge samples collected from all four existing Water Reclamation Plants (WRPs) in Singapore. Existing characterisation methods were applied and reviewed while alternative parameters and comparison bases were proposed. Chapter 5 reported thermal degradation behaviours and products evolution analysis of sludge samples by using analytical and experimental pyrolysis respectively and complementary. Complexity and heterogeneity of sludge were also identified and discussed. Chapter 6 described biomass composition analytical procedures developed for sludge. Main components in sludge were categorised and quantified based on extraction and isolation methods. Comparison and correlation study of thermochemical characteristics of all sludge samples collected with organic composition was also carried out. Chapter 7 discussed the findings for simulations analysis on characteristics of sludge based on the results from thermochemical characterisation study of sludge in Chapter 4, sludge biomass composition analysis in Chapter 6 and analysis of selected model compounds. Contributions of biomass composition identified for sludge samples to the thermochemical properties were analysed and discussed. Chapter 8 reported thermal degradation behaviours and products evolution analysis of sludge biomass components isolated in Chapter 6, model compounds selected and synthetic sludge formed. Applicability of model compounds and synthetic sludge to represent real waste sample was assessed and compared to results obtained from thermal degradation analysis of sludge samples collected in Chapter 5. Chapter 9 stated the summary of conclusions reached and recommendations suggested based on the results and discoveries found in this study.

Figure 1.2 Flowchart to illustrate structure and flow of this thesis.

2. Literature review

Literature review in this thesis attempted to establish groundwork of this study by analysing and summarising existing practices and ongoing research for sludge management related to thermal treatment and final disposal. General introduction of thermochemical conversion with the focus on advanced thermal processes and existing studies of sludge in the aspects including thermodynamics analysis, kinetics study and experimental research were also described in detail. Literature related to biomass composition analysis and thermal degradation behaviours of organic components were reviewed. Research gaps and current issues were then specified based on the findings from existing literature.

2.1. Waste management of sludge

2.1.1. General introduction

Holistic approach of sludge management addressed the sludge issues by considering the overall process of wastewater treatment, resource recovery from wastewater and sludge solids, sludge generation, reduction, final treatment and disposal (Englande and Reimers, 2001). Instead of viewing sludge as mixture of wastes as received and needed to be disposed of, holistic approach tried to reconsider the entire process and carried out research, technology development and engineering optimisation at any stage potentially beneficial. Sludge solids could be generated from different stages in a wastewater treatment facility. Primary sludge formed from coagulation, flocculation and sedimentation processes while secondary sludge generated during aerobic biological wastewater treatment process to digest and remove contaminants remained in water. The mixture of primary and secondary sludge commonly known as raw sludge could be directly dewatered by mechanical dewatering facility to form sludge cake for disposal or digested by anaerobic digestion process before dewatering. Waste sludge generated from wastewater treatment plants needed to be dewatered for subsequent handling and disposal because of high initial moisture content of around 95-98% (Guohua et al., 2006; Ning-Yi et al., 2013). Dewatering of sludge produced sludge cake with moisture content of 65-85% (Guohua et al.,

2006). Sludge dewatering was considered as one of the most difficult and costly processes in wastewater treatment (Jin et al., 2004). Conventional sludge dewatering techniques, such as centrifugation, belt filter presses and vacuum filtration, were commonly applied in wastewater treatment plant. However, these techniques showed concerns of low dewatering efficiency and thus high cost for subsequent treatment, due to difficulty of removing interstitial water in bio-flocs.

According to study on moisture distribution in sludge, four categories of water contents were presence namely free water, surface water, interstitial water and bound water (G. Chen et al., 2002; Tsang and Vesilind, 1990). Free water represented moisture that could be easily removed by mechanical process. Surface water was the moisture adsorbed and adhered on the surface of solid particles. Interstitial water was the moisture locked in the capillaries of dewatered cake or flocs of sludge solids. Bound water represented moisture in the cell and chemically bonded water. Biological sludge was much harder to be dewatered compared to primary sludge due to the presence of large amount of extracellular polymeric substances (EPS) and biological cells (Vaxelaire and Cezac, 2004). EPS and cells trapped water inside their structure and created negative charge repulsion between each other therefore caused difficulty in separating water from bio-solids.

Various conditioning and dewatering methods were established to tackle the problem but the efficiency and economics of sludge dewatering were still having significant room for improvements. Existing practices generally focused on three different perspectives to dewater sludge. Firstly, coagulation and flocculation of sludge solids for solids-water separation through charge neutralization and bridging of bio-solids by forming polymeric structure (Agarwal et al., 2005; Z. Zhang et al., 2010). Secondly, disruption on biological cells and polymeric structure for interstitial water release and better compressibility through enzymatic reactions (J. Lu et al., 2011) and cell lysis caused by thermal reaction (E. Neyens and Baeyens, 2003) or chemical oxidation (M.-C. Lu et al., 2003). Thirdly, facilitating water movement to reduce time of dewatering and to increase solids content through thermal assisted mechanical dewatering (Lee, 2006), physical filtration aids conditioning (Y. Qi et al., 2011), electrical field induced dewatering (Mahmoud et

al., 2010) and pH adjustment by lowering the pH to around 3 or raising the pH to 10 (Elisabeth Neyens et al., 2004). Novel methods which could improve the efficiency and reduce the energy usage during dewatering would benefit the whole treatment process especially for subsequent thermal treatment processes.

After mechanical dewatering processes, drying of sludge could further reduce moisture content of sludge to around 5-45% depended on desired amount of subsequent treatment processes (G. Chen et al., 2002). Thermal drying could be accomplished in direct, indirect, or combined drying systems. The selection of a particular dryer based on the initial and final moisture contents, properties of the solid products, the ability to operate and maintain the system, and the nature and capacity of sludge to be handled. In addition, thermal drying was considered as a good method to sterilise sludge in dealing with the concerns of viruses and pathogens (Guohua et al., 2006). Subsequent treatment or final disposal of sludge would determine final moisture content required. For agricultural and composting, the requirement of moisture content will be relatively higher since water was needed for the growth for plants and microorganism. For direct landfilling, the desired moisture content directly related to the trade-off between cost of drying and unit cost for sludge disposal into the landfill. The moisture in sludge was considered as a burden during incineration since energy will be required to heat the moisture into vapour and condense subsequently. Presence of low moisture content in sludge before incinerated was preferable. Advanced thermochemical conversion processes such as pyrolysis and gasification were on the other hand capable to utilise the moisture in sludge to improve heating value and hydrogen content of synthetic gas therefore could be promising options to convert sludge which was having significant amount of moisture into valuable synthetic products (De Andres et al., 2011a; Nipattummakul et al., 2010; Otto et al., 1979).

2.1.2. Environmental concerns

Rising demand in wastewater treatment and reclamation caused significant increase in amount of sludge generated during treatment processes. By producing treated water with acceptable quality for discharge and reuse, contaminants and undesirable

compounds were concentrated in sewage sludge (Spinosa, 2007). Contaminants commonly found in sludge were pathogens, heavy metals and organic pollutants such as polychlorinated biphenyl (PCB), dioxins, furans and polyaromatic hydrocarbons (PAHs) (Fonts et al., 2012). Existing disposal methods for sludge such as agricultural reuse, land applications, landfill and direct discharge into sea were potentially causing serious environmental and health concerns (Fytili and Zabaniotou, 2008; Spinosa, 2007). These methods could potentially cause leaching of heavy metals, transfer of toxic organic compounds and spread of pathogens to the surrounding environment, water resources, atmosphere and food chains of the ecosystem. Disposal of sewage sludge or wastes with organic contents in landfill could also cause increased greenhouse gases emission by microorganism activities and faced limitation of land availability (Ning-Yi et al., 2013).

In Singapore, sewage sludge was previously disposed in landfill after mechanical dewatering and thermal drying. Currently, sludge was incinerated before disposed to the landfill at Pulau Semakau. As a city state with more than 5.5 million of growing population but only about 720 km² of total land area, Singapore adopted waste minimisation & recycling (recycling rate at 61% in year 2015, targeting 70% by year 2030) and incineration as the main municipal solid wastes treatment methods for the country. Although incineration plants were capable to significantly reduce mass and volume of solid wastes including sludge residues, limited energy recovery from wastes and large amount flue gas would be generated. Efficient and comprehensive air pollution control system was needed to treat the flue gas to meet stringent limits before released to environment and incurred high cost because of the pollutants presence which included dioxins (PCDDs), furans (PCDFs), sulphur oxides (SO_x), nitrogen oxides (NO_x), hydrogen chloride (HCl), heavy metals and fly ash (Roy et al., 2011). Therefore alternative thermochemical conversion processes with high waste treatment rate and low land space requirement comparable to incineration but with potentially higher recovery of energy and lower environmental impacts were needed to be developed in Singapore as the next generation waste management methods.

2.2. Thermochemical conversion process

2.2.1. General introduction

Thermochemical conversion processes could be classified as pyrolysis and reactolysis (Warnecke, 2000). Pyrolysis was classified as a process of physical and chemical reactions that carried out without any input of other reactive materials but only with thermal energy. Pyrolysis consisted of complex thermal degradation with endothermic and exothermic reactions (Brown and Stevens, 2011). Products of pyrolysis were mainly oil and char with minor amount of gas (Fonts et al., 2009; Ji et al., 2011). Pyrolysis could be classified into different categories based on the heating rate and residence time applied. In general, fast pyrolysis was applied with the conditions of very high heating rates, heat transfer rates, short vapour residence time and finely ground feedstock to obtain higher liquids yield. Intermediate and slow pyrolysis with lower heating rates and longer residence time could generate higher solid and gas yields. Based on products distribution of the process, pyrolysis could be further designed and specified for generating liquids as biofuel, gases as syngas and solids as char adsorbent. Thermochemical properties and molecular structures of feedstock were found to be important in determination of products evolution and reaction rates at different operating conditions applied (Fonts et al., 2012; Manara and Zabaniotou, 2012).

In contrast, reactolysis was a process of physical and chemical reactions carried out with the presence of reactive materials such as oxygen, carbon dioxide, air and steam. Gasification was classified as a complex reactolysis process that utilised less than stoichiometric oxygen and/or other gasifying agents such as steam and carbon dioxide to react with the feedstock and generate synthetic gases (syngas). Main components of syngas were hydrogen gas (H_2), carbon monoxide (CO), methane (CH_4) and carbon dioxide (CO_2). Compare to combustion, gasification converted the chemical energy stored in sludge into chemical energy in syngas rather than heat in a net reducing environment. Gasification of sludge comprises a series of complex reactions (Dogru et al., 2002). Four basic steps happened during gasification including drying, pyrolysis, oxidation and reduction. Moisture content in feedstock released as water vapour during drying process. Light gases, tar and char residues

were generated from organic matters during pyrolysis through thermal degradation, volatilization and carbonization. Oxidation occurred when oxygen in air reacted with carbon monoxide, hydrogen and char residue with release of heat. Heat released will facilitate the subsequent endothermic reduction reaction. General reactions in thermochemical conversion processes were stated in three categories of reactions (Brown and Stevens, 2011; Mun et al., 2012).

Combustion and oxidation reactions:

Gasification and reduction reactions:

Thermal cracking:

However, thermochemical conversion reactions were highly complex in any thermal system and therefore complementary thermodynamics analysis, kinetics study and experimental research were needed for innovative reactor design and process optimisation for different types of feedstock.

2.2.2. Thermodynamics analysis

Thermodynamics analysis was applied to develop efficient biomass thermochemical conversion process and chemical synthesis technology. Gibbs free energy minimisation and exergy analysis were two of the common analytical methods used for thermochemical conversion processes (Shao et al., 2008; Tsatsaronis and Winhold, 1985; J. Zhang et al., 2007). Chemical equilibrium of gas composition released from pyrolysis and gasification could be calculated with minimisation of Gibbs free energy by assuming sufficient reaction time with representative feedstock composition, limited reactions considered and selected compounds in the system. During thermochemical conversion, chemical energy stored in the biomass would transform into thermal energy, work energy and chemical energy in the material produced such as oil, syngas, volatiles and char. Products with high chemical energy contents for subsequent utilization were important targets in advanced thermochemical processes such as pyrolysis and gasification, therefore exergy-based thermodynamic analysis was proposed (Tsatsaronis and Winhold, 1985). Exergy was defined as maximum amount of work could be obtained from a stream of materials, heat and work interactions by bringing this stream to environmental conditions (Ptasinski, 2008).

According to exergy-based analysis, efficiency of gasification reached maximum at carbon boundary where the amount of gasifying agent presence sufficient to convert all solid carbon into gaseous fuel and without any further conversion to heat (J. Prins et al., 2003; Palz et al., 1985; Prins, 2005; Ptasinski, 2008). Thermodynamics analysis also demonstrated that exergy efficiency of steam was higher compared to air/oxygen by considering biomass with molecular formula of $\text{CH}_{1.4}\text{O}_{0.59}\text{N}_{0.0017}$. Exergy efficiency for oxygen found to be 80.5% at equivalence ratio (ER) of 0.26 with reaction temperature of 764°C while for steam was calculated at 87.6% with steam-to-biomass ratio of 1.30kg/kg with reaction temperature of 460°C. However, kinetics of reactions resulted in significantly higher practical operation temperature compared to optimum temperatures found in thermodynamic analysis caused reduction of exergetic efficiency in gasifier and considered as the major exergy loss during conversion process of biomass-to-biofuel (Ptasinski, 2008). Feedstock with higher oxygen content required lower oxygen input for oxidation therefore causing

lower optimum gasifier temperature and reaction rate at carbon boundary. Thermodynamics analysis provided important information on thermochemical conversion processes but only in equilibrium states with limited understanding on reaction mechanisms and corresponding kinetics. In addition, practical operating conditions could also deviate from predicted optimum by thermodynamics simulations. Hence it was necessary to consider both thermodynamics and kinetics of thermochemical conversion systems with complementary results from experimental research to understand the processes and determine optimum operating parameters and designs suitable for different types of feedstock.

2.2.3. Kinetics study

Kinetics study could be carried out based on mass loss data collected by thermogravimetric analysis (TGA) for determination of rate equations and corresponding parameters, description of reaction mechanisms, and making predictions of reaction behaviours for any complex time-temperature profiles (Vyazovkin et al., 2011). Arrhenius model was one of the most important and commonly used models to describe kinetics of thermal reactions (Encinar et al., 2001; Otto et al., 1979; Thipkhunthod et al., 2006). Arrhenius model described thermal degradation behaviours by using kinetics parameters including rate constant (k), apparent activation energy (E_a) and pre-exponential factor (A). Differential data (DTG) and profiles could also be derived from mass loss curves. TGA could be further coupled with differential scanning calorimetry (DSC) and Fourier-transform infrared spectroscopy (FTIR) to measure heat flow and products evolved during reactions for more comprehensive understanding on thermal degradation behaviours at different temperatures, reacting conditions and for various types of feedstock (Grigante et al., 2010; Ischia et al., 2007).

Kinetic parameters of sludge pyrolysis found to be varied significantly among the published results. Activation energy, E_a of thermal degradation by pyrolysis could range from 17 to 332 kJ/mol while pre-exponential factor, $\log_{10} A$ could range from 0.50 to 12.80 and reaction order of the selected models, n could range from 0.92 to 15.00 for different sludge samples analysed (Font et al., 2005; Piatkowski and

Steinfeld, 2010; Thipkhunthod et al., 2006; Thipkhunthod et al., 2007; Urban and Antal Jr, 1982). Kinetic models and parameters stated in previously reported studies on sludge were generally correlation models and therefore not directly comparable because of different assumptions and conversion models used (Orfão et al., 1999; Thipkhunthod et al., 2006). Observations of varying activation energy and high reaction orders for fitted models also suggested different biomass composition degraded with multiple and complex reactions during thermal degradation of sludge (Stolarek and Ledakowicz, 2005; Urban and Antal Jr, 1982). Therefore, multiple stages degradation with different number of fractions from one to six or more were suggested to better describe pyrolysis of sludge based on moisture evaporation through drying, primary degradation of various organic matters in sludge such as biodegradable organics, microorganism and non-biodegradable materials, secondary degradation of char residues and inorganic matters decomposition during pyrolysis of sludge (Bengoa et al., 2011; J. A. Conesa et al., 1998; Font et al., 2005). Model fitting methods used for kinetics modeling were also facing issues on comparable fit of multiple statistically equivalent models with significantly different activation energies and mechanisms (Vyazovkin, 2000). Therefore, single heating rate experiment and single step model may not accurately describe mass loss kinetics of the highly complex sludge thermal degradations which consisted of different components reacted in multiple degradation stages.

Model-free isoconversional methods by using multiple heating rates in thermogravimetric analysis could be considered as alternative and suitable tools for kinetics analysis of sludge. Multiple heating rates TGA with simultaneous correlation could minimise errors in kinetics parameter analysis (Juan A. Conesa et al., 1995; Vyazovkin et al., 2014). Wide interval of heating rate used also contributed to results with higher reliability and closer to intrinsic kinetic characteristics of the samples (Font et al., 2005). Isoconversional methods 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 (Mo et al., 2013; Sbirrazzuoli et al., 2009). Isothermal predictions and complex time-temperature profiles could also be done by application of non-isothermal data and kinetics parameters determined in model-free isoconversional

methods to simulate the conversion degree versus time further support the use of these methods. Good isothermal conversion prediction could be obtained by using data of the activation energy obtained in isoconversional methods (Sbirrazzuoli et al., 2009). Improved predictions also demonstrated for isoconversional methods and conversion dependence E compared to model fitting methods (Vyazovkin, 2000). However, careful considerations needed when interpreting the rate constants due to the highly empirical characteristics of the determination procedures for kinetics parameters. Variation in the apparent activation energy, E_a determined in the experiments could be generally accounted by the following reasons as summarised in previous publication (Galwey, 2003). Firstly, E_a could be varied when the inherent reactivity altered as the physical and chemical properties of the reactants were changed caused by the reactions occurred. Secondly, E_a could be varied when the process was complex caused by the contributions from different components or reactions changed over the conversion process or alternative physical phenomenon occurred such as melting of reactants. Thirdly, computational artifacts could also significantly contribute to the variations of apparent activation energy.

Gasification of sludge and pyrolysed char residues found to be kinetics controlled processes since the performance and products generally different from the predictions based on thermodynamic equilibrium of the systems (Gil-Lalaguna et al., 2014). Significant differences in initial reaction temperatures, maximum degradation rates and corresponding temperatures, kinetics models and activation energies could be observed when using oxygen, steam and carbon dioxide as gasifying agents for comparison study. Carbon dioxide and steam started to react with sludge and char residues at temperature around 700°C while maximum degradation rates were reached at 900°C for H₂O and 950°C for CO₂ which was significantly higher than air or oxygen gasification that initiated at temperature around 400°C and reached maximum degradation rates at 550°C (Nowicki et al., 2011). Shrinking core model found to be fitted well for air/oxygen gasification with activation energy of 114kJ/mol and CO₂ gasification at 227kJ/mol while first-order model fitted well for steam gasification at 193kJ/mol (Bengoa et al., 2011). Therefore steam could be considered as thermodynamically favourable while air/oxygen was kinetically favourable in gasification. Therefore advanced

thermochemical conversion processes such as pyrolysis and gasification with air-steam mixtures as gasifying agents were promising technologies which could utilise moisture content in sludge for optimisation and improvement of overall performance (De Andres et al., 2011a; Fonts et al., 2012; Xie et al., 2010).

Calculation methods applied in this study for kinetics analysis were based on published kinetics studies (Khawam and Flanagan, 2005; Vyazovkin, 1996; Vyazovkin et al., 2011). Kinetics of thermochemical conversion processes could be described by general kinetics expression Equation 2.1 where conversion degree $\alpha = (m_i - m)/(m_i - m_f)$, heating rate $\beta = \frac{dT}{dt}$ and pressure $h(P) = P^n$ or $1 - P/P^0$. Modification applied and formed Equation 2.2. Rate constant, $k(T)$ described by Arrhenius model in Equation 2.3 could be simplified in to Equation 2.4. A , α , $f(\alpha)$ and $h(P)$ were constant at atmospheric pressure or constant pressure and at any point of conversion therefore $\frac{d}{dT^{-1}} \ln f(\alpha) + \frac{d}{dT^{-1}} \ln h(P) = 0$ and $\frac{d}{dT^{-1}} \ln A = 0$. Therefore, Equation 2.2 and 2.4 could be simplified in Equation 2.5. Simplification of general kinetics expression at constant conversion degree showed that dependence of reaction rate only on temperature. Activation energy, E_a found to be the single most important parameter related to the rate of reaction.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \quad \text{Equation 2.1}$$

$$\ln \frac{d\alpha}{dt} = \ln k(T) + \ln f(\alpha) + \ln h(P)$$

$$\frac{d}{dT^{-1}} \ln \frac{d\alpha}{dt} = \frac{d}{dT^{-1}} \ln k(T) + \frac{d}{dT^{-1}} \ln f(\alpha) + \frac{d}{dT^{-1}} \ln h(P) \quad \text{Equation 2.2}$$

$$k(T) = A \exp^{-\frac{E_a}{RT}} \quad \text{Equation 2.3}$$

$$\frac{d}{dT^{-1}} \ln k(T) = \frac{d}{dT^{-1}} \ln A \exp^{-\frac{E_a}{RT}}$$

$$\frac{d}{dT^{-1}} \ln k(T) = \frac{d}{dT^{-1}} \left[\ln A + \left(-\frac{E_a}{RT} \right) \right] \quad \text{Equation 2.4}$$

$$\frac{d}{dT^{-1}} \ln \frac{d\alpha}{dt} = \frac{d}{dT^{-1}} \left(-\frac{E_a}{RT} \right)$$

$$\frac{d}{dT^{-1}} \ln \frac{d\alpha}{dt} = -\frac{Ea}{R} \quad \text{Equation 2.5}$$

Differential method for non-isothermal isoconversion at constant pressure carried out by using Friedman analysis showed that Ea could be calculated based on the slope for the plot of $\ln (\beta d\alpha/dT) \propto -1/T_\alpha$ as described by Equation 2.6.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

$$\ln \frac{d\alpha}{dt} = \ln k(T) + \ln f(\alpha)$$

$$\ln \frac{d\alpha}{dt} = \ln A + \left(-\frac{E}{RT}\right) + \ln f(\alpha)$$

$$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E}{RT}$$

$$\ln \beta \frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E}{RT} \quad \text{Equation 2.6}$$

Integral method for non-isothermal isoconversion at constant pressure carried out by using OFW analysis with integral approximation, $\ln p(x) = -5.3305 - 1.052x$ showed that Ea could be calculated based on the slope for the plot of $\ln \beta \propto -1/T_\alpha$ as described by Equation 2.7 (Vyazovkin et al., 2011).

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

$$\beta \frac{d\alpha}{dT} = \left[A \exp^{-\frac{E}{RT}} \right] f(\alpha)$$

$$\int \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int \exp^{-\frac{E}{RT}} dT$$

$$\text{Let } g(\alpha) = \int \frac{d\alpha}{f(\alpha)} \text{ and } x = \frac{E}{RT} \text{ then } g(\alpha) = \frac{AE}{\beta R} \int \frac{\exp^{-x}}{x^2} dx$$

$$\ln g(\alpha) = \ln \frac{AE}{\beta R} + \ln p(x) \text{ where } p(x) = \int \frac{\exp^{-x}}{x^2} dx$$

$$\ln \beta = \ln \left(\frac{AE}{R} \right) - \ln g(\alpha) - 5.3305 - 1.052 \left(\frac{E}{RT} \right) \quad \text{Equation 2.7}$$

Predictions for thermal degradation could also be derived based on non-isothermal analysis (Vyazovkin, 1996). Equation 2.8 and 2.9 were applicable for isothermal prediction and non-isothermal prediction respectively.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

$$\int \frac{d\alpha}{f(\alpha)} = \int k(T)dt$$

$$g(\alpha) = t_{\alpha}A_{\alpha}\exp^{-E_{\alpha}/RT_0} \quad \text{Equation 2.8}$$

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

$$\beta \frac{d\alpha}{dT} = \left[A_{\alpha} \exp^{-\frac{E_{\alpha}}{RT}} \right] f(\alpha)$$

$$\int \frac{d\alpha}{f(\alpha)} = \frac{A_{\alpha}}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT$$

$$g(\alpha) = \frac{A_{\alpha}}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT \quad \text{Equation 2.9}$$

Assuming partial kinetics parameters including A_{α} , E_{α} and $f(\alpha)$ remain unchanged when isothermal reaction temperature changed, then Equation 2.8 and 2.9 were equal. Time of reaction t_{α} at temperature T could be described by Equation 2.10.

$$g(\alpha) = t_{\alpha}A_{\alpha}\exp^{-E_{\alpha}/RT_0} = \frac{A_{\alpha}}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT$$

$$t_{\alpha} = \left[\beta \exp^{-E_{\alpha}/RT_0} \right]^{-1} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT \quad \text{Equation 2.10}$$

Non-isothermal predictions for varying heating rates based on data of non-isothermal analysis could also be carried out. Temperature T_{α} of conversion α at heating rate β could be determined by Equation 2.11.

$$g(\alpha)_o = g(\alpha)$$

$$\frac{A_{\alpha}}{\beta_o} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT = \frac{A_{\alpha}}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT$$

$$\frac{1}{\beta} \int_0^{T_{\alpha}} \exp^{-\frac{E_{\alpha}}{RT}} dT - \frac{1}{\beta_o} \int_0^{T_{\alpha,o}} \exp^{-\frac{E_{\alpha}}{RT}} dT = 0 \quad \text{Equation 2.11}$$

2.2.4. Experimental research

2.2.4.1. Pyrolysis and gasification of sludge

Thermal degradation behaviours of sludge were found to be highly complex (Font et al., 2005; Gomez-Rico et al., 2005). Pyrolysis of sludge generally occurred at lower temperature compared to incineration and gasification processes. Therefore as temperature of reactor elevated with the presence of gasifying or combustion agents, sludge would thermally degrade by pyrolysis and followed by gasification or incineration of char formed or solid residues remained (Piatkowski and Steinfeld, 2010). Decomposition by concurrent pyrolysis and reactolysis reactions could also be observed when further heated to higher temperature. Reactivity of char residues produced from sludge found to be varied according to differences in gasification agents selected, types of sludge as initial feedstock, physical forms, chemical properties and preparation methods of char (Nilsson et al., 2012; Nowicki and Markowski, 2015). Presence of volatiles during gasification would also cause competition in consuming oxygen or other gasifying agents. Volatiles oxidised rapidly and consumed significant amount of oxygen before it diffused to the surface of char (Dogru et al., 2002). Therefore, analytical and experimental analysis of highly complex pyrolysis and gasification reactions with different characteristics should be carried out separately and complementary to provide more accurate data for system modelling. Multiple steps models with consideration of pyrolysis devolatilisation and gasification reactions were demonstrated to provide generally more accurate kinetics predictions (Di Blasi, 2009).

Pyrolysis of sludge produced gas, liquid and solid components with product distributions depended on operating temperature, residence time, pressure, turbulence, and characteristics of feedstock (Manara and Zabaniotou, 2012). Main constituents in gaseous products were hydrogen, carbon monoxide, carbon dioxide, methane and light hydrocarbon gases. Other gaseous compounds including HCN, NO_x, HCl and SO_x were also presence. Pyrolysis liquid from sludge was highly complex mixture with main constituents including water, hydrocarbons, organic acids, aromatics, and alcohols. Nitrogen and sulphur containing compounds were also detected in pyrolysis liquid which suggested the need of pre-treatment and

extraction processes before subsequent utilisation. Main solid constituents in char residues were solid carbon and inorganic contents. Instead of direct gasification of sludge, pyrolysed char solids could be used as a feedstock in gasifier and converted into synthetic gas by reacting with hot gases such as CO, CO₂, H₂O, H₂, and O₂. Char yield, structure and reactivity were important parameters for subsequent gasification and incineration design and modeling (Di Blasi, 2009). In addition to issues on complexity of modelling and control, direct gasification of sewage sludge also produced tar as by-products which would limit the applications of syngas but gasification of pyrolysed char could generate product gas with significantly lower tar contents while maintaining comparable energy efficiency and heating values of syngas (Cao et al., 2006; Gil-Lalaguna et al., 2014; He et al., 2012).

Based on previous studies, ash fusion of sludge initiated at temperature around 1010°C which went through softening, hemispherical and fluid stages at around 1185°C, 1215°C and 1425°C respectively (Chiang et al., 2011; Petersen and Werther, 2005). High ash content in sludge and 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. Therefore, improvements on performance for sludge gasification at lower operating temperature or avoidance on local overheating would be beneficial in both ash handling issues and energy efficiency considerations as discussed in thermodynamics analysis (Prins, 2005; Ptasiński, 2008). Detail feedstock characteristics analysis, innovative design on thermochemical process, proper selection of gasification agents and catalyst could contribute to this improvement.

2.2.4.2. Tar formation and removal

Tar was classified as a group of complex chemical compounds with molecular weight greater than benzene which formed during thermochemical conversion processes as volatiles in the pyrolyser or gasifier but condensed into liquids as temperature decreased (Kinoshita et al., 1994; Milne et al., 1998; Xu et al., 2010). The main contributors to tar formation in gasification of sludge were volatile organic matters released during the thermal degradations. High temperature

pyrolysis of sludge could also produce significant amount of polyaromatic hydrocarbons (PAH) through secondary reactions of volatile compounds (Dominguez et al., 2006). Tar tolerance limits for various applications were low, from 0.1 to 500 mg/m³ of syngas compare to the tar productions in gasification which were from 0.5 to 100 g/m³ (Han and Kim, 2008; Xu et al., 2010). Therefore, tar formation analysis, characterization and cracking were important issues for subsequent utilisation of syngas produced in biomass gasification. Tar could be categorised into five different groups which were (a) undetectable compounds, (b) heterocyclic, (c) light aromatic hydrocarbon, (d) light PAH, and (e) heavy PAH (H. Chen et al., 2011). Previous studies also showed that the dominant compounds in tar were benzene, toluene, naphthalene, xylene, styrene, phenol, indene, pyrene and poly-aromatic hydrocarbon (PAH) (Chun et al., 2012; Kinoshita et al., 1994; Phuphuakrat et al., 2010). Composition of major tar compounds, total number of tar species and tar yield were changed as the operating conditions of gasification were altered. Increased in the temperature of gasification led to the formation of tar species with less or no substituent group suggested that basic benzoic ring structure was relatively stable. Increase in both temperature and ER also promoted formation of PAH though reduced overall tar yield as illustrated in tar maturation scheme (H. Chen et al., 2011; Elliott, 1988). The scheme showed that the main components detected in tar mixtures changed from mixed oxygenates at 400°C, phenolic ethers at 500°C, alkyl phenolics at 600°C, heterocyclic ethers at 700°C, light PAH at 800°C to heavy PAH at 900°C as temperature of reaction elevated. In addition to temperature and ER, the type of biomass, steam content, operating pressure and design of gasifier were showed as important factors that affecting tar yield and its composition (Chun et al., 2012; Han and Kim, 2008). Tar removal could be classified into two main approaches which were primary and secondary methods (Devi et al., 2003). Primary methods included process modifications to reduce tar formation and cracking by heat or catalyst to convert tar into synthetic gas. Secondary methods include hot and cold gas cleaning to remove tar from the syngas stream. Scrubber, filter, cyclone and electrostatic precipitator were capable to remove most of the contaminants in syngas. Although secondary methods were proven to be effective and generally used, primary methods were getting increasing

attention to solve the tar issues. Tar removals through secondary methods reduced total energy recovery and generated liquid waste while primary methods recovered energy retained in tar and produced no waste. High operating temperature in gasifier reduced tar content and produced higher quality syngas with higher H₂ to CO ratio in product gas but faced with decreased energy efficiency and increased risk of ash sintering. Higher temperature would also promote the formation of stable tar such as PAH based on tar maturation scheme (L. Wang et al., 2008).

2.2.4.3. Sequential thermochemical conversion

Recently, different sequential thermochemical conversion systems were proposed to improve the modelling and control for process optimization and pollutants reduction (Ábrego et al., 2013; de Wild et al., 2009; Hernández et al., 2013). In general, biomass could be sequentially treated with thermal drying, torrefaction or pyrolysis to form volatile compounds for collections and char residues for subsequent gasification or incineration. Thermal degradations of biomass carried out in multiple stages with different reaction temperature and residence time selected based on the characteristics of targeted components in the feedstock could also produce targeting products separated directly by the process designed (Ábrego et al., 2013; de Wild et al., 2009). Removing of targeting pollutants included nitrogen and sulphur containing compounds such as NH₃ and H₂S could also be carried out by staged thermal degradations of sludge (Hernández et al., 2013). Two-stage gasifier system that separated pyrolysis and gasification processes of biomass also demonstrated excellent efficiency as a primary method in tar reduction and conversion (Devi et al., 2003). The operation of sequential thermal system relied on the control and stability of pyrolysis zone. Therefore, it was important to analyse and understand the pyrolysis characteristics and kinetics of sludge to develop an efficient and suitable thermochemical conversion process. Volatile compounds which consisted of condensable liquid and non-condensable gases separated from the char residues through pyrolysis could be utilised directly in combustion to provide the energy required for the entire thermochemical conversion system. Direct utilization of volatiles reduced energy loss caused by condensation and separation processes (Z. Wang et al., 2012).

2.2.4.4. Impacts of moisture and steam

Performance of air gasification also found to be improved with the increase of moisture content in sludge indicated the presence of H_2O in gasification enhanced the hydrogen gas generation and heating values of producer gas (Xie et al., 2010). Increase of moisture content in sludge on gasification also showed increased tar concentration, condensate liquid, H_2 and CO_2 volume percentage while reduction on CO production (Mun and Kim, 2013). Gasification of sludge with moisture could be considered similar to input of steam into air-gasification process. Introducing steam into gasification process improved hydrogen yield, aided tar cracking and improved quality of syngas by steam reforming reactions (De Andres et al., 2011b). However, extra energy input needed to increase temperature of steam and to promote endothermic reaction of steam with sludge should also be accounted for energy balance analysis (Corella et al., 2007; Nipattummakul et al., 2010). Steam gasification was highly endothermic therefore high temperature was both difficult to achieve and to control. Furthermore, water conversion in gasifier was typically less than 10% caused waste of energy on elevating the temperature of steam (Corella et al., 2007). The equilibrium of water-gas shift reaction was not achieved could account for the low water conversion rate (Petersen and Werther, 2005). Therefore, utilisation of air and steam mixture to couple both endothermic and exothermic reactions may improve the performance of sludge gasification. Endothermic reaction of H_2O and carbon could reduce the issue of thermal heat escape and local overheating in air gasification as oxygen resulted in vigorous exothermic combustion (Otto et al., 1979). Furthermore, if oxygen atom in steam could replace the requirement of oxygen gas in air then the ER required for gasification can be reduced. This will result in lower air requirement which means less nitrogen in the both gasifier and product gas. Therefore the volume of the gasifier and gas cleaning requirement can be lowered with the same feedstock input rate and the heating value of the syngas could be increased.

2.3. Biomass composition analysis

2.3.1. General introduction

Sludge is a complex waste mixture of different biochemical components and various synthetic or natural compounds. Main biochemical components identified in sludge were bacterial constituents such as nucleic acids, lipids, proteins and carbohydrates, corresponding decay products, undigested lignocellulosic materials, and inorganic contents (Manara and Zabaniotou, 2012). Biomass composition of sludge varied significantly due to differences in sources of wastewater and processes of sludge generation (Inoue et al., 1996; Jimenez et al., 2013; Ruggieri et al., 2008; Vriens et al., 1989). Diverse thermal degradation behaviours had been observed during thermochemical conversion and could be caused by both qualitative and quantitative variations of components in sludge (Thipkhunthod et al., 2006). Biomass composition in the waste mixtures could have different energy contents, reactivity of degradations and products released during the conversion due to variations in molecular structures, bond energy levels and physical structures of char formed (Channiwala and Parikh, 2002; Lv et al., 2010). Distinct thermochemical characteristics for different categories of compounds found in various types of biomass had been observed on the aspects of mass loss behaviours, heat of reactions and products evolution. Reactions between protein and lignin compounds with oxygen were demonstrated to be occurring at higher temperature compared to the oxidation of carbohydrates (Gomez-Rico et al., 2005; Kristensen, 1990). Xylan as a representative model compound for hemicellulose thermally degraded at lower temperature compared to cellulose in an inert environment (Orfão et al., 1999). During pyrolysis of lignocellulosic biomass, hemicellulose produced higher yield of CO₂, cellulose released more CO while lignin released more H₂ and CH₄ (Yang et al., 2007). Direct gasification of wood and biomass components also showed that the outputs gas composition of different types of woody biomass were similar to their respective major components (Hanaoka et al., 2005).

For sludge, composition also found to be very important in determination of thermal degradation behaviours and products evolution. Heterogeneity of sludge caused significant difficulties in understanding the pyrolysis and gasification pathways

since different and complex thermal degradation reactions occurred concurrently (Bengoa et al., 2011). Existing research classified sludge into three main fractions according to their corresponding thermal degradation temperature regions which were biodegradable materials degraded at 200-300°C, microorganisms at 300-400°C, and non-biodegradable polymers at 400-600°C (J. A. Conesa et al., 1997; Font et al., 2005). However, thermal stability of sludge may not correlate in a straightforward relationship to the degree of biodegradability as high thermal stability could also be observed for biodegradable materials such as proteins and lipids which thermally decompose at the range of 300-400°C (Kristensen, 1990; Thipkhunthod et al., 2007). Thermal degradation in a single temperature region could also involve more than a single category of biomass composition of sludge. Observations from lignocellulosic biomass thermal analysis showed that cellulose and hemicellulose decomposed actively in overlapping temperature regions at 300-350°C and at 250-320°C respectively while lignin decomposed in a wide temperature region from 150°C to 900°C (Biagini et al., 2006; Orfão et al., 1999; Thipkhunthod et al., 2006). Kinetics study of sludge pyrolysis further showed that high values of reaction order in the three suggested fractions indicating the presence of multiple compounds degraded simultaneously (Font et al., 2005). Fractional decomposition analysis based on comparison made to lignocellulosic biomass components also showed that sludge could be more complex and degrade differently in pyrolysis (Thipkhunthod et al., 2007). These findings suggested that main components of sludge and corresponding characteristics in thermochemical conversion processes needed to be further analysed and quantified. Existing composition analysis on sludge showed that about 33-50% of proteins, 6-10% of lipids and 3-20% of carbohydrates or fibres found in biological sludge samples after secondary treatment while relatively lower proteins contents at 18-24% and higher lipids contents at 10-18% found in primary, raw and digested sludge (Inoue et al., 1996; Jimenez et al., 2013; Manara and Zabaniotou, 2012). Limited study on sludge biomass components for thermochemical conversion processes found in the existing literature probably due to the complexity of composition in sludge.

2.3.2. Categorisation and quantification

Complete determination of biochemical compounds found in sludge would be highly challenging and complex. Since thermal degradation behaviours and products evolution of sludge could be more significantly affected by the differences between categories of main biomass components as compared to variations in molecular structure and chain length of compounds within the same category of biochemical components, biomass composition analysis of sludge should focus on the quantification of major composition instead of identifying all the compounds presence in sludge. Therefore biomass composition of sludge was divided into six categories for quantification and characterisation in this study. The six categories proposed in this study were ethanol extractives, water extractives, proteins contents, alkaline hydrolysed residues, acid digested residues and other organic matters. Further reviewed of existing literature was focused on these biomass components. Extractives were non-structural constituents. In general, hydrophobic extractives extracted by ethanol consisted of lipids, volatile fatty acids, waxes, pigments, resins, hydrocarbons and other hydrophobic materials while hydrophilic extractives extracted by water consisted of non-structural sugars, tannins, gums, colouring matters, alcohols, organic acids, nucleic acids and other intracellular substances (Edalatmanesh et al., 2010; Huang et al., 2010; Jimenez et al., 2013; Sluiter et al., 2010; Sun et al., 2004b). Hydrophobic extractives in sludge originated from a mixture of hydrophobic materials presence in the wastewater, phospholipids and cholesterol in cell membranes, metabolites of microorganisms, and by-products from cell lysis (Siddiquee and Rohani, 2011). Both polar and non-polar lipids in hydrophobic extractives of sludge. Polar lipids consisted of mainly phospholipids, steroids, and fatty acids while non-polar lipids consisted of mainly hydrocarbons, aromatics, and triglycerides. Ethanol as a polar organic solvent was selected for hydrophobic materials extraction from sludge to extract both polar and non-polar lipids in sludge. Polar organic solvents showed higher lipids extraction yield compared to non-polar solvents also supported that polar organic solvents were more suitable to extract widely diverse lipids in sludge (Dufreche et al., 2007). Ethanol and water extractions were also demonstrated to improve biomass compositional analysis on lignin and cellulose quantification through selective

removal of hydrophobic and hydrophilic extractives (Sluiter et al., 2010; Thammasouk et al., 1997). Therefore both extractions should be carried out before further isolation of other components in sludge.

No standardised method established for sludge protein analysis (Jimenez et al., 2013). Proteins content of sludge was commonly estimated by determination of elemental nitrogen content based on either Dumas method or Kjeldahl method and then multiplied by a factor of 6.25 (Ruggieri et al., 2008). Nitrogen-to-Protein factor (N-to-P) of 6.25 could be calculated from general protein molecular formula $C_{1656}H_{2620}N_{460}O_{494}S_{11}$ (Torabizadeh, 2011). However, significant amount of non-protein nitrogen presence in sludge varied the effective N-to-P factor significantly from 3.43 to 6.87 for different sludge samples and reduced the mean factor to 5.15 (Hattingh et al., 1967). In addition to protein polymers, microorganisms could also produce organic nitrogen in the forms of amino-sugar derivatives, nucleic acids and other organic molecules. Therefore, in general 70-80% of nitrogen contents in sludge could be contributed by amino acid nitrogen which represented total amount of protein contents in sludge (Kristensen, 1990; Vriens et al., 1989). Solubility of proteins in both of the extraction solvents, ethanol and water were demonstrated to be very low after unfolded at the temperature of extractions (Pace et al., 2004). Therefore ethanol and water extractions were suggested to be able to remove non-protein nitrogen and to improve estimation of protein contents in sludge. Alkaline hydrolysis and acid digestion were previously applied for isolations of biomass components. Alkaline hydrolysis was demonstrated to be able to isolate cellulose component and remove proteins, humic substances, hemicellulose and lignin in the sample (Li et al., 2014; Sun et al., 2004a). Cellulose isolated by sequential treatment of NaOH and H_2O_2 also showed higher molecular weight and crystallinity index with adequate purity of 94% compared to other isolation methods (Sun et al., 2004b). Acid digestion was demonstrated to be able to isolate acid insoluble lignin (Sluiter et al., 2010). Acid soluble lignin was assumed to be insignificant in sludge and only acid insoluble lignin was considered since acid soluble lignin weighted only about 6% of total lignin based on lignocellulosic biomass analysis. In addition, direct measurement of acid soluble lignin faced interference by other non-lignin components potentially presence in sludge that absorb UV in the same region (W.

Qi et al., 2011; Sluiter et al., 2010). Gravimetric corrections were suggested to be applied by determination of residual condensed protein and ash contents to improve estimation of alkaline hydrolysed and acid digested residues (Sluiter et al., 2010).

2.3.3. Thermochemical properties

Analysis of components in waste mixtures could also be carried out through thermogravimetric analysis system as thermochemical characteristics and thermal degradation behaviours of waste mixtures could be approximately accounted by using the summation of mass loss curves and degradation rate profiles of individual components respectively (Heikkinen et al., 2004). Devolatilization of biomass fuels could also be predicted by analyzing their chemical composition and summative law could be applied to predict the mass loss and volatilization of different species based on biomass composition of the feedstock (Biagini et al., 2006). The yield of volatiles and chars from lignocellulosic biomass could be estimated based on mass percentage of individual components and thermal degradation behaviours of lignocellulosic biomass could also be modelled by the summation kinetics model of the three major components which were cellulose, hemicellulose and lignin respectively (Orfão et al., 1999). Hence, superposition principle was applied in this study where degradation of waste represented by the summation of the degradation behaviours of individual component in the waste for simulations and synthetic sludge study based on the results from biomass composition analysis (Heikkinen et al., 2004). Products evolution during thermal degradation also analysed in this study because reaction stoichiometry was considered as an important aspect for comprehensive understanding of thermal decomposition of solids which included physical and chemical characterisation of the reactants and products (Galwey, 2003). Main permanent gases and volatile species categorised based on functional groups could be detected by FTIR system for products evolution analysis (Biagini et al., 2006). Therefore detection of volatile compounds released from sample during thermal degradation was also carried out by interconnected TGA-FTIR system. Char formation was an important parameter for kinetic model development during thermal degradation of sludge but it was not possible to determine experimentally

the mass of char formed during individual reaction and differentiated between char formed from different biochemical components and unreacted biomass solids (Urban and Antal Jr, 1982). Therefore, proximate analysis and analytical pyrolysis study of thermally induced degradations for individual components could potentially contribute in kinetics models development for sludge (Di Blasi, 2009).

2.4. Research gaps and current issues

Literature review carried out on waste management of sludge, thermochemical conversion process and biomass composition analysis revealed research gaps and current issues in thermal treatment and final disposal of sludge.

Heterogeneity of waste components in sludge created a significant challenge for waste management and resource recovery. Highly heterogeneous and complicated composition of sludge also increased the complexity in thermodynamics, kinetics and experimental research in thermal systems. Considerable amount of moisture, ash residues, contaminants, N and S containing compounds presence in sludge also caused potential problems in thermal system on energy recovery efficiency, ash sintering, fly ash generation and pollutants released. Therefore, holistic understanding on characteristics of sludge generated from different wastewater influents, stages of wastewater treatment plants, and with varying organic and inorganic composition needed to be established in order to develop flexible technologies for potential energy and resource recovery.

Characteristics of sludge found to be significantly different from traditional feedstock such as coal and lignocellulosic biomass. Current studies extensively focused on impacts of operating conditions in thermal system on sludge as showed in Table 2.1 and 2.2. Different operating parameters for pyrolysis and gasification studies on sludge were published including reactor designs, reaction types, operating temperatures, residence times, gas flow rates, feedstock input rates, gasifying agents applied, additives used and gasification ratios such as volume/mass-to-mass ratios, equivalence ratio (ER), gasifying ratio (GR), steam-to-biomass or carbon ratio (SB or SC). However, limited existing research studied the

impacts of composition and characteristics of sludge on thermochemical conversion processes. Therefore, comprehensive study needed to categorise and quantify the composition of sludge while correlating to the behaviours and performance of sludge in thermochemical conversion processes.

Thermochemical conversion processes such as pyrolysis, gasification and incineration were considered potential solutions in near future for sludge management although no general consensus was achieved on the most efficient and suitable method for sludge treatment and final disposal (Fonts et al., 2012). However, thermally induced degradation occurred in all single-stage or multiple-steps conversion processes and could be considered as primary reactions that important to system design and modelling. Therefore detail thermal degradation behaviours analysis could contribute to the research of sludge thermal conversion

Table 2.1: Comparison on pyrolysis studies of sludge.

Type of sample	Reactor design	Reaction type	Operating parameters				Research focus	Reference
			Temp °C	Residence time/Flowrate		Feedstock input		
				Solid	Gas			
Digested sludge	Fluidized bed	Fast	530	5.7min	3s	6-16g/min	Torrefaction pretreatment	Atienza-Martinez et al., 2015
Activated sludge	Fixed bed	Slow	400-800	60-100 min	-	10 g	Energy analysis	Agarwal et al., 2005
Digested sludge	Fluidized bed	Fast	550	-	100 ml/min	3 g/min	Sequential process	Ábrego et al., 2013
Activated sludge	Microwave ovens	Fast	1040	10 min	100 ml/min	15 g	Microwave pyrolysis	Dominguez et al., 2006
Digested sludge	Fluidized bed	Fast	550	4.5 g/min	4.5 L/min	4.5 g/min	Pyrolysis liquids	Fonts et al., 2009
Digested sludge	Fixed bed	Slow	450-850	12-150 min	100 ml/min	20 g	Yields distribution	Inguanzo et al., 2002
Primary Activated Digested	Fixed bed	Slow	250-500	-	20 min	5 g	Zeolite catalyst	Kim and Parker, 2008
Sewage sludge	Fixed bed	Slow	400-550	-	40 ml/min	50 g	Mass/energy balance	Z. Wang et al., 2012

Table 2.2: Comparison on gasification studies of sludge.

Type of sample	Reactor design	Gasifying agent	Operating paramters			Research focus	Reference
			Temp °C	Gasification ratio	Feedstock input		
Sewage sludge	Downdraft autothermal	Air	1000	2.28 - 2.34 m ³ /kg	3.70 kg/h	Autothermal	Dogru et al., 2002
Digested sludge	Two-stage Fludized bed	Air	770 - 807	0.17 - 0.20 ER	1000 g	Multiple additives	Mun and Kim, 2013
Dried sludge	Fixed bed allothermal	Steam	900	5.62 mol/mol SC	35 g	Steam input	Nipattummakul et al., 2010
Digested & undigested	Downdraft allothermal	Air	800	0.05 m ³ /h	100 g	Moisture 0-53%	Xie et al., 2010
Pyrolysed sludge char	Fixed bed	Steam CO ₂	750 - 850	100 ml/min	3 g	Sequential process	Ábrego et al., 2013
Dried sludge	Fludized bed allothermal	Air Steam	750 - 850	0.2 - 0.4 ER 0 - 1 g/g SB	1-2 g/min	Alumina 0-15%	De Andres et al., 2011a
Dried sludge	Fludized bed allothermal	Air Steam	750 - 850	0.3 ER 0 - 1 g/g SB	1.4 g/min	Multiple additives	De Andres et al., 2011b
Digested & char	Fludized bed allothermal	Air, O ₂ , Steam	770 - 850	0.8 - 1.1 g/g GR 0.12 - 0.32 ER 0.27 - 0.71 g/g SB	2.1 g/min	Comparison sludge/char	Gil-Lalaguna et al., 2014
Digested sludge	Fludized bed allothermal	Air	750 - 850	0.25 - 0.35 ER	2-5 g/min	Alumina	Manya et al., 2005
Pyrolysed sludge char	Fixed bed allothermal	Air	800 - 850	0.35 - 0.40 ER	20 g	Mass/energy balance	Z. Wang et al., 2012

3. General Materials and Methods

This chapter described the materials and methods generally used in this thesis. Detailed materials and methods for specific studies will be specified in respective chapters.

3.1. Sludge sampling

Sludge samples were collected from all four existing Water Reclamation Plants (WRPs) in Singapore. Changi WRP received wastewater from domestic sources only for while other WRPs (Ulu Pandan, Jurong and Kranji) were treating wastewater from industrial and domestic sources. Collection of sludge was carried out once in a month at one selected WRP. Sludge samples from Ulu Pandan and Changi WRPs were collected twice for comparison over different time while samples from Jurong and Kranji WRPs were collected once for comparison over different plants. Collection of Batch 1 and Batch 2 samples were carried out during the period of December 2012 to March 2013 and December 2013 to January 2014 respectively. Preliminary study showed that characteristics of digested, dewatered and dried sludge samples from the same plant were highly similar. Therefore, only one type of dewatered or dried sludge from each WRP was selected for further analysis. Drying system only existed in Changi WRP therefore dried samples were collected while dewatered samples were collected from three other WRPs as end products. Intermediate sludge samples before anaerobic digestion (AD) were also collected. Five types of sludge collected were primary, secondary, raw, dewatered and dried sludge. To obtain representative samples, at least 25L of liquids and 20kg of solids were collected. In total, 14 sludge samples were analysed and compared based on plant, type and batch categorisation. Primary sludge was categorised as residue from primary treatment where coagulation, flocculation, physical screening and sedimentation were used to remove solid residues from incoming wastewater. Cationic polyacrylamide was used as polymer additive for flocculation and sedimentation in WRPs. Secondary sludge was residue generated from activated sludge process. Raw sludge was mixture of primary and secondary sludge

before transferred into anaerobic digester with primary-to-secondary sludge mass ratio of 1.4-1.6. Dewatered sludge was residue collected after AD and mechanical dewatering. Dried sludge was residue collected after thermal drying. Figure 3.1 showed schematic of wastewater treatment system and collected samples.

Figure 3.1: Schematic representation of wastewater treatment system and different types of sludge samples collected from various treatment stages.

3.2. Sample pre-treatment

Sludge samples collected were dewatered by using centrifuge (liquid samples of primary, secondary and raw sludge) and dried in oven (all sludge samples collected) at 105°C for 24 hours. Dried samples were then comminuted by cutting mill to pass through a screen of 1.00mm in diameter into powder form. Impacts of particle size on thermochemical conversion processes and extraction and isolation analysis for biochemical components found to be diminished as size reduced and it could be considered as insignificant when less than 1.20mm (Bogomolov et al., 2013; Nilsson et al., 2012; Sluiter et al., 2010). Sludge in powder form was mixed manually to obtain homogenous sample. Due to the heterogeneity and complexity of contents in sludge, no sieving applied in order to obtain representative characteristics data. Model compounds in powder form and extractives from sludge were dried in oven at 60°C for 24 hours or until constant weight measured before analysed.

3.3. Analytical methods for physical properties

3.3.1. Heating value analysis

Higher Heating Value (HHV) of sample was determined by using Calorific Bomb (IKA C2000) according to ASTM E711. Lower Heating Value (LHV) could be obtained after deducting energy loss in water vaporisation with Equation 3.1, $LHV = HHV - 2.26 \times (9H/100)$ where LHV and HHV were lower and higher heating values expressed in MJ/kg, H was mass percentage of hydrogen in sludge, 2.26 MJ/kg was heat of vaporisation of water and digit nine referred to water produced during combustion in relation to hydrogen contents of sample.

3.3.2. Proximate analysis

Proximate analysis measured moisture content, volatile matter, fixed carbon and ash content in sample according to physical tests. Moisture of sample was recorded by measuring loss of mass after evaporating water content at 105°C in an oven for 24 hours. Volatile matter (VM) content of dried sample was determined as loss of mass after being heated in crucible using STA 449 Jupiter[®] (Netsch) to 950°C and maintained for 7 minutes in an inert environment with continuous flow of 60ml/min nitrogen gas according to ASTM D7582. Ash content of dried sample, Ash₅₅₀ and Ash₉₅₀ were recorded as the mass remained after being heated in a furnace at 550°C and 950°C for 3 hour respectively. 550°C was temperature commonly used to separate between volatile solids and fixed solids in sludge while 950°C was the standard temperature used in proximate analysis of coal and biomass. Fixed carbon (FC) was estimated by difference from the dry sample mass after subtracted ash and VM content for determination of non-inorganic char residues remained.

3.3.3. 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 capacity at constant pressure (C_p) was measured by using Differential Scanning Calorimetry (DSC) in STA 449 Jupiter[®] (Netszch). Heat fluxes of empty crucible without lid (Φ_0), crucible with reference materials (Φ_{ref}) and crucible with sample (Φ_s) were measured relative to an empty crucible (Höhne et al., 2003). Heat capacity estimated by using Equation 3.2, $C_s = (\frac{\Phi_s - \Phi_0}{\Phi_{ref} - \Phi_0} \times \frac{m_{ref}}{m_s}) C_{ref}$ where C_s and C_{ref} were heat capacity in J/g-K of sample and reference material respectively while m_s and m_{ref} in mg were the mass of sample and reference materials respectively. Correlation for general application could be further derived as Equation 3.3, $C_s \propto (\frac{\Phi_s - \Phi_0}{m_s})$. Heat capacity analysis should be carried out at temperature below thermal decomposition of sample therefore analytical pyrolysis of all sludge samples collected was carried out to determine the initial degradation temperature (Chen et al., 2014). In this study, temperature program started from initial temperature at 323K (50°C) for 10 minutes and raised to 403K (130°C) at 2.5K/min and maintained for 10 minutes before cooling down to 323K at same heating rate and the temperature program repeated once. Each test consisted of two cycles of heating and cooling segments. Mean heat flux was calculated from two cooling segments as the repeatability of these segments and consistency of the heat flux data were higher compared to heating segments. Heat fluxes of selected temperature region of 343K to 393K (70°C to 120°C) were recorded for C_p analysis. Reference materials used and corresponding specific heat fluxes at different temperature were showed in Table 3.1. By using Equation 3.3, multiple linear correlations at different temperatures for specific heat flux (mW/mg) with the mean C_p of reference materials were established and showed in Table 3.2 and Figure 3.2.

Table 3.1: Heat capacity and specific heat flux for reference materials.

Reference materials	Heat capacity C_p , J/g-K	Specific heat flux, mw/mg					
		343 K	353 K	363 K	373 K	383 K	393 K
Cellulose	1.58	-1.05	-1.06	-1.07	-1.08	-1.09	-1.10
Aluminium	0.91	-1.03	-1.04	-1.04	-1.05	-1.05	-1.04
Zinc	0.39	-1.02	-1.02	-1.02	-1.02	-1.02	-1.01
Gold	0.13	-1.00	-1.00	-1.00	-1.00	-1.00	-0.99

Table 3.2: Linear correlations of heat capacity and specific heat flux.

Temperature K	Linear correlations	Coefficients of determination, R^2
343	$C_1 = -28.27 \Phi_1 - 28.21$	0.9741
353	$C_2 = -23.13 \Phi_2 - 23.06$	0.9795
363	$C_3 = -19.72 \Phi_3 - 19.64$	0.9845
373	$C_4 = -17.42 \Phi_4 - 17.29$	0.9893
383	$C_5 = -15.63 \Phi_5 - 15.47$	0.9940
393	$C_6 = -13.88 \Phi_6 - 13.63$	0.9866

Figure 3.2: Linear correlations of C_p and specific heat flux for reference materials.

3.4. Analytical methods for chemical properties

3.4.1. Ultimate analysis

CHNS contents were determined by using Vario EL cube (Elementar) according to ASTM E870 and oxygen content was determined both by direct measurement using the same equipment and by calculation using the method of by difference according to ASTM D3176. Direct measurement of oxygen content was carried out by pyrolysis of sample at 1150°C with the presence of carbon materials according to ASTM D5622.

3.4.2. Functional group analysis

FTIR spectra of solid and liquid samples in condensed phase were collected by using Attenuated Total Reflection (ATR) with diamond crystal in FTIR System (Bruker). FTIR spectra of samples in gaseous or volatiles phase were collected with Mercury-Cadmium-Telluride (MCT) detector with continuous spectra collection at spectral resolution of 4 cm⁻¹. Mid-infrared region (MIR) from 4000 cm⁻¹ to 600 cm⁻¹ was applied (Ena Smidt et al., 2011; Smith, 1998). Spectra were analyzed according to absorbance bands identified and recorded in library databases and previous publications (Edalatmanesh et al., 2010; Reveille et al., 2003; Sluiter et al., 2010; Ena Smidt et al., 2011; E. Smidt and Meissl, 2007; Smith, 1998). Table 3.3 and 3.4 showed wavenumber of peaks, corresponding functional groups and suggested compounds determined for condensed phase and gaseous or volatiles phase respectively (Biagini et al., 2006; Ferrasse et al., 2003; Tian et al., 2014; Yang et al., 2007). Samples in condensed phase analysed including sludge samples collected, char and ash residues formed from pyrolysis and combustion of sludge samples, biomass composition extracted and isolated, model compounds selected and synthetic sludge formed. Samples in gaseous or volatiles phase analysed including gases and volatile compounds evolved during thermal degradation of the solid and liquid samples studied.

Table 3.3: Functional groups and suggested compounds of FTIR spectra.

Wavenumber	Functional groups	Suggested compounds
3710 - 3620	O–H	Inorganic hydroxyl groups
3500 - 3200	O–H, N–H	Alcohols, acids, amides, amines
3080 - 3070	C–H	Unsaturated hydrocarbon, aromatics
2980 - 2850	C–H	Saturated hydrocarbon, ethers, lipids
1750 - 1640	C=O	Aldehyde, ketone, acids, esters, amides
1680 - 1595	C=C	Unsaturated carbon chain backbones
1650 - 1580	C=O, N–H	Amides, amines
1600 - 1500	Rings	Aromatics, lignin
1550 - 1500	N–O	Nitro group
1540 - 1510	N–H	Amides
1525 - 1470	Rings	Aromatics
1460 - 1440	C–H	Saturated hydrocarbon, ethers, lipids
1440 - 1395	O–H, COO ⁻	Carboxylic acids, alcohols
1430 - 1390	C–N	Primary amides
1450 - 1330	S–O	Sulphur organics compound
1400 - 1300	O–H	Alcohols
1395 - 1365	C–H	Saturated hydrocarbon, aldehyde, lipids
1390 - 1330	N–O	Nitro compounds
1350 - 1250	C–N	Amines
1340 - 1310	S–O	Sulphur organic compounds
1320 - 1250	C–O	Carboxylic acids
1250 - 1000	C–O, C–N	Polysaccharides, alcohols, esters, amides, amines
1240 - 1135	S–O	Sulphur organic compounds
1240 - 1085	P=O	Phospholipids
1210 - 1070	C–O–C	Polysaccharides, ether
1200 - 940	Inorganic	Silicates, sulphates, phosphates, clay minerals
960 - 900	O–H	Carboxylic acids
920 - 880	C=C–H, C–O–C	Unsaturated-carbon, aromatics, glycosidic-bonds
890 - 820	C–O–C	Ether
850 - 650	C–H	Unsaturated hydrocarbon, aromatics
810 - 750	Inorganic	Silicates, nitrites, minerals
800 - 600	C–Cl	Halogenated organic compounds
750 - 700	N–H, Inorganic	Amides, amines, carbonates, nitrates
700 - 680	Rings	Aromatics
680 - 610	Inorganic	Sulphates

Table 3.4: Functional groups and suggested compounds for TGA-FTIR spectra.

Wavenumber	Peaks identified	Functional groups	Suggested compounds
4000 – 3500	3853, 3736, 3649	O-H	Water vapour
3500 – 3100	3590, 3582	C-OH	Phenol, carboxylic acids
	3334	N-H	Ammonia, NH ₃
	3314, 3308, 665	C≡N	Cyano compounds
3100 – 2800	3077	C-H	Benzoic acids
	3059	C-H	Benzene, toluene, phenol, amine
	3017, 1305	C-H	Methane
	2970, 2954, 2917	C-H	Alkane, alkene, ketone, alcohol
	2934, 2836	C-H	Cyclo-alkane
	2892	C-H	Ether
3100 – 2600	2728, 2704	H-Cl	Hydrochloric acid
2600 – 2000	2359, 2344, 669	C=O	Carbon dioxide, CO ₂
	2250	C≡N	Fulminic acid, HCNO
	2238, 2217	N-O	Nitrous oxide, N ₂ O
	2178, 2167, 2112	C≡O	Carbon monoxide, CO
	2063	C=O=S	Carbonyl sulfide
2000 – 1250	1653, 1541, 1508	O-H	Water vapour
1900 – 1800	1900, 1850	N-O	Nitrogen oxides
1800 – 1600	1799, 1779, 1758	C = O	Carboxylic acids, esters, amides
	1769	C = O	Benzoic acids
	1739, 1738, 1730	C = O	Ketones, amides
	1604	C-OH	Phenols
1600 – 1250	1590, 1327, 1275	C=O, N-H	Amides
	1541, 1526	C-S	Carbon disulphide, CS ₂
	1482, 1471, 1442	C-H	Alkanes, alkenes, benzene
	1380, 1370	S-O	Sulphur dioxide, SO ₂
1250 – 1000	1246	C-O-C	Esters
	1194, 1167	C-O-C	Ether
	1187, 1179, 1120	C-OH	Phenol, carboxylic acids,
	1066, 1054	C-OH	Alcohol
1000 – 600	998, 968, 913	C=C	Alkene
	966, 931	N-H	Ammonia, NH ₃
	780, 758	N-H	Amine
	771	C-Cl	Chloro-compounds
	749, 713	Aromatics	Phenol, benzoic Acids
	728, 690, 673	Aromatics	Toluene, benzene
	726	C=C, rings	Furans
	714, 712	H-C ≡ N	Cyanide

3.5. Analytical methods for pyrolysis

3.5.1. Thermal analysis

Analytical pyrolysis was carried out in STA 449 Jupiter[®] (Netsch) inter-connected with FTIR system (Bruker). Simultaneous thermal analysis (STA) was carried out where TGA measured mass loss data of sludge thermal degradation while simultaneously DSC measured heat transfer signals based on temperature differences between crucible with samples and reference crucible in heating chamber. Heat of pyrolysis, $\Delta H_{\text{pyrolysis}}$ was measured at main degradation region of the samples studied. Linear baseline was established for DSC signals recorded and the area under the curve was calculated as heat of pyrolysis.

9.00 $\pm$ 0.50mg of sample placed in alumina, Al₂O₃ crucible and heated using temperature programme with constant heating rate from initial temperature at 100°C to final temperature at 950°C. Multiple heating rates of 5, 10, 15, 20, and 25 K/min were applied with reference to thermal analysis data collection procedure suggested by ICTAC Kinetics Committee (Sergey Vyazovkin et al., 2014). Continuous nitrogen flow of 60 ml/min was supplied to provide inert environment inside the heating chamber and to transfer volatile compounds evolved from thermal degradation for FTIR detection. Five different heating rates were used in this study to provide reliable determination of kinetic parameters. No lid for crucible was used to reduce secondary char formation reactions. Continuous flow of nitrogen gas at 60ml/min was supplied to provide inert environment and to remove volatile compounds released from heating chamber while maintaining atmospheric pressure of the system.

Systematic errors of STA system could be reduced by calibration using reference metals, blank run with empty crucible and initialization stage at 100°C with nitrogen flow for 30 minutes before experiment. Temperature and DSC signals were calibrated by using at least five different metals as reference compounds with distinctive melting temperature and heat of melting. Metals were selected based on individual melting temperature as compared to the temperature range of experiments. Blank run with empty crucible before sample testing allowed

background correction for buoyancy effects on mass measured. Initialization stage removed any residual moisture in the pre-dried samples and purged out any residual air inside heating chamber to maintain inert environment for study with focus on thermally induced degradations.

3.5.2. Products evolution analysis

STA system was connected to FTIR equipped with MCT detector by transfer-line and flowcell maintained at 200°C to transfer volatile compounds evolved from thermal degradation of sample. Based on pyrolysis of model compounds with single peak of degradation in DTG and single peak of absorbance detected in FTIR, the time needed for volatile compounds to transfer from STA system to FTIR detector was estimated at an average of 5 minutes for heating rate at 10K/min or 50°C difference on TGA data and FTIR spectra recorded. Correction was carried out accordingly to determine the reaction temperature for volatile compounds as identified in FTIR spectra.

Gas samples collected from experimental pyrolysis system 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 released during pyrolysis of sludge which were hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂) by using Thermal Conductivity Detector (TCD) while methane (CH₄) and C₂ to C₅ hydrocarbon gases by using Flame Ionization Detector (FID) (Dominguez et al., 2006; Inguanzo et al., 2002). 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% CH₄, 1.0% CO, 3.0% CO₂, 0.1% O₂ and 14.7% C₂-C₅ gases.

3.6. Statistical analysis

Statistics analysis used in this study were showed in Equation 3.4-3.7 for calculation of mean, standard deviation (SD) and relative standard deviation (RSD%) and Coefficient of determination (R²). Equations 3.8-3.10 were used to analyse the usage of two different calculation methods and compare estimated values with measured data.

$$\text{Mean, } \mu = \frac{\sum x}{n} \quad \text{Equation 3.4}$$

$$\text{Standard deviations, } SD = \sqrt{\frac{\sum (x-\mu)^2}{(n-1)}} \quad \text{Equation 3.5}$$

$$\text{Relative standard deviations, } RSD\% = \frac{SD}{\mu} \times 100\% \quad \text{Equation 3.6}$$

$$\text{Coefficient of determination, } R^2 = \left[\frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}} \right]^2 \quad \text{Equation 3.7}$$

$$\text{Bias Error, } \epsilon_{\text{Bias}} = \text{Data}_{\text{measured}} - \text{Data}_{\text{calculated}} \quad \text{Equation 3.8}$$

$$\text{Absolute Error, } \epsilon_{\text{Abs}} = \sqrt{(\epsilon_{\text{Bias}})^2} \quad \text{Equation 3.9}$$

$$\text{Percentage of Error, } \epsilon_{\%} = \frac{\epsilon_{\text{Abs}}}{\text{Data}_{\text{measured}}} \times 100\% \quad \text{Equation 3.10}$$

4. Comprehensive characterisation study of sludge for advanced thermochemical conversion processes

Findings in this chapter were summarised and published as an original research paper: Chan, W.P. and Wang, J.-Y. (2016) “Comprehensive characterisation of sewage sludge for thermochemical conversion processes – Based on Singapore survey.” *Waste Management*, Vol. 54, pp. 131-142.

4.1. Introduction

Differences in sources of wastewater and wastewater treatment technology applied were resulting in significant variations on the characteristics of sludge generated (Fytli and Zabaniotou, 2008; Spinosa, 2007). Due to the complex nature, characterisation of sludge should also be carried out specifically to the targeting treatment and disposal methods (Sanin et al., 2011). Hence, characterisation study specifically for thermochemical conversion processes was necessary for sludge generated from all WRPs in Singapore which functioned as both wastewater treatment and water reclamation facilities in order to develop and optimise suitable technology for sludge thermal treatment and its final disposal. Existing studies extensively focus on anaerobic digested sludge as final solid residues from wastewater treatment plants (Fonts et al., 2012). In this study, comparison analysis extended to different types of sludge in order to achieve a more comprehensive understanding on sludge generated from different stages of wastewater treatment processes. Sludge samples were collected based on type, plant and batch categorisations. Properties for sludge handling and storage such as physical appearance, pH and density were determined. Physical properties included heating value, proximate analysis, heat capacity and chemical properties included ultimate analysis, inorganic composition and functional groups based on FTIR spectra were determined for all sludge samples collected (Arena, 2012). Further analyses were carried out based on measured data including residual energy, heating value correlation, char residues components analysis, mass balance equations, oxidation of inorganics and ash sintering study.

4.2. Materials and Methods

4.2.1. Physical properties

4.2.1.1. Physical appearance, pH and density analysis

Physical appearances of sludge were recorded based on colour, odour, and structural form. pH tests were carried out by using two methods. In the first method, sludge samples were wetted by deionised water and tested directly with semi-solid portable pH meter D-51E (HORIBA). In second method, US EPA Method 9054D was used. 20g of sludge was placed in a 100-ml beaker with addition of 30ml deionised water. The mixtures were continuous stirred for 5 minutes and allowed to settle for 15 minutes. pH of solutions was measured by pH meter. Bulk density of sludge was estimated by dividing mass of sample measured in measuring cylinder with fixed sample volume of 20 cm³. Pellet density of sludge was estimated by dividing mass of pellet with volume measured. Sludge pellet at average height of 3.64mm were prepared by using milled sludge powder pressed in a die with 12.17mm diameter at 5MPa for 1 minute using mechanical hydraulic pelletiser.

4.2.1.2. Heating value analysis

HHV and LHV of sludge were measured and recorded on dry basis (db), dry ash free basis (daf), and total inorganic contents free basis (icf). Heating value on daf was calculated based on ash content of sludge at 550°C where only inorganic fixed solids remained after combustion. Heating value on icf was calculated by using total inorganic contents (TI) based on the summation of inorganic matter (IM), halogens and inorganic CHNSO contents in sludge. Both daf and icf were used to eliminate the apparent underestimation effect on heating values caused by the presence of inorganic contents in order to quantify and understand the intrinsic characteristics of organic matters in sludge. Ash content was frequently used in existing research as an approximation to the amount of inorganic compounds in sludge. However, ash content of sludge significantly overestimated inorganic content in sludge due to oxidation of inorganic elements as demonstrated in inorganic composition and ultimate analysis in this study. Therefore, icf basis was suggested as an improved estimation basis for heating values quantification of organic matters.

Residual energy analysis was carried out based on heating value and moisture content of sludge samples collected. Residual energy content $Q_{Residual}$ was determined by using Equation 4.1, $Q_{Residual} = Q_o - Q_w$ where total sludge energy content $Q_o = m_o h_o$ and evaporation energy loss $Q_w = m_w h_w$. Mass balance of sewage sludge $m_o + m_w = 1$ where m_o and m_w were the mass fractions of sludge solids and moisture respectively in the sludge samples as received while h_o and h_w were LHV in db and latent heat of evaporation. Moisture content in sludge said to be at critical level when zero residual energy remained where any reduction of moisture below this level would result in net positive residual energy for recovery. At zero residual energy $Q_{Residual} = 0$, then $Q_o = Q_w$ and critical moisture content calculated by using Equation 4.2 derived as $m_{w,critical} = 1 - h_w / (h_o + h_w)$. 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 $h_{effective}$ when net recoverable energy determined. Therefore the practical level of $Q_{Residual}$ and $m_{w,critical}$ would be lower.

A unified correlation for calculating HHV (db) of a sample from its elemental composition was developed (Channiwala and Parikh, 2002) and showed as Equation 4.3, $HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$. Where C, H, S, O, N and A represent the carbon, hydrogen, sulphur, oxygen, nitrogen and ash mass percentage in the sample respectively expressed in db. 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 all sludge samples when oxygen contents and inorganic contents data determined by different methods. Therefore, two separate calculations of HHV with the above correlation were carried out by using different oxygen and inorganics mass percentage (mass%). Calculation 1 was based on direct measurement of oxygen contents and indirect calculation of IM contents. Calculation 2 was based on oxygen contents determined using by difference method and direct measurement of ash contents at 950°C. This correlation established based on empirical results and could be used to calculate heating value of sample from its elemental composition when HHV measurement was not available. When both HHV and elemental composition data were available,

the correlation could be used for cross verification on the accuracy of measured data. The correlation could also be useful when dealing with complex and unknown waste samples in order to identify any irregular characteristics compared to other feedstock for thermochemical conversion processes.

4.2.1.3. Proximate analysis

Moisture content of sludge was recorded in as received basis. Ash content of dried sludge was measured at 550°C and 950°C. Organic matters in sludge would be combusted and formed gaseous volatile compounds at 550°C while inorganics would be partially decomposed and the residues either remained inert or oxidised to form solids ash residues. Further inorganics decomposition and oxidation would occur as sludge heated to 950°C suggested by the results of proximate and ultimate analysis in this study. Multiple heating rates programmes with 5, 10, 15, 20, 25 K/min were applied to measure VM content and mean was calculated. However, oxidation of inorganic matter in sludge during ash forming test overestimated the inorganic residuals presence in char and therefore underestimated the FC. Fixed Residues (FR) was proposed in this study to improve the estimation on the inorganic residues remained in sludge solids after thermally degraded in inert environment or pyrolysed. Fixed Residues (FR) was estimated by difference from the dry sample mass after subtracted inorganic matters (IM) and VM content. IM content was calculated based on mass balance equations developed by ultimate analysis in this study. Ratio of Ash₉₅₀/IM and apparent degree of oxidation (O_D) describing the oxidation of IM to ash for sludge were also calculated by assuming Ash₉₅₀ represented oxidised IM where $O_D = (Ash_{950} - IM)/IM \times 100\%$. For comparison, CHNS data of char solids at 950°C was considered and used as representative data to account for the mass% of non-inorganic residues. CHNS data of Char₉₅₀ were calculated based on the CHNS of char produced from sludge pyrolysis in inert nitrogen gas environment at 500°C for 40 minutes and subtracted by CHNS of Ash₅₅₀ which would decompose into volatiles at 950°C. Oxygen content of Char₉₅₀ was assumed to be irrelevant because most of the oxygen compounds in sludge were released at 950°C and most of the oxygen remained in char would be bounded with inorganic compounds and be categorised as part of the IM. In order to further analyse impacts of IM contents, level of O_D , and intrinsic

distribution ratio ($R = VM/FR$) on apparent distribution ratio of sludge samples ($R^* = VM/FC$), simulations based on relationships of these four parameters were developed. VM released could be determined by intrinsic distribution ratio R after considered the mass of IM. Based on Equation 4.7 derived, three independent variables which were IM, R and O_D accounted for variations in dependent variable R^*/R . Three sets of simulations were carried out where each single parameter was used as independent variable and other two parameters were fixed at constant values using data from proximate analysis of sludge as reference values.

For sample consisted organic matters only,

$$\frac{VM}{FR} = R = R:1 \text{ therefore } VM = 100\% \times \frac{R}{R+1}$$

For sample consisted both organic and inorganic matters,

$$VM = (100\% - IM) \times \frac{R}{R+1}$$

For oxidation of inorganic matters,

$$Ash = IM \times \left(\frac{O_D}{100} + 1\right) \text{ where } O_D = (Ash_{950} - IM)/IM \times 100\%$$

$$R^* = \frac{VM}{FC} \text{ and } R^* = \frac{(100-IM) \times \frac{R}{R+1}}{100 - \left[(100-IM) \times \frac{R}{R+1}\right] - \left[IM \times \left(\frac{O_D}{100} + 1\right)\right]}$$

$$\frac{R^*}{R} = \frac{(100-IM)}{100 + \left[R - R\left(\frac{O_D}{100} + 1\right) - \left(\frac{O_D}{100} + 1\right)\right] \times IM} \quad \text{Equation 4.4}$$

4.2.2. Chemical properties

4.2.2.1. Ultimate analysis

Ultimate analysis carried out through direct determination provided approximately total measurement of elemental contents, $CHNSO_{Total}$ as the summation of both organic and inorganic $CHNSO$ contents in sludge. $CHNSO_{Inorganic}$ content of sludge was estimated by carrying out ultimate analysis on Ash_{550} and calculated in dry sludge basis (dsb). $CHNSO_{Organic}$ was calculated based on Equation 4.5. O direct determination partially or minimally measured oxygen from inorganic oxides in sludge due to strong resistant to decomposition. This amount of oxygen was

assumed to be insignificant in sludge samples based on the findings from previous studies that suggested metals content of sludge were mainly in the form of leachable organic fractions (Hernandez et al., 2011; Zorpas et al., 2001). Non-metals oxides such as SiO₂ remained as inert inorganics. Therefore, direct determination of CHNSO_{Total} could approximately represent the total CHNSO of organics and inorganics in sludge other than inert oxides which were categorized as inorganic matters. Significant amount of oxides formed in ash residues of sludge after combustion but due to strong resistant to decomposition of the oxides, amount of oxygen added to ash residues during combustion would not significantly increase oxygen contents of CHNSO_{Inorganic} direct measurement. Therefore, CHNSO_{Inorganic} would mainly account for decomposition of carbonates, nitrates and sulfates that remained after combustion of sludge at 550°C (Vassilev and Tascon, 2003). Thus, mass balance approximation showed as Equation 4.5 could be formed. In addition to CHNSO_{Total} measured, sludge also consisted of inorganic matters and halogens. Release of halogens through combustion was measured in this study and the inorganic matters (IM) was calculated by difference. The approximated mass balance for sludge and inorganics could be represented by the Equation 4.6 and 4.7. Using by difference method, oxygen content determined with Equation 4.8.

$$CHNSO_{Total} \cong CHNSO_{Organic} + CHNSO_{Inorganic} \quad \text{Equation 4.5}$$

$$CHNS_{Total} + O_{Total} + IM + Halogens \cong 100\% \quad \text{Equation 4.6}$$

$$TI \cong IM + Halogens + CHNSO_{Inorganic} \quad \text{Equation 4.7}$$

$$CHNS_{Total} + O_{difference} + Ash_{950} + Halogens \cong 100\% \quad \text{Equation 4.8}$$

However, determination of O_{Total} and O_{difference} of sludge samples collected showed significant deviations based on the results obtained in this study. Both values cannot be used interchangeably. During ash formation analysis, sludge was combusted. High temperature oxidative environment transformed the inorganic matters into ash residues that remained as solids and released volatile inorganics into gas phase. Mass balance could be described by the Equation 4.9. Assuming negligible volatile inorganics released other than CHNSO_{Inorganic} already accounted compared to residues remained during ash formation analysis, Equation 4.9 could be further

simplified into Equation 4.10. This assumption was based on previous studies which showed that most of the inorganics of sludge retained in solids residue during thermochemical conversion such as pyrolysis and gasification while heavy metals showed partial retention (Fytili and Zabaniotou, 2008; Hernandez et al., 2011). This assumption supported by inorganic elements analysis in this study which demonstrated that most of the inorganic elements in sludge were non-volatile ash forming elements. Equations 4.12 could be derived by using Equations 4.6, 4.8, 4.10 and 4.11. Therefore, the deviations found in two methods for oxygen contents determination could be accounted by the oxidation of inorganics in sludge.

$$IM + O_{oxidation} = Volatile\ Inorganics + Ash_{950} \quad \text{Equation 4.9}$$

$$IM + O_{oxidation} \cong Ash_{950} \quad \text{Equation 4.10}$$

$$O_{Total} - O_{difference} = O_{deviation} \quad \text{Equation 4.11}$$

$$O_{deviation} \cong Ash_{950^{\circ}C} - IM \cong O_{oxidation} \quad \text{Equation 4.12}$$

Molecular formula of sludge could be determined by converting dry basis CHNSO contents into molar basis. Molar basis CHNSO could be calculated by dividing mass% with respective molecular weight and could be normalized by dividing all molar basis data with the moles of C presence respectively. Quantification of total organic carbon was also carried out by reacting 2.0 M HCl solutions with sludge samples to remove inorganic carbon in the form of carbon dioxide (Schumacher, 2002). Both untreated and treated samples were tested for Total Carbon (TC) and Total Organic Carbon (TOC) in Multi N/C@ UV (AnalytikJena).

4.2.2.2. Inorganic composition analysis

For quantification of halogens released during combustion, sludge weighted 0.50 ± 0.05 g was combusted in Calorific Bomb (IKA C2000) with 5ml of Na_2CO_3 solution (50g/L) according to ASTM D808 and then tested by Ion Chromatography System (Dionex ICS-1100) to quantify the concentration of anions presence. Combustions tests were duplicated and halogen anions detections were triplicated. Mean values of mass% in db of detected fluoride, chloride and bromide ions were calculated. For quantification of other inorganic elements, sludge was treated with

acids digestion in Ethos One Microwave Digestion System (Milestone) using US-EPA Method 3052 and DIN EN 13346 (for phosphorus) and then sent to Optima 8000 ICP-OES Spectrometer (Perkin-Elmer) for inorganic elements detection. Acids digestion tests were duplicated and ICP-OES detections were triplicated.

Inorganic elements were categorised into four groups as major ash forming elements, minor elements, trace elements and non-detectable elements according to mass% in sludge respectively. Major ash forming elements and their corresponding oxides in sludge identified in previous studies were SiO_2 , Al_2O_3 , TiO_2 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , and P_2O_5 (Dunnu et al., 2010; Wang et al., 2012; Werle, 2014). Silica (SiO_2) was calculated based on differences between mass% of Ash_{950} and mass% of oxides of the other main ash forming elements. It was assumed that major ash forming elements were in oxides form and other inorganic elements were presence in insignificant amount in ash residues. Silicon element in sludge was calculated based on its mass% in silica. Inorganic elements having average mass% of more than and less than 50ppm in dsb among the 14 different sludge samples collected were categorised into minor and trace elements respectively. Minor elements detected in this study were Copper (Cu), Zinc (Zn), Barium (Ba), Chromium (Cr), Manganese (Mn), Nickel (Ni), Tin (Sn) and Strontium (Sr) while trace elements detected were Lead (Pb), Antimony (Sb), Silver (Ag), Arsenic (As), Cadmium (Cd), Cobalt (Co), Molybdenum (Mo) and Vanadium (V). Non-detectable elements were Selenium (Se), Beryllium (Be), Thallium (Tl) and Mercury (Hg) with less than 2ppm in dsb detected in all sludge samples tested.

Fusibility test adequately predicted sintering of ashes from biomass therefore adopted in this study to analyse sintering characteristics of ash residues from sludge (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, softening temperature, hemispherical temperature, and fluid temperature. Initial deformation temperature (IDT) measured at initial deformation stage when the first rounding of the apex of ash cone occurred. Softening temperature (ST) measured at the ash cone fused down into a spherical

lump in which the height is equal to width of the base. Hemispherical temperature (HT) reached when the ash cone fused down into a hemispherical lump in which height is half of the width of the base. Fluid Temperature (FT) recorded when the fused ash spread out and forms a nearly flat layer. The difference between IDT and FT was calculated as fusion temperature range. Base-to-acid ratio with and without phosphate ($R_{B/A}$ and $R_{B+P/A}$) as showed in Equation 4.13 and 4.14 were used as indicators in this study in order to estimate sintering characteristics of ash residues from sludge samples. 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 showed in Table 4.1 and 4.2 (Dunnu et al., 2010; Wang et al., 2012; Werle, 2014). Fusion temperatures of the sludge samples collected from WRPs in Singapore were calculated by using linear correlations developed.

$$R_{B/A} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{Al_2O_3 + SiO_2 + TiO_2} \quad \text{Equation 4.13}$$

$$R_{B+P/A} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5}{Al_2O_3 + SiO_2 + TiO_2} \quad \text{Equation 4.14}$$

Table 4.1: Fusibility of ash residues from sludge.

Sludge	Oxides ratio		Fusion temperature °C				References
	$R_{B/A}$	$R_{B+P/A}$	IDT	ST	HT	FT	
A	0.38	0.66	1210	1267	1456	1510	(Wang et al., 2012)
B	0.45	0.79	1110	1189	1322	1460	
C	0.97	1.42	994	1039	1105	1160	
D	0.61	0.65	1160	1165	1195	1210	(Dunnu et al., 2010)
E	1.06	1.66	840	1140	1190	1200	(Werle, 2014)

Table 4.2: Linear correlations of $R_{B/A}$ and $R_{B+P/A}$ with fusion temperatures.

Oxides ratio	Fusion temperature	Linear correlation	Coefficients of determination, R^2
$R_{B/A}$	IDT 1	$T_I = -443.45 R_I + 1370.60$	0.8414
	ST 1	$T_S = -217.97 R_S + 1311.30$	0.6519
	HT 1	$T_H = -371.98 R_H + 1511.80$	0.6906
	FT 1	$T_F = -460.03 R_F + 1627.30$	0.7418
$R_{B+P/A}$	IDT 2	$T_I = -304.06 R_I + 1377.80$	0.9357
	ST 2	$T_S = -121.93 R_S + 1286.30$	0.4824
	HT 2	$T_H = -188.19 R_H + 1448.60$	0.4180
	FT 2	$T_F = -225.00 R_F + 1541.10$	0.4197

4.3. Results and Discussion

4.3.1. Properties on handling and storage

Physical appearance, pH and density were important properties for sludge handling and storage. Observations on sludge showed that type of sludge corresponding to treatment methods and stages was main factor affecting physical appearances of sludge (Sanin et al., 2011). 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, secondary sludge was in fluffy form and different from primary sludge and anaerobic digested sludge where both were in granular powder form after milling. Raw sludge had mixed appearances of primary and secondary sludge. Results showed that anaerobic digested sludge were more stabilized and easier to handle with less odour issues compared to sludge samples collected before AD. Results of pH and density were showed in Table 4.3. pH test carried out by both methods showed similar results and average values were calculated. pH values of sludge were slightly and relatively acidic ranging from 4.44 to 5.84 compared to previous studies probably due to pre-treatment steps applied (dewatered, dried, and milled) and long-term storage of samples (Sanin et al., 2011). Slightly acidic nature of sludge would not expected to be causing problems in sludge handling (even after long-term storage) as feedstock for thermochemical conversion processes (Hernandez et al., 2011).

Bulk and pellet density were important parameters to be considered on the aspect of transportation and feeder design (Dogru et al., 2002). Bulk density of sludge varied significantly and with mean of $0.66 \pm 0.22 \text{g/cm}^3$ and relative standard deviation of 33.67RSD% comparable to earlier study (Ruggieri et al., 2008). Primary sludge showed highest bulk density of 0.93g/cm^3 while secondary sludge recorded lowest bulk density of 0.22g/cm^3 . Bulk density of raw sludge was generally lower than sludge samples after anaerobic digestion (AD) probably due to the presence of significant amounts of low density secondary sludge. Pellet density of sludge was more consistent with mean of $1.38 \pm 0.09 \text{g/cm}^3$ and 6.58RSD%. Pellet density was higher for sludge with more ash residues as shown in Figure 4.1. Strong correlation

existed between ash content and pellet density but only a weak correlation found for bulk density suggested that physical forms played a more important role in determination of bulk density of sludge. This study showed that significant variation existed in bulk densities of different type of sludge and could lead to complex handling and transportation issues. Variation in bulk density mainly resulted by the type of sludge and partially by differences in ash contents. This issue could be resolved by pelletizing. Transportation volume could also be reduced by about 50% since density doubled in average during pelletizing.

Table 4.3: Sample label with pH, bulk and pellet density for sludge.

Batch	Plant	Type	Sample label	pH	Density g/cm ³	
					Bulk	Pellet
1	Ulu Pandan	Raw	UR	4.79	0.54	1.30
		Dewatered	UD	4.44	0.76	1.37
	Changi	Primary	CP	4.68	0.93	1.30
		Secondary	CS	5.01	0.22	1.35
		Dried	CY	5.53	0.74	1.47
	Jurong	Raw	JR	4.43	0.66	1.46
		Dewatered	JD	5.05	0.79	1.61
	Kranji	Raw	KR	4.62	0.63	1.30
		Dewatered	KD	4.37	0.96	1.38
2	Ulu Pandan	Raw	UsR	5.07	0.55	1.31
		Dewatered	UsD	4.48	0.71	1.33
	Changi	Primary	CsP	5.21	0.83	1.34
		Secondary	CsS	5.82	0.22	1.32
		Dried	CsY	5.69	0.76	1.46
Mean ± standard deviations						
All samples collected				4.94 ± 0.48	0.66 ± 0.22	1.38 ± 0.09
Samples before AD (P, S, and R)				4.95 ± 0.43	0.57 ± 0.25	1.34 ± 0.06
Samples after AD (D and Y)				4.93 ± 0.58	0.79 ± 0.09	1.43 ± 0.10
Range				4.44 – 5.82	0.22 – 0.96	1.30 – 1.61

Figure 4.1: Correlations of bulk and pellet density of sludge with Ash₉₅₀ contents.

4.3.2. Physical Properties

4.3.2.1. 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 total inorganic contents free basis (icf) in Table 4.4. HHV and LHV on db varied significantly with mean values of $17.41 \pm 2.36 \text{ MJ/kg}$ at 13.56RSD% and $16.23 \pm 2.22 \text{ MJ/kg}$ at 13.67RSD% respectively. Inverse correlations were found for both HHV and LHV on db with the ash contents and TI since energy contents were contributed mainly by organic matters in sludge. Presence of inorganics was the main factor that caused significant variation in dry basis HHV and LHV as ash contents at 550°C varied from 15.28 to 51.06 mass% and TI varied from 10.71 to 44.09 mass% for different sludge samples collected. Heating values of sludge generally higher than 12MJ/kg indicated that all dry

sludge samples were suitable for thermochemical conversion processes such as incineration, gasification and pyrolysis (Arena, 2012; Tsai and Chou, 2006).

Heating values of sludge in daf and icf were more consistent. HHV and LHV in daf of sludge were having mean values of 24.52 ± 1.34 MJ/kg at 5.46RSD% and 22.86 ± 1.29 MJ/kg at 5.64RSD% respectively. HHV and LHV in icf of sludge were having mean values of 22.43 ± 1.14 MJ/kg at 5.08RSD% and 20.91 ± 1.12 MJ/kg at 5.36RSD% respectively. The consistency of HHV and LHV in both daf and icf showed that the energy contents of organic matters in sludge among different batches, types and plants were similar. As ash contents overestimated the amount of inorganics in the sludge due to oxidation, daf basis heating values were higher than the icf basis. Therefore, heating value in icf was proposed as an alternative parameter to improve estimation on heating values of organics in sludge. Mean LHV in icf 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 samples collected after AD were having lower heating values in db mainly due to higher mass% of inorganics. Biodegradation of organic matters during AD caused concentration effect of inorganics. Mean values of HHV and LHV in daf and icf of sludge samples before AD were slightly higher than sludge samples collected at the stages after AD indicated anaerobic process biodegraded organic compounds with relatively higher energy contents or transformed organic matters in sludge into compounds with slightly lower heating values.

Based on residual energy analysis, dewatered and dried sludge samples showed positive residual energy contents of 0.24 to 12.44 MJ/kg of sludge indicated the available of net recoverable energy contents while wet sludge samples included primary, secondary and raw sludge showed negative residual energy contents -0.89 to -1.91 MJ/kg of sludge indicated the need of moisture removal before energy recovery. Critical moisture content, $m_{w,critical}$ calculated based on LHV in db of sludge ranged from 84.46 to 89.54 mass% as showed in Table 4.4. In order to be able to recover energy from the sludge, moisture content of sludge needed to be reduced to below the critical level. Figure 4.2 (a) and (b) further showed that the residual energy of sludge reduced greatly and the demand of LHV in sludge

elevated tremendously when the moisture content of sludge increased above 80 mass%. Based on thermodynamic equilibrium, moisture content in sludge should also be reduced to be lower than 19.0 mass% in order to achieve efficient thermochemical conversion inside a gasifier (Ptasinski et al., 2007). Therefore, further improvement on dewatering and drying processes and considerations of the potential of re-utilization of the water vapour generated during drying were important to sustain the wastewater treatment system and to achieve energy recovery from sludge.

Calculated results of HHV correlation were showed in Table 4.5. By using oxygen contents directly measured instead of determined from by difference method and using IM instead of ash contents to represent the inorganics in sludge, mean of $\epsilon_{\%}$ calculated was reduced from 5.28% to 3.86%. Bias errors were illustrated in Figure 4.3 further showed that $\epsilon_{\text{Bias } 1}$ data were randomly distributed around zero for all sludge samples but $\epsilon_{\text{Bias } 2}$ data were below zero for most sludge samples. Mean values of $\epsilon_{\text{Bias } 1}$ and $\epsilon_{\text{Bias } 2}$ were at 0.02MJ/kg and -0.76MJ/kg. These observations demonstrated that HHV 2 making over-predictions similar to the findings in previous study for sludge (Niessen, 2010). Calculation 2 overestimated HHV of sludge mainly because of the underestimation of oxygen content if compared to Calculation 1. The used of IM also helped to reduce the underestimation on HHV by reducing the overestimation of inorganics in sludge. ϵ_{Abs} of both methods showed that the errors were in average less than 1.00MJ/kg indicated that the usage of correlation for HHV calculation of sludge was acceptable. The results also indicated that sludge samples were comparable to other feedstock as correlation between heating values and elemental composition could be formed.

Table 4.4: Heating value and residual energy analysis of sludge.

Sample label	HHV (MJ/kg)			LHV (MJ/kg)			M_w	Energy content, MJ			$M_{w,critical}$
	db	daf	icf	db	daf	icf		Q_o	Q_w	$Q_{residual}$	
UR	20.49	24.19	22.95	19.35	22.61	21.45	98.40	0.31	2.22	-1.91	89.54
UD	17.41	24.18	21.19	16.15	22.43	19.65	86.40	2.20	1.95	0.24	87.72
CP	17.53	23.93	21.92	16.34	22.30	20.43	93.30	1.09	2.11	-1.01	87.85
CS	19.66	24.17	22.34	18.34	22.55	20.84	93.30	1.22	2.11	-0.89	88.97
CY	14.47	23.85	21.62	13.48	22.22	20.13	6.55	12.59	0.15	12.44	85.64
JR	17.13	26.96	23.50	15.92	25.06	21.84	97.90	0.33	2.21	-1.88	87.57
JD	13.19	26.95	23.59	12.28	25.26	22.11	73.40	3.27	1.66	1.61	84.46
KR	20.52	26.59	24.14	19.19	24.87	22.57	97.40	0.49	2.20	-1.71	89.39
KD	15.66	23.19	20.27	14.44	21.39	18.69	83.80	2.34	1.89	0.45	86.47
UsR	19.41	24.46	23.61	18.13	22.85	22.06	98.28	0.31	2.22	-1.91	88.92
UsD	17.48	23.14	21.80	16.29	21.56	20.31	84.11	2.59	1.90	0.69	87.82
CsP	18.20	24.53	22.73	17.03	22.95	21.27	93.85	1.05	2.12	-1.07	88.28
CsS	18.65	24.08	23.14	17.45	22.53	21.66	94.16	1.02	2.13	-1.11	88.54
CsY	13.89	23.00	21.16	12.97	21.46	19.75	4.65	12.36	0.11	12.26	85.16
Mean $\pm$ standard deviations											
All sample	17.41 ± 2.36	24.52 ± 1.34	22.43 ± 1.14	16.23 ± 2.22	22.86 ± 1.29	20.91 ± 1.12	78.96 ± 31.88	2.94 ± 4.14	1.78 ± 0.72	1.16 ± 4.86	87.60 ± 1.59
Before AD	18.95 ± 1.28	24.87 ± 1.26	23.04 ± 0.72	17.69 ± 1.22	23.21 ± 1.10	21.51 ± 0.68	95.82 ± 2.36	0.73 ± 0.40	2.17 ± 0.05	-1.44 ± 0.45	88.63 ± 0.70
After AD	15.35 ± 1.81	24.05 ± 1.49	21.60 ± 1.11	14.28 ± 1.65	22.39 ± 1.47	20.11 ± 1.13	56.49 ± 39.68	5.89 ± 5.11	1.28 ± 0.89	4.62 ± 6.01	86.21 ± 1.37
Range	13.19 – 20.52	23.00 – 26.96	20.27 – 24.14	12.28 – 19.35	21.39 – 25.26	18.69 – 22.57	4.65 – 98.40	0.31 – 12.59	0.11 – 2.22	-1.91 – 12.44	84.46 – 89.54

Figure 4.2: (a) Residual energy at different moisture contents in percentage and (b) moisture contents at zero residual energy for different lower heating values.

Table 4.5: HHV of sludge estimated by Calculation 1 and 2.

Sample Label	Calculation 1, MJ/kg				Calculation 2, MJ/kg			
	HHV 1	$\epsilon_{\text{Bias 1}}$	$\epsilon_{\text{Abs 1}}$	$\epsilon_{\% 1}$	HHV 2	$\epsilon_{\text{Bias 2}}$	$\epsilon_{\text{Abs 2}}$	$\epsilon_{\% 2}$
UR	18.94	1.55	1.55	7.55	19.39	0.95	0.95	4.61
UD	18.57	-1.16	1.16	6.67	19.51	-2.29	2.29	13.14
CP	17.51	0.02	0.02	0.11	18.33	-0.64	0.64	3.63
CS	20.14	-0.49	0.49	2.48	20.75	-1.24	1.24	6.32
CY	14.18	0.29	0.29	2.01	14.90	-0.52	0.52	3.58
JR	17.55	-0.42	0.42	2.45	18.45	-1.57	1.57	9.17
JD	11.91	1.28	1.28	9.70	12.70	0.17	0.17	1.30
KR	20.57	-0.05	0.05	0.25	21.33	-0.89	0.89	4.35
KD	17.22	-1.56	1.56	9.99	18.16	-2.61	2.61	16.64
UsR	19.64	-0.23	0.23	1.20	19.96	-0.66	0.66	3.38
UsD	17.93	-0.44	0.44	2.54	18.40	-1.07	1.07	6.11
CsP	17.64	0.56	0.56	3.09	18.30	-0.06	0.06	0.31
CsS	18.27	0.38	0.38	2.05	18.69	-0.07	0.07	0.35
CsY	13.35	0.54	0.54	3.88	14.00	-0.15	0.15	1.08
Mean	17.39	0.02	0.64	3.86	18.06	-0.76	0.92	5.28
SD	2.55	0.85	0.52	3.28	2.50	0.95	0.72	4.39

Figure 4.3: Distribution of bias errors for Calculation 1 and 2 on HHV estimation.

4.3.2.2. Proximate Analysis

Proximate analysis studied thermal processes related characteristics included moisture, VM, FC, and ash contents. Multiple heating rates TGA could be useful to analyse heterogeneous waste residues by obtaining mean data to account for the variations in samples and by observing any significant trend in char formation and volatile mass loss at different heating rates. Variation in char residues formation for different heating rates could be observed and mean values of char residues remained were calculated and showed in Table 4.6. No significant alteration on char formation by heating rates in the range of 5-25 K/min. However, fluctuation caused by heterogeneity of sludge and random errors of experiments could be identified. VM represented by the mass loss recorded. After determination of VM and char residues, further quantification of inorganic components needed for FC calculation.

Table 4.6: Char residues of sludge by multiple heating rate TGA analysis.

Sample Label	Char residues at 950°C - Multiple heating rates TGA						
	5 K/min	10 K/min	15 K/min	20 K/min	25 K/min	Mean	SD
UR	30.61	30.08	28.91	30.56	29.88	30.01	0.69
UD	38.95	37.58	39.08	38.17	36.49	38.05	1.07
CP	38.48	37.67	34.53	35.79	36.71	36.64	1.55
CS	33.19	32.05	33.55	32.91	31.09	32.56	0.99
CY	48.25	49.31	48.18	48.03	49.02	48.56	0.57
JR	35.86	39.88	41.64	41.06	38.89	39.47	2.28
JD	52.25	53.74	51.97	53.14	51.08	52.44	1.04
KR	36.46	35.88	36.33	34.79	35.25	35.74	0.71
KD	41.58	43.18	43.48	43.77	44.43	43.29	1.06
UsR	27.08	26.25	31.19	27.35	32.80	28.93	2.88
UsD	32.85	34.92	33.93	34.44	34.90	34.21	0.86
CsP	33.95	34.94	35.38	35.29	37.16	35.34	1.16
CsS	33.01	33.75	32.46	32.20	33.24	32.93	0.62
CsY	48.25	49.95	48.34	50.08	48.03	48.93	1.00

Results of proximate analysis for all sludge samples collected were summarised in Table 4.7. Wet samples included raw, primary and secondary sludge were collected from different plants and moisture contents ranged from 93.30 to 98.40 mass% as received. Moisture contents of sludge samples dewatered by mechanical processes in Ulu Pandan, Jurong and Kranji WRPs varied significantly and ranged from 73.40

to 86.40 mass% comparable to previous study (F.Y.Wang et al., 2008). Thermal drying further reduced the moisture contents of two batches of dried sludge from Changi WRP to an average of 5.60 mass%. Dewatering facilities existed in all four WRPs but thermal dryer existed only at Changi WRP and operated with energy supplied by combustion of biogas generated from onsite anaerobic digestion. VM was the most abundant components and ranged from 47.56 to 71.07 mass% in db except for J-D as VM was slightly lower than Ash₉₅₀ content. FC and FR calculated by difference were important parameters to determine non-inorganic residues remained in char after pyrolysed at 950°C in an inert environment. FC underestimated non-inorganic residues due to apparent mass gained of inorganic contents in char when combusted and oxidised at 950°C to form ash residues. Data showed that mean FC calculated at 10.51 ± 3.32 mass% significantly lower than mean FR calculated at 18.71 ± 3.47 mass%. FR and IM were proposed to replace FC and Ash₉₅₀ to improve quantification on residual components remained after pyrolysis. For comparison, CHNS of Char₉₅₀ was calculated in dsb to represent the mass% of non-inorganic residues in char. FC data underestimated the residues as represented by CHNS_{char} data from -9.40 to -2.46 mass% with mean difference at -6.35 mass%. FR data randomly under- and over-estimated residues for different sludge samples from -2.66 to 5.96 mass% with mean difference of 1.85 mass%. FR slightly overestimated the residues in average could be accounted by random errors of experiments and heterogeneity of sludge characteristics. Therefore, it was demonstrated that use of FR and IM for quantification of non-inorganic residues in char could potentially improve the accuracy of the estimation.

Contents of VM, FC and FR were mainly affected by both presence of inorganics and intrinsic characteristics of organic and inorganic matters in sludge. Higher inorganic contents would lead to generally lower amounts of VM, FC and FR in db because of less organic matters available. In order to observe intrinsic characteristics of organic matters, distributions of VM, FC and FR calculated in dry ash free basis (daf) and inorganic matters free basis (imf) respectively were showed in Table 4.8. Results showed that VM, FC and FR contents were similar across all the sludge samples collected from different plants, types and batches and agreed well with the findings on the similarity in heating values of sludge organics. Data

also showed that VM contents of sludge samples before AD were slightly higher while the corresponding FC and FR were slightly lower. These observations suggested that AD process transformed organic matters in sludge to compounds that produced less VM and formed more char residues upon heating in an inert environment. VM/FC or VM/FR ratios were indicators for distributions of volatile matters released and char residues formed. VM/FC ratios of sludge samples collected were relatively high compared to common feedstock in thermochemical conversion processes (Channiwala and Parikh, 2002) as showed in Table 4.9. For coal, VM/FC ratios 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 value at 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 of 3.40 ± 0.78 comparable to other biomass and wastes. These observations further supported the hypothesis of FC underestimation caused by oxidation of inorganics in sludge during ash contents determination tests. Distribution ratios of VM/FC or VM/FR would also be affected by intrinsic characteristics of organic matters in sludge and by the impact of inorganics on volatilization during thermal degradation. It was demonstrated in previous studies that inorganics in feedstock could promote char formation reactions (Fonts et al., 2012). However, no significant correlations found in this study between VM/FR or VM/FC ratios with the IM or Ash₉₅₀ in sludge probably because composition of organic and inorganic matters also changed when comparing sludge samples with different IM or Ash₉₅₀. Changes in organic matters altered the intrinsic distribution ratio while changes in inorganic composition could alter relative abundance of active components such as alkaline metals. In addition, increased of the amount of inorganics in sludge could also caused more decomposition of sulphates and carbonates therefore released more volatiles reduced the apparent mass gained on promoting char formation. Therefore, the changes in the amount of ash and IM did not contribute observable alterations to the distributions of VM, FC and FR. Hence, intrinsic characteristics and composition of the inorganic and organic matters in sludge would be the main factors that determined the distribution ratios and needed to be studied in further details.

Table 4.7: Proximate and residues analysis proposed for sludge.

Sample Label	Moisture contents	Mass% in db						Difference in mass%	
		VM	FC	Ash ₉₅₀	FR	IM	CHNS _{Char}	FC - CHNS _{Char}	FR - CHNS _{Char}
UR	98.40	69.99	16.24	13.77	21.66	8.35	21.29	-5.05	0.37
UD	86.40	61.95	11.91	26.14	23.28	14.78	18.56	-6.65	4.71
CP	93.30	63.36	8.36	28.28	18.28	18.36	17.75	-9.40	0.53
CS	93.30	67.44	15.32	17.24	22.68	9.88	17.96	-2.64	4.72
CY	6.55	51.44	10.00	38.57	18.85	29.72	16.23	-6.24	2.61
JR	97.90	60.53	5.34	34.13	16.36	23.11	14.33	-9.00	2.02
JD	73.40	47.56	4.43	48.01	14.06	38.38	12.58	-8.16	1.47
KR	97.40	64.26	13.69	22.05	22.93	12.81	16.97	-3.27	5.96
KD	83.80	56.71	11.85	31.44	23.20	20.09	17.47	-5.62	5.73
UsR	98.28	71.07	9.25	19.69	13.16	15.77	15.82	-6.58	-2.66
UsD	84.11	65.79	11.21	23.00	17.00	17.21	19.03	-7.82	-2.03
CsP	93.85	64.66	9.11	26.24	17.17	18.17	16.49	-7.38	0.69
CsS	94.16	67.07	10.68	22.26	15.75	17.18	16.07	-5.40	-0.32
CsY	4.65	51.07	9.77	39.15	17.59	31.33	15.49	-5.72	2.10
Mean ± standard deviations									
All sample		61.64 ±7.33	10.51 ±3.32	27.86 ±9.50	18.71 ±3.47	19.65 ±8.44	16.86 ±2.12	-6.35 ±1.95	1.85 ±2.70
Before AD		66.05 ±3.52	11.00 ±3.76	22.96 ±6.47	18.50 ±3.58	15.45 ±4.87	17.09 ±2.05	-6.09 ±2.47	1.41 ±2.78
After AD		55.75 ±7.04	9.86 ±2.81	34.39 ±9.30	19.00 ±3.64	25.25 ±9.28	16.56 ±2.37	-6.70 ±1.07	2.44 ±2.72
Minimum		47.56	4.43	13.77	13.16	8.36	12.58	-9.40	-2.66
Maximum		71.07	16.24	48.01	23.28	38.38	21.29	-2.64	5.96

Table 4.8: Distributions of VM, FC and FR.

Sample Label	Mass% in daf			Mass% in imf		
	VM	FC	VM/FC	VM	FR	VM/FR
UR	81.17	18.83	4.31	76.37	23.63	3.23
UD	83.87	16.13	5.20	72.69	27.31	2.66
CP	88.35	11.65	7.58	77.61	22.39	3.47
CS	81.49	18.51	4.40	74.83	25.17	2.97
CY	83.72	16.28	5.14	73.18	26.82	2.73
JR	91.89	8.11	11.34	78.73	21.27	3.70
JD	91.49	8.51	10.74	77.19	22.81	3.38
KR	82.43	17.57	4.69	73.70	26.30	2.80
KD	82.72	17.28	4.79	70.97	29.03	2.44
UsR	88.49	11.51	7.69	84.37	15.63	5.40
UsD	85.44	14.56	5.87	79.47	20.53	3.87
CsP	87.65	12.35	7.10	79.01	20.99	3.76
CsS	86.27	13.73	6.28	80.98	19.02	4.26
CsY	83.94	16.06	5.23	74.38	25.62	2.90
Mean $\pm$ standard deviations						
All Sample	85.64 ± 3.50	14.36 ± 3.50	6.45 ± 2.24	76.68 ± 3.67	23.32 ± 3.67	3.40 ± 0.78
Before AD	85.97 ± 3.88	14.03 ± 3.88	6.67 ± 2.35	78.20 ± 3.42	21.80 ± 3.42	3.70 ± 0.83
After AD	85.20 ± 3.20	14.80 ± 3.20	6.16 ± 2.27	74.65 ± 3.41	25.35 ± 3.14	3.00 ± 0.53

Table 4.9: Proximate analysis of reference materials.

Type of feedstock	Mass% in db			VM/FC ratio
	VM	FC	Ash ₉₅₀	
Stalks	62.90	19.90	17.20	3.16
Bagasse	73.78	14.95	11.27	4.94
Wood	82.14	15.77	2.09	5.21
Anthracite	1.34	90.60	8.06	0.01
Bituminous	33.45	60.25	6.30	0.56
Lignite	49.47	46.03	4.50	1.07
Refuse derived fuels	72.00	17.60	10.40	4.09

Despite the fact that use of ash content could cause errors in estimation of FC in char residues and heating values of organic matters in sludge, it still considered as an important engineering parameter that accurately determined the amount of inorganic residues remained after sludge being treated in oxidative thermochemical

conversion processes such as incineration and air/oxygen gasification. Ash content of sludge analyzed at 550°C and 950°C respectively as combustion temperatures and results showed in Table 4.10. Ash₅₅₀ varied from 15.28 to 51.06 mass% while Ash₉₅₀ varied from 13.77 to 48.01 mass%. These two data were applicable to different operating temperatures. Ash₅₅₀ was suitable for modelling of incineration operated at 700-800°C and below while Ash₉₅₀ was suitable for modelling of gasification with air or oxygen operated at 900-1000°C and higher. After AD, sludge samples were having higher ash contents because of biodegradation of organic matters and accumulation of inorganics. Ash contents of samples from Jurong WRP were higher compared to other WRPs and could be caused by industrial wastewater influent with higher concentration of inorganics. Dried sludge samples from Changi WRP were having the highest ash content among samples collected there, followed by primary sludge and lowest ash contents found in secondary sludge. These observations were resulted from physical screening during primary treatment and accumulation of inorganics during AD treatment. Ratios of Ash₉₅₀/IM and apparent degree of oxidation, O_D showed that significant oxidation of inorganics at different degrees could be observed. O_D ranged from 24.96 to 76.94% with mean at 47.07 ±19.59% and higher for sludge before AD. Variations in OD could be explained by correlations established with inorganic elements in sludge as illustrated in Figure 4.4. Relative mass% of inorganic element was calculated with reference to IM contents by using $Relative\ Mass\% = (Mass\%_{element}/IM) \times 100\%$ for individual element and summation of detected elements. No significant correlation could be formed for individual element 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 composition analysis in this study. Positive correlations indicated that as relative mass% of inorganic elements increased, O_D would also increase. IM represented the inorganic contents in sludge after excluding CHNSO_{Inorganic} and combustion released halogen contents. As the summation of detected inorganic elements approaching IM contents calculated, 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.

Figure 4.4: Correlations of apparent degree of oxidation, O_D with relative mass% of inorganic elements presence in inorganic matters of sludge.

In general, ratios of Ash_{550}/Ash_{950} greater than 1.00 indicated that ash contents at 950°C were lower except for CP and CsP. Reduction of mass for Ash_{950} was resulted by decomposition of inorganics including carbonates, sulphates and other volatile inorganics at temperature higher than 550°C. Inorganics in sludge should not be considered as inert because both oxidation and decomposition of inorganics occurred at elevated temperature and in oxidative environment as observed in previous study on mineral phase transformation analysis (Hernandez et al., 2011). Results of primary sludge samples suggested that more mass gained from oxidation of IM at 950°C and less mass loss from decomposition of inorganics above 550°C occurred as supported by low $CHNSO_{Inorganic}$ measured in ultimate analysis of Ash_{550} for CP and CsP. Therefore increased of ash contents at higher temperature combustion could be observed. $CHNSO_{Inorganic}$ would decompose and release as volatiles at 950°C. However reductions in mass% of Ash_{950} compared to Ash_{550} were lower than $CHNSO_{Inorganic}$ measured indicated mass gained by Ash_{950} at high temperature combustion through oxidation of inorganics. Apparent mass increased by oxidation could be calculate based on the assumptions that the expected mass loss caused only by complete decomposition of CHNSO contents of Ash_{550} and

mass gained caused only by the oxidation of inorganic matters. Results supported that ash contents overestimated inorganics in sludge and showed that inorganics actively participated in high temperature thermochemical conversion processes. Compared to sludge, underestimation of FC contents in the char caused by the oxidation of inorganics may not be significant in the coal and other biomass due to the following reasons. (i) 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. (ii) Significant inorganics decompose at elevated temperature for coal compensated for the oxidation of remaining inorganics therefore no significant net mass gained in ash contents. Theoretical amount of ash measured for coal should be more than inorganic matters but comparable or even lower values of ash contents in coal than IM were commonly detected due to the decomposition and volatilization (Vassilev and Tascon, 2003). Mass loss behaviours of IM in coal were caused by decomposition of coal minerals (clay minerals, sulfides, carbonates and sulfates), partial volatilization of elements, and loss of adsorbed and combined water. (iii) Inorganics in sludge were in leachable organic fractions which could be easily oxidised (Hernandez et al., 2011).

Simulations developed based on proposed intrinsic distribution ratio, $R = VM/FR$ illustrated the above reasons that caused sludge samples to behave distinctively. Simulations of R^*/R carried out at (a) $O_D = 45\%$ with variations in IM at three distinct R, (b) IM = 20 mass% with variations in R at three distinct O_D , and (c) $R = 3.50$ with variations in O_D at three distinct IM were showed in Figure 3.7. Simulations were developed using mean values of the data obtained from sludge samples for IM = 19.65 mass%, $R = 3.40$, $O_D = 47.07\%$ and $Ash_{950} = 27.85$ mass% as reference values to fix one of the parameters in each simulation as constant. All simulations showed that the deviation of R^* from R increased as the IM, R and O_D increased. Simulations also demonstrated that the deviations became significance at $R^*/R > 1.20$ when in general, IM > 10.00 mass%, $R > 1.00$, $O_D > 20.00$ mass% and $Ash_{950} > 12.00$ mass% respectively. Proximate analysis showed that properties of sludge were in the range where deviations could be significantly observed for R^*/R . By observing the separations of three simulated curves in individual simulation, impacts on R^*/R found to be highest when IM changed and followed by O_D and R.

Table 4.10: Ash contents analysis for sludge.

Sample Label	Mass% in db								Ratio of Ash ₉₅₀ /IM	Apparent degree of oxidation, O _D	Ratio of A ₅₅₀ /A ₉₅₀
	Ash ₅₅₀		Ash ₉₅₀		IM	Difference A ₅₅₀ - A ₉₅₀	CHNSO of Ash ₅₅₀	Apparent increased			
	Mean	SD	Mean	SD							
UR	15.28	0.11	13.77	0.33	8.35	1.51	2.06	0.55	1.65	64.90	1.11
UD	27.99	0.16	26.14	0.07	14.78	1.85	2.86	1.01	1.77	76.94	1.07
CP	26.74	0.20	28.28	0.09	18.36	-1.54	1.29	2.82	1.54	54.06	0.95
CS	18.68	0.03	17.24	0.62	9.88	1.44	1.75	0.31	1.75	74.56	1.08
CY	39.35	0.07	38.57	0.26	29.72	0.78	2.91	2.13	1.30	29.78	1.02
JR	36.48	0.25	34.13	0.07	23.11	2.35	3.33	0.98	1.48	47.67	1.07
JD	51.06	0.34	48.01	0.04	38.38	3.05	5.11	2.05	1.25	25.09	1.06
KR	22.83	0.24	22.05	0.35	12.81	0.78	1.83	1.05	1.72	72.08	1.04
KD	32.48	0.18	31.44	0.19	20.09	1.04	2.30	1.26	1.56	56.50	1.03
UsR	20.66	0.30	19.69	0.14	15.77	0.97	1.89	0.91	1.25	24.83	1.05
UsD	24.43	0.17	23.00	0.10	17.21	1.43	2.41	0.98	1.34	33.61	1.06
CsP	25.81	0.10	26.24	0.12	18.17	-0.43	1.50	1.93	1.44	44.38	0.98
CsS	22.54	0.16	22.26	0.23	17.18	0.29	1.97	1.68	1.30	29.56	1.01
CsY	39.59	0.20	39.15	0.02	31.33	0.44	2.81	2.38	1.25	24.96	1.01
Mean ± Standard Deviation											
All Sample	28.85 ±9.83		27.85 ±9.50		19.65 ±8.44	1.00 ±1.14	2.43 ±0.97	1.43 ±0.74	1.47 ±0.20	47.07 ±19.59	1.04 ±0.04
Before AD	23.63 ±6.37		22.96 ±6.47		15.45 ±4.87	0.67 ±1.22	1.95 ±0.61	1.28 ±0.82	1.52 ±0.18	51.51 ±18.51	1.04 ±0.05
After AD	35.82 ±9.60		34.39 ±9.30		25.25 ±9.28	1.43 ±0.93	3.07 ±1.03	1.64 ±0.62	1.41 ±0.21	41.15 ±21.08	1.04 ±0.02

Figure 4.5: Simulations of apparent-to-intrinsic distribution ratio R^*/R at three different conditions of (a) apparent degree of oxidation $OD = 45\%$, (b) $IM = 20$ mass% and (c) $R = 3.50$.

4.3.2.3. Heat capacity analysis

Results for heat capacity analysis at temperature from 343K to 393K (from 70°C to 120°C) were showed in Table 4.11. C_p of sludge increased gradually as temperature elevated illustrated in Figure 3.8 similar to previous studies on biomass (Chen et al., 2014; Dupont et al., 2014; Mark, 2007; Morad et al., 2000). Mean C_p was calculated at $1.68 \pm 0.26 \text{ J/g-K}$ based on the average of recorded data at different temperatures and was lower than the assumed value of around 2.00 J/g-K in previous studies based on heat capacity of general organic and inorganic materials (Agarwal et al., 2015; Kim and Parker, 2008). However, significant variation could be observed as heat capacities measured varied from 1.33 J/g-K to 2.18 J/g-K for different sludge samples as illustrated in Figure 4.6. Direct measurement of C_p for feedstock therefore improved the accuracy of energy audit and modelling. C_p of sludge samples collected before AD measured at mean of $1.78 \pm 0.27 \text{ J/g-K}$ higher than after AD measured at mean of $1.55 \pm 0.21 \text{ J/g-K}$. This observation mainly caused by higher inorganic contents in sludge samples after AD as the heat capacity of inorganics generally lower than organic matters (Kim and Parker, 2008). Comparison among two batches of sludge samples for Ulu Pandan and Changi WRPs showed quantitative differences indicated time variations caused by probably characteristics of wastewater influents could be observed.

Table 4.11: Heat capacity analysis of sludge.

Sample Label	Heat Capacity in dry basis, $C_p \text{ J/g-K}$						Mean $\pm$ SD
	343K	353K	363K	373K	383K	393K	
UR	1.75	1.81	1.89	2.01	2.12	2.29	1.98 ± 0.21
UD	1.44	1.46	1.55	1.62	1.70	1.82	1.60 ± 0.15
CP	1.40	1.43	1.46	1.55	1.66	1.81	1.55 ± 0.16
CS	1.74	1.78	1.83	1.93	2.05	2.23	1.93 ± 0.19
CY	1.38	1.43	1.48	1.57	1.68	1.86	1.57 ± 0.18
JR	1.58	1.62	1.66	1.75	1.85	2.01	1.74 ± 0.16
JD	1.24	1.25	1.27	1.35	1.42	1.57	1.35 ± 0.13
KR	1.46	1.50	1.53	1.61	1.69	1.85	1.61 ± 0.15
KD	1.19	1.22	1.26	1.34	1.41	1.57	1.33 ± 0.14
UsR	1.97	2.01	2.14	2.23	2.32	2.39	2.18 ± 0.17
UsD	1.69	1.72	1.82	1.93	2.04	2.20	1.90 ± 0.20
CsP	1.12	1.18	1.26	1.37	1.49	1.73	1.36 ± 0.22
CsS	1.69	1.71	1.75	1.85	2.01	2.39	1.90 ± 0.27
CsY	1.38	1.38	1.45	1.54	1.64	1.79	1.53 ± 0.16

Figure 4.6: Heat capacity analysis. (a) C_p of sludge at temperature from 343K to 393K and (b) mean values of C_p calculated for different sludge samples.

4.3.3. Chemical Properties

4.3.3.1. Ultimate Analysis

Results of ultimate analysis for sludge samples and ash residues were showed in Table 4.12 and 4.13. 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 ultimate analysis of sludge, C was the dominant element followed by O, H, N and S according to the mass% in db. pH values of sludge ranged from 4.44 to 5.84 and were lower than 7.40 indicated no significant presence of carbonates in sludge samples collected (Schumacher, 2002). This indication supported by the sludge TC/TOC ratios which were ranged from 1.01 to 1.10 as showed in Table 4.14. Therefore C contents in sludge samples collected from WRPs in Singapore were mainly organic carbon. This observation further supported by mass% of C in ash residues was in average contributing only about 0.58% to the total C in sludge. Based on ultimate analysis for ash residues, O and S contents were partially contributed by inorganics at 5.67% and 13.54% contribution respectively. C, H and N contents were mainly contributed by organic matters with less than 1.00% contribution in average from inorganics in sludge. By using ultimate analysis for sludge and ash samples, CHNSO contents of organic matters in sludge could be calculated. Data for $\text{CHNSO}_{\text{organic}}$, $\text{CHNSO}_{\text{inorganic}}$, $\text{CHNSO}_{\text{Total}}$, halogens contents, IM and TI were showed in Table 4.15.

By determination of $\text{CHNSO}_{\text{Total}}$ and halogens contents released during combustion, IM could be calculated by approximated mass balance as described by Equation 4.6. IM represented the main portion of inorganics in sludge which included inorganic elements in various forms such as inert oxides, heavy metals, minerals, and volatile inorganics. Total inorganic contents were calculated by using Equation 4.7. Compared to ash contents measured, IM and TI contents were lower indicated the mass gained during ash formation analysis. Therefore, IM and TI were proposed to be used as indicators to represent the amount of inorganics in sludge. IM was suitable to account for the inorganics remained in char residues after pyrolysis at 950°C by assuming insignificant release of volatile inorganics while TI was suitable to account for total inorganic contents initially in sludge.

Table 4.12: Ultimate analysis of sludge samples.

Sample Label	CHNSO _{Total} of sludge in db, Mass%									
	C		H		N		S		O	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
UR	43.56	0.10	5.64	0.04	5.81	0.07	5.47	0.29	30.87	0.61
UD	39.88	0.08	6.20	0.01	6.04	0.02	5.62	0.09	27.29	0.59
CP	37.92	1.03	5.89	0.33	7.55	0.38	4.57	0.35	25.33	0.30
CS	43.98	1.88	6.48	0.62	3.87	0.05	5.30	0.42	30.11	0.17
CY	31.71	1.83	4.88	0.31	5.03	0.30	4.81	0.45	23.41	0.31
JR	37.16	0.59	5.94	0.12	4.33	0.09	5.37	0.03	23.39	0.36
JD	27.44	1.15	4.07	0.46	3.21	0.14	5.43	0.12	20.85	0.40
KR	43.79	2.51	6.56	0.84	5.63	0.18	5.44	0.36	25.42	0.42
KD	36.51	0.36	5.98	0.03	6.64	0.06	5.38	0.11	25.04	0.21
UsR	42.68	0.31	6.28	0.03	4.96	0.03	4.26	0.03	25.91	0.37
UsD	39.50	0.20	5.85	0.03	5.91	0.03	4.59	0.00	26.78	0.59
CsP	38.36	0.32	5.76	0.06	6.80	0.04	5.48	0.05	25.18	0.55
CsS	40.24	0.16	5.89	0.11	3.46	0.01	5.43	0.01	27.55	0.25
CsY	30.42	0.12	4.56	0.01	4.83	0.03	5.20	0.02	23.45	0.57
Mean±SD	38.08 ±5.15		5.71 ±0.72		5.29 ±1.29		5.17 ±0.43		25.75 ±2.68	

Table 4.13: Ultimate analysis of ash residues.

Sample Label	CHNSO of Ash ₅₅₀ in dsb, Mass%									
	C		H		N		S		O	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
UR	0.14	0.00	0.02	0.01	0.02	0.00	0.49	0.02	1.40	0.06
UD	0.26	0.01	0.02	0.00	0.04	0.00	0.88	0.02	1.67	0.06
CP	0.13	0.01	0.01	0.00	0.03	0.00	0.25	0.05	0.86	0.14
CS	0.25	0.00	0.01	0.00	0.03	0.00	0.52	0.02	0.93	0.11
CY	0.32	0.03	0.01	0.00	0.07	0.01	0.81	0.01	1.70	0.20
JR	0.29	0.02	0.01	0.00	0.04	0.00	1.16	0.01	1.83	0.15
JD	0.33	0.03	0.02	0.00	0.06	0.01	1.76	0.01	2.94	0.27
KR	0.18	0.00	0.01	0.00	0.03	0.00	0.45	0.02	1.16	0.02
KD	0.19	0.01	0.01	0.00	0.04	0.00	0.54	0.02	1.51	0.08
UsR	0.18	0.01	0.01	0.00	0.03	0.00	0.58	0.00	1.09	0.05
UsD	0.22	0.01	0.01	0.00	0.04	0.00	0.74	0.01	1.40	0.01
CsP	0.14	0.00	0.01	0.00	0.03	0.00	0.33	0.01	0.99	0.07
CsS	0.22	0.00	0.01	0.00	0.03	0.00	0.57	0.01	1.15	0.02
CsY	0.21	0.01	0.02	0.00	0.05	0.00	0.79	0.03	1.74	0.02
Mean±SD	0.22 ± 0.07		0.01 ± 0.00		0.04 ± 0.01		0.70 ± 0.38		1.46 ± 0.53	
% Total	0.58		0.18		0.76		13.54		5.67	

Table 4.14: Total carbon and total organic carbon analysis.

Batch	Plant	Type	Mass% in db		TC/TOC Ratio
			TC	TOC	
1	Ulu Pandan	Raw	43.56	40.58	1.07
		Dewatered	39.88	36.38	1.10
	Changi	Primary	37.92	37.58	1.01
		Secondary	43.98	41.97	1.05
		Dried	31.71	30.67	1.03
	Jurong	Raw	37.16	34.79	1.07
		Dewatered	27.44	26.58	1.03
	Kranji	Raw	43.79	41.68	1.05
		Dewatered	36.51	35.04	1.04
	Mean $\pm$ SD			37.99 $\pm$ 5.68	36.14 $\pm$ 5.13
RSD%			14.94	14.20	2.46

Table 4.15: Summary of CHNSO elements and inorganic contents.

Sample Label	Mass% in dsb					
	CHNSO of sludge			Halogens contents	IM	TI
	Organics	Inorganics	Total			
UR	89.29	2.06	91.35	0.30	8.35	10.71
UD	82.17	2.86	85.03	0.20	14.78	17.83
CP	79.98	1.29	81.26	0.38	18.36	20.02
CS	87.99	1.75	89.75	0.38	9.88	12.01
CY	66.93	2.91	69.84	0.45	29.72	33.07
JR	72.86	3.33	76.19	0.70	23.11	27.14
JD	55.91	5.11	61.02	0.60	38.38	44.09
KR	85.00	1.83	86.83	0.36	12.81	15.00
KD	77.26	2.30	79.55	0.36	20.09	22.74
UsR	82.20	1.89	84.09	0.14	15.77	17.80
UsD	80.21	2.41	82.62	0.16	17.21	19.79
CsP	80.07	1.50	81.57	0.25	18.17	19.92
CsS	80.60	1.97	82.57	0.26	17.18	19.40
CsY	65.65	2.81	68.46	0.21	31.33	34.35
Mean	77.58	2.43	80.01	0.34	19.65	22.42
SD	9.28	0.97	8.51	0.16	8.44	9.28

CHNSO contents were important input to form molecular formula for sludge and used in simulations of thermochemical conversion processes (Dominguez et al., 2006; Shao et al., 2008). Molecular formula of sludge was calculated based on the data from ultimate analysis showed in Table 4.16. Data of ultimate analysis of sludge organic matters and sludge using by difference method were also calculated based on Equation 4.5 and 4.8. 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 (Ptasinski et al., 2007; Ruggieri et al., 2008; Vriens et al., 1989). Mean molecular formulas summarized for sludge samples collected, organic matters in sludge and ash residues formed at 550°C were $C_{1.00}H_{1.80}N_{0.12}S_{0.05}O_{0.51}$, $C_{1.00}H_{1.81}N_{0.12}S_{0.04}O_{0.48}$ and $C_{1.00}H_{0.70}N_{0.15}S_{1.16}O_{5.11}$ respectively. Molecular formula for sludge sample and organic matter were highly similar since $CHNSO_{Inorganic}$ only represented small part of $CHNSO_{Total}$. Significantly lower H, slightly higher N and significantly higher S and O observed for ash residues indicated presence of mainly carbonates, nitrates and sulphates with inorganic bounded moisture contents but absence of C-H functional groups generally found in organic matters. Variations could be observed for different sludge samples but most showed high similarity. For Changi WRP, it could be observed that secondary sludge samples were having lower H and N contents in the normalized molar basis compared to primary and dry sludge samples. Low N contents in secondary sludge could indicate lower amount of proteins or other non-protein nitrogenous compounds. Low H contents could indicate lower amount of lipids or higher contents of polysaccharides. However, further biomass composition analysis needed to clarify the variations in characteristics of different sludge samples. Based on thermodynamics study, feedstock with O/C ratio of lower than 0.40 recommended to be gasified at about 927°C and the temperature increased to 1227°C when O/C ratio further reduced to 0.30 (Ptasinski, 2008). Molecular formula of sludge formed by O_{Total} showed O/C ratio of 0.51 while for $O_{difference}$, O/C ratio reduced to 0.31 in average. Therefore, significant errors could be caused by using $O_{difference}$ for thermodynamic modelling. O_{Total} should be used in pyrolysis and gasification analysis on reactions modelling but $O_{difference}$ could be used for stoichiometric and equivalent ratio calculation. Ultimate analysis in molar basis for selected model compounds was showed in Table 4.17. Proteins and lignocellulosic

biomass components such as cellulose, xylan, and lignin were showing much lower H/C ratios compared to sludge while sucrose and lipids model compounds such as cholesterol and glyceryl lipids were having relatively higher H/C ratios. Sucrose and polysaccharides such as cellulose and xylan were showing much higher O/C ratios compared to sludge while lignin, proteins and lipids were having relatively lower O/C ratios. Results of comparison indicated that sludge could be complex mixtures of different categories of compounds.

Table 4.16: Molecular formula of sludge samples collected.

Sample Label	Molecular formula of sludge					H/C ratio	O/C ratio	H/O ratio	H/N ratio
	C	H	N	S	O				
UR	1.00	1.55	0.11	0.05	0.53	1.55	0.53	2.92	13.58
UD	1.00	1.87	0.13	0.05	0.51	1.87	0.51	3.64	14.39
CP	1.00	1.86	0.17	0.05	0.50	1.86	0.50	3.72	10.91
CS	1.00	1.77	0.08	0.05	0.51	1.77	0.51	3.44	23.44
CY	1.00	1.85	0.14	0.06	0.55	1.85	0.55	3.33	13.57
JR	1.00	1.92	0.10	0.05	0.47	1.92	0.47	4.07	19.22
JD	1.00	1.78	0.10	0.07	0.57	1.78	0.57	3.13	17.75
KR	1.00	1.80	0.11	0.05	0.44	1.80	0.44	4.13	16.31
KD	1.00	1.97	0.16	0.06	0.51	1.97	0.51	3.82	12.61
UsR	1.00	1.77	0.10	0.04	0.46	1.77	0.46	3.88	17.73
UsD	1.00	1.78	0.13	0.04	0.51	1.78	0.51	3.50	13.87
CsP	1.00	1.80	0.15	0.05	0.49	1.80	0.49	3.66	11.86
CsS	1.00	1.76	0.07	0.05	0.51	1.76	0.51	3.42	23.84
CsY	1.00	1.80	0.14	0.06	0.58	1.80	0.58	3.11	13.20
Mean	1.00	1.80	0.12	0.05	0.51	1.80	0.51	3.55	15.88
SD	0.00	0.10	0.03	0.01	0.04	0.10	0.04	0.36	4.06

Table 4.17: Ultimate analysis for model compounds in molar basis.

Model Compounds	Molar Basis					H/O Ratio	H/N Ratio
	C	H	N	S	O		
Cholesterol	1.00	1.70	0.00	0.00	0.04	46.00	-
Glyceryl Tri-Oleate	1.00	1.82	0.00	0.00	0.11	17.33	-
Glyceryl Tri-Palmitate	1.00	1.92	0.00	0.00	0.12	16.33	-
Cellulose	1.00	1.67	0.00	0.00	0.83	2.00	-
Xylan	1.00	1.60	0.00	0.00	0.80	2.00	-
Lignin	1.00	1.19	0.00	0.00	0.29	4.10	-
Sucrose	1.00	1.83	0.00	0.00	0.92	2.00	-
Proteins	1.00	1.58	0.28	0.07	0.30	5.27	5.64

Results of oxygen contents determined by two different methods were showed in Table 4.18. Significant differences quantified as $O_{\text{deviation}}$ could be observed. Differences in O contents determined ranged from 5.09 to 11.37 mass% in db. Since $O_{\text{difference}}$ calculated based on Ash_{950} , $O_{\text{deviation}}$ was mainly caused by apparent mass gained of inorganics during ash formation analysis as suggested by Equation 4.12. $O_{\text{difference}}/O_{\text{Total}}$ ratio showed mean of 0.67 ± 0.11 indicated that calculated values of $O_{\text{difference}}$ only accounted about 67% in average of the total O contents in sludge. Slightly higher of $O_{\text{deviation}}$ in average for sludge samples after AD probably because of higher amount of inorganics and therefore more oxidation of inorganics occurred. Total O contents released from sludge and available in 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 total O contents released from sludge but $O_{\text{difference}}$ would be more suitable to account for the O contents available in the system for thermochemical reactions other than oxidation of inorganics. Therefore direct measurement of O_{Total} was recommended for molecular formula formation of sludge 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 presence of O_2 for system modelling, stoichiometric analysis and equivalence ratios calculations. The phenomenon of significant $O_{\text{deviation}}$ determined for sludge in this study was distinctive when compared to other fuel feedstock such as lignocellulosic biomass and coal. High oxygen contents and low amount of IM were generally found in lignocellulosic biomass. Therefore $O_{\text{oxidation}}$ was not significant compared to the O_{Total} . Decomposition of inorganic components in coal caused the mass of ash residues determined comparable to initial mass of inorganics (Vassilev and Tascon, 2003). Therefore no significant underestimation of oxygen contents could be observed. Low oxygen and high carbon contents in coal led to high stoichiometric requirement of oxygen supply for complete combustion also reduced importance of initial oxygen contents found in coal. However, large amount of ash residues and O contents in sludge caused the accurate estimation of O contents to be important.

Table 4.18: Oxygen contents analysis for sludge.

Sample Label	Oxygen contents, Mass% in db			$O_{\text{Difference}} / O_{\text{Total}}$
	O_{Total}	$O_{\text{difference}}$	$O_{\text{deviation}}$	
UR	30.87	25.45	5.42	0.82
UD	27.29	15.92	11.37	0.58
CP	25.33	15.41	9.92	0.61
CS	30.11	22.74	7.37	0.76
CY	23.41	14.56	8.85	0.62
JR	23.39	12.37	11.02	0.53
JD	20.85	11.22	9.63	0.54
KR	25.42	16.19	9.23	0.64
KD	25.04	13.68	11.35	0.55
UsR	25.91	21.99	3.92	0.85
UsD	26.78	20.99	5.79	0.78
CsP	25.18	17.12	8.06	0.68
CsS	27.55	22.47	5.09	0.82
CsY	23.45	15.63	7.82	0.67
Mean $\pm$ Standard Deviation				
All Sample	25.75 ± 2.68	17.55 ± 4.37	8.20 ± 2.43	0.68 ± 0.11
Before AD	26.72 ± 2.60	19.22 ± 4.54	7.50 ± 2.52	0.71 ± 0.12
After AD	24.47 ± 2.40	15.34 ± 3.24	9.13 ± 2.15	0.62 ± 0.09
Range	20.85 – 30.87	11.22 – 25.45	3.92 – 11.37	0.53 – 0.85

4.3.3.2. Inorganic composition analysis

Inorganic composition analysis provided basic data for pollution concerns of inorganics, ash residues expected to be generated and also potential of inorganics in participating in conversion processes by promoting char formation during pyrolysis and catalytic reactions during gasification (de Lasa et al., 2011; Fonts et al., 2012). Results of combustion released halogens were showed in Table 4.19. Fluoride, chloride and bromide were detected and summations of these elements were considered as total halogens released. Halogen contents determined were not representing the total amount of halogens in sludge but only the halogen elements that released during combustion. Halogens remained bounded with ash residues in solid form were classified as part of the IM. The determination of total halogens released provided basis for pollution analysis and helped to improve mass balance equations and theoretical calculations when calculating IM and $O_{\text{difference}}$. Results

showed that total halogens released during combustion varied among different sludge samples collected with mean of 0.34 ± 0.16 mass% and relatively lower when compared to previous study (Manara and Zabaniotou, 2012). Significant amount of total halogens detected for sludge samples from Jurong WRP compared to other plants caused by the presence of higher amount of fluoride. In average, more fluoride released than chloride and followed by bromide during combustion. However for sludge samples from Ulu Pandan WRP, more chloride and less fluoride released during combustion were detected.

Table 4.19: Combustion released halogens from sludge.

Sample Label	Mass% in dsb			
	Fluoride	Chloride	Bromide	Total halogens
UR	0.04	0.21	0.05	0.30
UD	0.03	0.13	0.04	0.20
CP	0.25	0.12	0.01	0.38
CS	0.27	0.10	0.01	0.38
CY	0.38	0.06	0.01	0.45
JR	0.55	0.14	0.01	0.70
JD	0.49	0.10	0.01	0.60
KR	0.26	0.08	0.01	0.36
KD	0.27	0.07	0.02	0.36
UsR	0.03	0.10	0.02	0.14
UsD	0.04	0.11	0.02	0.16
CsP	0.11	0.14	0.01	0.25
CsS	0.12	0.13	0.01	0.26
CsY	0.13	0.07	0.01	0.21
Mean $\pm$ SD	0.21 ± 0.17	0.11 ± 0.04	0.02 ± 0.01	0.34 ± 0.16

Results of inorganic elements detected were showed in Table 4.20, 4.21 and 4.22. Major ash forming elements detected were similar to previous studies (Dunnu et al., 2010; Wang et al., 2012; Werle, 2014). Measurements of inorganic elements 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, contents of inorganic elements detected were quantitatively varying among different sludge samples collected but qualitatively similar. For major ash forming elements determined, Si, Al, Fe, Ca, and P were presence in relatively higher amount in sludge samples while Ti, Mg,

Na and K were present with less than 1.00 mass% in db in average. Significantly higher P contents could be found in primary sludge as compared to secondary sludge similar to the findings in previous study (F. Y. Wang et al., 2008). For minor elements detected in sludge, Cu and Zn were in relatively higher amount with more than 1000 mg/kg in average compared to Ba, Cr, Mn, Ni, Sn, and Sr. For trace elements detected, Pb, Co, Mo, and V were in higher amount with more than 10 mg/kg in average while Sb, Ag, As and Cd were present with lower amounts. 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 other WRPs. This observation mainly caused by the higher total amount of inorganics in J-R and J-D and also the characteristics of industrial wastewater influent. Changi WRP treated wastewater from domestic sources only while other three WRPs treated wastewater from mixed of domestic and industrial sources. The influent of wastewater from industrial sources may contribute significantly to the amount of inorganic elements detected. Summary of inorganic elements was showed in Table 4.23. Results showed that most of the inorganic elements in sludge were non-volatile ash forming elements with a mean of 14.77 ± 4.97 mass% in db and $96.78 \pm 2.49\%$ in relative composition, followed by minor elements with mean at 0.55 ± 0.63 mass% and $3.14 \pm 2.44\%$ and trace elements with mean of 0.01 ± 0.02 mass% and $0.07 \pm 0.06\%$. Relatively higher composition of minor and trace elements were found in sludge samples collected from Jurong and Kranji WRP indicated the impacts of wastewater influent from industrial sources to the distribution of inorganic elements in sludge. Inorganic elements analysis indicated that extra care needed to be taken for sludge samples from Jurong WRP compared to other plants. Surprisingly low P contents could also be observed for J-R and J-D.

Table 4.20: Major ash forming elements in sludge.

Sample Label	Major ash forming elements, Mass% in dsb									
	Si	Al	Ti	Fe	Ca	Mg	Na	K	P	Total
UR	2.52	0.91	0.01	1.33	1.57	0.21	0.09	0.15	0.82	7.62
UD	5.42	1.86	0.02	2.43	2.33	0.39	0.09	0.28	1.39	14.20
CP	5.04	1.68	0.01	1.33	1.50	0.78	0.15	0.82	3.41	14.72
CS	4.23	1.31	0.01	0.88	1.69	0.13	0.09	0.12	0.70	9.15
CY	9.71	2.83	0.02	1.92	2.70	0.55	0.07	0.31	1.97	20.08
JR	9.79	2.11	0.04	2.74	2.86	0.35	0.16	0.34	0.00	18.39
JD	13.51	3.08	0.06	3.74	4.01	0.50	0.21	0.44	0.27	25.80
KR	5.77	1.01	0.01	1.30	1.92	0.29	0.08	0.23	1.03	11.64
KD	8.02	0.88	0.01	2.54	1.95	0.64	0.07	0.18	2.13	16.42
UsR	4.77	1.53	0.02	1.45	1.58	0.16	0.07	0.28	0.69	10.55
UsD	5.24	1.53	0.02	2.02	1.93	0.33	0.06	0.26	1.02	12.41
CsP	5.52	1.88	0.02	1.33	1.44	0.53	0.16	0.60	2.24	13.70
CsS	5.61	1.53	0.01	1.07	2.12	0.17	0.22	0.20	0.89	11.82
CsY	9.93	3.16	0.02	2.04	2.10	0.62	0.06	0.32	1.99	20.24
Mean	6.79	1.81	0.02	1.87	2.12	0.40	0.11	0.32	1.32	14.77
SD	2.97	0.75	0.01	0.79	0.69	0.20	0.06	0.19	0.92	4.97

Table 4.21: Minor elements in sludge.

Sample Label	Minor elements, mg/kg in dsb								
	Cu	Zn	Ba	Cr	Mn	Ni	Sn	Sr	Total
UR	803	778	250	33	81	56	51	48	2100
UD	1338	1126	408	49	159	86	77	82	3324
CP	493	1041	224	129	91	51	28	64	2120
CS	373	1092	167	108	67	52	8	36	1904
CY	565	1494	277	167	120	73	27	75	2799
JR	3497	9543	380	1480	234	1155	193	228	16710
JD	3890	12683	541	1766	379	1638	310	273	21480
KR	651	3287	181	81	69	162	77	26	4533
KD	995	9210	249	101	110	166	72	43	10945
UsR	783	547	192	31	76	46	49	37	1762
UsD	1237	837	291	40	138	62	98	60	2762
CsP	499	1030	213	127	102	46	48	72	2136
CsS	396	928	181	100	91	52	38	49	1834
CsY	658	1299	264	163	133	64	50	84	2716
Mean	1156	3207	273	312	132	265	80	84	5509
SD	1116	4063	105	560	84	490	80	73	6285

Table 4.22: Trace elements in sludge.

Sample Label	Trace elements, mg/kg in dsb								
	Pb	Sb	Ag	As	Cd	Co	Mo	V	Total
UR	24	0	9	7	0	0	11	8	59
UD	34	0	14	13	0	4	15	18	98
CP	13	0	0	6	0	4	7	10	39
CS	20	4	6	8	3	4	12	9	65
CY	23	0	3	11	0	5	10	19	71
JR	127	41	37	0	29	58	25	86	403
JD	204	50	45	5	38	105	37	133	616
KR	35	5	0	10	0	3	10	10	72
KD	41	0	0	9	0	4	13	6	73
UsR	23	2	4	5	0	2	9	15	60
UsD	31	2	7	6	0	3	13	15	77
CsP	22	4	2	5	0	3	10	10	57
CsS	22	5	3	5	0	3	12	9	60
CsY	29	5	2	7	0	5	12	18	78
Mean	46	8	9	7	5	15	14	26	131
SD	53	16	14	3	12	30	8	37	166

Table 4.23: Summary of inorganic elements in sludge.

Sample Label	Mass% in dsb				Relative Composition %		
	Major	Minor	Trace	Total	Major	Minor	Trace
UR	7.62	0.21	0.01	7.84	97.25	2.68	0.08
UD	14.20	0.33	0.01	14.54	97.65	2.29	0.07
CP	14.72	0.21	0.00	14.94	98.55	1.42	0.03
CS	9.15	0.19	0.01	9.35	97.89	2.04	0.07
CY	20.08	0.28	0.01	20.36	98.59	1.37	0.03
JR	18.39	1.67	0.04	20.10	91.49	8.31	0.20
JD	25.80	2.15	0.06	28.01	92.11	7.67	0.22
KR	11.64	0.45	0.01	12.10	96.19	3.75	0.06
KD	16.42	1.09	0.01	17.52	93.71	6.25	0.04
UsR	10.55	0.18	0.01	10.73	98.30	1.64	0.06
UsD	12.41	0.28	0.01	12.69	97.76	2.18	0.06
CsP	13.70	0.21	0.01	13.92	98.42	1.53	0.04
CsS	11.82	0.18	0.01	12.01	98.42	1.53	0.05
CsY	20.24	0.27	0.01	20.52	98.64	1.32	0.04
Mean	14.77	0.55	0.01	15.33	96.78	3.14	0.07
SD	4.97	0.63	0.02	5.44	2.49	2.44	0.06

Results of inorganic composition analysis for ash were showed in Table 4.24 and 4.25. Oxides in ash residues could be classified into acidic and basic constituents (Dunnu et al., 2010). SiO_2 , Al_2O_3 and TiO_2 were considered as acidic oxides while Fe_2O_3 , CaO , MgO , Na_2O , K_2O , and P_2O_5 were considered as basic oxides. Composition of oxides in sludge samples collected found to be comparable to previous studies (Wang et al., 2012; Werle, 2014). Main acidic constituents were SiO_2 and Al_2O_3 while main basic constituents were P_2O_5 , Fe_2O_3 and CaO . Other oxides included TiO_2 , MgO , Na_2O , and K_2O were presence in minor amounts. Based on relative composition analysis, SiO_2 found to be the dominant components in ash with mean of $50.99 \pm 7.09\%$. Al_2O_3 , P_2O_5 , CaO , and Fe_2O_3 were also major components presence with $12.29 \pm 2.61\%$, $11.47 \pm 6.85\%$, $11.07 \pm 2.56\%$, and $9.68 \pm 2.63\%$ respectively. MgO , K_2O , Na_2O and TiO_2 were minor components presence with only $2.37 \pm 0.94\%$, $1.43 \pm 0.77\%$, $0.59 \pm 0.33\%$, and $0.12 \pm 0.04\%$ respectively. Composition of oxides measured was used in ash sintering study and results were showed in Table 4.26. Fusion temperatures estimated by two calculation methods were similar with less than 50°C difference in average. Based on the calculation, IDT of sludge 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). Significant variations of about $100\text{--}200^\circ\text{C}$ among different sludge samples could be observed. Slightly higher of $R_{B/A}$ and $R_{B+P/A}$ could be observed for sludge before AD resulted in lower fusion temperatures. However these differences were relatively small and could be caused by the variations in wastewater influent instead of treatment processes applied as supported by the comparison made on two batches of sludge samples collected from Ulu Pandan and Changi WRPs that showed significant fluctuations on inorganic elements, oxides ratios and fusion temperatures. To optimize the utilization of sludge in thermochemical conversion processes, more detail analysis needed to further clarify effects of fluctuations in characteristics of inorganics to ash sintering.

Low ash fusion temperature compared to other biomass was one of the main concerns in sludge gasification. High temperature in gasifier could produce higher quality syngas and H_2 to CO ratio in product gas but faced with risks of ash melting and agglomeration. Undesired ash sintering could cause declined in energy

efficiency, increased in maintenance cost and increased frequency of unscheduled shutdown of the thermochemical conversion system (Dogru et al., 2002; Wang et al., 2012). Gasification with uniform operating temperature lower than ash slagging temperature reduced risk of sintering and volatilization of inorganic elements into syngas (L. Wang et al., 2008). Therefore improvements on performance for sludge thermochemical conversion at lower operating temperature and avoidance of local overheating would be beneficial in both ash handling and energy efficiency considerations as suggested in thermodynamics analysis (Prins, 2005; Ptasiński, 2008). IDT and FT indicated initial and complete deformation of ash residues respectively. Therefore, IDT should be considered when to avoid ash sintering in the systems while FT should be considered if sintered ash residues were expected as by-products. Fusion temperature range of sludge found to be ranged from 246 to 252°C for calculation 1 based on $R_{B/A}$ and ranged from 192 to 244°C for calculation 2 based on $R_{B+P/A}$. Large fusion temperature range indicated the presence of inorganic components that having significantly different melting temperatures. Care needed to be taken when estimating fusion temperatures of feedstock based on inorganic elements analysis as ash fusion temperatures 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 estimation based on oxides ratios such as Base-to-Acid ratios ($R_{B/A}$ and $R_{B+P/A}$) was only applicable to samples with similar distribution and mineral characteristics of inorganic components. $R_{B/A}$ could also be used as preliminary indicator for refractory materials used in reactor of targeted feedstock (Routschka, 2008). $R_{B/A}$ of sludge ranged from 0.27 to 0.67 and could be classified as neutral ash residues. Carbon graphite, chromite, alumina, and silica carbide were recommended as refractory materials. Measured oxides composition of sludge samples could be changed by different sources of wastewater or treatment methods then the selection of refractory material should be altered accordingly. For $R_{B/A}$ of less than 0.25 indicated the presence of acidic ash residues therefore the recommended refractory materials were silica and zirconia while for $R_{B/A}$ of greater than 0.75 indicated the presence of basic ash residues therefore the recommended refractory materials were magnesia, dolomite and chromite.

Table 4.24: Mass% of major ash forming oxides.

Sample Label	Mass% of major ash forming oxides in dsb									
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	Ash ₉₅₀
UR	5.38	1.72	0.02	1.91	2.19	0.35	0.13	0.18	1.88	13.77
UD	11.59	3.51	0.03	3.48	3.25	0.64	0.12	0.33	3.18	26.14
CP	10.78	3.17	0.02	1.90	2.09	1.29	0.20	0.99	7.82	28.28
CS	9.05	2.47	0.02	1.26	2.37	0.21	0.12	0.14	1.61	17.24
CY	20.77	5.36	0.03	2.74	3.78	0.91	0.10	0.37	4.51	38.57
JR	20.95	3.98	0.07	3.91	4.00	0.58	0.22	0.41	0.00	34.13
JD	28.90	5.82	0.09	5.35	5.60	0.82	0.28	0.53	0.61	48.01
KR	12.35	1.91	0.02	1.85	2.68	0.49	0.10	0.27	2.36	22.05
KD	17.16	1.66	0.02	3.64	2.73	1.06	0.09	0.22	4.87	31.44
UsR	10.21	2.89	0.03	2.08	2.21	0.26	0.10	0.34	1.58	19.69
UsD	11.22	2.89	0.03	2.88	2.70	0.55	0.08	0.31	2.34	23.00
CsP	11.80	3.55	0.03	1.90	2.01	0.87	0.21	0.72	5.14	26.24
CsS	11.99	2.89	0.02	1.53	2.96	0.28	0.30	0.24	2.04	22.26
CsY	21.24	5.97	0.03	2.91	2.93	1.03	0.09	0.39	4.57	39.15
Mean	14.53	3.41	0.03	2.67	2.97	0.67	0.15	0.39	3.04	27.85
SD	6.34	1.43	0.02	1.13	0.97	0.34	0.08	0.23	2.11	9.50

Table 4.25: Relative composition of oxides in ash residues.

Sample Label	Relative Composition of Oxides in Ash, Mass%								
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
UR	39.11	12.49	0.14	13.85	15.94	2.57	0.93	1.34	13.63
UD	44.34	13.43	0.12	13.31	12.44	2.45	0.47	1.27	12.16
CP	38.11	11.22	0.09	6.73	7.40	4.57	0.72	3.50	27.66
CS	52.52	14.32	0.13	7.30	13.72	1.22	0.68	0.81	9.31
CY	53.87	13.89	0.08	7.11	9.80	2.35	0.25	0.96	11.69
JR	61.39	11.67	0.20	11.46	11.72	1.70	0.65	1.22	0.00
JD	60.19	12.12	0.20	11.15	11.67	1.72	0.58	1.11	1.27
KR	56.03	8.65	0.10	8.41	12.17	2.21	0.47	1.24	10.71
KD	54.57	5.27	0.07	11.57	8.68	3.38	0.28	0.68	15.50
UsR	51.87	14.68	0.13	10.54	11.22	1.33	0.49	1.71	8.03
UsD	48.77	12.57	0.12	12.54	11.75	2.40	0.35	1.35	10.16
CsP	44.99	13.53	0.10	7.25	7.67	3.33	0.81	2.74	19.58
CsS	53.88	12.98	0.11	6.87	13.30	1.26	1.36	1.08	9.16
CsY	54.24	15.24	0.09	7.44	7.49	2.63	0.22	0.99	11.66
Mean	50.99	12.29	0.12	9.68	11.07	2.37	0.59	1.43	11.47
SD	7.09	2.61	0.04	2.63	2.56	0.94	0.31	0.77	6.85

Table 4.26: Fusion temperatures calculated for ash residues of sludge.

Sample label	$R_{B/A}$	Fusion Temperature 1				$R_{B+P/A}$	Fusion Temperature 2			
		IDT 1	ST 1	HT 1	FT 1		IDT 2	ST 2	HT 2	FT 2
UR	0.67	1074	1165	1263	1319	0.93	1094	1173	1273	1331
UD	0.52	1141	1199	1319	1389	0.73	1157	1198	1312	1377
CP	0.46	1165	1210	1339	1414	1.02	1067	1161	1256	1311
CS	0.35	1214	1234	1380	1464	0.49	1228	1226	1356	1430
CY	0.30	1237	1246	1400	1488	0.47	1234	1228	1359	1434
JR	0.37	1209	1232	1376	1459	0.37	1267	1242	1380	1459
JD	0.36	1210	1232	1377	1461	0.38	1262	1240	1377	1456
KR	0.38	1203	1229	1371	1453	0.54	1213	1220	1346	1419
KD	0.41	1189	1222	1359	1438	0.67	1174	1205	1323	1390
UsR	0.38	1202	1229	1371	1453	0.50	1226	1225	1355	1429
UsD	0.46	1166	1211	1340	1415	0.63	1187	1210	1331	1400
CsP	0.37	1206	1230	1373	1456	0.71	1163	1200	1316	1382
CsS	0.36	1213	1234	1379	1463	0.49	1228	1226	1356	1430
CsY	0.27	1251	1253	1411	1503	0.44	1245	1233	1366	1443
Mean $\pm$ standard deviations										
All sample	0.40 $\pm$ 0.10	1191 $\pm$ 44	1223 $\pm$ 22	1361 $\pm$ 37	1441 $\pm$ 46	0.60 $\pm$ 0.20	1196 $\pm$ 60	1213 $\pm$ 24	1336 $\pm$ 37	1407 $\pm$ 44
Before AD	0.42 $\pm$ 0.11	1186 $\pm$ 48	1220 $\pm$ 23	1357 $\pm$ 40	1435 $\pm$ 49	0.63 $\pm$ 0.23	1186 $\pm$ 71	1209 $\pm$ 29	1330 $\pm$ 44	1399 $\pm$ 53
After AD	0.39 $\pm$ 0.09	1199 $\pm$ 42	1227 $\pm$ 21	1368 $\pm$ 35	1449 $\pm$ 44	0.55 $\pm$ 0.14	1210 $\pm$ 43	1219 $\pm$ 17	1345 $\pm$ 27	1417 $\pm$ 32
Minimum	0.27	1074	1165	1263	1319	0.37	1067	1161	1256	1311
Maximum	0.67	1251	1253	1411	1503	1.02	1267	1242	1380	1459

4.3.3.3. Functional groups analysis

FTIR spectra provided information of functional groups detected and indirectly indicated the group of chemical compounds presence. This information was more crucial for pyrolysis and gasification system 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 4.7 showed the FTIR spectra of all sludge samples collected and ash residues after combustion at 550°C. FTIR of sludge showed qualitative similarities and quantitative variations among different sludge samples and comparable to previous research (Grube et al., 2006). FTIR spectra of ash residues showed the characteristics of inorganics and similar to spectra of sludge, no significant qualitative differences but identifiable quantitative differences observed. By comparing FTIR spectra of sludge samples and ash residues, contribution of peaks by organic and inorganic contents could be identified and differentiated to provide a better understanding to the functional groups presence in sludge. However care needed to be taken when carried out FTIR analysis of waste. Complex mixtures in waste caused overlapping of peaks and diverse peaks shifting (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. Direct determination of chemical compounds and detail 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. Wavenumber of detected peaks were recorded in Table 4.27 and assigned with corresponding functional groups and suggested chemical compounds based on literature and databases (Edalatmanesh et al., 2010; Reveille et al., 2003; Sluiter et al., 2010; E. Smidt and Meissl, 2007).

Inorganic bounded O-H groups with wavenumber of 3700 and 3620cm⁻¹ could be observed in sludge samples but not in ash residues. It showed that residual moisture contents remained in sludge after drying at 105°C but removed after combustion at 550°C. Broad peaks at 3600–3100cm⁻¹ region could be contributed by O-H and N-H functional groups suggested the presence of alcohols, acids, amides and amines.

Multiple peaks showed at $3100\text{--}2600\text{cm}^{-1}$ region were caused by C-H groups of unsaturated hydrocarbons and aromatics at 3076cm^{-1} and saturated hydrocarbons, ethers, and lipids at 2925cm^{-1} . C=O functional groups 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 1535cm^{-1} . Multiple peaks showed in the region of $1450\text{--}1350\text{ cm}^{-1}$ could be attributed to C-H groups for saturated hydrocarbon, ethers, and lipids at 1445cm^{-1} and O-H groups for acids and alcohols at 1415cm^{-1} . Peak at 1375cm^{-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 1314cm^{-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 FTIR spectra of sludge samples and ash residues. By considering the organic composition in sludge samples, peaks at 1220cm^{-1} , 1158cm^{-1} and 1030cm^{-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 1028cm^{-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 of sludge and ash residues, peaks at 1080 and 1008cm^{-1} were 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 797cm^{-1} , for carbonates and nitrates at 779cm^{-1} , amides, amines and halogenated compounds at 750cm^{-1} , aromatics and alcohols at 694 cm^{-1} and sulphates at 668cm^{-1} . In general, broad and overlapping peaks were observed throughout the FTIR spectra of sludge samples and ash residues suggested that complex mixture presence 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 in sludge.

Figure 4.7: FTIR spectra of (a) sludge samples collected from WRPs in Singapore and (b) ash residues produced from combustion of sludge at 550°C.

Table 4.27: Functional groups and suggested compounds for FTIR spectra.

Wavenumber of peaks		Functional groups	Suggested compounds
3700 - 3600	3700	O-H	Inorganic O-H
	3620		
3600 - 3100	3280	O-H	Alcohols, acids
		N-H	Amides, amines
3100 - 2600	3076	C-H	Unsaturated hydrocarbon, aromatics
	2925, 2853	C-H	Saturated hydrocarbon, ethers, lipids
1800 - 1450	1710	C=O	Aldehyde, ketone, acids, esters, amides
	1635	C=C	Unsaturated carbon chain backbones
		C=O, N-H	Amides, amines
	1535, 1518	Rings	Aromatics
		N-H, N-O	Amides, nitro compounds
1450 - 1300	1445	C-H	Saturated hydrocarbon, ethers, lipids
	1415	O-H	Carboxylic acids, alcohols
	1375	C-N	Primary amides
		S-O	Sulphur organic compounds
		O-H	Alcohols, polysaccharides
	1314	C-N, S-O	Amines, sulphur organic compounds
		C-O	Carboxylic acids
1300 - 900	1220, 1158	C-O	Polysaccharides, alcohols, esters
		C-N	Amides, amines
	1030	C-O-C	Polysaccharides, ether
	1028	-P=O-	Phosphates, nucleic acids, phospholipids
	1080, 1008	Inorganic	Phosphates, silicates, sulphates, clay minerals
	913	C-H, O-H, C-O-C	Unsaturated hydrocarbon, aromatics, carboxylic acids, glycosidic linkages
900 - 600	797	Inorganic	Minerals, silicates
	779	Inorganic	Carbonates, nitrates
	750	N-H, C-Cl	Amides, amines, halogenated compounds
	694	Rings, O-H	Aromatics, alcohols
	668	Inorganic	Sulphates

4.4. Conclusions

Comprehensive characterisation on physical and chemical properties of sludge specifically for thermochemical conversion was carried out for all existing WRPs in Singapore with total 14 different sludge samples collected based on type, plant, and batch categorisation. Sludge generated in Singapore WRPs could be classified as suitable feedstock for thermochemical conversion processes with positive residual energy (after dewatering/drying treatment), 77.58% organic contents and LHV of 16.24MJ/kg on dry basis average. Qualitative similarities and quantitative variations of different sludge samples were identified and discussed. The categorisations of sludge samples based on type, plant and batch were all showing different thermochemical properties. Due to significant differences in physical forms, primary sludge showed highest bulk density of 0.93g/cm^3 while secondary sludge recorded lowest bulk density of 0.22g/cm^3 . Sludge after AD treatment also recorded relatively higher bulk ($+0.22\text{g/cm}^3$) and pellet ($+0.09\text{g/cm}^3$) density compared to before AD. For comparison of mean values, HHV & LHV of sludge samples collected before AD was higher than after AD by 3.51 MJ/kg (db), 0.82 MJ/kg (daf) and 1.42 MJ/kg (icf). Proximate analysis on dry basis showed that relatively higher VM ($+10.30\%$) and FC ($+1.14\%$) but lower Ash₉₅₀ (-11.43%), FR (-0.50%), and IM (-9.80%) found in sludge before AD treatment. Differences in organic and inorganic contents also caused heat capacity of sludge before AD to be higher by 0.23 J/g-K compared to dewatered and dried sludge where overall mean C_p was calculated at $1.68 \pm 0.26\text{ J/g-K}$. Considering oxygen contents (Mass%, db) in sludge, higher O_{Total} ($+2.25\%$) and $O_{\text{difference}}$ ($+3.88\%$) but lower $O_{\text{deviation}}$ (-1.63%) observed for primary, secondary and raw sludge in average indicated oxidation of inorganic components occurred in a lesser extent for sludge samples collected before AD.

Existing characterisation methods for determination of sludge physical and chemical properties were also analysed and reviewed using collected samples. Oxidation of inorganics during ash forming analysis found to be causing significant deviations on characterisation analysis included oxygen contents determination, char residues analysis and other parameters related to quantification of ash contents in sludge. Results in this study showed that $O_{\text{difference}}$ accounted for only 68.13% of

O_{Total} in sludge, FC accounted for only 56.17% of FR in char residues, HHV & LHV on daf basis were higher than on icf basis by 2.02 MJ/kg and Ash₉₅₀ contents higher than TI by 24.22% and IM by 47.07% in average. Hence, alternative parameters included fixed residues (FR), inorganic matters (IM) and total inorganic contents (TI) and bases for comparison included inorganic matters free basis (imf) and total inorganic contents free basis (icf) were proposed for better estimation, reliable comparison and improved understanding on thermochemical characteristics of sludge. Analytical procedure proposed was comparable to existing characterisation methods and could be applied directly and complementary.

Detail thermochemical characterisation of sludge suggested the applications of different parameters and quantification methods for incineration, pyrolysis and gasification respectively due to differences in operating conditions and reacting environments. Distributions of sludge components (CHNSO_{Organics} and other inorganic contents) in inert (pyrolysis) and oxidative (combustion) environments at different temperatures were significantly different and summarised in Figure 4.8 and 4.9. Gasification 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 presence in sludge. Results of this study also confirmed distinctive behaviours of sludge as compared to traditional feedstock such as coal and lignocellulosic biomass. Therefore further research was suggested on characteristics and behaviours of sludge in thermochemical conversion processes in the aspects of kinetics study, products evolution and organic composition analysis.

Figure 4.8: Distributions of organics and inorganics in sludge for pyrolysis.

Figure 4.9: Distributions of organics and inorganics in sludge for combustion.

5. Thermal degradation behaviours and products evolution analysis of sludge by analytical and experimental pyrolysis

Findings in this chapter were summarised and published as an original research paper: Chan, W.P. and Wang, J.-Y. (2016) “Comparison study on thermal degradation behaviours and product distributions for various types of sludge by using TG-FTIR and fixed bed pyrolysis.” *Journal of Analytical and Applied Pyrolysis*, Vol. 121 pp. 177-189.

5.1 Introduction

Analytical pyrolysis of sludge aimed to determine thermal degradation behaviours as the primary reactions in thermochemical conversion processes such as pyrolysis, gasification and combustion. Thermal degradation behaviours including mass loss characteristics, kinetics of thermally induced degradations and products evolution during the reactions were important aspects in process modelling and reactor design (Kandiyoti et al., 2006). Kinetics analysis could be carried out based on mass loss data collected by TGA-DTG for determination of rate equations and corresponding parameters, description of reaction mechanisms, and making predictions of reaction behaviours for any complex time-temperature profiles (Sergey Vyazovkin et al., 2011). Hence, multiple heating rates analysis and model-free isoconversional methods were selected for carrying out analytical pyrolysis on 14 different sludge samples collected for thermal degradation behaviours analysis and comparison study. Differential and integral isoconversional methods by Friedman and Ozawa-Flynn-Wall (OFW) analysis respectively for non-isothermal conversion were used in this study. Details of calculation methods were based on published studies as described in literature review of this thesis (Khawam and Flanagan, 2005; Sergey Vyazovkin, 1996; Sergey Vyazovkin et al., 2011). Reaction stoichiometry was also considered as an important aspect for comprehensive understanding of thermal decomposition of solids which included physical and chemical characterisation of the reactants and products (Galwey, 2003). Therefore main permanent gases and volatile compounds categorised based on functional groups detected in interconnected TGA-FTIR system were analysed and compared for product

evolution analysis (Biagini et al., 2006). Existing experimental pyrolysis studies on different types of sludge at different reaction temperatures showed distinct amounts of yields and different chemical compounds distributed in solids, liquids and gases (Conesa et al., 1998; Kim and Parker, 2008). However, limited understanding had been achieved on the impacts of sludge composition on the corresponding pyrolysis products. Hence, comparison study by experimental pyrolysis was carried out to complement the results of analytical pyrolysis on determination of thermal degradation behaviours and products evolution analysis for different sludge samples collected based on plant, type and batch categorization. Yield distributions and energy requirements for pyrolysis process were measured and calculated. Char residues produced were further characterized by considering both physical and chemical properties included heat capacity, heating value, ultimate analysis and functional groups analysis by using FTIR system. Considering the distinctive characteristics of sludge as compared to other biomass, nitrogen and sulphur contents were presence significantly and causing concerns of pollutants released during application of thermal treatment. Therefore, distributions of CHNSO elements in solid residues and volatile components during pyrolysis of sludge were also important characteristics to be considered for process design and pollution control. Gas composition was determined by GC-TCD/FID for identification and calculation of relative abundance for main gaseous compounds detected.

5.2. Materials and Methods

5.2.1. Analytical pyrolysis

14 different sludge samples based on type, plant, and batch categorisation collected from Water Reclamation Plants (WRPs) in Singapore were analysed. TGA mass loss data in mass% were measured in dry basis (db) and corresponding DTG data in %/min were derived based on numerical differentiation. For comparing different sludge samples with varying amounts of inorganic matters and char residues, TGA and DTG in volatile basis (vb) were calculated based on Equation 5.1 and 5.2. DTG data recorded in %/min were also divided by heating rate, β to convert into %/°C by using $R_{\%/^{\circ}C} = R_{\%/min}/\beta$ to compare degradation rate measured at different heating rates. Degree of conversion was 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. Mean TGA, DTG and α were calculated based on data collected from experiments of five different heating rates.

$$\text{TGA in volatile basis, } M_{vb} = \left[1 - \frac{100 - M_{db}}{100 - Char_{db}} \right] \times 100\% \quad \text{Equation 5.1}$$

$$\text{DTG in volatile basis, } R_{vb} = \left[\frac{100}{100 - Char_{db}} \right] \times R_{db} \quad \text{Equation 5.2}$$

Kinetics computational procedure developed by ICTAC Kinetics Committee was adopted and applied to analyse all the sludge samples collected (Sergey Vyazovkin et al., 2011). Both differential method by Friedman analysis and integral method by Ozawa-Flynn-Wall (OFW) analysis were applied to determine apparent activation energy, E_a as a function of conversion, α according to the mathematical expressions developed in previous studies and by using analytical software from Netzsch Thermokinetics (Mo et al., 2013; Sbirrazzuoli et al., 2009; Sergey Vyazovkin, 2000). Standard deviations of E_a determined were calculated by using Equation 5.3, $SD_m = \sqrt{S_{yx}^2 / SS_{xx}}$ where $S_{yx}^2 = \sum_{i=1}^n (y_i - \hat{y})^2 / (n - 2)$ and $SS_{xx} = \sum_{i=1}^n (x_i - \bar{x})^2$ based on linear regression analytical method (Seber and Lee, 2012).

Baselines corrections were carried out on TGA-FTIR spectra collected based on the absorbance measured at $2500 \pm 100 \text{ cm}^{-1}$ because no peak detection and generally parallel spectra observed at this wavenumber region. TGA-FTIR spectra collected at different temperatures within the primary degradation regions of three types of sludge samples from Changi WRP were selectively illustrated and analysed. Direct comparisons of 10 important peaks identified were carried out after the absorbance normalized to the mass of organic matters presence in respective sludge samples.

5.2.2. Experimental pyrolysis

Sludge samples were weighted at $20.00 \pm 2.00 \text{ g}$ on quartz boat as carrier and inserted into horizontal quartz tube reactor. Nitrogen gas supplied at flow rate of 600 ml/min to maintain inert environment in the reactor and to flush out any volatile compounds produced during experiments. Pyrolysis reactor was hold at 100°C as initial temperature for 10 minutes. After initialization, pyrolysis reactor was further heated up to reaction temperature at heating rate of 25 K/min . All 14 sludge samples

were pyrolysed to final temperature of 500°C and CsY was selected for further analysis at pyrolysis temperatures of 200°C, 300°C, and 400°C separately. Reactor maintained at pyrolysis temperature with total experimental time of 50 minutes and then allowed to cool down for char samples collection. Pyrolysis temperatures of sludge were selected based on primary degradation region and apparent peaks in DTG profiles identified by analytical pyrolysis in this study. Selection of pyrolysis temperature at 500°C and below 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 (Agarwal et al., 2015; Di Blasi, 2009). Total energy required for pyrolysis included heat required to raise initial temperature of feedstock to targeting reaction temperature and heat required for pyrolysis reactions. This was calculated based on heat capacity and $\Delta H_{\text{pyrolysis}}$ of sludge. Heat capacity of sludge was measured at temperature interval from 70°C to 120°C (343K to 393K) lower than the initial temperature of thermal degradation. $\Delta H_{\text{pyrolysis}}$ for sludge was measured at main degradation region ranged from 200°C to 500°C. Mass of char solids collected was recorded as total solids yield. Solid residues remained was commonly known as char and consisted of three major components which were inorganic matters initially presence in sludge, unreacted organic residues and char formed during pyrolysis. The summation of unreacted organic matters and char formed during pyrolysis were categorised as residual char. Residual char was calculated by the difference between total solids yield and inorganic matters mass% in sludge. Solids residues collected were further characterized by considering both physical and chemical properties which included heat capacity, heating values, ultimate analysis and FTIR spectra for functional groups analysis. Ultimate analysis of solid residues carried out with direct determination of CHNS contents and indirect calculation of O contents by difference using IM contents. Significant oxidation of inorganics in sludge could be observed during ash forming analysis as discussed in Chapter 3 therefore estimation of inorganics in char solids was carried out with IM instead of ash contents.

Volatile compounds released during pyrolysis were allowed to condense inside condensation tubes connected in series and placed in ice bath. Mass of the condensable liquids was recorded as liquid yield. Gas yield was then calculated by

difference. Gas collection was carried out by using gas bag at the gas outlet of the pyrolysis system after the collection of condensable liquids. Gas samples collected were tested using GC-FID/TCD/TCD (Agilent Technologies 7890B). Gases detected from sludge pyrolysis were CO₂, CO, CH₄, H₂ and other hydrocarbon gases. Detected hydrocarbon gases during sludge pyrolysis 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 in this study. Relative abundance in volume percentage was calculated by assuming the volume of other gas components such as NH₃, HCN, HCl, H₂S, and SO₂ were insignificant when compared to the main gas components detected.

5.3. Results and Discussion

5.3.1. Multiple heating rates TGA-DTG analysis

Impacts of heating rates on TGA and DTG were generally comparable for all 14 different sludge samples studied. Therefore, data for three types of sludge samples collected from Changi WRP, CsP, CsS and CsY were selected for illustration and showed in Table 5.1. Plots of multiple heating rates TGA in mass% and DTG in %/°C and %/min on vertical axes with temperature in °C and time in minutes on horizontal axes respectively for Changi dried sludge, CsY were also showed in Figure 5.1 for illustration. Based on data obtained, thermal degradation of sludge could be generally divided into primary and secondary degradations where majority of the volatile compounds released during primary degradations at low temperature with high mass loss rate and continuous decomposition occurred during secondary degradations at high temperature with low mass loss rate. Similarly primary devolatilization and secondary thermolysis also observed during previous studies on pyrolysis of lignocellulosic biomass and sludge where main mass loss occurred at a specific temperature range depending on the composition and followed by slow and continuous mass loss (Bengoa et al., 2011; Biagini et al., 2006; Thipkhunthod et al., 2006). Primary degradation region of sludge generally occurred at 100-500°C while secondary degradation region occurred at 500-950°C. Residual mass of sludge in db

were compared at 500°C and 950°C respectively. Corresponding relative% of volatiles released was calculated. Data showed that release of volatiles at both temperatures remained consistent at different heating rates used in this study. For comparison purposes, initial and terminate temperatures for sludge in primary degradation regions under different heating rates were determined when degradation rate of $-0.02\%/^{\circ}\text{C}$ was reached. Multiple apparent peaks could be observed while peaks with maximum degradation rates were compared.

Based on the multiple heating rates TGA, highly similar and poorly separated mass loss curves from 100 to 950°C could be observed for all sludge samples at different heating rates used. Mass% in db recorded at 500°C and 950°C and relative% of volatiles released in both primary and secondary degradation regions appeared to be closely similar with random deviations. These results observed probably because sludge samples were less affected by the heat transfer conditions as compared to other biomass feedstock (Urban and Antal Jr, 1982). Poor separation of TGA curves could be also due to heterogeneity in composition which caused random errors among the mass loss data and therefore less significant shift of TGA curves to higher temperature at higher heating rates observed. In addition, thermal degradations of organic matters in sludge could be highly sensitive to temperature indicating high activation energy, E_a therefore less affected by heating rates used. Variations in sludge composition and mass of char residues formed at different heating rates also caused random crossing on mass loss curves as observed for all sludge samples collected (Urban and Antal Jr, 1982).

Based on multiple heating rates DTG of sludge, heterogeneity of composition in sludge samples could also be observed as the DTG profiles plotted randomly varied at different heating rates. Shifts of initialization and terminating temperatures for primary degradation region, peaks at maximum degradation rate and other apparent peaks to slightly higher temperatures and degradation rates could also be found in DTG profiles when higher heating rates were used. Heterogeneity of the inorganic contents in sludge could also be observed based on the apparent peaks at temperature region of higher than 500°C in some of the samples tested. Higher heating rates also caused the thermal degradation of sludge samples occurred in

much shorter time intervals and therefore slightly lower resolution of the apparent peaks could be observed. In general, thermal degradation behaviours of sludge samples collected were highly similar at different heating rates within the range of 5 to 25 K/min used in this study. Therefore, mean TGA and DTG were calculated based on the data measured for further comparison among different sludge samples. Kinetics analysis was also carried out by using the data collected in multiple heating rates TGA-DTG. Heterogeneity in organic and inorganic composition of sludge samples indicated the importance of the analysis of representative samples and the potential advantages of forming synthetic sludge with well controlled and modifiable composition to improve the accuracy and consistency of thermal degradation behaviours study.

Results of TGA-DTG for all sludge samples were summarised with mean values calculated based on multiple heating rates analysis in Table 5.2. Mean TGA-DTG calculated in dry basis (db) and volatile basis (vb) were also illustrated in Figure 5.2. Thermal degradation behaviours of sludge were quantitatively varied but qualitatively similar as highly comparable mass loss curves in TGA and generally overlapping degradation rate profiles in DTG could be observed. By comparing mean TGA-DTG calculated, variations observed in db mainly caused by presence of different amounts of inorganic matters in sludge samples and variations in vb mainly caused by differences in organic and inorganic composition of sludge. Initial and terminating temperatures in primary degradation region determined based on the selected degradation rate of $-0.02\%/^{\circ}\text{C}$ 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. Based on the apparent changes of slope in mass loss curves of mean TGA which indicated the different stages of degradation, 500°C also appeared to be a good estimated temperature for the end of primary degradation region for sludge.

Both initial and terminating temperatures of sludge samples after anaerobic digestion (AD) treatment included dewatered (UD, UsD, JD and KD) and dried (CY and CsY) sludge were slightly higher as compared to sludge samples before AD included raw (UR, UsR, JR and KR), primary (CP and CsP), and secondary (CS and CsS) sludge. Determination of 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 by DTG with broad and multiple apparent peaks could be observed for all sludge samples collected in both db and vb. The temperatures at maximum degradation rate ranged from $274.9 \pm 9.1^{\circ}\text{C}$ to $346.4 \pm 13.5^{\circ}\text{C}$ with degradation rates in db ranged from $-0.16\%/^{\circ}\text{C}$ to $-0.54\%/^{\circ}\text{C}$ for different sludge samples. Maximum degradation rates in vb and corresponding temperatures for primary sludge samples were similar to the dewatered and dried sludge samples. Secondary sludge samples, CS and CsS showed significantly higher degradation rates at temperature around 340°C and much lower degradation rates at temperature above 400°C in both db and vb as compared to all other sludge samples. Raw sludge samples showed mixed behaviours of primary and secondary sludge samples.

By comparing the mean DTG profiles, dewatered and dried sludge samples showed relatively higher degradation rate at temperature above 400°C as compared to raw, primary, and secondary sludge samples. However both maximum degradation rates and their corresponding recorded temperatures were generally lower for sludge samples collected after AD treatment. These observations indicated that the thermal degradations of sludge samples after AD were slightly more distributed which suggested the presence of more diverse composition and larger amounts of recalcitrant organic matters or other non-biodegradable materials that decomposed at higher temperature. In average, more than 50 mass% of solids in db degraded during thermal degradation of sludge and more than 80 relative% of total mass loss caused by release of volatile compounds in the primary degradation region. Significant lower relative% for volatiles released before 500°C could be observed for sludge samples collected from Jurong WRP probably because of secondary char degradation and the decomposition of significant amount of inorganics at higher temperature such as carbonates and sulphates. Higher relative% for volatiles released before 500°C could also be observed for secondary sludge samples. In

general, mass% in db for char residues at 500°C and 900°C for sludge samples after AD treatment were higher mainly due to the presence of more inorganic matters. Less volatile compounds released in relative% during primary 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.

Apparent peaks identified for thermal degradations in primary degradation region of all sludge samples were comparable. In general, three apparent broad peaks could be observed. The first apparent peak occurred at $276.8 \pm 5.2^\circ\text{C}$ with degradation rate of $-0.28 \pm 0.05\%/^\circ\text{C}$, while second and third apparent peaks could be observed at $326.2 \pm 10.7^\circ\text{C}$ and $414.7 \pm 11.1^\circ\text{C}$ with degradation rates of $-0.33 \pm 0.12\%/^\circ\text{C}$ and $-0.13 \pm 0.02\%/^\circ\text{C}$ by considering mean values calculated. Peaks observed in DTG could be used to identify the main components in the waste mixtures. Peaks observed in DTG could represent the composition in sludge as different components degraded with distinct characteristics (Heikkinen et al., 2004). Comparison on DTG of all sludge samples suggested that different but comparable components with varying amounts presence in the waste mixtures. Isolation and identification of thermal degradation behaviours of individual group of components could therefore help to improve the understanding on pyrolysis of sludge.

Table 5.1: Multiple heating rates TGA-DTG of CsP, CsS and CsY sludge.

Sample label	K/min	Initial Temp °C	Maximum degradation		Terminate Temp °C	Mass% in dry basis		Volatiles released in relative%	
			Temp °C	Rate %/min		500 °C	950 °C	100°C - 500 °C	500°C - 950 °C
CsP	5	152.2	261.0	-1.50	527.5	44.13	34.68	85.53	14.47
	10	164.1	272.6	-3.35	526.8	44.34	36.17	87.20	12.80
	15	157.9	282.3	-5.20	536.2	45.10	36.85	86.94	13.06
	20	163.9	287.3	-7.24	552.9	44.22	36.93	88.44	11.56
	25	172.2	287.8	-8.23	540.4	47.64	38.98	85.81	14.19
Mean ± SD		162.1 ± 7.5	278.2 ± 11.4		536.8 ± 10.7	45.09 ± 1.48	36.72 ± 1.55	86.79 ± 1.17	13.21 ± 1.17
CsS	5	154.9	323.1	-2.62	510.2	39.68	30.89	87.28	12.72
	10	175.5	332.3	-5.32	514.2	40.22	33.75	90.23	9.77
	15	170.9	342.6	-8.14	529.5	39.60	32.46	89.43	10.57
	20	170.4	337.5	-11.12	532.6	39.30	32.20	89.53	10.47
	25	170.4	336.1	-13.96	533.8	40.50	33.74	89.81	10.19
Mean ± SD		168.4 ± 7.9	334.3 ± 7.3		524.1 ± 11.0	39.86 ± 0.49	32.61 ± 1.20	89.26 ± 1.15	10.74 ± 1.15
CsY	5	167.0	312.9	-1.11	537.7	58.51	48.25	80.17	19.83
	10	173.0	316.8	-2.31	538.4	58.32	49.95	83.27	16.73
	15	188.8	325.1	-3.37	558.3	59.15	48.34	79.07	20.93
	20	197.7	338.2	-4.94	554.5	59.86	50.08	80.41	19.59
	25	170.4	334.0	-6.86	569.1	57.88	48.03	81.06	18.94
Mean ± SD		179.4 ± 13.2	325.4 ± 10.8		551.6 ± 13.5	58.74 ± 0.77	48.93 ± 1.00	80.80 ± 1.56	19.20 ± 1.56

Figure 5.1: Multiple heating rates (a) TGA (b) DTG on temperature and (c) TGA and (d) DTG on time of CsY sludge.

Table 5.2: Summary of multiple heating rates TGA -DTG of sludge.

Sample label	Initial Temp °C	Maximum degradation		Terminate Temp °C	Mass% in db		Volatiles released in relative%	
		Temp °C	Rate %/°C		500°C	950°C	100-500°C	500-950°C
UR	137.3 ± 19.7	340.7 ± 7.7	-0.40 ± 0.02	558.8 ± 9.9	41.96 ± 1.51	31.42 ± 1.22	84.63 ± 0.80	15.37 ± 0.80
UD	162.0 ± 5.8	277.5 ± 8.2	-0.28 ± 0.03	589.2 ± 29.0	50.37 ± 0.70	38.87 ± 0.77	81.20 ± 0.76	18.80 ± 0.76
CP	161.5 ± 5.9	318.4 ± 9.2	-0.31 ± 0.02	545.9 ± 3.5	47.23 ± 0.82	37.57 ± 1.03	84.55 ± 0.86	15.45 ± 0.86
CS	185.4 ± 7.1	346.4 ± 13.5	-0.61 ± 0.05	553.0 ± 22.3	41.40 ± 2.72	32.76 ± 1.04	87.13 ± 2.84	12.87 ± 2.84
CY	165.9 ± 5.8	318.6 ± 6.6	-0.26 ± 0.02	547.5 ± 6.5	57.95 ± 0.95	48.56 ± 0.57	81.75 ± 1.41	18.25 ± 1.41
JR	161.5 ± 10.8	322.4 ± 4.4	-0.29 ± 0.03	551.6 ± 9.4	52.47 ± 2.38	40.29 ± 2.40	79.58 ± 1.05	20.42 ± 1.05
JD	171.9 ± 11.0	320.4 ± 7.1	-0.16 ± 0.02	570.4 ± 25.9	66.07 ± 0.83	53.14 ± 0.83	72.43 ± 1.83	27.57 ± 1.83
KR	163.8 ± 6.3	327.8 ± 17.2	-0.33 ± 0.03	540.5 ± 27.2	44.24 ± 0.93	35.75 ± 0.73	86.80 ± 0.87	13.20 ± 0.87
KD	163.3 ± 3.5	310.9 ± 4.4	-0.26 ± 0.02	543.0 ± 13.9	53.00 ± 0.50	43.29 ± 1.06	82.89 ± 1.06	17.11 ± 1.06
UsR	162.4 ± 5.7	342.0 ± 11.8	-0.38 ± 0.02	540.6 ± 15.2	39.21 ± 2.69	29.71 ± 2.72	86.47 ± 1.02	13.53 ± 1.02
UsD	156.4 ± 10.4	274.9 ± 9.1	-0.32 ± 0.02	573.3 ± 5.0	45.39 ± 2.02	34.37 ± 1.68	83.20 ± 2.00	16.80 ± 2.00
CsP	162.1 ± 7.5	278.2 ± 11.4	-0.33 ± 0.02	536.8 ± 10.7	45.09 ± 1.48	36.72 ± 1.55	86.79 ± 1.17	13.21 ± 1.17
CsS	168.4 ± 7.9	334.3 ± 7.3	-0.54 ± 0.01	524.1 ± 11.0	39.86 ± 0.49	32.61 ± 1.20	89.26 ± 1.15	10.74 ± 1.15
CsY	179.4 ± 13.2	325.4 ± 10.8	-0.24 ± 0.02	551.6 ± 13.5	58.74 ± 0.77	48.93 ± 1.00	80.80 ± 1.56	19.20 ± 1.56
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
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	14.36 ± 2.87
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

Figure 5.2: Mean data for sludge on (a) TGA (b) DTG in dry basis and (c) TGA (d) DTG in volatile basis.

5.3.2. Kinetics analysis

Activation energy for thermal degradation of sludge was determined by differential method using Friedman analysis and integral method using Ozawa-Flynn-Wall (OFW) analysis. Plots of activation energy, E_a related to conversion, α for all sludge samples collected were showed in Figure 5.3. E_a increased steadily at the initial conversion stage where $\alpha < 0.20$, and then 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 presence of reversible reactions (S. Vyazovkin, 2001; Sergey Vyazovkin et al., 2011). Reversible reactions could be caused by simultaneous mass loss and mass gain at high temperature where mass loss caused by volatiles released from sludge solids or by secondary char degradation and mass gain caused by solids formation through carbonization of volatile compounds and char forming reactions. Significant carbonization products could be observed on the upper parts of crucible distance from solid residues after end of pyrolysis suggested reversibility of mass changed by carbonization of volatiles released. Negative values of E_a could be observed mainly caused by the crossover of TGA mass loss curves at high temperature due to heterogeneity of sludge composition (Urban and Antal Jr, 1982).

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 initial and ending stages (Sbirrazzuoli et al., 2009). Therefore mean values of E_a for sludge samples collected were calculated as indicators only based on the E_a measured in the main degradation region and results were showed in Table 5.3. Standard deviations (SD) showed were indicators of the consistency of E_a within the selected region. Results showed that mean values for different sludge samples varied significantly. These variations could be caused by the differences in the composition 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. Difference between the mean values of activation energy determined by Friedman and OFW methods calculated at 19.7kJ/mol or 10.88% and comparable to the systematic deviations found in previous research (S. Vyazovkin, 2001). 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 clarify the details of 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 (Sergey Vyazovkin, 1996). Considering the relationship of temperature and 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 5.4. Second section could be classified as major degradation section where the temperature-conversion plot showed strong linearity with R^2 of 0.9685. Degradation of sludge samples occurred mainly 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 samples 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 inorganic contents 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 the temperature boundaries of the three sections. Generally, the temperature-conversion relationships agreed well with the selected temperature of 500°C as the boundary to separate between primary and secondary degradation regions of the sludge as

discussed in the multiple heating rates TGA and DTG analysis. Temperatures for sludge samples collected from Jurong WRP at conversion, $\alpha = 0.80$ were much higher compared to all other plants due to presence of significant amount of inorganic contents that decomposed at higher temperature compared to organic matters that generally decomposed at temperature below 500°C .

Figure 5.3: Activation energy of sludge by (a) Friedman and (b) OFW analysis.

Table 5.3: Mean activation energy and temperature-conversion data.

Sample label	Activation Energy, E in kJ/mol				Temperature °C at conversion α			
	Friedman analysis		OFW analysis					
	Mean	SD	Mean	SD	$\alpha = 0.01$	$\alpha = 0.20$	$\alpha = 0.80$	$\alpha = 0.99$
UR	229.7	25.2	202.4	30.7	195.8	277.2	459.3	910.9
UD	240.8	61.3	209.2	58.2	153.4	270.7	488.2	915.4
CP	183.6	5.1	161.1	6.8	156.1	262.1	458.8	925.3
CS	98.3	48.1	99.3	32.1	185.8	290.6	443.3	889.4
CY	319.4	648.7	288.0	539.5	150.9	273.1	481.7	944.3
JR	203.8	49.3	182.1	34.1	127.4	267.7	506.7	917.4
JD	78.4	73.3	69.7	52.5	128.4	284.6	608.5	926.4
KR	58.7	145.3	52.4	115.1	167.4	261.2	441.8	914.9
KD	226.8	225.8	211.6	170.0	154.4	260.2	468.3	934.3
UsR	156.7	31.6	135.3	21.6	139.4	262.2	445.3	907.9
UsD	158.3	266.6	142.1	203.6	120.0	262.7	468.8	919.8
CsP	178.5	6.8	150.5	6.3	127.9	260.2	443.8	927.4
CsS	212.1	162.2	187.8	128.6	174.3	272.1	414.9	909.3
CsY	190.5	42.8	167.7	32.9	125.7	278.9	493.4	925.7
Mean $\pm$ standard deviations								
All sample	181.1 $\pm$ 69.2		161.4 $\pm$ 61.4		150.5 $\pm$ 23.9	270.2 $\pm$ 9.8	473.1 $\pm$ 46.0	919.2 $\pm$ 13.2
Before AD	165.2 $\pm$ 58.9		146.4 $\pm$ 50.0		159.3 $\pm$ 50.0	269.2 $\pm$ 10.5	451.7 $\pm$ 26.1	912.8 $\pm$ 11.8
After AD	202.4 $\pm$ 81.5		181.4 $\pm$ 73.8		138.8 $\pm$ 15.7	271.7 $\pm$ 9.3	501.5 $\pm$ 53.4	927.7 $\pm$ 10.4

5.3.3. Products evolution analysis

Qualitative and semi-quantitative comparisons on the volatile compounds released during thermal degradations of sludge were carried out based on peaks identification and absorbance normalisation. TGA-FTIR spectra for CsP, CsS and CsY sludge samples at different temperatures within primary degradation region were selectively illustrated in Figure 5.4. Wavenumber of peaks identified in the spectra and corresponding functional groups were recorded and showed in Table 5.4. The main functional groups detected in TGA-FTIR system included O-H, N-H, C-O, C-H, H-C≡N and C=C groups. Gaseous compounds identified were methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), water vapour (H₂O), ammonia (NH₃), and hydrogen cyanide (HCN). Ten selected peaks identified in TGA-FTIR spectra at (a) 3032 cm⁻¹ (C=C-H), (b) 3016 cm⁻¹ (CH₄), (c) 2974 cm⁻¹ (C-H), (d) 2359 cm⁻¹ (CO₂), (e) 2173 cm⁻¹ (CO), (f) 1541 cm⁻¹ (H₂O), (g) 1176 cm⁻¹ (C-O), (h) 966 cm⁻¹ (NH₃), (i) 951 cm⁻¹ (C=C) and (j) 712 cm⁻¹ (HCN) were compared and showed in Figure 5.5. Absorbance measured were normalised to the mass of organic matters presence in the Cs-P, Cs-S and Cs-Y sludge samples respectively for comparison. Distinct characteristics of volatile compounds released according to the reaction temperatures and types of sludge samples could be observed in TGA-FTIR spectra collected for Cs-P, Cs-S and Cs-Y sludge samples during primary thermal degradations. 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 (Hernández et al., 2013). 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 release of water vapours gradually increased as temperature elevated to 500°C. Release of water vapour during pyrolysis could be caused by dehydration of organic components (Conesa et al., 1998). Dehydration of hydrated inorganic compounds in sludge could also contribute to the release of water vapour as suggested by comparison made for the FTIR spectra of sludge samples and char solids. Peaks identified in solids FTIR spectra at 3700cm⁻¹ corresponding to O-H functional

groups for inorganic compounds reduced in absorbance as temperature increased and diminished from the solids residues collected after pyrolysis at 500°C. CO₂, CO, C-O functional groups and NH₃ detection reached maximum at temperature region from 300°C to 400°C corresponding to the second apparent peak in DTG. 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 recalcitrant organic matters, non-biodegradable materials and char residues decomposed. Similar volatiles compounds released 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 CO₂, CO and C-O containing compounds released from Cs-S during thermal degradation but higher absorbance detected at 966 cm⁻¹ indicated relatively more NH₃ released from Cs-P and Cs-Y. More C-H and C=C-H containing compounds also released from Cs-Y at above 400°C. Comparable release of methane, H₂O, HCN, and C=C functional groups could be observed for all three types of sludge.

Table 5.4: Peaks identified in TGA-FTIR spectra for CsP, CsS and CsY.

Suggested compounds	Wavenumber of peaks identified		
	CsP	CsS	CsY
Methane, CH ₄	3016	3016	3016
Carbon dioxide, CO ₂	2359	2359	2359
Carbon monoxide, CO	2187	2187	2187
Water vapour, H ₂ O	1541	1541	1541
Ammonia, NH ₃	966	966	966
Hydrogen cyanide, HCN	712	712	712
C-H groups	3032	3032	3032
	2974	2974	2968
	2959	2959	2959
	2939	2939	2935
	-	2820	-
C-O groups	1176	1176	1176
	-	1105	1105
C=C groups	951	951	951
	-	-	908
	-	742	-
	719	719	-

Figure 5.4: Comparison of TGA-FTIR spectra for (a) CsP, (b) CsS and (c) CsY in primary degradation region from 250-500°C.

Figure 5.5: Comparison of peaks identified in TGA-FTIR spectra for CsP, CsS and CsY. (a) 3032 cm^{-1} (C=C-H), (b) 3016 cm^{-1} (CH_4), (c) 2974 cm^{-1} (C-H), (d) 2359 cm^{-1} (CO_2), (e) 2173 cm^{-1} (CO), (f) 1541 cm^{-1} (H_2O), (g) 1176 cm^{-1} (C-O), (h) 966 cm^{-1} (NH_3), (i) 951 cm^{-1} (C=C) and (j) 712 cm^{-1} (HCN).

5.3.4. Yield distributions analysis

During pyrolysis, organic components in sludge would be thermally degraded to release liquids and gases as volatile compounds and to form char as solids residues. Inorganic components in sludge generally remained as solids with the release of insignificant amount of volatile inorganics as compared to organic decomposition. Yield distributions for experimental pyrolysis at 500°C of 14 different sludge samples collected were showed on dry basis (db) and inorganic matters free basis (imf) in Table 5.5. Results of yield distribution were quantitatively different and qualitatively similar among different sludge samples analysed and were also comparable to findings in previous research on pyrolysis of sludge (Fonts et al., 2012). Yield distributions in db showed that significant variations in solids, liquids and gases yields could be observed when comparing different types of sludge samples collected. Variations were caused by differences in amounts of inorganic matters presence and characteristics of organic composition in sludge. Solid residues recorded highest mass% in db followed by liquids and gases due to presence of high amounts of inorganics. In average, solid residues after pyrolysis at 500°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 of sludge pyrolysis could be caused by apparent effects of IM presence and interaction effects with the organic components. Mass% of IM increased the apparent solid yields and reduced the apparent liquid and gas yields. IM could also promote char forming reactions and catalytic decomposition which increased solids yield and reduced liquids yield (Fonts et al., 2012). Biomass composition of 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 presence. Different organic components such as lipids, proteins, and carbohydrates could produce distinctive yield distributions.

Yield distributions in imf basis were calculated for comparison among different sludge samples by removing the apparent effects of mass% of IM on the measured data (db). In average, liquids recorded highest mass% in imf basis followed by solids and gases. Total volatiles and liquids yield from dewatered and dried sludge samples after treated by AD were lower than the samples collected before AD

which included raw, primary and secondary sludge samples in both db and imf bases. Solid yields in 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 in imf basis indicated that organic matters presence released relatively less permanent gases but slightly higher in db as relatively higher mass% of organic matters presence. After treated by AD, sludge samples in average 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 (V/S) and liquid/gas (L/G) 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 when all sludge samples were considered. Both ratios were higher in average 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 composition of sludge were suggested to be having significant impacts on the results of pyrolysis. Since organic matters were mainly decomposed during pyrolysis at 500°C, further analysis on the biomass composition of sludge could help to understand and predict the yield distributions from pyrolysis of different types of sludge samples

Correlations for yield distributions with IM contents and CHNSO elemental composition in sludge were established and showed in Figure 5.6. Yield distributions in db and imf were used to form linear regression plots and to illustrate increasing and reducing trends of solid, liquid and gas yields as IM contents varied. In db, strong correlations could be found. Solid yields increased with R^2 of 0.8606 while liquids yields decreased with R^2 of 0.7824 when the mass% of IM increased. Gas yields in db slightly reduced with IM increased. Observations in db showed apparent effects of increased IM contents on increasing solid yields and reducing yields of liquids and gases since mass% in db of organic matters available for thermal decomposition reduced. In imf, 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 mass% of IM increased. Gas yields in imf slightly increased with IM increased. Observations on data in imf showed that interaction effects of IM with volatile compounds could be presence for promoting char formation, liquids cracking and gas production but less significant as compared to the apparent effects found in yield distributions in db. These observations could be also explained by the variations in biomass composition of sludge which determined the intrinsic characteristics of yield distribution and also the differences in inorganic composition 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 composition study was important to determine other factors affecting yield distribution of sludge pyrolysis.

Solid, liquid, and gas yields in imf were correlated with total mass% of element in db, in imf and organic mass% of element in imf for CHNSO elements separately and collectively. Results showed that strong correlations with $R^2 > 0.50$ could only be observed on solid and liquid yields with carbon (C) element and could not be found in all other elements examined individually. No significant correlation could be formed for gas yields with any individual CHNSO elements. However, weak correlations with $R^2 > 0.35$ could be found between gas yields and summation of HNSO contents. Correlations found to be improved statistically when considered organic C contents in imf as compared to total C contents in both db and imf. By using organic element contents in imf, apparent effects of IM and inorganic CHNSO contents on the contents of elements in sludge could be reduced. CHNSO of organic matters were determined by difference using CHNSO of sludge samples and ash residues measured. Results of correlation analysis showed that increasing organic C contents in imf for different sludge samples 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. Considering the composition 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 in imf were equal to 100%, increased of C contents could also be represented by decreased of the summation of HNSO contents. Therefore, the results also could indicate that the presence of more reactive functional groups with HNSO elements could promote more char formation reactions and caused higher solids yield during pyrolysis similar to the observations of side-groups elimination that produced specific fragments during thermal degradation while backbone remained would further transformed by aromatisation, char formation and backbone scission (Crompton, 2013). Correlation of gas yields also showed similar results supporting the observations for char formation reactions where sludge samples with higher organic HNSO contents in 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 correlations with yield distributions were complex and obscure.

Table 5.5: Yield distributions of sludge pyrolysis at 500°C.

Sample label	Yield distributions of sludge pyrolysis at 500°C								
	Mass% in db						Mass% in imf		
	Inorganic matters	Residual char	Total solids	Liquid	Gas	Total volatiles	Solid	Liquid	Gas
UR	8.35	30.63	38.98	46.43	14.59	61.02	33.42	50.66	15.92
UD	14.78	32.90	47.68	35.30	17.02	52.32	38.61	41.42	19.97
CP	18.36	27.18	45.54	33.69	20.77	54.46	33.30	41.26	25.44
CS	9.88	28.72	38.60	42.66	18.74	61.40	31.87	47.34	20.79
CY	29.72	27.40	57.12	22.17	20.71	42.88	38.99	31.54	29.47
JR	23.11	28.45	51.56	35.28	13.16	48.44	37.00	45.88	17.12
JD	38.38	24.83	63.21	25.68	11.11	36.79	40.29	41.68	18.03
KR	12.81	28.71	41.52	40.20	18.28	58.48	32.93	46.11	20.97
KD	20.09	31.31	51.40	29.63	18.97	48.60	39.18	37.08	23.74
UsR	15.77	22.55	38.32	43.78	17.90	61.68	26.77	51.98	21.25
UsD	17.21	27.81	45.02	37.49	17.49	54.98	33.59	45.28	21.13
CsP	18.17	24.77	42.94	36.88	20.17	57.05	30.27	45.08	24.65
CsS	17.18	22.49	39.67	39.13	21.20	60.33	27.16	47.25	25.60
CsY	31.33	24.73	56.06	25.97	17.98	43.95	36.00	37.82	26.18
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	53.03 ±7.86	34.24 ±4.34	43.60 ±5.54	22.16 ±3.85
Before AD	15.45 ±4.87	26.69 ±3.06	42.14 ±4.54	39.76 ±4.39	18.10 ±2.88	57.86 ±4.54	31.59 ±3.42	46.94 ±3.32	21.47 ±3.65
After AD	25.25 ±9.28	28.16 ±3.35	53.42 ±6.69	29.37 ±5.97	17.21 ±3.26	46.59 ±6.69	37.78 ±2.50	39.14 ±4.76	23.09 ±4.24

Figure 5.6: Correlations analysis for (a) solid, (b) liquid and (c) gas yields with mass% of inorganic matters and (d) solid, (e) liquid and (f) gas yields with CHNSO contents in sludge.

5.3.5. Energy requirements analysis

Results of total energy requirements calculated based on assumed initial temperature at 25°C and pyrolysis temperature of 500°C were showed in Table 5.6. Heat of reaction during pyrolysis found to be ranged from endothermic to exothermic depending on main reactions involved for different types of feedstock and testing conditions (Rath et al., 2003). Heat of reactions for all sludge samples collected were slightly endothermic or near autothermic and ranging from 22 to 78J/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 endothermic

devolatilization and exothermic char forming reactions occurred concurrently (Rath et al., 2003; Urban and Antal Jr, 1982). Heating requirement to raise the temperature of sludge found to be the main energy needed as compared to heat of reaction measured. In average, heat of reaction and heating requirement represented 5.67% and 94.33% respectively of total energy requirement at 0.85 ± 0.13 MJ/kg for pyrolysis. Energy requirement for sludge pyrolysis comparable to energy required for pyrolysis of different types of biomass that ranged from 0.80 to 1.60MJ/kg (Daugaard and Brown, 2003; Yang et al., 2013). Higher total energy requirements observed for sludge samples collected before AD treatment mainly due to the higher heat capacities measured which caused by the presence of more organic contents (Kim and Parker, 2008).

5.3.6. Solid products analysis

HHV results of char solids collected were also showed in Table 5.6 with significant variations of HHV in db and imf could be observed. Mean HHV of Char_{500C} measured at 11.84 ± 2.60 MJ/kg in db comparable to previous studies (Inguanzo et al., 2002; Wang et al., 2012). Mean HHV of char in imf at 19.83 ± 2.23 MJ/kg slightly lower than HHV of sludge in imf at 21.62 ± 1.13 MJ/kg suggested the intrinsic energy contents of organic matters in sludge slightly 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 solid yields observed. These observations indicated that differences in organic composition not only affected the energy contents in sludge but also char solids formed in pyrolysis.

Results of ultimate analysis on Char_{500C} in dry basis and normalised molar basis were showed in Table 5.7 and 5.8. According to the mass contents in db, element with highest mass% was carbon (C) measured at 30.69 ± 7.61 mass% followed by

oxygen (O) at 20.35 ± 4.86 mass%, nitrogen (N) at 3.97 ± 0.98 mass%, sulphur (S) at 3.43 ± 0.66 mass% and hydrogen (H) with only 1.09 ± 0.3 mass%. In addition to the CHNSO contents, IM presence with significant amount of 40.48 ± 11.04 mass% in average. In imf basis, C contents calculated at 51.56% in average and significantly lower than lignocellulosic biomass pyrolysed at similar conditions (Di Blasi, 2009). 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 samples collected after AD treatment as compared to raw, primary and secondary sludge samples collected before AD treatment. Based on CHNSO data in normalised molar basis, sludge samples before and after AD treatment were highly similar with slightly more S and O. Significantly more sulphur and oxygen contents could also be found in samples collected from Jurong WRP (JR and JD) mainly due to the presence of inorganic components such as sulphates and carbonates. Molecular formula of Char_{500C} could be formed for individual sludge samples for subsequent analysis while in average $C_{1.00}H_{0.42}N_{0.11}S_{0.05}O_{0.52}$ represented the char solids. Compared to average molecular formula of sludge $C_{1.00}H_{1.80}N_{0.12}S_{0.05}O_{0.51}$ determined in characterisation study, only H was significantly reduced. Residual CHNSO contents of char solids in relative percentage to the initial contents in respective sludge samples were calculated and showed in Table 5.8. In average, less than 10% of H but more than 30% of C, N, S and O contents were remained in the char solids which agreed with the changes in molecular formula formed. Sludge samples after AD treatment generally retained more CHNSO contents after pyrolysis probably due to relatively more char solids formation as suggested in yield distributions analysis of pyrolysis and relatively more inorganic contents with carbonates and sulphates that degraded only at higher temperature as suggested in ultimate analysis of ash residues. Significant release of 65.14% N and 68.55% S contents in average could be observed after pyrolysis of sludge at 500°C. Therefore, subsequent utilization of char solids by gasification and incineration could be having lower concerns of NO_x and SO_x pollutants as compared to using sludge as feedstock directly since fuel bound nitrogen contents were more important in NO_x formation compared to nitrogen gas in the air at temperature below 1500°C (H. Chen et al., 2011; Mura et al., 2013).

Table 5.6: Energy requirements for pyrolysis and heating values of char.

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	db		imf	dsb	Residual HHV in %
	Mean	SD				Mean	SD			
UR	1.98	0.21	940	41	981	14.63	0.13	18.62	5.70	27.83
UD	1.60	0.15	760	40	800	12.64	0.07	18.32	6.03	34.62
CP	1.55	0.16	737	72	809	12.32	0.00	20.64	5.61	32.00
CS	1.93	0.19	916	55	972	15.81	0.02	21.25	6.10	31.05
CY	1.57	0.18	745	44	788	9.22	0.16	19.22	5.27	36.41
JR	1.74	0.16	829	36	864	9.26	0.13	16.78	4.77	27.88
JD	1.35	0.13	642	46	719	6.44	0.04	16.40	4.07	30.86
KR	1.61	0.15	763	22	785	13.28	0.05	19.20	5.51	26.86
KD	1.33	0.14	632	33	664	10.61	0.01	17.41	5.45	34.82
UsR	2.18	0.17	1034	66	1119	13.25	0.06	22.52	5.08	26.17
UsD	1.90	0.2	902	78	997	13.55	0.04	21.93	6.10	34.88
CsP	1.36	0.22	645	48	693	12.39	0.07	21.48	5.32	29.23
CsS	1.90	0.27	903	50	953	13.51	0.14	23.83	5.36	28.73
CsY	1.53	0.16	727	40	767	8.84	0.07	20.03	4.95	35.65
Mean $\pm$ standard deviations										
All sample	1.68 $\pm$ 0.26		798 $\pm$ 125	48 $\pm$ 16	846 $\pm$ 132	11.84 $\pm$ 2.60		19.83 $\pm$ 2.23	5.38 $\pm$ 0.56	31.21 $\pm$ 3.54
Before AD	1.78 $\pm$ 0.27		846 $\pm$ 126	49 $\pm$ 16	895 $\pm$ 131	13.06 $\pm$ 1.92		20.54 $\pm$ 2.26	5.43 $\pm$ 0.40	28.72 $\pm$ 2.00
After AD	1.55 $\pm$ 0.21		734 $\pm$ 98	47 $\pm$ 16	781 $\pm$ 112	10.22 $\pm$ 2.62		18.89 $\pm$ 1.97	5.31 $\pm$ 0.75	34.54 $\pm$ 1.92

Table 5.7: Ultimate analysis of char collected after pyrolysis at 500°C.

Sample label	Ultimate analysis of Char _{500C} , Mass% in dry basis									
	C		H		N		S		O _{difference}	IM
	Mean	SD	Mean	SD	Mean	SD	Mean	SD		
UR	45.26	0.99	1.64	0.05	5.68	0.14	3.72	0.05	22.27	21.42
UD	32.40	0.19	1.11	0.03	4.26	0.04	3.65	0.07	27.58	30.99
CP	31.15	0.20	1.00	0.04	4.85	0.04	2.91	0.04	19.78	40.31
CS	39.75	0.29	1.51	0.03	4.00	0.02	3.39	0.02	25.76	25.59
CY	23.66	0.40	0.87	0.02	3.06	0.06	2.94	0.04	17.44	52.02
JR	22.25	0.28	0.73	0.04	2.99	0.05	4.73	0.05	24.47	44.82
JD	16.18	0.17	0.48	0.01	1.96	0.02	4.71	0.04	15.95	60.72
KR	33.71	0.08	1.07	0.03	4.45	0.05	3.24	0.06	26.67	30.86
KD	27.51	0.21	0.84	0.02	4.03	0.07	3.13	0.14	25.41	39.08
UsR	34.00	0.31	1.21	0.04	4.52	0.04	3.63	0.14	15.47	41.16
UsD	34.99	0.18	1.24	0.02	4.71	0.02	3.59	0.06	17.25	38.23
CsP	31.20	0.11	1.11	0.03	4.69	0.02	2.58	0.08	18.11	42.32
CsS	34.64	0.55	1.44	0.05	3.42	0.03	3.08	0.06	14.11	43.30
CsY	22.96	0.12	0.94	0.01	2.97	0.04	2.68	0.07	14.56	55.89
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
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
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

Table 5.8: Ultimate analysis in normalised molar basis and residual CHNSO contents in relative% of Char_{500C}.

Sample label	Char _{500C} in normalised molar basis				Residual CHNSO of Char _{500C} in relative%				
	H	N	S	O _{difference}	C	H	N	S	O _{difference}
UR	0.43	0.11	0.03	0.37	40.50	11.33	38.10	26.53	28.13
UD	0.41	0.11	0.04	0.64	38.75	8.57	33.65	30.95	48.19
CP	0.39	0.13	0.03	0.48	37.40	7.77	29.27	28.95	35.57
CS	0.46	0.09	0.03	0.49	34.89	9.02	39.89	24.68	33.02
CY	0.44	0.11	0.05	0.55	42.63	10.18	34.75	34.95	42.55
JR	0.39	0.12	0.08	0.82	30.87	6.33	35.63	45.41	53.96
JD	0.36	0.10	0.11	0.74	37.27	7.49	38.57	54.79	48.34
KR	0.38	0.11	0.04	0.59	31.96	6.79	32.83	24.74	43.56
KD	0.37	0.13	0.04	0.69	38.73	7.21	31.15	29.86	52.18
UsR	0.43	0.11	0.04	0.34	30.53	7.39	34.95	32.69	22.89
UsD	0.42	0.12	0.04	0.37	39.87	9.51	35.88	35.21	29.00
CsP	0.43	0.13	0.03	0.44	34.92	8.29	29.62	20.19	30.89
CsS	0.50	0.08	0.03	0.31	34.16	9.68	39.23	22.51	20.32
CsY	0.49	0.11	0.04	0.48	42.30	11.61	34.48	28.87	34.80
Mean ± standard deviations									
All sample	0.42 ±0.04	0.11 ±0.01	0.05 ±0.02	0.52 ±0.16	36.77 ±4.00	8.65 ±1.64	34.86 ±3.38	31.45 ±9.22	37.38 ±10.83
Before AD	0.43 ±0.04	0.11 ±0.02	0.04 ±0.02	0.48 ±0.17	34.40 ±3.38	8.32 ±1.64	34.94 ±4.11	28.21 ±7.93	33.54 ±11.00
After AD	0.42 ±0.05	0.11 ±0.01	0.05 ±0.03	0.58 ±0.14	39.93 ±2.14	9.09 ±1.68	34.75 ±2.45	35.77 ±9.68	42.51 ±8.96

5.3.7. Operating temperature analysis

Experimental pyrolysis at different operating temperatures could be considered as isothermal studies to complement the non-isothermal studies carried out by analytical pyrolysis. Pyrolysis at 200°C, 300°C, 400°C and 500°C were carried out separately on dried sludge samples from Changi WRPs collected during second batch of sampling, denoted as CsY. Results of yield distributions, heat capacity analysis, HHV data and ultimate analysis on CsY sludge and char solids collected after pyrolysis were showed in Table 5.9, 5.10, 5.11 and 5.12. Heat capacity and HHV data of ash residues after combustion of CsY at 550°C were also included. IM content in CsY was assumed to be constant throughout the experiments. Therefore reduction on total solids yields indicated the decreased in mass% of residual char remained. Solid yields gradually decreased as temperature elevated accompanied by the increased of total volatiles released. Decomposition of sludge solids into liquids and gases measured from 200°C agreed with analytical pyrolysis of sludge as TGA-FTIR showed that main volatile compounds released at low temperature were water vapour and carbon dioxide similar to the torrefaction treatment of biomass (de Wild et al., 2009). Significant reduction of solids could be observed when temperature increased to 300°C while liquids and gases compounds were produced almost equally in mass% recorded. Gas yields at 300°C and 400°C remained consistent indicating the reduction of solids mass in this temperature region converted mainly into liquids. Liquid yields at 400°C and 500°C remained consistent indicated solids decomposed mainly into gases in this temperature region comparable to findings in previous study (Inguanzo et al., 2002). Ratios of V/S increased as solids decomposed into volatiles while ratios of L/G fluctuated depending on release of liquids and gases at different temperature regions. Results showed that pyrolysis mechanisms for sludge were highly complex as yields of solids, liquids and gases were needed to be described individually at different thermal degradation stages.

Heat capacities were measured at constant pressure, C_p for CsY sludge, char solids and ash residues from 70°C to 120°C (343K to 393K) and mean values were calculated in dry basis (J/g-K) and dry sludge basis (J/g of Sludge-K). Heat capacity in dsb was calculated based on the heat capacity measured in db and mass% of solid residues remained. Heat capacities of all samples increased gradually as

temperature elevated similar to the observations found in previous studies on biomass and char (Q. Chen et al., 2014; Dupont et al., 2014; Mark, 2007; Morad et al., 2000). Comparison study of sludge, char solids, and ash residues aimed to understand and quantify the changes in heat capacity as sludge thermally degraded through pyrolysis at different temperatures and also when combusted. In dry basis, results showed that the heat capacity of sludge gradually decreased when pyrolysed to form char solids and combusted to form ash residues. For CsY, average values of heat capacity decreased from 1.53J/g-K for sludge to 1.08J/g-K in db and 0.61J/g-K in dsb for Char_{500C} comparable to previous study on biomass char analysis (Dupont et al., 2014). Reduction of mean values indicated the destruction of organic matters with higher C_p into residual char with lower C_p . C_p in db of Char_{500C} and Ash_{550C} were similar indicated that residual char solids formed from organic matters at 500°C were having comparable C_p with inorganics at around 1.08J/g-K. In dry sludge basis, heat capacities of char solids and ash residues reduced more significantly as compared to CsY sludge due to concurrent reductions on both heat capacities measured and mass of solids residues remained. Energy requirements for heating reduced by 29.41% in db and 60.13% in dsb when Char_{500C} instead of sludge heated to operating temperature of gasification or incineration at 700°C and above therefore supporting the application of sequential thermochemical conversion process. For process modelling, linear regressions could be formed separately for mean values of heat capacity, $C_p = 1.6063 - 0.001 T$ with R^2 of 0.9669 in db and $C_p = 1.7042 - 0.0023 T$ with R^2 of 0.9687 in dsb based on data collected for CsY. T represented temperature of pyrolysis and ranged from 100°C to 500°C. Since primary degradation region of sludge ended at around 500°C, therefore C_p of char solids in db produced at higher temperature that consisted of mainly residual char and IM were expected to be similar to Char_{500C} and Ash_{550C}.

Results of HHV analysis of char solids collected after pyrolysis of CsY at different temperatures were showed in Table 5.10. HHV data recorded in db and dsb were gradually decreased as temperature increased from 100°C to 500°C caused by thermal degradation of sludge and released volatile compounds with energy contents. However, HHV data in imf were first increased as temperature elevated to 300°C then decreased when further pyrolysed to higher temperature until 500°C.

These observations indicated that the release of volatile compounds with relatively lower energy contents in temperature regions of 100°C to 300°C and release of volatile compounds with relatively higher energy contents occurred from 300°C to 500°C respectively. Residual HHV data showed that energy contents remained in char solids gradually reduced to 35.65% as temperature of pyrolysis elevated until 500°C. Most significant reduction in energy contents with about 50% decreased could be observed from 200°C to 400°C.

Ultimate analysis in dry basis, normalised molar basis and residual CHNSO contents were calculated and showed in Table 5.11 and 5.12. By comparing residual CHNSO contents and molecular formula of char solids, elements released as volatile compounds could be identified at corresponding temperature. In dry basis, CHNSO contents were generally decreased and IM steadily increased as CsY sludge pyrolysed to form char solids at gradually elevated temperature from 200°C to 500°C. C and N contents in db appeared to be increase slightly at 200°C as H, S and O contents reduced more significantly. At 200°C, significant reduction of H and O indicated dehydration reactions on organic matters and release of moisture bounded to inorganic compounds in sludge. These suggested reactions supported by the release of water vapour at low temperature as observed in analytical pyrolysis study by using TGA-FTIR. Reduction of S contents could be due to degradation of simple and low molecular weight sulphur containing organic compounds. Slight reduction on C and N contents could be accounted by the release of CO, CO₂ and NH₃ observed. As temperature increased to 300°C, most significant reduction in all CHNSO elements could be observed indicating the main thermal degradation reactions occurred. N contents could also decompose into condensable liquids. Based on previous studies, liquids collected from sludge pyrolysis were having pH from 8 to 10 different from the acidic pyrolysis liquid from lignocellulosic biomass due to the presence of ammonia and nitrogen-containing compounds derived from the protein in sludge and could be separated into aqueous and organic phases with significantly different characteristics (Fonts et al., 2012; Manara and Zabaniotou, 2012). Reduction of CHNSO elements continued as temperature elevated to 400°C. However, only slight reduction could be observed as temperature increased from 400°C to 500°C indicated ending of primary degradation reactions.

Table 5.9: Yield distributions of CsY pyrolysis.

Sample Label	Yield distributions of Cs-Y pyrolysis											
	Mass% in db						Mass% in imf				Ratio	
	IM	Residual char	Total solids	Liquid	Gas	Total volatiles	Solid	Liquid	Gas	Total volatiles	Volatiles/Solid	Liquid/Gas
Char _{200C}	31.33	57.68	89.01	6.22	4.78	11.00	83.98	9.06	6.96	16.02	0.19	1.30
Char _{300C}	31.33	38.84	70.17	15.64	14.19	29.83	56.56	22.78	20.67	43.44	0.77	1.10
Char _{400C}	31.33	28.77	60.10	25.72	14.17	39.89	41.90	37.46	20.64	58.10	1.39	1.82
Char _{500C}	31.33	24.73	56.06	25.97	17.98	43.95	36.00	37.82	26.18	64.00	1.78	1.44

Table 5.10: Heat capacity and HHV data of CsY sludge, char and ash.

Sample Label	Heat Capacity, J/g-K										Higher Heating Value, MJ/kg				
	db								dsb		db		imf	dsb	Residual HHV in%
	343K	353K	363K	373K	383K	393K	Mean	SD	Mean	SD	Mean	SD			
CsY	1.38	1.38	1.45	1.54	1.64	1.79	1.53	0.16	1.53	0.16	13.89	0.02	21.16	13.89	100.00
Char _{200C}	1.28	1.31	1.32	1.39	1.49	1.65	1.41	0.14	1.25	0.13	14.44	0.05	22.29	12.86	92.53
Char _{300C}	1.07	1.08	1.15	1.22	1.35	1.62	1.25	0.21	0.88	0.15	12.38	0.07	22.37	8.69	62.53
Char _{400C}	1.05	1.06	1.14	1.21	1.29	1.49	1.21	0.17	0.73	0.10	9.71	0.03	20.28	5.83	41.99
Char _{500C}	0.97	0.94	0.98	1.05	1.15	1.40	1.08	0.17	0.61	0.10	8.84	0.07	20.03	4.95	35.65
Ash _{550C}	0.93	0.95	1.02	1.09	1.16	1.36	1.08	0.16	0.43	0.06	0.00	0.00	0.00	0.00	0.00

Table 5.11: Ultimate analysis in dry basis of Cs-Y sludge and char solids.

Sample label	Ultimate analysis in dry basis, Mass%									O by difference	Inorganic matters
	C		H		N		S				
	Mean	SD	Mean	SD	Mean	SD	Mean	SD			
CsY	30.42	0.12	4.56	0.01	4.83	0.03	5.20	0.02	23.45	31.33	
Char _{200C}	32.24	0.34	3.82	0.04	5.14	0.03	5.08	0.02	18.52	35.20	
Char _{300C}	29.61	0.01	2.50	0.03	4.22	0.02	4.37	0.06	14.64	44.65	
Char _{400C}	24.29	0.21	1.40	0.06	3.38	0.04	3.88	0.05	14.92	52.14	
Char _{500C}	22.96	0.12	0.94	0.01	2.97	0.04	2.68	0.07	14.56	55.89	

Table 5.12: Ultimate analysis in normalised molar basis and residual CHNSO contents in relative% of Cs-Y sludge and char solids.

Sample label	Ultimate analysis in normalised molar basis					Residual CHNSO in relative%				
	C	H	N	S	O	C	H	N	S	O
CsY	1.00	1.80	0.14	0.06	0.58	100.00	100.00	100.00	100.00	100.00
Char _{200C}	1.00	1.42	0.14	0.06	0.43	94.32	74.58	94.63	87.03	70.30
Char _{300C}	1.00	1.01	0.12	0.06	0.37	68.29	38.47	61.29	59.04	43.82
Char _{400C}	1.00	0.69	0.12	0.06	0.46	47.99	18.44	42.01	44.82	38.23
Char _{500C}	1.00	0.49	0.11	0.04	0.48	42.30	11.61	34.48	28.87	34.80

5.3.8. FTIR spectra analysis

Thermal degradation behaviours of sludge could be described based on the functional groups identified by comparing FTIR spectra of sludge samples, char solids and ash residues collected after drying, pyrolysis and combustion. Figure 5.7 showed that high similarity could be observed in the FTIR spectra of Char_{500C} of different types of sludge samples. High similarity suggested comparable chemical compounds and functional groups detectable by FTIR in char solids formed during sludge pyrolysis and therefore FTIR spectra of CsY related solid samples were selected and focused for further analysis. FTIR spectra of collected sludge samples, char solids and ash residues as CsY sludge pyrolysed at different temperatures and combusted were qualitatively compared and illustrated in Figure 5.7. Apparent peaks observed were recorded in Table 5.13. Changed of the apparent peaks could be observed when sludge samples were pyrolysed to form char solids and combusted to form ash residues. As temperature elevated, absent of peak at 1220 cm⁻¹ was observed for Char_{200C} corresponding to degradation of C-O or C-N functional groups of polysaccharides, alcohols, esters, amides and amines. Char_{300C} further showed peaks diminished at 1518 cm⁻¹, 1415 cm⁻¹, and 1314 cm⁻¹ corresponding to decomposition of N-H, N-O, O-H, C-N, S-O, C-O functional groups and aromatic rings of amides, amines, nitro compounds, carboxylic acids, sulphur organic compound, and aromatic compounds. Further peaks reduction could be observed when CsY sludge pyrolysed at higher temperature. Peaks at 3225 cm⁻¹, 3077 cm⁻¹, 2925 cm⁻¹, 1710 cm⁻¹, and 1635 cm⁻¹ were diminished for Char_{400C} corresponding to degradation of O-H, N-H, C-H, C=O, and C=C functional groups of alcohols, carboxylic acids, amides, amines, saturated and unsaturated hydrocarbon, aromatics, esters, ethers, aldehyde and ketone were also absent. Char_{500C} showed that peaks at 3700 cm⁻¹, 1030 cm⁻¹, and 913 cm⁻¹ corresponding to O-H, C-O-C, P-O, and C-H functional groups of hydroxyl groups bounded in inorganic compounds, polysaccharides, ethers, phospholipids, unsaturated hydrocarbon, and aromatic compounds were diminished. FTIR spectra of ash residues combusted at 550°C showed only peaks of inorganic compounds at 1008 cm⁻¹, 797 cm⁻¹, 779 cm⁻¹ and 668 cm⁻¹. Peaks at 1600 cm⁻¹, 1445 cm⁻¹, and 1375 cm⁻¹ corresponding to C=C, N-H, N-O, C-H, C-N, S-O, O-H functional groups and

aromatic rings of saturated and unsaturated hydrocarbon, amides, amines, sulphur organic compound, polysaccharides, and aromatic compounds were diminished after combustion. FTIR spectra analysis demonstrated that different peaks diminished and corresponding functional groups decomposed at different stages of pyrolysis and combustion complementing the data for thermal degradation behaviours of sludge.

Figure 5.7: FTIR spectra of (a) char solids for CsP, CsS, and CsY sludge after pyrolysis at 500°C and (b) comparison of CsY sludge, char solids and ash residues.

Table 5.13: Apparent peaks in FTIR spectra of CsY sludge, char and ash.

Regions	Peaks identified for CsY						Functional groups	Suggested compounds
	Sludge	Char Solids				Ash		
	100°C	200°C	300°C	400°C	500°C	550°C		
3700 - 3600	3700	3700	3700	3700	-	-	O-H	Inorganic O-H
3600 - 3100	3225	3225	3225	-	-	-	O-H, N-H	Alcohols, carboxylic acids, amides, amines
3100 - 3000	3077	3077	3077	-	-	-	C-H	Unsaturated hydrocarbon, aromatics
3000 - 2800	2925	2925	2925	-	-	-	C-H	Saturated hydrocarbon, ethers, lipids
1800 - 1600	1710	1710	1710	-	-	-	C=O	Aldehyde, ketone, acids, esters, amides
	1635	1635	1635	-	-	-	C=C, C=O, N-H	Unsaturated hydrocarbon, amides, amines
	1600	1600	1600	1600	1600	-	C=C, N-H, Ring	Hydrocarbon, amides, amines, aromatics
1600 - 1450	1518	1518	-	-	-	-	Ring, N-H, N-O	Aromatics, amides, nitro compounds
1450 - 1300	1445	1445	1445	1445	1445	-	C-H	Saturated hydrocarbon, ethers, lipids
	1415	1415	-	-	-	-	O-H	Carboxylic acids, alcohols
	1375	1375	1375	1375	1375	-	C-N, S-O, O-H	Amides, sulphur organics, polysaccharides
	1314	1314	-	-	-	-	C-N, S-O, C-O	Amines, sulphur organics, carboxylic acids
1300 -900	1220	-	-	-	-	-	C-O, C-N	Polysaccharides, alcohols, esters, amides, amines
	1030	1030	1030	1030	-	-	C-O-C, -P=O-	Polysaccharides, ether, phospholipids
	1008	1008	1008	1008	1008	1008	Inorganic	Phosphates, silicates, sulphates, minerals
	913	913	913	913	-	-	C-H, O-H, C-O-C	Unsaturated hydrocarbon, aromatics, organic acids, glycosidic linkages
900 - 600	797	797	797	797	797	797	Inorganic	Minerals, silicates
	779	779	779	779	779	779	Inorganic	Carbonates, nitrates
	750	750	750	750	-	-	N-H, C-Cl	Amides, amines, halogenated compounds
	694	694	694	694	-	-	Rings, O-H	Aromatics, alcohols
	668	668	668	668	668	668	Inorganic	Sulphates

5.3.9. Gas composition analysis

Results of gas composition analysis from all sludge samples pyrolysis at 500°C and CsY sludge pyrolysis at different temperatures were showed in Table 5.14 and 5.15. Illustrations of gas composition analysis were showed in Figure 5.8. Qualitative similarities and quantitative variations could be generally observed. Based on the results of 500°C pyrolysis for all sludge samples collected, CO₂ showed highest relative abundance of 52.64 ±5.71% in average comparable to the pyrolysis of lignocellulosic biomass (de Wild et al., 2009). H₂ presence with mean relative abundance of 20.89 ±6.61% and then followed by CO at 11.35 ±3.48%, CH₄ at 9.26 ±1.91%, and C₂ to C₅ gases at 5.80 ±1.37%. Heating values of product gases calculated at 12.10 ±3.05MJ/m³ for HHV and at 10.98 ±1.88 MJ/m³ for LHV. Significant quantitative variations in all the gas components detected indicating differences in composition 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 (UR and UsR) released significant higher amount of H₂ and different from all other sludge samples collected before AD treatment while sludge samples from Jurong WRP (JR and JD) released significantly lower amount of CO and CH₄. Secondary sludge from Changi WRP (CS and CsS) showed comparable gas composition among the two batches of samples but primary sludge samples reduced the release of CO by more than 50% when compared CP to CsP.

Based on results of CsY sludge pyrolysis at different pyrolysis temperatures, only CO₂ and CO detected at 200°C agreed with C-O functional groups released from FTIR spectra analysis on Char_{200C} and HHV analysis which suggested the release of volatile compounds with low energy contents in average at lower temperature of pyrolysis. Emission of combustible gases with high energy contents included H₂, CO, CH₄ and C₂ to C₅ gases gradually increased as temperature of pyrolysis elevated. Significant increase in relative abundance for all combustible gases could be observed at 400°C and 500°C comparable to the findings in previous study

(Calvo et al., 2004). Presence of about 38.60% 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 inhibitions (Di Blasi, 2009). These gases could be separated when sludge samples were first pyrolysed and removed then the char solid residues were subsequently gasified or incinerated. These observations also supporting the application of sequential thermochemical conversion processes.

Table 5.14: Gas composition analysis of sludge pyrolysis at 500°C.

Sample label	Gas composition in relative abundance, volume%				
	H ₂	CO	CO ₂	CH ₄	C ₂ - C ₅
UR	33.16	9.47	44.78	8.41	4.18
UD	17.09	10.77	59.17	8.15	4.83
CP	16.31	13.48	52.24	10.75	7.12
CS	13.29	16.93	56.11	8.13	5.54
CY	21.21	11.69	49.12	11.50	6.47
JR	22.84	6.62	60.37	5.64	4.53
JD	32.21	7.71	48.58	6.22	5.28
KR	14.00	15.27	52.79	9.80	8.02
KD	20.74	11.76	49.27	11.46	6.77
UsR	22.58	10.23	49.16	10.99	7.04
UsD	15.68	13.23	57.32	8.66	5.11
CsP	17.38	6.24	60.21	10.40	5.77
CsS	16.13	16.75	55.54	8.35	3.23
CsY	29.82	8.78	42.26	11.22	7.25
Mean $\pm$ standard deviations					
All samples	20.89 $\pm$ 6.61	11.35 $\pm$ 3.48	52.64 $\pm$ 5.71	9.26 $\pm$ 1.91	5.80 $\pm$ 1.37
Before AD	19.46 $\pm$ 6.57	11.87 $\pm$ 4.33	53.90 $\pm$ 5.33	9.06 $\pm$ 1.79	5.68 $\pm$ 1.65
After AD	22.79 $\pm$ 6.75	10.66 $\pm$ 2.06	50.95 $\pm$ 6.25	9.53 $\pm$ 2.20	5.95 $\pm$ 1.00

Table 5.15: Gas composition analysis of CsY sludge pyrolysis.

Pyrolysis Temp °C	Gas composition in relative abundance, volume%				
	H ₂	CO	CO ₂	CH ₄	C ₂ - C ₅
100	0.00	0.00	0.00	0.00	0.00
200	0.00	2.22	97.78	0.00	0.00
300	8.99	3.86	85.85	1.04	0.26
400	12.98	9.74	65.44	5.62	5.58
500	29.82	8.78	42.26	11.22	7.25

Figure 5.8: Gas composition in relative volume% of pyrolysis for (a) 14 different sludge samples at 500°C and (b) CsY from 200°C to 500°C.

5.4. Conclusions

Analytical and experimental pyrolysis were applied to compare all 14 sludge samples collected and showed that thermal degradation behaviours and product distributions of different sludge samples studied were qualitatively similar and quantitatively different. These observations suggested the presence of waste mixtures with comparable components in varying amounts in sludge.

Multiple heating rates TGA-DTG showed that poorly separated mass loss curves, random variations of degradation rate profiles and char residues remained could be observed suggested that heterogeneity in sludge significantly affected thermal degradation behaviours. Mean TGA-DTG showed that results in db and vb influenced by contents of inorganic matters presence and composition of organics and inorganics in sludge respectively. Impacts of sludge categorisation by types based on different treatment processes applied and by plants with different sources of wastewater were identified and discussed. In average, relatively lower initial and terminating temperatures for primary degradation region of sludge samples collected before AD could be observed lowered by 3.7°C and 18.6°C respectively where mean values of overall sludge samples collected at $164.4 \pm 11.0^\circ\text{C}$ and $551.9 \pm 16.7^\circ\text{C}$ respectively. Three apparent broad peaks could be observed in general. First apparent peak occurred at $276.8 \pm 5.2^\circ\text{C}$ with degradation rate of $-0.28 \pm 0.05\%/^\circ\text{C}$, while second and third apparent peaks could be observed at $326.2 \pm 10.7^\circ\text{C}$ and $414.7 \pm 11.1^\circ\text{C}$ with degradation rates of $-0.33 \pm 0.12\%/^\circ\text{C}$ and $-0.13 \pm 0.02\%/^\circ\text{C}$ respectively by considering mean values calculated. Apparent peaks with maximum degradation rates in DTG profiles showed that lower temperature and degradation rates could be observed for sludge samples collected after AD at 21.7°C and $0.15\%/^\circ\text{C}$ respectively. Mass% (db) of char residues formed during pyrolysis at 500°C and 950°C showed that more solids remained for AD digested sludge at 11.32% and 9.92% higher than sludge before AD respectively. Considering the release of volatiles in two degradation regions separately, sludge samples collected before AD showed higher released during primary degradation with $85.65 \pm 2.87\%$ while AD digested samples showed higher released during secondary degradation with $19.62 \pm 4.00\%$ in relative percentage. Kinetics and products evolution studies revealed the complexity of degradation behaviours. As

sludge heated over wide range of temperature, various components were degraded at different temperatures with varying reactivity and products evolution therefore resulted in the variations of apparent activation energy (E_a) and volatile compounds released depend on temperature and conversion degree. In addition, competitive reactions such as formation of char and carbonization of volatile compounds also complicated the thermally induced reactions. Primary and secondary decomposition of sludge at low and high temperature and degradation kinetics of organic and inorganic contents in sludge should also be studied separately in details. Separation of primary and secondary degradation region of sludge solids by using 500°C as temperature boundary showed in this study could also contribute to improve kinetics parameters estimation and models development.

Products of experimental pyrolysis were collected and analysed to complement results obtained from analytical pyrolysis. Total volatiles and liquids yields of sludge samples after treated by AD were lower than primary, secondary and raw sludge in average on db (-11.27% and -10.39%) and imf (-6.18% and -7.80%) bases. Solid yields on db (+11.28%) and imf (+6.19%) bases 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 (-1.62%) indicated that organic matters presence released relatively less permanent gases but slightly higher on db (+0.89%) as relatively higher mass% of organic matters presence compared to dewatered and dried sludge. Thus after treated by AD, sludge samples in average 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 during pyrolysis. Distribution ratios V/S ranged from 1.48 to 2.74 and L/G ranged from 1.07 to 3.18. Both ratios were higher in average for sludge samples collected before AD at 2.20 and 2.26 while lower for after AD at 1.66 and 1.77 respectively. Energy requirement analysis also showed that with higher heat capacity (+0.23J/g-K) measured for sludge samples before AD, higher energy requirement for heating and total energy needed (+0.11MJ/kg) for pyrolysis could be observed. HHV of Char_{500C} showed 13.06 ± 1.92 MJ/kg and 10.22 ± 2.62 MJ/kg for sludge samples collected before and after AD. Higher HHV observed for sludge before AD but

lower relative percentage of residual energy in char at $28.72 \pm 2.00\%$ compared to after AD at $34.54 \pm 1.92\%$ of initial sludge samples. Gas composition results at 500°C pyrolysis for all sludge samples collected showed that CO_2 recorded highest relative abundance at $52.64 \pm 5.71\%$ in average, H_2 presence with mean relative abundance of $20.89 \pm 6.61\%$ and then followed by CO at $11.35 \pm 3.48\%$, CH_4 at $9.26 \pm 1.91\%$, and C_2 to C_5 gases at $5.80 \pm 1.37\%$.

Comparison study based on different pyrolysis temperatures selected further provided important information on thermal degradation behaviours during different stages of reaction. Comprehensive understanding on the degradation behaviours of sludge could therefore be established by determination of yield distributions, total energy requirements, details characteristics of char solids including heat capacity, heating value, elemental contents, and functional groups and also gas composition. Analysis of char solids produced during pyrolysis could help to indirectly determine the progress of the reactions at different temperature and thermal degradation stages. Thermal degradation behaviours and products distribution of sludge found to be varied according to the operating conditions and also composition of sludge. Hence, thermal degradation behaviours and products evolution of sludge could be concluded as the outcome of interactions between sludge characteristics and operating conditions applied. Understanding on mechanism and modelling of thermochemical conversion processes would be limited if only operating conditions were considered in details. In order to understand and describe complex behaviours of sludge thermal degradation, individual contributing components and corresponding characteristics should be identified and studied. Organic composition determination was therefore important to identify and quantify impacts and kinetics of individual components on sludge thermochemical conversion processes.

6. Biomass composition analysis of sludge

Findings in this chapter were summarised and submitted for publication as parts of an original research paper: Characterisation of sludge for thermochemical conversion processes based on biomass composition analysis and simulation study of thermochemical properties.

6.1. Introduction

Biomass composition analysis was carried out to determine the distribution of organic components in sludge. Analytical procedure proposed in this study focused on the quantification of main organic components in sludge instead of identifying all the compounds that presence since thermal degradation behaviours and products evolution of sludge could be more significantly affected by the differences in categories of main biomass components presence as compared to variations in molecular structure, chain length and substituent groups of compounds within same category of biomass composition. Biomass composition of sludge also varied significantly due to differences in sources of wastewater and treatment processes applied (Inoue et al., 1996; Jimenez et al., 2013; Ruggieri et al., 2008; Vriens et al., 1989). Therefore comparison study based on sludge biomass composition analysis was carried out to achieve a more comprehensive understanding of sludge generated from various stages of wastewater treatment processes and different wastewater influents. Correlations study was also carried out to determine the impacts of sludge organic composition on physical and chemical properties of sludge related to thermochemical conversion processes.

6.2. Materials and Methods

6.2.1. Categorisation for biomass composition of sludge

Biomass composition of sludge was divided into six categories which were ethanol extractives (EE), water extractives (WE), proteins, alkaline hydrolysed residues (AHR), acid digested residues (ADR) and other organic matters (OOM). Flowchart for extraction and isolation procedures was illustrated in Figure 6.1. Results of composition analysis were recorded in db and calculated in dsb and icf. To obtain representative data, all tests were carried out in triplicate and sludge samples were analysed without sieving due to heterogeneity and complexity in composition.

Figure 6.1: Categorisation flowchart for biomass composition analysis of sludge.

6.2.2. Extractives analysis

Ethanol extraction was carried out according to ASTM E1690 to quantify hydrophobic extractives in sludge. $20.00 \pm 1.00\text{g}$ of sludge placed in cellulose thimble for Soxhlet extraction using Ethanol (ACS Grade, 95% purity) for 24 hours with about 4–5 solvent cycles per hour and achieved 100–120 solvent exchanges in total. Solid residue was then dried in oven at 60°C for 24 hours. Mass loss after ethanol extraction was measured and recorded as EE. Water extraction was carried out subsequently to remove hydrophilic materials. $20.00 \pm 1.00\text{g}$ of EER placed in cellulose thimble for Soxhlet extraction using deionised water for 6 hours according to recommendations stated in Laboratory Analytical Procedure (LAP) of National Renewable Energy Laboratory (NREL) on Determination of Extractives in Biomass. Solid residue was dried in oven at 60°C for 24 hours and mass loss after water extraction was measured and recorded as WE. Solid residue of sludge extracted by both ethanol and water was classified as EFR and used for subsequent analysis.

6.2.3. Proteins content

Dumas method measured the Dumas-Nitrogen (DN) content in sample through complete combustion and nitrogen gas quantification by using Vario EL cube (Elementar). Kjeldahl Method measured the nitrogen content in sample through a series of procedures using concentrated acids and heavy metal catalysts to convert nitrogen in the sample to ammonia and quantified by titration. Kjeldahl-Nitrogen (KN) determination was carried out by TUV-SUD Singapore using Method TTS-CHM-TM-003/03. In order to reduce the interference of non-protein nitrogen in protein contents estimation, nitrogen content of EFR determined by Dumas method and calculated in dsb was proposed and used in subsequent sludge biomass composition analysis. In total, four different calculations were applied and compared including DN and KN of sludge with multiplier of 6.25, DN of EFR multiplied with N-to-P factor of 6.25 and DN of sludge multiplied with reduced N-to-P factor of 5.15 for protein contents estimation.

6.2.4 Alkaline hydrolysis and acid digestion

Sequential treatment of 10.00 ± 0.50 g EFR was carried out in 300 ml of 0.5M NaOH followed by 0.5%, 1.0%, 1.5%, 2.0%, and 3.0% of H_2O_2 in 200 ml 0.5M NaOH, and 200 ml of 2M NaOH at 55°C for 2 hours at each step to determine AHR which represented components in sludge similar to cellulose (Sun et al., 2004). Soluble extractives were removed by centrifugations and washings after each step of treatment. Solid residues were retained and dried in oven at 105°C . Mass of final residue was recorded as AHR after gravimetric correction of ash residues and nitrogenous contents. Acid digestion of EFR was carried out according to ASTM 1721 to determine ADR which represented lignin, aromatics compounds and humic substances in sludge. 0.30 ± 0.01 g of EFR was placed in test tube followed by the addition of 3.00 ± 0.01 ml of 72% sulfuric acid. The mixture was stirred for one minute and placed in warm room at 30°C for 2 hours. Sample mixture was stirred every 15 minutes to achieve complete mixing and wetting. The mixture was then transferred to a glass bottle and diluted to 4% sulfuric acid by adding 84.00 ± 0.04 ml of deionized water. Glass bottle was carefully sealed and placed in an autoclave for 1 hour at $121 \pm 3^\circ\text{C}$. Solid residues were washed and centrifuged to remove any hydrolyzed materials. Acid insoluble material was measured gravimetrically and recorded as ADR after drying in an oven at 105°C and corrected for ash residues and nitrogenous contents.

6.2.5. Other organic matters

Lipids, simple sugars, proteins, cellulose, and lignin were quantified based on the sequential extraction and isolation procedures. All results obtained were calculated in dsb. Therefore residuals were categorized as OOM and mass% was calculated by difference after considered the above five categories of organic composition and total inorganic contents presence in sludge. Consider major chemical compounds could be presence in sludge, polysaccharides and hemicelluloses were suggested as the main components in the category of OOM in this study.

6.2.6. Characterisation study on sludge components

FTIR analysis provided a simple, fast and economical method to compare different categories of sludge composition. Functional groups identifications helped to determine main components presence in waste mixtures (Wingender et al., 1999). Glycosidic bonds (Carbohydrates–O–R) presence in the polysaccharides linked in linear or branched structures. Peptide (R–CO–NH–R') bonds presence in abundance in proteins polymers while the major type of linkage in nucleic acids was phosphodiester (R–O–P–O–R') bonds. Lipids were mainly linked with ester (R–CO–O–R') and C–C bonds while phenolic compounds and sugars in humic substances and lignin were having significant amount of ether (R–O–R') and C–C bonds. The characteristics peak numbers were 1654, 1540 cm^{-1} for protein, 2925, 2855 cm^{-1} for lipids, 1160, 1080, 1030 cm^{-1} for polysaccharides and 1510 cm^{-1} for lignin (Grube et al., 2006). Peak numbers were used as references but shift of peaks on FTIR spectra occurred for different waste mixtures. Shift of peaks indicated presence of identical functional groups with different chemical constituents in the overall structure of the compounds (Francioso et al., 2010).

Heating values of EER and EFR were measured directly and then heating values of extractives were calculated by difference in dsb. Distribution of energy contents in extractives and solvent extracted residues were also calculated. CHNS contents of EER and EFR were measured and molecular formulas were formed. Comparison made on ash tests of solvent extracted residues and sludge samples suggested that no significant amount of inorganics dissolved into extractives similar to previous extraction study on sludge (Boocock et al., 1992). Therefore, inorganic contents in solvent extracted residues were calculated from initial inorganic contents in sludge by assuming insignificant loss of inorganics into extractives. CHNS of ethanol and water extractives were estimated qualitatively by comparing elemental composition measured for sludge and the corresponding solvent extracted residues.

6.3. Results and Discussion

6.3.1. Extractives analysis

Results of extractives analysis in db and icf were showed in Table 6.1. Data in db showed extractives contents as measured while data calculated in icf allowed comparison among different sludge samples made on organics only basis. Contents of EE and WE varied significantly among different sludge samples. Total extractives of sludge showed mean values of 18.82 ± 4.70 mass% in db and 24.09 ± 4.56 mass% in icf indicated that extractives were major components in biomass composition of sludge. EE and WE contents were higher and lower respectively in sludge collected before AD as compared to after AD treatment indicated that lipids and other hydrophobic materials were degraded while simple sugars, organic acids, alcohols and intracellular substances were formed and remained in sludge solids during AD. For Changi WRP, primary sludge showed higher WE contents while secondary sludge showed higher EE contents. Dried sludge was relatively low in both extractives. Activated sludge process produced secondary sludge with higher lipids contents compared to primary sludge generated from sedimentation and dried sludge collected after AD. Total extractives followed the order of primary > secondary > dried sludge in both db and icf for the two batches of sludge samples collected. WE contents among two batches of Ulu Pandan raw sludge and EE contents among two batches of Changi primary sludge varied significantly. Contents of both extractives among batches of Ulu Pandan dewatered sludge, Changi secondary and dried sludge were more consistent. These observations could be explained by considerations on treatment processes. Raw and primary sludge were significantly affected by variation of wastewater characteristics as primary sludge formed from direct settling of solids and floatation of greases in the incoming wastewater while raw sludge formed from mixing of primary and secondary sludge. However, secondary and AD digested sludge were more consistent suggesting regulating effect of aerobic and anaerobic biodegradation processes on characteristics of sludge generated. Lower total extractives after AD in db and icf indicated the accumulation of inorganic contents, structural biomass components recalcitrant to biodegradation and other non-biodegradable materials.

Results of HHV analysis for extractives calculated from direct measurements of solvent extracted residues were showed in Table 6.2 in db and dsb. By using extractives contents presence in sludge and HHV data, energy distributions were also calculated. Significant variations in HHV could be observed for all extractives and solvent extracted residues among different sludge samples collected due to differences in inorganic contents in sludge and composition of organic matters. EFR showed lower HHV compared to EER and sludge because of reduction in organic matters during solvent extractions. With lipids as major components, EE was estimated at higher mean HHV of $42.41 \pm 6.59 \text{ MJ/kg}$ and contributed higher proportion of energy contents of $20.67 \pm 7.79\%$ to sludge. With carbohydrates as major components, WE was estimated at lower mean HHV of $21.24 \pm 4.96 \text{ MJ/kg}$ and contributed lower proportion of energy content of $11.70 \pm 4.50\%$ to sludge. Main portion of sludge energy contents at $67.63 \pm 5.66\%$ remained in EFR. Based on mean HHV values for extractives and residues, it could be observed that energy distribution of sludge affected by both mass and type of biomass composition. Mean HHV of EE for sludge before AD was lower compared to after AD but comprised of higher percentage of energy contents because presence of higher contents in sludge. For WE and EFR, slightly higher mean HHV for sludge before AD could be observed while represented lower percentage of energy contents in sludge as compared to sludge after AD. In general, HHV results supported that the EE and WE were comparable among different sludge samples collected and having comparable characteristics to lipids and carbohydrates compounds respectively.

Results of CHNS contents of solvent extracted residues were showed in Table 6.3. Quantitative variations and qualitative similarities for all sludge samples according to the categorisation of types, plants and batches could be observed. Mean values of CHNS calculated in normalised molar basis were used to form the molecular formula for sludge $\text{C}_{1.00}\text{H}_{1.8045}\text{N}_{0.1202}\text{S}_{0.0518}$, EER $\text{C}_{1.00}\text{H}_{1.7797}\text{N}_{0.1353}\text{S}_{0.0481}$, and EFR $\text{C}_{1.00}\text{H}_{1.8100}\text{N}_{0.1290}\text{S}_{0.0456}$. Based on the molecular formula of solids, EE was estimated to be having relatively higher H and S with lower N molar contents while WE was estimated to be having higher N and S with lower H molar contents. High H/C ratio in EE suggested lipids as main components while nitrogen contents indicated presence of phospholipids. Low H/C ratio in WE suggested sugars as

main components while high N/C ratio also indicated presence of nucleic acids, amines and nitrogenous compounds agreed with FTIR spectra analysis. Sulphur containing compounds were extracted by both extractions. No significant difference could be observed for molecular formula of sludge and solvent extracted residues showed that elemental analysis of waste samples hardly distinguished different complex mixtures. These observations supported the need for biomass composition analysis for sludge and applicability of categories established in this study.

FTIR spectra of extractives were showed in Figure 6.2. High similarity observed for spectra of EE and WE respectively indicated the compounds in both extractives were comparable among different sludge samples. For EE, broad peak at 3200cm^{-1} indicated presence of O-H functional groups of carboxylic acids, alcohols, sterol lipids and phospholipids. Strong and narrow peaks indicated presence of significant amount of C-H groups, at 3048cm^{-1} for unsaturated hydrocarbon and aromatics while at $2926, 2854\text{cm}^{-1}$ for saturated hydrocarbon, ethers and lipids. Strong peaks at 1730cm^{-1} indicated presence of C=O groups of aldehyde, ketone, carboxylic acids, esters and lipids while multiple peaks at 1461 and 1370cm^{-1} indicated presence of C-H groups of hydrocarbon, ethers and lipids. Multiple peaks overlapped in fingerprint regions of $1300\text{-}600\text{cm}^{-1}$ could be observed. Strong peaks at $1226, 1170, 1045$ and 960cm^{-1} indicated presence of lipids mixture comparable to the spectra of model compounds such as glyceryl-tripalmitate, asolectin (phospholipids) and cholesterol (sterol lipids). For WE, broad peaks extended from $3400\text{-}3000\text{cm}^{-1}$ indicated presence of O-H and N-H groups from alcohols, acids, amides and amines. Weak peaks observed at 2949cm^{-1} indicated that the proportions of C-H groups were smaller in water extractives. Strong broad peaks at 1620cm^{-1} indicated presence of N-H groups of amines and nitrogenous compounds while strong peaks at 1405cm^{-1} indicated the presence of O-H groups of alcohols and carbohydrates. Multiple peaks at $1230, 1060, \text{ and } 1000\text{cm}^{-1}$ indicated the presence of C-O-C groups of carbohydrates and ethers in water extractives. The signature peaks of protein compounds at 1654 and 1540cm^{-1} (Grube et al., 2006) were absent in FTIR spectra of EE suggested that protein remained in sludge solids while non-protein nitrogen extracted into extractives. For FTIR spectra of water extractives, broad peaks observed at $1650\text{-}1540\text{cm}^{-1}$ region could be caused by the presence of amines,

nucleic acids, amino acids, and other nitrogenous compounds instead of proteins because of the low solubility of proteins in water after unfolded during extractions (Pace et al., 2004). These observations supported the hypothesis that calculations based on EFR nitrogen contents could improve the estimation of protein contents in the sludge by excluding non-protein nitrogen contents.

Figure 6.2: FTIR spectra of (a) ethanol and (b) water extractives from sludge.

Table 6.1: Extractives analysis of sludge.

Sample label	Mass% in db					Mass% in icf				
	EE		WE		Total extractives	EE		WE		Total extractives
	Mean	SD	Mean	SD		Mean	SD	Mean	SD	
UR	11.92	1.05	12.49	1.55	24.41	13.35	1.17	13.99	1.73	27.34
UD	5.28	0.68	12.88	1.34	18.16	6.43	0.83	15.67	1.63	22.10
CP	5.77	0.91	17.07	0.25	22.84	7.21	1.14	21.34	0.31	28.56
CS	11.10	0.98	7.56	2.04	18.65	12.61	1.11	8.59	2.32	21.20
CY	3.55	0.59	8.54	0.92	12.09	5.31	0.88	12.76	1.37	18.06
JR	11.15	2.14	4.42	1.72	15.56	15.30	2.94	6.06	2.36	21.36
JD	6.64	0.65	8.07	1.27	14.71	11.88	1.16	14.43	2.28	26.31
KR	14.36	1.29	9.59	2.44	23.95	16.90	1.51	11.28	2.87	28.18
KD	4.16	0.25	13.47	0.57	17.63	5.38	0.33	17.44	0.74	22.82
UsR	14.86	2.99	5.41	3.43	20.26	18.08	3.63	6.58	4.17	24.65
UsD	7.05	1.66	14.24	1.32	21.29	8.78	2.07	17.75	1.65	26.54
CsP	12.07	0.81	14.24	1.79	26.31	15.07	1.01	17.79	2.23	32.86
CsS	12.94	0.78	4.42	1.73	17.36	16.05	0.97	5.48	2.15	21.54
CsY	3.61	0.11	6.69	0.95	10.30	5.50	0.16	10.19	1.45	15.69
Mean $\pm$ standard deviations										
All sample	8.89 $\pm$ 4.13		9.93 $\pm$ 4.10		18.82 $\pm$ 4.70	11.27 $\pm$ 4.70		12.81 $\pm$ 4.97		24.09 $\pm$ 4.56
Before AD	11.77 $\pm$ 2.79		9.40 $\pm$ 4.79		21.17 $\pm$ 3.79	14.32 $\pm$ 3.37		11.39 $\pm$ 5.87		25.71 $\pm$ 4.24
After AD	5.05 $\pm$ 1.53		10.65 $\pm$ 3.24		15.70 $\pm$ 4.10	7.21 $\pm$ 2.64		14.71 $\pm$ 2.90		21.92 $\pm$ 4.36
Range	3.55 – 14.86		4.42 – 17.07		10.30 – 26.31	5.31 – 18.08		5.48 – 21.34		15.69 – 32.86

Table 6.2: Heating value analysis for extractives and solvent extracted residues.

Sample label	HHV in MJ/kg								Energy distribution, %		
	EER		EFR		EE		WE		EE	WE	EFR
	db	dsb	db	dsb	db	dsb	db	dsb			
UR	18.23	16.05	17.38	13.14	37.23	4.44	23.34	2.91	21.66	14.22	64.12
UD	15.68	14.85	13.99	11.45	48.47	2.56	26.42	3.40	14.70	19.54	65.76
CP	16.33	15.39	15.88	12.26	37.25	2.15	18.33	3.13	12.26	17.85	69.89
CS	15.84	14.08	15.30	12.45	50.27	5.58	21.62	1.63	28.37	8.31	63.31
CY	13.16	12.69	12.33	10.84	50.07	1.78	21.70	1.85	12.29	12.80	74.90
JR	13.34	11.85	12.44	10.50	47.30	5.27	30.51	1.35	30.79	7.87	61.34
JD	10.37	9.68	10.33	8.81	52.90	3.51	10.73	0.87	26.64	6.56	66.80
KR	16.41	14.05	15.76	11.98	45.04	6.47	21.59	2.07	31.52	10.09	58.39
KD	14.51	13.90	13.62	11.22	42.27	1.76	19.90	2.68	11.22	17.12	71.66
UsR	16.57	14.11	16.20	12.92	35.68	5.30	21.94	1.19	27.32	6.11	66.57
UsD	16.14	15.00	16.02	12.61	35.22	2.48	16.80	2.39	14.19	13.69	72.12
CsP	16.15	14.20	15.88	11.70	33.11	4.00	17.58	2.50	21.96	13.76	64.28
CsS	15.94	13.88	15.30	12.65	36.91	4.78	27.83	1.23	25.60	6.59	67.80
CsY	12.84	12.38	12.37	11.09	42.07	1.52	19.13	1.28	10.92	9.22	79.86
Mean $\pm$ standard deviations											
All sample	15.11 ± 2.03	13.72 ± 1.63	14.49 ± 2.00	11.69 ± 1.16	42.41 ± 6.59	3.68 ± 1.65	21.24 ± 4.96	2.04 ± 0.81	20.67 ± 7.79	11.70 ± 4.50	67.63 ± 5.66
Before AD	16.10 ± 1.34	14.20 ± 1.23	15.52 ± 1.41	12.20 ± 0.83	40.35 ± 6.26	4.75 ± 1.29	22.84 ± 4.40	2.00 ± 0.77	24.93 ± 6.28	10.60 ± 4.22	64.46 ± 3.65
After AD	13.78 ± 2.13	13.08 ± 1.99	13.11 ± 1.92	11.00 ± 1.24	45.16 ± 6.51	2.27 ± 0.74	19.11 ± 5.22	2.08 ± 0.94	14.99 ± 5.91	13.16 ± 4.82	71.85 ± 5.22

Table 6.3: Elemental analysis of solvent extracted residues from sludge.

Sample label	Mass% in db								Normalised molar basis, C = 1.00					
	EER				EFR				EER			EFR		
	C	H	N	S	C	H	N	S	H	N	S	H	N	S
UR	39.02	5.65	6.00	4.02	39.18	6.05	5.41	3.98	1.74	0.13	0.04	1.85	0.12	0.04
UD	34.18	5.09	5.55	4.39	32.20	4.78	4.93	3.78	1.79	0.14	0.05	1.78	0.13	0.04
CP	33.12	5.15	7.13	3.94	33.83	5.14	6.89	3.80	1.87	0.18	0.04	1.82	0.17	0.04
CS	37.93	5.56	3.82	3.20	38.00	5.59	3.64	3.44	1.76	0.09	0.03	1.76	0.08	0.03
CY	29.01	4.27	5.03	3.75	28.67	4.28	4.84	3.36	1.76	0.15	0.05	1.79	0.14	0.04
JR	28.42	4.20	4.32	3.83	28.32	4.31	4.10	3.14	1.77	0.13	0.05	1.82	0.12	0.04
JD	21.60	3.12	3.14	4.45	20.92	3.09	2.92	4.21	1.73	0.12	0.08	1.77	0.12	0.08
KR	35.75	5.21	5.70	3.85	36.59	5.40	5.57	3.57	1.75	0.14	0.04	1.77	0.13	0.04
KD	31.38	4.68	5.90	4.34	30.52	4.73	5.32	4.01	1.79	0.16	0.05	1.86	0.15	0.05
UsR	37.58	5.60	5.41	3.78	36.58	5.59	4.97	3.92	1.79	0.12	0.04	1.83	0.12	0.04
UsD	36.27	5.43	5.86	3.39	35.13	5.39	5.21	3.99	1.80	0.14	0.03	1.84	0.13	0.04
CsP	33.12	4.94	6.80	4.86	32.86	4.96	6.29	4.48	1.79	0.18	0.05	1.81	0.16	0.05
CsS	36.46	5.44	3.33	5.03	36.66	5.53	3.17	4.45	1.79	0.08	0.05	1.81	0.07	0.05
CsY	27.76	4.14	4.95	4.80	27.35	4.13	4.77	4.12	1.79	0.15	0.06	1.81	0.15	0.06
Mean $\pm$ standard deviations														
All sample	32.97 ± 4.88	4.89 ± 0.73	5.21 ± 1.20	4.12 ± 0.55	32.63 ± 5.04	4.92 ± 0.78	4.86 ± 1.11	3.88 ± 0.39	1.78 ± 0.03	0.14 ± 0.03	0.05 ± 0.01	1.81 ± 0.03	0.13 ± 0.03	0.05 ± 0.01
Before AD	35.17 ± 3.47	5.22 ± 0.48	5.31 ± 1.38	4.06 ± 0.60	35.25 ± 3.47	5.32 ± 0.52	5.01 ± 1.29	3.85 ± 0.47	1.78 ± 0.04	0.13 ± 0.04	0.04 ± 0.01	1.81 ± 0.03	0.12 ± 0.03	0.04 ± 0.01
After AD	30.03 ± 5.20	4.45 ± 0.82	5.07 ± 1.03	4.19 ± 0.52	29.13 ± 4.86	4.40 ± 0.78	4.66 ± 0.88	3.91 ± 0.31	1.78 ± 0.02	0.14 ± 0.01	0.05 ± 0.01	1.81 ± 0.03	0.14 ± 0.01	0.05 ± 0.01

6.3.2. Protein contents

Table 6.4 showed nitrogen and proteins contents of sludge measured and calculated based on four different calculation methods respectively. In general, N and protein contents of sludge varied with type, plant and batch categorisations. Mean values of N and protein contents in dsb calculated for sludge samples collected before and after AD were similar. However, inorganic contents were higher in AD digested sludge therefore protein contents in icf were also relatively higher as showed in Table 6.7. N and protein contents were also found to be significantly higher in primary sludge and lower in secondary sludge. These observations suggested that high protein contents settled into primary sludge from wastewater influent and partially digested during AD. KN/DN ratios could vary from 0.15 to 1.40 in biomass (Simonne et al., 1997). However, KN/DN ratios of sludge measured in this study varied from 0.87 to 1.31 with mean at 0.96 ± 0.13 showing that both Kjeldahl and Dumas methods determined similar nitrogen contents in sludge. Therefore Dumas method was recommended for N contents determination for sludge since it reduced the time of testing and avoided using concentrated acids and heavy metal catalysts. DN of EFR were lower than the DN of sludge indicated the removal of nitrogen during solvent extractions. Ratios of DN of EFR to DN of sludge varied from 0.66 to 0.91 with a overall mean of 0.75 ± 0.07 agreed well with the previous estimation that suggested the presence of 70-80% protein-nitrogen in sludge (Vriens et al., 1989). The hypothesis of protein estimation improved by using DN of EFR also supported by lowest mean values of calculated protein contents indicated the removal of non-protein nitrogen contents from sludge before nitrogen-to-protein conversion. Mean values of four different protein contents calculated were in the following order, DN of sludge $\times 6.25$ ($33.16 \pm 7.96\%$) $>$ KN of sludge $\times 6.25$ ($31.64 \pm 6.48\%$) $>$ DN of sludge $\times 5.15$ ($27.32 \pm 6.56\%$) $>$ DN of EFR $\times 6.25$ ($24.62 \pm 4.92\%$). Reduced Nitrogen-to-Protein (N-to-P) factor of 5.15 was also applied and illustrated (Hattingh et al., 1967). However variation in non-protein nitrogen as showed in DN of EFR/sludge ratios could not be accounted in the calculation by using a fixed and reduced factor. Therefore determination of nitrogen contents of EFR with N-to-P multiplication factor of 6.25 was recommended and used in this study for sludge biomass composition analysis and subsequent study.

Table 6.4: Proteins contents analysis of sludge.

Sample label	Nitrogen contents in dsb, Mass%						Nitrogen contents ratio		Proteins contents in dsb, Mass%			
	DN sludge		KN sludge		DN EFR		KN/DN	DN of EFR/Sludge	N-to-P 6.25			N-to-P 5.15
	Mean	SD	Mean	SD	Mean	SD			DN sludge	KN sludge	DN EFR	DN sludge
UR	5.74	0.29	5.22	-	4.09	0.09	0.91	0.71	35.85	32.60	25.55	29.54
UD	6.04	0.02	5.46	-	4.03	0.03	0.90	0.67	37.72	34.10	25.20	31.08
CP	7.55	0.38	7.14	-	5.32	0.01	0.94	0.70	47.21	44.60	33.25	38.90
CS	3.87	0.07	3.60	-	2.96	0.03	0.93	0.77	24.20	22.50	18.53	19.94
CY	5.03	0.30	4.82	-	4.25	0.04	0.96	0.85	31.45	30.10	26.58	25.92
JR	4.33	0.09	4.10	-	3.47	0.09	0.95	0.80	27.06	25.60	21.66	22.30
JD	3.33	0.11	4.35	-	2.49	0.03	1.31	0.75	20.81	27.20	15.57	17.15
KR	5.78	0.06	5.14	-	4.24	0.14	0.89	0.73	36.16	32.10	26.47	29.79
KD	6.64	0.06	5.76	-	4.38	0.07	0.87	0.66	41.52	36.00	27.38	34.21
UsR	4.96	0.03	-	-	3.97	0.03	-	0.80	31.00	-	24.79	25.54
UsD	5.91	0.03	-	-	4.10	0.06	-	0.69	36.92	-	25.62	30.42
CsP	6.80	0.04	-	-	4.78	0.02	-	0.70	42.48	-	29.87	35.01
CsS	3.46	0.01	-	-	2.69	0.10	-	0.78	21.62	-	16.83	17.81
CsY	4.83	0.03	-	-	4.37	0.02	-	0.91	30.20	-	27.34	24.89
Mean $\pm$ standard deviations												
All sample	5.31 $\pm$ 1.27		5.06 $\pm$ 1.04		3.94 $\pm$ 0.79		0.96 $\pm$ 0.13	0.75 $\pm$ 0.07	33.16 $\pm$ 7.96	31.64 $\pm$ 6.48	24.62 $\pm$ 4.92	27.32 $\pm$ 6.56
Before AD	5.31 $\pm$ 1.43		5.04 $\pm$ 1.36		3.94 $\pm$ 0.88		0.92 $\pm$ 0.02	0.75 $\pm$ 0.04	33.20 $\pm$ 8.91	31.48 $\pm$ 8.50	24.62 $\pm$ 5.52	27.35 $\pm$ 7.34
After AD	5.30 $\pm$ 1.17		5.10 $\pm$ 0.63		3.94 $\pm$ 0.72		1.01 $\pm$ 0.20	0.75 $\pm$ 0.10	33.10 $\pm$ 7.33	31.85 $\pm$ 3.96	24.62 $\pm$ 4.52	27.28 $\pm$ 6.04

6.3.3. Summary of sludge biomass composition

Alkaline hydrolysis and acid digestion were carried out separately on EFR. Contents of AHR and ADR recorded in dsb and icf were showed in Table 6.5 and 6.6 with the summary of all organic categories which included OOM calculated using by-difference method. Total inorganic contents (TI) in sludge samples were also showed for 100% mass closure of sludge composition. Composition of sludge distributed among six organic categories with contents in icf ranged from the lowest at $5.97 \pm 2.30\%$ for AHR which represented cellulose in sludge, $11.27 \pm 4.70\%$ for EE which represented lipids, $12.81 \pm 4.97\%$ for WE which represented simple sugars, organic alcohols, acids and other intracellular substances, $17.14 \pm 7.19\%$ for ADR which represented lignin and aromatics compounds, $20.83 \pm 9.73\%$ for OOM which represented polysaccharides and other compounds in sludge, to the highest at $31.98 \pm 6.61\%$ for protein contents estimated. Summarised results suggested that categorisation used in this study was satisfactory because all categories showed appropriate proportion in sludge. If content of any category was too low then the category could be ignored and combined with another category as it is insignificant and content of any category was too high then further division of would be needed to have a better understanding of the organic matters within the category. Biomass composition analysis of sludge also showed that significant variations could be observed according to differences in types, plants and batches. Consider data from all sludge samples in average, contents of organics followed the order of proteins > OOM > ADR > WE > EE > AHR in db and icf. Considering sludge samples collected before AD, mean contents followed different order of proteins > OOM > EE > ADR > WE > AHR. Considering sludge samples collected after AD, mean contents also followed different order of proteins > ADR > WE > OOM > EE > AHR. Proteins appeared to be the most dominant biomass composition and AHR which represented amount of cellulose appeared to be the minor component in all sludge samples collected. Relative abundance of other components varied among different sludge samples. Mass% in icf of EE and OOM were significantly lower in AD digested sludge mainly because lipids and polysaccharides were consumed during anaerobic digestion (Li et al., 2014). These components were relatively higher in secondary sludge suggested generation and accumulation of lipids and

polysaccharides in sludge solids during activated sludge process. Mass% in icf of proteins, AHR and ADR were significantly higher in sludge samples collected after AD mainly because non-biodegradable matters and aromatic compounds remained during AD processes therefore showed higher relative composition in AD digested sludge (Li et al., 2014). WE contents also higher in sludge after AD mainly because the digestion processes of sludge degraded polysaccharides into simple sugars and organic alcohols which could be extracted by water extractions.

Figure 6.3 showed FTIR spectra of EER, EFR, AHR and ADR for all sludge samples collected. In general, high similarities could be observed among sludge samples for different category of residues. These observations suggested that residues isolated from different sludge samples were having similar functional groups and comparable chemical compounds in respective biomass composition categories. Results supported the application of analytical procedure developed in this study for sludge samples of different types, plants, batches. For EER and EFR, no significant difference could be observed when compared to sludge. Detail peaks and functional groups identification could be referred to sludge characterisation in Chapter 3. For AHR, FTIR spectra showed the presence of mainly O-H, C-O, C-O-C and inorganic functional groups. O-H groups could be observed at 3700cm^{-1} for inorganic bounded O-H and at 3300cm^{-1} , 1415cm^{-1} , and at 913cm^{-1} for O-H in organic matters. C-O and C-O-C groups of glycosidic linkage could be observed at peaks of 1220cm^{-1} , 1158cm^{-1} , 1030cm^{-1} and 912cm^{-1} . For ADR, FTIR spectra analysis showed the presence of mainly C-H, C=O, C=C and aromatic rings functional groups. C-H groups observed at 2972cm^{-1} and 2837cm^{-1} , C=O and C=C groups in $1700\text{-}1600\text{cm}^{-1}$ region with broad peaks at 1680cm^{-1} and 1653cm^{-1} and aromatic rings at 1510cm^{-1} . Figure 6.4 compared dried sludge from Changi WRP (CsY) with respective solid residues and extractives. No qualitative difference could be observed for EER and EFR as compared to CsY sludge. However, significant differences could be observed for AHR, ADR and extractives when compared to sludge. These observations suggested that complex nature of the chemical compounds in sludge could be better characterized after extraction and isolation procedures that could separate different categories of biomass composition.

Table 6.5: Biomass composition analysis for sludge in db.

Sample label	Mass% in dry basis (db)											
	EE		WE		Proteins		AHR		ADR		OOM	TI
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD		
UR	11.92	1.05	12.49	1.55	25.55	0.55	4.53	0.49	14.12	0.41	20.68	10.71
UD	5.28	0.68	12.88	1.34	25.20	0.20	4.26	0.18	11.80	0.07	22.75	17.83
CP	5.77	0.91	17.07	0.25	33.25	0.07	4.83	0.38	5.39	0.23	13.67	20.02
CS	11.10	0.98	7.56	2.04	18.53	0.17	8.64	0.85	10.91	0.74	31.26	12.01
CY	3.55	0.59	8.54	0.92	26.58	0.24	5.83	0.53	17.56	0.04	4.87	33.07
JR	11.15	2.14	4.42	1.72	21.66	0.56	2.93	0.10	10.68	0.60	22.03	27.14
JD	6.64	0.65	8.07	1.27	15.57	0.20	5.58	0.88	13.38	0.07	6.66	44.09
KR	14.36	1.29	9.59	2.44	26.47	0.88	3.09	0.25	11.25	0.27	20.23	15.00
KD	4.16	0.25	13.47	0.57	27.38	0.42	5.53	0.79	23.81	0.16	2.91	22.74
UsR	14.86	2.99	5.41	3.43	24.79	0.17	2.82	0.50	12.63	0.03	21.70	17.80
UsD	7.05	1.66	14.24	1.32	25.62	0.35	2.41	0.44	20.93	0.34	9.97	19.79
CsP	12.07	0.81	14.24	1.79	29.87	0.11	4.22	0.17	5.43	0.13	14.26	19.92
CsS	12.94	0.78	4.42	1.73	16.83	0.61	3.97	0.87	14.71	0.07	27.74	19.40
CsY	3.61	0.11	6.69	0.95	27.34	0.14	4.79	0.14	10.05	0.11	13.16	34.35
Mean $\pm$ standard deviations												
All sample	8.89 $\pm$ 4.13		9.93 $\pm$ 4.10		24.62 $\pm$ 4.92		4.53 $\pm$ 1.60		13.05 $\pm$ 5.14		16.56 $\pm$ 8.57	22.42 $\pm$ 9.28
Before AD	11.77 $\pm$ 2.79		9.40 $\pm$ 4.79		24.62 $\pm$ 5.52		4.38 $\pm$ 1.88		10.64 $\pm$ 3.54		21.45 $\pm$ 5.98	17.75 $\pm$ 5.22
After AD	5.33 $\pm$ 1.59		11.16 $\pm$ 3.26		24.76 $\pm$ 4.14		4.40 $\pm$ 1.46		16.92 $\pm$ 5.26		10.04 $\pm$ 6.59	28.65 $\pm$ 10.21
Range	3.55 – 14.86		4.42 – 17.07		15.57 – 33.25		2.41 – 8.64		5.39 – 23.81		2.91 – 31.26	10.71 – 44.09

Table 6.6: Biomass composition analysis for sludge in icf.

Sample label	Mass% in inorganic contents free basis (icf)										
	EE		WE		Proteins		AHR		ADR		OOM
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
UR	13.35	1.17	13.99	1.73	28.61	0.61	5.08	0.55	15.81	0.46	23.16
UD	6.43	0.83	15.67	1.63	30.67	0.25	5.18	0.21	14.36	0.09	27.68
CP	7.21	1.14	21.34	0.31	41.57	0.09	6.04	0.48	6.74	0.29	17.09
CS	12.61	1.11	8.59	2.32	21.06	0.19	9.82	0.97	12.40	0.84	35.53
CY	5.31	0.88	12.76	1.37	39.71	0.37	8.70	0.79	26.24	0.06	7.28
JR	15.30	2.94	6.06	2.36	29.72	0.77	4.02	0.14	14.66	0.83	30.23
JD	11.88	1.16	14.43	2.28	27.84	0.37	9.99	1.58	23.94	0.13	11.92
KR	16.90	1.51	11.28	2.87	31.14	1.03	3.64	0.29	13.24	0.32	23.80
KD	5.38	0.33	17.44	0.74	35.44	0.55	7.15	1.03	30.82	0.21	3.76
UsR	18.08	3.63	6.58	4.17	30.16	0.21	3.43	0.61	15.36	0.04	26.40
UsD	8.78	2.07	17.75	1.65	31.94	0.43	3.00	0.55	26.09	0.42	12.43
CsP	15.07	1.01	17.79	2.23	37.30	0.14	5.27	0.21	6.78	0.17	17.80
CsS	16.05	0.97	5.48	2.15	20.88	0.76	4.92	1.08	18.25	0.09	34.41
CsY	5.50	0.16	10.19	1.45	41.65	0.22	7.30	0.22	15.31	0.17	20.05
Mean ± standard deviations											
All sample	11.27 ± 4.70		12.81 ± 4.97		31.98 ± 6.61		5.97 ± 2.30		17.14 ± 7.19		20.83 ± 9.73
Before AD	14.32 ± 3.37		11.39 ± 5.87		30.05 ± 7.11		5.28 ± 2.04		12.90 ± 4.18		26.05 ± 6.96
After AD	7.44 ± 2.48		15.14 ± 2.88		34.17 ± 5.01		6.33 ± 2.71		23.26 ± 6.12		13.65 ± 7.98
Range	5.31 – 18.08		5.48 – 21.34		20.88 – 41.65		3.00 – 9.99		6.74 – 30.82		3.76 – 35.53

Figure 6.3: FTIR spectra of (a) EER, (b) EFR, (c) AHR and (d) ADR from sludge.

Figure 6.4: FTIR spectra of CsY sludge with (a) solid residues and (b) extractives.

6.3.4. Correlation analysis

Correlations study was performed based on results from biomass composition analysis, data of physical and chemical properties from sludge characterisation analysis and yield distributions from experimental pyrolysis. Data recorded were compared to the contents in icf for six categories of sludge biomass components individually to identify linear correlations. HHV, LHV, VM/FR ratio and C contents were correlated positively to the contents of EE in sludge as illustrated in Figure 6.5 (a), (b) and (c). These observations supported the application of EE to represent lipids and hydrocarbons components in sludge which were having relatively higher energy contents, carbon contents and generally released more volatiles when thermally degraded. In average, contents of EE in sludge only measured at 11.27 ± 4.70 mass% in icf. Therefore the main portions of these properties did not contributed by EE but contributed by other components in sludge. However, differences in EE contents could account for the quantitative variations of sludge samples collected probably because of the significantly higher energy density, volatile matters and carbon contents in EE as compared to other components. No significant correlations could be observed for other categories of biomass suggested that these components were having comparable characteristics among each other on these properties. EE could therefore be used as a good indicator for estimation of HHV, LHV, VM/FR ratio and C contents of sludge. N contents correlated positively to WE, proteins and the summation of these two categories of biomass composition as illustrated in Figure 6.5 (d). These observations suggested that WE and proteins were main contributors to the nitrogen contents in sludge. N contents in sludge mainly originated from proteins while significant amount of amines, amino acids and other nitrogen containing compounds were also presence and soluble in water therefore found in WE as suggested in FTIR analysis. Bulk density of sludge correlated negatively with EE and OOM while correlated positively with WE and proteins. Results were illustrated in Figure 6.6 (a) and (b). These observations suggested that EE represented lipids and OOM represented mainly polysaccharides were having relatively lower density while water soluble substances and proteins were having higher density. Therefore changes in biomass composition of sludge could affect the

bulk density measured. Solid and liquid yields of sludge pyrolysis at 500°C correlated strongly with contents of EE and OOM. As EE and OOM contents in icf increased in sludge samples collected, solids yields decreased and liquid yields increased as illustrated in Figure 6.6 (c) and (d). These observations suggested that EE and OOM thermally degraded to form more condensable volatile compounds. These identified behaviours were similar to the thermal degradations of lipids and polysaccharides in general.

The identified correlations suggested that physical and chemical properties of sludge could be partially explained and quantified based on the biomass composition analysis methodology and categorisation developed in this study. No significant linear correlations could be observed for the characteristics discussed with any other categories of sludge biomass components. In addition, no significant correlations could be observed for HSO contents, heat capacity, heat of pyrolysis, pH, pellet density and gas yields of sludge pyrolysis at 500°C with biomass composition of sludge. Parameters with strong correlations suggested strong dependence of the properties on individual category of biomass components while weak or unidentified correlations suggested that the properties discussed were determined by overall composition of sludge. Since the contributions to characteristics of sludge by different biomass components of sludge were quantitatively different while qualitatively similar, simple and direct relationships were generally difficult to obtain. Further study needed to analyse and quantify the characteristics of individual category of biomass composition for better understanding on thermochemical conversion of sludge.

Figure 6.5: Correlations for biomass composition with (a) HHV and LHV, (b) VM/FR ratio, (c) carbon and (d) nitrogen contents.

Figure 6.6: Correlations for biomass composition with (a) (b) Bulk density in db, (c) solid and (d) liquid yields at 500°C pyrolysis.

6.4. Conclusions

In conclusion, biochemical components in sludge could be appropriately categorised and quantified by using biomass composition analysis developed in this study. Analytical procedure developed also suggested to be able to improve estimation of proteins content and to account for most of the major components in sludge. Based on characterisation of isolated components, properties of compounds found in sludge were identified and discussed. Comparison study for different sludge samples collected based on types, plants and batches showed qualitative similarities and quantitative variations agreed well with the results obtained in previous chapters. In average (icf), sludge consisted of $11.27 \pm 4.70\%$ of EE, $12.81 \pm 4.97\%$ of WE, $31.98 \pm 6.61\%$ of proteins, $5.97 \pm 2.30\%$ of AHR, $17.14 \pm 7.19\%$ of ADR, and $20.83 \pm 9.73\%$ of OOM. Mass contents for total extractives and EE of primary, secondary and raw sludge in average were higher than sludge after AD treatment on db by +5.47% and +6.02% while on icf by +3.79% and +7.11% respectively. OOM was also higher by +11.41% (db) and +12.40% (icf). On the contrary, WE of sludge before AD lower than AD digested sludge by -1.25% (db) and -3.32% (icf). Proteins, AHR and ADR contents of sludge before AD were also relatively lower than dewatered and dried sludge in average by -0.14%, -0.02% and -6.28% on db while -4.12%, -1.05% and -10.36% on icf respectively.

Qualitatively similar results on biomass composition analysis of sludge also provided the insights of why existing studies carried out to compare different sludge samples were unable to identify significant impacts of sludge composition on thermochemical characteristics and thermal degradation behaviours. Characterisation of components isolated from sludge also showed distinctive properties as compared to the initial waste mixtures sampled. These observations supported the hypothesis of composition analysis for main components in sludge could improve the understanding of sludge in thermochemical conversion processes. Correlation analysis also identified and discussed the impacts of organic composition on the characteristics of sludge in both aspects for chemical and physical properties. Further analytical study of sludge could be carried out based on the biomass composition analysis developed to understand the characteristics of individual components in thermochemical conversion processes.

Since the properties and composition of sludge varied depending on sludge types, collection batches and operating conditions of WRPs, it was recommended for operators of thermal systems to establish characteristic profiles (thermochemical properties and composition) of sludge received based on the categorisation proposed in this thesis (type, plant and batch) and then followed by detailed analysis on how the characteristics (statistical dispersion) affected the corresponding performance of targeted systems which would be different for incineration, gasification or pyrolysis. Optimisation of thermochemical conversion processes could then be performed based on the results of composition analysis and further study on properties of individual components. Instead of only direct testing of sludge with complex, heterogeneous and uncertain composition, optimisation study for thermal reactors could be initiated with individual components analysis followed by modeling for the impacts on alteration of composition and operating parameters. In addition, application of controlled components could also help to improve the accuracy and consistency for determination of degradation kinetics and products evolution. Controlled components study could be carried out by using model compounds that can represent the characteristics of major components in sludge.

7. Simulation study on thermochemical properties of sludge by biomass composition analysis and model compounds selection

Findings in this chapter were summarised and submitted for publication as parts of an original research paper: Characterisation of sludge for thermochemical conversion processes based on biomass composition analysis and simulation study of thermochemical properties.

7.1. Introduction

Simulation study of thermochemical properties of sludge based on the results of biomass composition analysis and model compounds selected for respective category of sludge composition were carried out. Based on categorisation and quantification of biochemical components in sludge by biomass composition analysis, model compounds from different categories of organic matters were selected and characterised. Selection of model compounds was also made with reference to published literature for identification of dominant chemical compounds potentially presence in sludge. Methodology developed in this study for comprehensive characterisation of sludge was applied. Thermochemical characteristics for biomass and waste could be estimated as the summation of individual components presence in the mixtures (Biagini et al., 2006; Heikkinen et al., 2004; Orfão et al., 1999). Therefore, superposition principle was applied to physical and chemical properties determined for individual model compounds and corresponding category of sludge biomass composition. Results obtained supported the applicability of the methods for sludge biomass composition analysis and model compounds selection proposed. Characteristics of individual components and impacts on properties of sludge could also be quantitatively estimated based on the results of simulations.

7.2. Materials and Methods

7.2.1. Selection and characterisation of model compounds

Model compounds selected in this study were showed in Table 7.1. For EE, model compounds were selected from three common lipids groups found in wastewater and microorganisms which were glycerol lipids, sterol lipids and phospholipids with reference to lipids classification study (Sud et al., 2007). Details chemical components analysis of hydrophobic extractives also identified main compounds in sludge included fatty acids, sterol lipids, phospholipids and hydrocarbons (Siddiquee and Rohani, 2011). Fatty acids of C₁₀₋₂₂ with mostly stearic, palmitic, and oleic acids were found in sludge. Main steroids in sludge were coprostanol and cholestanol with chain lengths ranging from C₂₇₋₂₉ formed from biodegradation of cholesterol. Non-polar lipids in sludge included linear alkylbenzene, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and alkanes with aliphatic, cyclic and branched structures (Jardé et al., 2005; Reveille et al., 2003). Hence, asolectin and cholesterol were selected to represent phospholipids and sterol lipids respectively while triglycerides of palmitate, stearate and oleate acids were selected to represent fatty acids and glycerol lipids in ethanol extractives of sludge. Triglycerides analysed in this study showed comparable characteristics, therefore glyceryl tripalmitate was selected for further study. For WE, sucrose was selected as model compounds to represent easily soluble hydrophilic materials in sludge. Actual composition of WE was highly complex where organic alcohols, acids, amines and other intracellular substances could also presence but sucrose was selected based on simplicity and dominant appearance. Analysis of chemical components in water soluble materials from corn stover and switchgrass showed that hydrophilic extractives of biomass predominantly consisting of carbohydrates in which primarily were simple sugars such as glucose, fructose, sucrose and other oligomeric sugars (Chen et al., 2007; Chen et al., 2010).

Proteins existed as heterogeneous and complex mixtures in sludge and no standard model compound or mixture available. Therefore, ON Whey Isolates with protein content of 81.48 mass% was selected to represent protein mixtures in sludge similar to previous study (Jimenez et al., 2013). Cellulose and lignin isolated from

lignocellulosic biomass were selected as model compounds for alkaline hydrolysed residues and acid digested residues based on biomass composition analysis (Sluiter et al., 2010). OOM represented residual organics which consisted of diverse groups of compounds. Polysaccharides as one of the main components in sludge were expected to be dominant compounds in residual organics since this group of biochemical component was not accounted by other five categories of composition found in sludge. Therefore five types of storage or structural polysaccharides were characterised in this study included amylopectin, pectin, starch, glycogen and xylan. Starch, glycogen and xylan were selected for further simulations and synthetic sludge study based on the results of characterisation. Whey isolates obtained from local distributors while all other model compounds for lipids, carbohydrates, and lignocellulosic biomass components were purchased from Sigma-Aldrich. Thermochemical characteristics of model compounds were determined which including VM, FC, $\Delta H_{\text{pyrolysis}}$ and HHV. Elemental contents of model compounds were obtained from product specification sheets provided and calculated from general molecular formula for proteins and lignin (Tolbert et al., 2014; Torabizadeh, 2011). Heat capacity (C_p) of model compounds and sludge biomass composition were estimated based on reference compounds in literature and listed in Table 7.2 and 7.3 (Boerio-Goates, 1991; Dupont et al., 2014; Kim and Parker, 2008; Mark, 2007; Morad et al., 2000).

Table 7.1: Selected model compounds.

Category	Model compound	Description
Proteins	Whey isolates	Mixtures with 81.48 mass% proteins
Lipids	Asolectin	Phospholipids
	Cholesterol	Sterol lipids
	Glyceryl tripalmitate	Triglyceride - palmitate acids
	Glyceryl tristearate	Triglyceride - stearate acids
	Glyceryl trioleate	Triglyceride - oleate acids
Carbohydrates	Amylopectin	Glucose branched polymer
	Pectin	Structural heteropolysaccharide
	Glycogen	Animal glucose storage
	Starch	Plant glucose storage
	Sucrose	Simple disaccharides
Lignocellulose	Cellulose	Linear chain of glucose polymer
	Xylan	Hemicellulose, heteropolymers of xylose
	Lignin	Complex polymer of aromatic alcohol

Table 7.2: Heat capacity of reference compounds from literature.

Reference compounds	Heat capacity, C_p in J/g-K		References
	Range	Mean	
Organic materials	2.10 – 2.50	2.30	(Kim and Parker, 2008)
Inorganic materials	0.80 – 1.30	1.05	(Kim and Parker, 2008)
Oil and fats	2.16 – 2.49	2.33	(Morad et al., 2000)
Proteins	1.85 – 2.40	2.25	(Mark, 2007)
Glucose	1.21 – 1.42	1.32	(Boerio-Goates, 1991)
Lignocellulosic biomass	1.30 – 1.82	1.56	(Dupont et al., 2014)

Table 7.3: Estimated mean heat capacity for biomass composition of sludge.

Biomass composition of sludge	Reference compounds	Mean C_p , J/g-K
Ethanol extractives, EE	Oil and fats	2.33
Water extractives, WE	Glucose	1.32
Proteins	Proteins	2.25
Alkaline hydrolysed residues, AHR	Lignocellulosic biomass	1.56
Acid digested residues, ADR		
Other organic matters, OOM		
Organic contents	General organic materials	2.30
Inorganic contents	General inorganic materials	1.05

7.2.2. Simulation analysis

Thermochemical characteristics included heat capacity, heating value, proximate and ultimate analysis could be calculated based on composition of individual compounds with superposition principle (Tillman, 2012). Characteristics of selected model compounds obtained by both direct measurements and indirect calculation were showed in Table 7.4 and 7.5. Mean values were calculated to represent the six categories of biomass components in sludge. Simulations were carried out by using Equation 7.1, $W_s P_s = \sum_{i=1}^n W_i P_i$ where W_s and W_i were mass% in db of sludge and individual components while P_s and P_i were mean values of the thermochemical parameters for sludge and individual components respectively. Simulations of heat capacity for sludge, C_p were carried out with two different methods for comparison. First method was developed in this study to calculate heat capacity of sludge based on data from biomass composition analysis and mean heat capacities of different type of reference compounds recorded in the literature. Heat capacities of sludge were estimated by the summation of the multiplication of mass% of components and their corresponding mean heat capacities. Second method was adopted from literature to calculate the heat capacity of sludge based on mass% of organic and inorganic contents in sludge with the estimated heat capacity of general organic and inorganic materials (Agarwal et al., 2015; Kim and Parker, 2008). Heat capacity, heating value, heat of pyrolysis, distribution of volatiles and char residues by proximate analysis and CHNSO contents of organic matters by ultimate analysis were simulated and compared to data obtained from direct measurements.

Table 7.4: Thermochemical characteristics of model compounds.

Biomass composition	Model compounds	HHV, MJ/kg		$\Delta H_{\text{pyrolysis}}$ in J/g		VM/FC Ratio		Mass% in db	
		Measurement	Mean	DSC	Mean	Measurement	Mean	VM	FC
EE	Asolectin	29.26	35.86	286.98	217.54	5.10	133.96	99.26	0.74
	Cholesterol	41.67		153.34		211.23			
	Glyceryl tripalmitate	36.66		212.30		185.54			
WE	Sucrose	16.48	16.48	220.65	220.65	4.93	4.93	83.12	16.88
Proteins	Whey Isolates	22.71	22.71	80.92	80.92	2.96	2.96	74.77	25.23
AHR	Cellulose	16.43	16.43	115.10	115.10	5.03	5.03	83.41	16.59
ADR	Lignin	26.52	26.52	-106.61	-106.61	1.19	1.19	54.34	45.66
OOM	Xylan	15.90	16.14	-2.47	45.89	2.47	2.99	74.97	25.03
	Glycogen	16.02		-42.47		2.81			
	Starch	16.50		182.60		3.70			

Table 7.5: Elemental contents analysis of model compounds.

Biomass composition	Model compounds	Mass% in db					Mean values of CHNSO, Mass%				
		C	H	N	S	O	C	H	N	S	O
EE	Asolectin	70.13	11.40	1.64	-	16.83	76.68	11.81	0.55	-	10.96
	Cholesterol	83.96	11.89	-	-	4.15					
	Glyceryl tripalmitate	75.94	12.15	-	-	11.91					
WE	Sucrose	42.11	6.42	-	-	51.47	42.11	6.42	-	-	51.47
Proteins	Whey isolates	53.44	7.04	17.32	0.95	21.26	53.44	7.04	17.32	0.95	21.26
AHR	Cellulose	44.53	6.20	-	-	49.28	44.53	6.20	-	-	49.28
ADR	Lignin	66.67	6.67	-	-	26.67	66.67	6.67	-	-	26.67
OOM	Xylan	45.45	6.06	-	-	48.48	44.41	6.19	-	-	49.40
	Glycogen	43.24	6.31	-	-	50.45					
	Starch	44.53	6.20	-	-	49.28					

7.3. Results and Discussion

7.3.1. Characterisation of model compounds

Results of model compounds characterisation were showed in Table 7.6. VM contents found to be main components in all compounds tested followed by moderate contents of FC and low amounts of Ash₉₅₀. In general, lipids generated highest amount of VM during thermal degradation followed by polysaccharides, proteins and lignin and VM/FC ratios varied accordingly. Variation could also be observed within lipids and polysaccharides groups. Triglycerides and cholesterol consisted of mainly C and H contents releasing higher VM compared to asolectin as phospholipids model compound consisted of phosphorus, N and O contents forming more FC. Starch, glycogen, amylopectin, cellulose were glucose polymers but showed different characteristics during thermal degradations because of different molecular structures. Polysaccharides with branched, heterogeneous and amorphous structure were observed to form more solid residues classified as FC such as xylan, pectin and glycogen. Main components in lignocellulosic biomass which were xylan, cellulose and lignin behaved distinctively in almost all aspects. Heat of pyrolysis, $\Delta H_{\text{pyrolysis}}$ varied significantly for different model compounds. Pyrolysis reactions for lipids and proteins were endothermic, for lignin was exothermic and could ranged from endothermic to exothermic for different types of polysaccharide. Linear regressions in Figure 7.1 demonstrated that $\Delta H_{\text{pyrolysis}}$ in J/g for model compounds reduced from endothermic to exothermic values with increasing char yield comparable to previous studies (Rath et al., 2003; Yang et al., 2007) Based on linear regressions, autothermic pyrolysis expected to be occurred at VM $\approx$ 70.44%, FC $\approx$ 29.56% and VM/FC ratio $\approx$ 2.38. Heating values of model compounds showed significant categorical characteristics and closely related to carbon contents. Lipids showed highest HHV followed by lignin, proteins, and polysaccharides.

FTIR spectra of model compounds were showed in Figure 7.2. For whey isolates, broad peaks at 3275 and 2928cm⁻¹ showed N-H and C-H functional groups respectively. Strong double peaks at 1632 and 1517cm⁻¹ indicated presence of C=O and N-H signature groups of amides and proteins while 1391 and 1235cm⁻¹ showed the presence of C-N groups. For lipids model compounds, detail analysis of FTIR

spectra based on three types of lipids included phospholipids, sterol and glycerol lipids. Broad peak at 3424cm^{-1} for cholesterol indicated O-H groups and wide peak at 3291cm^{-1} indicated both O-H and N-H groups for asolectin. No detection of these groups in triglycerides. Multiple peaks at 2912 and 2851cm^{-1} showed the presence of C-H groups with mainly saturated carbon backbone for tripalmitate and tristearate with sharp peaks and mixing of saturated and unsaturated carbon backbone for cholesterol, asolectin and trioleate. Single strong peak at 1738 and 1170cm^{-1} indicated the presence of C=O and C-O-C groups respectively and only significantly observed for phospholipids and triglycerides. Peaks around 1050cm^{-1} could indicate C-O groups for asolectin and cholesterol and also inorganics for asolectin. For carbohydrates, generally similar spectra could be observed. Broad peaks at 3300cm^{-1} showed O-H functional groups, 2920cm^{-1} showed C-H groups while peaks at 1160 , 1080 , and 889cm^{-1} showed C-O-C groups and 1050cm^{-1} showed C-O groups. For FTIR spectra of lignocellulosic biomass components, xylan and cellulose were highly similar to carbohydrates. For lignin, peaks could be observed at 1600cm^{-1} for C=C groups, 1510cm^{-1} for rings and aromatics groups, 1265cm^{-1} for C-O groups while peaks at 1125cm^{-1} and 1030cm^{-1} for C-O-C groups. FTIR analysis of model compounds provided important information to understand and compare with biomass components isolated from sludge.

Figure 7.1: Heat of pyrolysis for model compounds at different VM or FC mass%.

Table 7.6: Characterisation of model compounds.

Model compounds	Mass% in db			VM/FC ratio	$\Delta H_{\text{pyrolysis}}$ in J/g	HHV in MJ/kg	Molar basis					Moisture as received
	VM	FC	Ash				C	H	N	S	O	
Whey Isolates	72.68	24.52	2.80	2.96	80.92	22.71	1.00	1.58	0.28	0.01	0.30	3.81
Asolectin	83.60	16.40	-	5.10	286.98	29.26	1.00	1.95	0.02	-	0.18	-
Cholesterol	99.53	0.47	-	211.23	153.34	41.67	1.00	1.70	-	-	0.04	-
Glyceryl Tripalmitate	99.46	0.54	-	185.54	212.30	36.66	1.00	1.92	-	-	0.12	-
Glyceryl Tristearate	99.99	0.01	0.01	9999.00	619.50	39.73	1.00	1.93	-	-	0.11	0.47
Glyceryl Trioleate	99.69	0.31	-	320.30	405.40	39.55	1.00	1.82	-	-	0.11	-
Amylopectin	80.73	19.27	-	4.19	-107.43	16.26	1.00	1.67	-	-	0.83	-
Pectin	66.40	33.60	-	1.98	-76.42	14.78	1.00	1.67	-	-	1.17	-
Glycogen	73.78	26.22	0.02	2.81	-42.47	16.50	1.00	1.67	-	-	0.83	8.87
Starch	78.69	21.28	-	3.70	182.60	16.02	1.00	1.75	-	-	0.88	-
Sucrose	83.12	16.88	-	4.93	220.65	16.48	1.00	1.83	-	-	0.92	-
Cellulose	83.35	16.58	0.08	5.03	115.10	16.43	1.00	1.67	-	-	0.83	8.01
Xylan	71.21	28.79	-	2.47	-2.47	15.90	1.00	1.60	-	-	0.80	-
Lignin	52.58	44.19	3.23	1.19	-106.61	26.52	1.00	1.20	-	-	0.30	5.94

Figure 7.2: FTIR Spectra of (a) proteins, (b) lipids, (c) carbohydrates and (d) lignocellulosic biomass model compounds.

7.3.2. Simulations analysis

Results for heat capacity simulation of sludge, C_p based on two different calculation methods were showed in Table 7.7. Calculated data showed that heat capacity was mainly contributed by organics. Based on calculation 1, proteins contributed largely to C_p because of relatively higher contents in sludge and higher mean heat capacity. EE and OOM also contributed significantly to C_p for sludge samples collected before AD while ADR and inorganic contents contributed significantly for sludge after AD. Based on calculation 2, organics contributed largely to C_p of sludge. Sludge before AD showed higher C_p because of higher organic contents. By comparing the two methods, calculation 2 used in literature showed higher values of C_p because of higher mean values assumed for organics in sludge at around 2.30J/g-K (Agarwal et al., 2015; Kim and Parker, 2008). Proteins and lipids were having C_p close to the general value assumed but simple sugars, lignin and carbohydrates which including polysaccharides, xylan and cellulose were having lower mean C_p at around 1.32J/g-K for glucose and 1.56 J/g-K for lignocellulosic biomass. Therefore, lower C_p values assigned for the biomass components reduced the overall estimation for sludge. Statistics analysis was applied to determine accuracy and consistency of the simulated data. Results of statistics analysis for simulated C_p values compared to direct measurements on sludge using DSC were showed in Table 7.8 and the distributions of bias errors were illustrated in Figure 7.3. Considerably overestimation by calculation 2 using general materials method could be observed compared to slightly underestimation made in calculation 1 by using biomass composition analysis of sludge. Data showed that relative% of ϵ_{Abs} reduced from 21.04% for calculation 2 to 11.39% for calculation 1. Distributions of bias errors also showed that calculation 2 consistently overestimated C_p except for UsR sludge while random errors of estimation could be generally observed for calculation 1. Therefore, simulation analysis of heat capacity suggested that improvement of C_p estimation could be achieved by categorisation of biochemical components in sludge. Biomass composition analysis categorised organics in sludge into better defined groups of compounds improved the understanding and estimation of thermochemical characteristics of sludge. Simulations also supported the applicability of biomass composition analysis developed in this study.

Table 7.7: Heat capacity analysis for sludge simulation.

Sample label	Heat capacity of sludge in db, J/g-K										
	Method 1 - Biomass composition of sludge								Method 2 – General materials		
	EE	WE	Proteins	AHR	ADR	OOM	Inorganic contents	Total	Organic contents	Inorganic contents	Total
UR	0.28	0.16	0.57	0.07	0.22	0.32	0.11	1.74	2.05	0.11	2.17
UD	0.12	0.17	0.57	0.07	0.18	0.35	0.19	1.65	1.89	0.19	2.08
CP	0.13	0.23	0.75	0.08	0.08	0.21	0.21	1.69	1.84	0.21	2.05
CS	0.26	0.10	0.42	0.13	0.17	0.49	0.13	1.69	2.02	0.13	2.15
CY	0.08	0.11	0.60	0.09	0.27	0.08	0.35	1.58	1.54	0.35	1.89
JR	0.26	0.06	0.49	0.05	0.17	0.34	0.28	1.65	1.68	0.28	1.96
JD	0.15	0.11	0.35	0.09	0.21	0.10	0.46	1.47	1.29	0.46	1.75
KR	0.33	0.13	0.60	0.05	0.18	0.32	0.16	1.75	1.96	0.16	2.11
KD	0.10	0.18	0.62	0.09	0.37	0.05	0.24	1.63	1.78	0.24	2.02
UsR	0.35	0.07	0.56	0.04	0.20	0.34	0.19	1.74	1.89	0.19	2.08
UsD	0.16	0.19	0.58	0.04	0.33	0.16	0.21	1.66	1.84	0.21	2.05
CsP	0.28	0.19	0.67	0.07	0.08	0.22	0.21	1.72	1.84	0.21	2.05
CsS	0.30	0.06	0.38	0.06	0.23	0.43	0.20	1.67	1.85	0.20	2.06
CsY	0.08	0.09	0.62	0.07	0.16	0.21	0.36	1.59	1.51	0.36	1.87
Mean $\pm$ SD											
All sample	0.21 ± 0.10	0.13 ± 0.05	0.55 ± 0.11	0.07 ± 0.02	0.20 ± 0.08	0.26 ± 0.13	0.24 ± 0.10	1.66 ± 0.08	1.78 ± 0.21	0.24 ± 0.10	2.02 ± 0.12
Before AD	0.27 ± 0.07	0.13 ± 0.06	0.56 ± 0.12	0.07 ± 0.03	0.17 ± 0.06	0.33 ± 0.09	0.19 ± 0.05	1.71 ± 0.04	1.89 ± 0.12	0.19 ± 0.05	2.08 ± 0.07
After AD	0.12 ± 0.03	0.14 ± 0.04	0.56 ± 0.10	0.08 ± 0.02	0.25 ± 0.08	0.16 ± 0.11	0.30 ± 0.11	1.60 ± 0.07	1.64 ± 0.23	0.30 ± 0.11	1.94 ± 0.13

Table 7.8: Heat capacity estimation compared to measured data.

Sample label	Heat capacity, C_p (J/g-K) in db						
	DSC data	Biomass composition method			General materials method		
		C_p 1	ϵ_{bias} 1	ϵ_{Abs} 1	C_p 2	ϵ_{bias} 2	ϵ_{Abs} 2
UR	1.98	1.74	0.24	0.24	2.17	-0.19	0.19
UD	1.60	1.65	-0.05	0.05	2.08	-0.48	0.48
CP	1.55	1.69	-0.14	0.14	2.05	-0.50	0.50
CS	1.93	1.69	0.24	0.24	2.15	-0.22	0.22
CY	1.57	1.58	-0.01	0.01	1.89	-0.32	0.32
JR	1.74	1.65	0.10	0.10	1.96	-0.22	0.22
JD	1.35	1.47	-0.12	0.12	1.75	-0.40	0.40
KR	1.61	1.75	-0.15	0.15	2.11	-0.51	0.51
KD	1.33	1.63	-0.30	0.30	2.02	-0.69	0.69
UsR	2.18	1.74	0.44	0.44	2.08	0.10	0.10
UsD	1.90	1.66	0.24	0.24	2.05	-0.15	0.15
CsP	1.36	1.72	-0.36	0.36	2.05	-0.69	0.69
CsS	1.90	1.67	0.24	0.24	2.06	-0.16	0.16
CsY	1.53	1.59	-0.05	0.05	1.87	-0.34	0.34
Mean	1.68	1.66	0.02	0.19	2.02	-0.34	0.35
SD	0.26	0.08	0.23	0.12	0.12	0.22	0.20

Figure 7.3: Distribution of bias errors for heat capacity calculation.

Results of HHV simulation were showed in Table 7.9. In average, ϵ_{Abs} of less than 1.00MJ/kg or 4.31% of sludge HHV could be observed indicated good estimation of heating values by biomass composition analysis developed. Bias errors randomly distributed as positive and negative values indicated low systematic errors. In average, simulated data underestimated HHV of sludge by 0.31MJ/kg or 1.78%. The overall underestimation could be explained by considering the higher mean values of HHV found for EE and WE in Chapter 6 at 42.41MJ/kg and 21.24MJ/kg as compared to model compounds for lipids and simple sugars at 35.86MJ/kg and 16.48MJ/kg respectively. The simulation also generally made underestimation for sludge samples collected before AD and overestimation for AD digested sludge samples. HHV of sludge was mainly contributed by proteins at 32.69% of total energy contents. Similar to C_p , EE and OOM contributed significantly to HHV of sludge before AD while ADR contributed significantly to HHV of sludge after AD.

For comparison, four published HHV correlations were selected where three selected from a historical survey and one as the of unified correlation obtained (Channiwala and Parikh, 2002). Dulong's equation was selected as one of the earliest attempt to establish correlation for HHV, where $\text{HHV} = 0.3383C + 1.443(H-(O/8)) + 0.0942S$. Correlation established by Institue of Gas Technology (IGT) was selected as one of the most generalised HHV equation derived for coal samples, where $\text{HHV} = 0.341C + 1.323H + 0.0685 - 0.0153A - 0.1194 (O + N)$. Correlation established based on wastewater sludge was selected as comparison for current study, where $\text{HHV} = 0.2322C + 0.7655H - 0.072O + 0.0419N + 0.0698S + 0.0262Cl + 0.1814P$ (Niessen, 2002). Unified correlation (Equation 4.4) was also selected as one of the most recent attempt (Channiwala and Parikh, 2002). As discussed in Chapter 4, Section 4.3.2.1. Heating value analysis, two calculations for Equation 4.4 were carried out with suggested improvement by using O contents (by direct measurement) and IM contents (estimated by difference) in Calculation 1.

Results of the statiscal analysis of these four correlations compared to simulation carried out in this study were summarised in Table 7.10. Results showed that ϵ_{Abs} of Calculation 1 (Chapter 4) and Simulation (Chapter 7) are relatively lower in average at 0.64 and 0.75 MJ/kg respectively compared to all other HHV correlations. If

considered sludge samples collected before and after AD separately, Calculation 1 showed lowest ϵ_{Abs} at 0.46 MJ/kg for sludge samples before AD while simulation by biomass composition analysis showed lowest ϵ_{Abs} at 0.68 MJ/kg for sludge samples after AD. These two calculation methods also showed that underestimation could be observed for mean values of all samples and before AD in average while overestimation could be observed for mean values of sludge samples after AD. Both methods showed comparable accuracy and advantages over other correlations.

Results for $\Delta H_{\text{pyrolysis}}$ simulation and direct measurement by DSC for sludge were showed in Table 7.11. Relatively significant differences could be observed between $\Delta H_{\text{pyrolysis}}$ measured and calculated at 37.20% in average with absolute difference at 17.83J/g. Since pyrolysis reactions of sludge were slightly endothermic and near autothermic, relative% of random errors were higher though with only slight different when consider the absolute values. By considering mean of total energy requirement at $846 \pm 132\text{J/g}$ for sludge pyrolysis at 500°C calculated in Chapter 5, mean absolute error of simulation at 17.83J/g or 2.11% of the total energy requirement was generally acceptable. $\Delta H_{\text{pyrolysis}}$ was higher for sludge samples collected before AD because of the presence of higher organic contents in db. Detail analysis based on biomass composition of sludge and model compounds showed that extractives and proteins were significantly contributed to the endothermic requirements of pyrolysis. AHR and OOM contributed slightly because of the low mass% of AHR and also mixed of endothermic and exothermic reactions among the model compounds selected to represent OOM of sludge. Xylan and glycogen showed exothermic behaviours while starch endothermic decomposed. ADR and lignin exothermic decomposed and reduced the overall heat of pyrolysis of sludge.

Table 7.9: Heating value analysis for sludge simulation.

Sample label	Heating value, MJ/kg in db									
	Biomass composition of sludge						Total	HHV data	ϵ_{Bias}	ϵ_{Abs}
	EE	WE	Proteins	AHR	ADR	OOM				
UR	4.27	2.06	5.80	0.74	3.54	3.34	19.76	20.49	0.73	0.73
UD	1.89	2.12	5.72	0.70	3.02	3.67	17.13	17.41	0.28	0.28
CP	2.07	2.81	7.55	0.79	1.37	2.21	16.80	17.53	0.73	0.73
CS	3.98	1.25	4.21	1.42	2.78	5.04	18.68	19.66	0.98	0.98
CY	1.27	1.41	6.04	0.96	4.55	0.79	15.01	14.47	-0.55	0.55
JR	4.00	0.73	4.92	0.48	2.59	3.55	16.28	17.13	0.85	0.85
JD	2.38	1.33	3.54	0.92	3.26	1.08	12.50	13.19	0.69	0.69
KR	5.15	1.58	6.01	0.51	2.99	3.26	19.50	20.52	1.02	1.02
KD	1.49	2.22	6.22	0.91	6.22	0.47	17.52	15.66	-1.86	1.86
UsR	5.33	0.89	5.63	0.46	3.19	3.50	19.00	19.41	0.41	0.41
UsD	2.53	2.35	5.82	0.40	5.33	1.61	18.03	17.48	-0.54	0.54
CsP	4.33	2.35	6.78	0.69	1.31	2.30	17.76	18.20	0.44	0.44
CsS	4.64	0.73	3.82	0.65	3.06	4.48	17.38	18.65	1.27	1.27
CsY	1.29	1.10	6.21	0.79	2.53	2.12	14.05	13.89	-0.16	0.16
Mean $\pm$ SD										
All sample	3.19 ± 1.48	1.64 ± 0.68	5.59 ± 1.12	0.74 ± 0.26	3.27 ± 1.35	2.67 ± 1.38	17.10 ± 2.08	17.41 ± 2.36	0.31 ± 0.84	0.75 ± 0.44
Before AD	4.22 ± 1.00	1.55 ± 0.79	5.59 ± 1.25	0.72 ± 0.31	2.60 ± 0.83	3.46 ± 0.96	18.15 ± 1.28	18.95 ± 1.28	0.80 ± 0.29	0.80 ± 0.29
After AD	1.81 ± 0.55	1.76 ± 0.54	5.59 ± 1.03	0.78 ± 0.21	4.15 ± 1.45	1.62 ± 1.16	15.71 ± 2.20	15.35 ± 1.81	-0.36 ± 0.88	0.68 ± 0.61

Table 7.10: Comparison of HHV correlations

Sample label	Simulation		Dulong's equation		IGT for coal		Wastewater sludge		Unified correlation			
									Calculation 1		Calculation 2	
	ϵ_{Bias}	ϵ_{Abs}	ϵ_{Bias}	ϵ_{Abs}	ϵ_{Bias}	ϵ_{Abs}	ϵ_{Bias}	ϵ_{Abs}	ϵ_{Bias}	ϵ_{Abs}	ϵ_{Bias}	ϵ_{Abs}
UR	0.73	0.73	2.67	2.67	2.70	2.70	5.43	5.43	1.55	1.55	0.95	0.95
UD	0.28	0.28	-0.64	0.64	-0.08	0.08	-0.12	0.12	-1.16	1.16	-2.29	2.29
CP	0.73	0.73	0.35	0.35	1.10	1.10	-0.24	0.24	0.02	0.02	-0.64	0.64
CS	0.98	0.98	0.36	0.36	0.34	0.34	3.14	3.14	-0.49	0.49	-1.24	1.24
CY	-0.55	0.55	0.47	0.47	1.12	1.12	-2.32	2.32	0.29	0.29	-0.52	0.52
JR	0.85	0.85	-0.31	0.31	0.35	0.35	-1.18	1.18	-0.42	0.42	-1.57	1.57
JD	0.69	0.69	1.28	1.28	1.98	1.98	-3.26	3.26	1.28	1.28	0.17	0.17
KR	1.02	1.02	0.32	0.32	0.89	0.89	2.36	2.36	-0.05	0.05	-0.89	0.89
KD	-1.86	1.86	-1.32	1.32	-0.51	0.51	-2.28	2.28	-1.56	1.56	-2.61	2.61
UsR	0.41	0.41	0.18	0.18	0.46	0.46	2.62	2.62	-0.23	0.23	-0.66	0.66
UsD	-0.54	0.54	0.07	0.07	0.45	0.45	1.28	1.28	-0.44	0.44	-1.07	1.07
CsP	0.44	0.44	0.94	0.94	1.65	1.65	1.15	1.15	0.56	0.56	-0.06	0.06
CsS	1.27	1.27	1.00	1.00	1.11	1.11	2.50	2.50	0.38	0.38	-0.07	0.07
CsY	-0.16	0.16	0.76	0.76	1.40	1.40	-2.20	2.20	0.54	0.54	-0.15	0.15
Mean $\pm$ Standard deviations												
All sample	0.31 ± 0.84	0.75 ± 0.44	0.44 ± 0.94	0.76 ± 0.68	0.93 ± 0.85	1.01 ± 0.73	0.49 ± 2.56	2.15 ± 1.36	0.02 ± 0.85	0.64 ± 0.52	-0.76 ± 0.96	0.92 ± 0.79
Before AD	0.80 ± 0.29	0.80 ± 0.29	0.69 ± 0.90	0.77 ± 0.83	1.08 ± 0.80	1.08 ± 0.80	1.97 ± 2.06	2.33 ± 1.58	0.16 ± 0.67	0.46 ± 0.48	-0.52 ± 0.79	0.76 ± 0.53
After AD	-0.36 ± 0.88	0.68 ± 0.61	0.10 ± 0.95	0.76 ± 0.48	0.73 ± 0.94	0.93 ± 0.70	-1.48 ± 1.70	1.91 ± 1.08	-0.18 ± 1.08	0.88 ± 0.52	-1.08 ± 1.14	1.14 ± 1.08

Table 7.11: Heat of pyrolysis analysis for sludge simulation.

Sample label	Heat of pyrolysis, J/g in db									
	Biomass composition of sludge						Total	DSC data	ϵ_{Bias}	ϵ_{Abs}
	EE	WE	Proteins	AHR	ADR	OOM				
UR	25.93	27.56	20.68	5.22	-15.05	9.49	73.82	41.30	-32.52	32.52
UD	11.49	28.42	20.39	4.90	-12.58	10.44	63.06	40.05	-23.01	23.01
CP	12.55	37.67	26.90	5.56	-5.74	6.27	83.22	71.84	-11.38	11.38
CS	24.14	16.68	14.99	9.94	-11.63	14.34	68.45	55.15	-13.30	13.30
CY	7.73	18.84	21.51	6.71	-18.72	2.24	38.29	43.87	5.58	5.58
JR	24.25	9.74	17.52	3.37	-11.39	10.11	53.62	35.56	-18.06	18.06
JD	14.45	17.81	12.60	6.43	-14.27	3.06	40.07	46.31	6.24	6.24
KR	31.25	21.16	21.42	3.56	-12.00	9.28	74.67	21.72	-52.95	52.95
KD	9.04	29.73	22.16	6.36	-25.38	1.33	43.24	32.86	-10.38	10.38
UsR	32.32	11.93	20.06	3.25	-13.46	9.96	64.05	66.15	2.10	2.10
UsD	15.33	31.42	20.73	2.77	-22.31	4.58	52.52	78.29	25.77	25.77
CsP	26.25	31.42	24.17	4.86	-5.79	6.54	87.46	47.63	-39.83	39.83
CsS	28.15	9.75	13.62	4.57	-15.68	12.73	53.13	50.20	-2.93	2.93
CsY	7.85	14.77	22.13	5.51	-10.71	6.04	45.58	40.02	-5.56	5.56
Mean $\pm$ Standard deviations										
All sample	19.34 ± 8.97	21.92 ± 9.05	19.92 ± 3.98	5.21 ± 1.84	-13.91 ± 5.48	7.60 ± 3.93	60.08 ± 15.93	47.93 ± 15.54	-12.16 ± 20.43	17.83 ± 15.31
Before AD	25.61 ± 6.08	20.74 ± 10.58	19.92 ± 4.46	5.04 ± 2.16	-11.34 ± 3.78	9.84 ± 2.75	69.80 ± 12.57	48.69 ± 16.21	-21.11 ± 19.01	21.63 ± 18.32
After AD	10.98 ± 3.33	23.50 ± 7.16	19.92 ± 3.66	5.45 ± 1.47	-17.33 ± 5.78	4.62 ± 3.31	47.13 ± 9.26	46.90 ± 16.04	-0.23 ± 16.75	12.76 ± 9.23

Results for simulation on distribution of volatile matters and char solids were showed in Table 7.12 and 7.13. Simulated data were compared to two parameters fixed carbon (FC) and fixed residues (FR) as discussed in sludge characterisation study in Chapter 3. FR was proposed to replace FC because of inorganics overestimation by ash residues quantification. Simulated data of VM/FC ratio clearly supported the proposal of this parameter while agreed well with the VM/FR data from direct measurements of sludge samples. VM/FC ratios measured for sludge largely higher than VM/FR and simulated data because of the underestimation of FC caused by overestimation of ash contents. Randomly distributed bias errors also indicated insignificant systematic error on the simulation. Detail analysis based on biomass composition of sludge showed that components in sludge contributed differently to the release of volatile matters and the formation of char solids. In general, volatiles released contributed by all components in sludge with varying amounts while char solids mainly formed from three groups of components which were proteins, ADR and other organic matters. In average, these three groups represented 69.95% of organics while accounted for 86.73% of FC formed. Ethanol extractives as simulated by using lipids model compounds decomposed mainly into volatiles and contributed less than 1.00% on FC though represented 11.27% of organics in sludge. Since char formation could not be measured directly during thermogravimetric analysis, data from proximate analysis were generally used for kinetics equations and quantification of char formation reactions. However, characterisation study of complex waste mixtures such as sludge showed that different components thermally degraded at different temperature regions therefore proximate analysis data for individual steps would be needed. Biomass composition analysis of sludge separated the sludge components into six different categories with distinct distributions of VM and FC provided important data and basic for novel methodology development on multiple step kinetics modelling study for sludge and other waste mixtures.

Results of sludge simulation on elemental composition were showed in Table 7.14. Elemental composition calculated based on model compounds showed comparable contents and expected variations with the data of organic matters in sludge. The variations were expected because biomass composition analysis in this study

focused only on main categories of biochemical components in sludge. CHNSO_{Organic} data were calculated by difference using the CHNSO_{Total} of sludge and CHNSO_{Inorganic} of ash residues after combustion of sludge at 550°C. In general, overestimation could be observed for C and O contents while underestimation could be observed for H, N and S contents as illustrated in Figure 7.4. In average, C and O simulations overestimated the contents by 3.88 mass% in db or 10.54% in relative percentage and 0.72 mass% or 5.01% respectively while H, N and S simulations underestimated contents by 0.15 mass% or 5.11%, 0.94 mass% or 16.74% and 4.23 mass% or 94.72% respectively. Since estimations of H and O contents agreed very well with the CHNSO_{Organic} data of sludge, the overestimation of C contents was probably caused by underestimation of N and S containing compounds. Underestimation of N contents caused by the selection of sucrose as model compound to represent the water extractives from sludge. Since extraction also removed non-protein nitrogen contents therefore nitrogen containing compounds such as nucleic acids and other intracellular substances were not accounted in this simulation study. Significant underestimation of S contents caused by absent of individual categorisation for sulphur containing compounds in sludge based on the biomass composition analysis method applied. Sulphur containing compounds were highly diverse and consisted of amino acids, vitamins, thiols and enzymes that could be extracted during ethanol and water extractions. Polysaccharides with sulphur and alkylbenzene sulphonate from laundry detergents could also presence. However polysaccharides as categorised in the other organic matters in this study were represented by glycogen, starch and xylan. These commonly found carbohydrates were generally sulphur-free. Therefore, further analysis could be carried out to determine the main sulphur containing compounds presence in sludge so that the corresponding model compounds could be selected and added into the category of extractives and OOM.

Table 7.12: Comparison of VM/FC and VM/FR ratios with simulated data

Sample label	Direct measurement		Simulated VM/FC ratio	ϵ_{Bias}	ϵ_{Abs}
	VM/FC	VM/FR			
UR	4.31	3.23	3.25	-0.02	0.02
UD	5.20	2.66	3.04	-0.38	0.38
CP	7.58	3.47	3.44	0.03	0.03
CS	4.40	2.97	3.34	-0.37	0.37
CY	5.14	2.73	2.64	0.09	0.09
JR	11.34	3.70	3.24	0.46	0.46
JD	10.74	3.38	2.98	0.40	0.40
KR	4.69	2.80	3.45	-0.65	0.65
KD	4.79	2.44	2.56	-0.12	0.12
UsR	7.69	5.40	3.34	2.06	2.06
UsD	5.87	3.87	2.75	1.12	1.12
CsP	7.10	3.76	3.77	-0.01	0.01
CsS	6.28	4.26	3.15	1.11	1.11
CsY	5.23	2.90	2.92	-0.02	0.02
Mean $\pm$ SD					
All sample	6.45 $\pm$ 2.24	3.40 $\pm$ 0.78	3.13 $\pm$ 0.34	0.26 $\pm$ 0.72	0.49 $\pm$ 0.59
Before AD	6.67 $\pm$ 2.35	3.70 $\pm$ 0.83	3.37 $\pm$ 0.19	0.33 $\pm$ 0.88	0.59 $\pm$ 0.70
After AD	6.16 $\pm$ 2.27	3.00 $\pm$ 0.53	2.82 $\pm$ 0.19	0.18 $\pm$ 0.53	0.36 $\pm$ 0.41

Figure 7.4: Distribution of bias errors for organic CHNSO contents calculation.

Table 7.13: Distributions analysis of thermal degradation for sludge simulation.

Sample label	Distribution of volatile matters and char solids, Mass%													
	EE		WE		Proteins		AHR		ADR		OOM		Simulated total	
	VM	FC	VM	FC	VM	FC	VM	FC	VM	FC	VM	FC	VM	FC
UR	13.25	0.10	11.63	2.36	21.40	7.22	4.24	0.84	8.59	7.22	17.36	5.80	76.46	23.54
UD	6.38	0.05	13.03	2.65	22.93	7.74	4.32	0.86	7.80	6.56	20.75	6.93	75.22	24.78
CP	7.16	0.05	17.74	3.60	31.08	10.49	5.04	1.00	3.66	3.08	12.81	4.28	77.50	22.50
CS	12.52	0.09	7.14	1.45	15.74	5.31	8.19	1.63	6.74	5.66	26.63	8.89	76.96	23.04
CY	5.27	0.04	10.60	2.15	29.69	10.02	7.26	1.44	14.26	11.98	5.46	1.82	72.54	27.46
JR	15.19	0.11	5.04	1.02	22.23	7.50	3.36	0.67	7.96	6.69	22.67	7.57	76.44	23.56
JD	11.79	0.09	12.00	2.44	20.82	7.02	8.33	1.66	13.01	10.93	8.93	2.98	74.88	25.12
KR	16.77	0.13	9.38	1.90	23.29	7.86	3.03	0.60	7.19	6.05	17.84	5.96	77.51	22.49
KD	5.34	0.04	14.49	2.94	26.50	8.94	5.97	1.19	16.75	14.07	2.82	0.94	71.87	28.13
UsR	17.94	0.13	5.47	1.11	22.55	7.61	2.86	0.57	8.35	7.01	19.79	6.61	76.96	23.04
UsD	8.72	0.07	14.76	3.00	23.88	8.06	2.51	0.50	14.18	11.91	9.32	3.11	73.36	26.64
CsP	14.96	0.11	14.78	3.00	27.89	9.41	4.39	0.87	3.68	3.09	13.35	4.46	79.05	20.95
CsS	15.93	0.12	4.56	0.93	15.61	5.27	4.11	0.82	9.92	8.33	25.80	8.61	75.92	24.08
CsY	5.46	0.04	8.47	1.72	31.14	10.51	6.09	1.21	8.32	6.99	15.03	5.02	74.51	25.49
Mean $\pm$ SD														
All sample	11.19 ± 4.67	0.08 ± 0.03	10.65 ± 4.13	2.16 ± 0.84	23.91 ± 4.94	8.07 ± 1.67	4.98 ± 1.92	0.99 ± 0.38	9.31 ± 3.91	7.83 ± 3.28	15.61 ± 7.29	5.21 ± 2.43	75.66 ± 2.05	24.34 ± 2.05
Before AD	14.22 ± 3.35	0.11 ± 0.02	9.47 ± 4.88	1.92 ± 0.99	22.47 ± 5.31	7.58 ± 1.79	4.40 ± 1.70	0.88 ± 0.34	7.01 ± 2.27	5.89 ± 1.91	19.53 ± 5.22	6.52 ± 1.74	77.10 ± 0.96	22.90 ± 0.96
After AD	7.16 ± 2.62	0.05 ± 0.02	12.23 ± 2.41	2.48 ± 0.49	25.83 ± 4.02	8.71 ± 1.36	5.75 ± 2.08	1.14 ± 0.41	12.38 ± 3.57	10.41 ± 3.00	10.39 ± 6.54	3.47 ± 2.18	73.73 ± 1.35	26.27 ± 1.35

Table 7.14: Elemental contents analysis for sludge simulation.

Sample Label	CHNSO of sludge organic composition, Mass% in db									
	Calculated based on biomass composition					Ultimate analysis of sludge organic contents				
	C	H	N	S	O	C	H	N	S	O
UR	48.16	6.46	4.49	0.24	29.18	43.43	5.62	5.79	4.98	29.47
UD	42.54	5.66	4.39	0.24	28.94	39.62	6.19	6.00	4.74	25.62
CP	41.04	5.61	5.79	0.32	27.00	37.79	5.88	7.52	4.32	24.46
CS	46.31	6.27	3.27	0.18	31.54	43.73	6.47	3.84	4.77	29.18
CY	36.73	4.65	4.62	0.25	20.29	31.39	4.86	4.97	4.00	21.71
JR	39.59	5.32	3.81	0.21	23.03	36.87	5.93	4.29	4.22	21.55
JD	30.44	3.98	2.73	0.15	17.51	27.11	4.06	3.15	3.68	17.91
KR	47.07	6.37	4.66	0.25	26.66	43.61	6.55	5.60	4.99	24.26
KD	42.87	5.37	4.77	0.26	23.62	36.32	5.97	6.60	4.84	23.52
UsR	45.82	6.17	4.37	0.24	24.99	42.50	6.27	4.93	3.68	24.82
UsD	43.98	5.66	4.48	0.24	25.02	39.28	5.84	5.87	3.85	25.38
CsP	42.72	5.92	5.24	0.28	25.44	38.22	5.75	6.77	5.15	24.18
CsS	42.55	5.73	2.98	0.16	26.01	40.02	5.88	3.43	4.86	26.41
CsY	34.54	4.53	4.75	0.26	21.06	30.21	4.54	4.78	4.41	21.71
Mean $\pm$ SD										
All sample	41.74 ± 5.00	5.55 ± 0.73	4.31 ± 0.85	0.23 ± 0.05	25.02 ± 3.76	37.86 ± 5.18	5.70 ± 0.73	5.25 ± 1.29	4.46 ± 0.51	24.30 ± 3.05
Before AD	44.16 ± 3.10	5.98 ± 0.40	4.33 ± 0.95	0.24 ± 0.05	26.73 ± 2.62	40.77 ± 2.88	6.04 ± 0.34	5.27 ± 1.42	4.62 ± 0.50	25.54 ± 2.69
After AD	38.52 ± 5.46	4.98 ± 0.69	4.29 ± 0.78	0.23 ± 0.04	22.74 ± 4.01	33.99 ± 5.17	5.24 ± 0.87	5.23 ± 1.22	4.25 ± 0.48	22.64 ± 2.87

7.4. Conclusions

Characterisation study of materials and model compounds selected showed considerable differences on thermochemical parameters and contents (mass% on db) measured or estimated which including HHV (15.90-41.67 MJ/kg), VM (52.58-99.99%), FC (0.01-44.19%), C_p (0.80-2.50 J/g-K), C (42.11-83.96%), H (6.06-12.15%), N (0.55-17.32%) and O (4.15-51.47%). Heat of pyrolysis of model compounds also ranged from exothermic to endothermic during thermal degradation where $\Delta H_{\text{pyrolysis}}$ recorded from -107.43 to 619.50 J/g. FTIR spectra illustrated distinctive peaks could be observed for different categories of biomass components and specific compounds in the corresponding categories. Therefore in general, thermochemical properties could be contributed uniquely by different biomass components in the sludge. Simulation analysis carried out in this study also demonstrated that biomass composition analysis and model compounds selection methodology developed in this study could satisfactory categorise main components presence and simulate thermochemical characteristics of sludge. Heat capacity of sludge could be estimated with improved accuracy where in average, ϵ_{bias} and ϵ_{Abs} calculated at 0.02 and 0.19 J/g-K respectively by using results of biomass composition and data from model compounds. Other characteristics simulated including heating value ($\epsilon_{\text{bias}} = 0.31$ and $\epsilon_{\text{Abs}} = 0.75$ MJ/kg), heat of pyrolysis ($\epsilon_{\text{bias}} = -12.16$ and $\epsilon_{\text{Abs}} = 17.83$ J/g), distribution of volatiles and char ($\epsilon_{\text{bias}} = 0.26$ and $\epsilon_{\text{Abs}} = 0.49$), and elemental composition (ϵ_{Abs} at 0.15-4.23 mass%) also showed good agreements with expected variations compared to the measured data of sludge. Combination of biomass composition analysis and thermochemical characteristics simulation also provided insights on specific characteristics of individual biochemical components in sludge and contributions to the overall thermochemical properties of sludge. These insights were important for understanding on thermal degradation behaviours and products evolution of sludge and also crucial for mechanisms determination and models development.

8. Thermal degradation behaviours and products evolution analysis of biomass components, model compounds and synthetic sludge

Findings in this chapter were summarised for publication as parts of an original research paper: Formation of synthetic sludge as a tool for system modelling and performance study in thermochemical conversion processes based on thermal degradation behaviours and biomass composition analysis of sludge.

8.1. Introduction

Thermal degradation behaviours and products evolution analysis of model compounds selected and sludge biomass components isolated were carried out to further characterise individual components identified, compare to selected model compounds and provide important data for synthetic sludge simulation and formation. Synthetic sludge study was carried out to address two important issues in the research of sludge thermochemical conversion. First issue was uncertainty in kinetics analysis and modelling caused by heterogeneity of sludge as waste mixtures. Second issue was limited studies and understanding developed on impacts of sludge composition to thermochemical processes since existing research focused extensively on impacts of operating conditions such as temperature, pressure and other engineering parameters on performance of conversion processes (Atienza-Martinez et al., 2015; Calvo et al., 2004; Fonts et al., 2012; Gomez-Rico et al., 2005; Inguanzo et al., 2002) With the proposed methodology on sludge biomass composition analysis, model compounds selection and formation of synthetic sludge, sample with controlled composition could be used for complex analysis and modelling with improved consistency. Composition of sludge could also be manipulated as one of the control parameters to develop comprehensive study on impacts of feedstock characteristics on thermochemical conversion processes. Synthetic sludge was formed based on the data collected with CsY as reference waste sample. Multiple heating rate TGA-DTG analysis and kinetics study were carried out for synthetic sludge and compared to collected sludge sample.

8.2. Materials and Methods

Thermal degradation behaviours and products evolution studies of sludge samples, biomass components, model compounds and synthetic sludge were carried out. Sludge samples collected from Changi WRP and corresponding biomass components isolated were selected for detail analysis and comparison study. Initial and terminate temperatures of primary degradation were determined for comparison. Degradation rates of 1.00%/min and 0.20%/min in db were selected as rates to define the temperatures. Samples with small amount of inorganics included model compounds, synthetic sludge and extractives from sludge were analysed based on rate of 1.00%/min. Samples with large amount of inorganic contents included sludge, EER, EFR, ADR and AHR were analysed based on rate of 0.20%/min because of significant inorganic contents reduced apparent thermal degradation rate in db. Initial temperature defined as the temperature when thermal degradation rate increased to the selected rate from start of experiment and terminate temperature defined as the temperature when degradation rate reduced to the selected rate after main degradation region. Maximum degradation defined as peak with the highest degradation rate in DTG profiles. Mass% in db at 500°C and 950°C were also determined. This selection of temperatures was based on terminate temperatures of primary degradation region for sludge and proximate analysis. Relative mass% of volatiles released was calculated based on mass loss at 100-500°C and 500-950°C regions in percentage of overall mass loss which represented total volatiles released. Synthetic sludge was formed by physically mixing of selected model compounds with reference to the mass% determined in sludge biomass composition analysis. The selection was also based on the results of model compounds characterisation, thermochemical characteristics simulations and thermal degradation behaviours study. Chang dried sludge CsY was selected as reference waste sample in this study. Ash residue formed from combustion of CsY sludge at 550°C was mixed with synthetic sludge to represent the inorganic contents in sludge. Thermochemical characteristics of synthetic sludge could be simulated based on model compounds selected and FTIR spectra of synthetic sludge with and without ash residue were collected. Thermal degradation behaviours and products evolution studies of synthetic sludge were also carried out by using interconnected TGA-FTIR system.

8.3. Results and Discussion

8.3.1. Model compounds analysis

Results of thermal degradation behaviours study for model compounds were summarised in Appendix E and illustrated in Figure 8.1 and 8.2. TGA-DTG analysis of model compounds showed that main degradation of most model compounds occurred in narrow temperature region of about 100°C during primary degradations while proteins, asolectin, sucrose, xylan and lignin degraded primarily in relative broader temperature region of about 200°C and above. Maximum degradation temperatures and rates generally varied among the compounds tested from 234.3 to 414.7°C and from -2.44 to -22.04%/min. However, high similarity could be observed for triglycerides lipids with fatty acids having differences in chain length and double bonds. Glucose polymers included amylopectin, starch and glycogen also degraded with highly similar TGA mass loss curves. DTG profiles of pectin and xylan showed similar maximum degradation peak at temperature around 234°C but xylan also showed multiple degradation peaks. Volatiles primarily released at temperature lower than 500°C similar to sludge and significant secondary degradation at 500°C and above could only be observed for pectin, xylan and lignin. For other compounds, thermal degradations mainly occurred in primary degradation region as represented by more than 94.0% of total mass loss. The results suggested that compounds with heterogeneous structures and components such as pectin, xylan and lignin could initiate degradation at lower temperature but released more volatiles during secondary degradation at higher temperature.

Thermal degradation stages of model compounds within primary degradation region also illustrated that most compounds degraded with single narrow peak in DTG profiles while proteins, asolectin, sucrose, xylan and lignin degraded with broad peak or multiple apparent peaks. Proteins mixture degraded over broad temperature region and reached maximum degradation rate at above 300°C indicated relatively high thermal stability. The resistant to degradation could be partly caused by the strong double and triple carbon-nitrogen bonds (Kristensen, 1990; Thipkhunthod et al., 2007). Peaks of degradation for lipids compound were at higher temperature of around 350-420°C. Cellulose and lignin were having degradation peaks at around

340°C while most of the carbohydrates showed degradation peak at temperature around 300°C and below. TGA mass loss curves and mass% in db at 950°C also provided information of the distribution of volatiles and char. Different amounts of char could be found among the compounds except for cholesterol and triglycerides which were almost completely converted into volatiles. These observations also suggested that char formation tendency may not directly correlate to the thermal stability of sample.

Cellulose and lignin were treated with the sludge biomass composition quantification procedures of alkaline hydrolysis for AHR and acid digestion for ADR respectively to observe the impact of alkaline and acid treatment on the compounds in the aspect of thermal degradation behaviours analysis. Results were illustrated in Figure 8.3. Alkaline hydrolysed cellulose, AH-Cellulose and acid digested lignin, AD-Lignin were showing different thermal degradation characteristics compared to model compounds tested as received. AH-Cellulose degraded with broader peak at lower temperature and rate while forming significantly more char solids and releasing relatively more volatiles during secondary degradation at high temperature. AD-Lignin showed significant mass loss at low temperature probably due to the adsorbed moisture and sulphate residues supported by H₂O and SO₂ detection by TGA-FTIR. After devolatilisation of these interfering residues, AD-Lignin degraded gradually over a wide temperature region comparable to lignin. These observations suggested that alkaline and acid treatments could be suitable for AHR and ADR quantifications but care needed to be taken for components isolation and analysed in further thermal study.

In general, distinctive thermal degradation behaviours could be observed for model compounds analysed in this study. Data of TGA-DTG for model compounds could be used to compare with degradation behaviours of sludge and corresponding biomass components. Results could also be used to carry out simulations and calculate TGA-DTG data for mixtures of model compounds and synthetic sludge.

Table 8.2: TGA-DTG analysis of model compounds.

Category	Model compounds	Initial °C	Maximum degradation		Terminate °C	Mass% in db		Volatiles released in relative%	
			Temp °C	Rate %/min		500°C	950°C	100-500°C	500-950°C
Proteins	Whey isolates	223.2	313.4	-7.08	431.9	30.78	27.32	95.24	4.76
Lipids	Asolectin	198.9	369.8	-6.24	451.6	20.17	16.40	95.49	4.51
	Cholesterol	241.1	345.9	-20.06	385.4	0.47	0.47	100.00	0.00
	Glyceryl tripalmitate	322.4	414.6	-20.25	466.7	0.54	0.54	100.00	0.00
	Glyceryl tristearate	328.3	411.7	-19.38	467.2	0.00	0.00	100.00	0.00
	Glyceryl trioleate	344.1	414.3	-16.92	474.6	1.44	0.31	98.87	1.13
Carbohydrates	Amylopectin	276.3	308.3	-21.12	360.5	21.96	19.27	96.67	3.33
	Pectin	207.5	234.9	-16.99	350.9	38.69	33.60	92.33	7.67
	Glycogen	254.0	293.4	-20.29	342.8	30.41	26.22	94.33	5.67
	Starch	270.8	299.6	-22.04	373.5	24.93	21.31	95.40	4.60
	Sucrose	219.1	285.2	-7.93	398.8	21.32	16.88	94.66	5.34
Lignocellulosic biomass	Cellulose	261.7	344.3	-15.78	370.6	19.22	16.65	96.92	3.08
	Xylan	201.8	234.3	-7.42	346.5	34.96	28.79	91.33	8.67
	Lignin	249.7	337.7	-2.44	436.1	57.81	47.42	80.24	19.76
Alkaline/Acid treated residue	AH-Cellulose	210.8	303.5	-6.67	359.5	35.54	25.50	86.53	13.47
	AD-Lignin	159.7	217.0	-5.65	281.0	47.91	35.79	81.12	18.88

Table 8.3: Thermal degradation stages of model compounds.

Category	Model compounds	Thermal degradation stages, T (°C) and R (%/min) at 10K/min									
		Initial stage		Apparent peak 1		Apparent peak 2		Apparent peak 3		Terminate stage	
		T	R	T	R	T	R	T	R	T	R
Proteins	Whey isolates	223.2	-1.00	299.5	-6.52	313.4	-7.08	-	-	431.9	-1.00
Lipids	Asolectin	198.9	-1.00	287.3	-2.99	369.8	-6.24	417.6	-1.83	451.6	-1.00
	Cholesterol	241.1	-1.00	-	-	345.9	-20.06	-	-	385.4	-1.00
	Glyceryl tripalmitate	322.4	-1.00	-	-	414.6	-20.25	459.2	-1.23	466.7	-1.00
	Glyceryl tristearate	328.3	-1.00	-	-	411.7	-19.38	457.5	-1.63	467.2	-1.00
	Glyceryl trioleate	344.1	-1.00	-	-	414.3	-16.92	-	-	474.6	-1.00
Carbohydrates	Amylopectin	276.3	-1.00	-	-	308.3	-21.12	-	-	360.5	-1.00
	Pectin	207.5	-1.00	234.9	-16.99	-	-	-	-	350.9	-1.00
	Glycogen	254.0	-1.00	-	-	293.4	-20.29	-	-	342.8	-1.00
	Starch	270.8	-1.00	-	-	299.6	-22.04	-	-	373.5	-1.00
	Sucrose	219.1	-1.00	227.1	-6.78	285.2	-7.93	-	-	398.8	-1.00
Lignocellulosic biomass	Cellulose	261.7	-1.00	-	-	344.3	-15.78	-	-	370.6	-1.00
	Xylan	201.8	-1.00	234.3	-7.42	282.3	-5.47	-	-	346.5	-1.00
	Lignin	249.7	-1.00	-	-	337.7	-2.44	-	-	436.1	-1.00
Alkaline/Acid treated residues	AH-Cellulose	210.8	-1.00	268.6	-4.75	303.5	-6.67	396.7	-1.05	359.5	-1.00
	AD-Lignin	159.7	-1.00	217.0	-5.65	-	-	-	-	281.0	-1.00

Figure 8.1: Model compounds analysis. (a) TGA (b) DTG for proteins. (c) TGA (d) DTG for lipids.

Figure 8.2: Model compounds analysis. (a) TGA (b) DTG for carbohydrates. (c) TGA (d) DTG for lignocellulosic biomass.

Figure 8.3: Model compounds analysis. (a) TGA (b) DTG for alkaline treated cellulose. (c) TGA (d) DTG for acid treated lignin.

8.3.2. Sludge biomass components analysis

Results of thermal degradation behaviours study for sludge samples collected from Changi WRP and corresponding components isolated by biomass composition analysis were showed in Table 8.4, 8.5 and 8.6. TGA-DTG plots were illustrated in Figure 8.4, 8.5 and 8.6. Primary (CsP), secondary (CsS) and dried (CsY) sludge samples collected during second batch of sampling were analysed and compared. Sludge samples collected, EER and EFR were showing highly similar thermal degradation behaviours for all three types of sludge respectively suggested that the extraction processes isolated extractives without significantly affected the thermal degradation behaviours of the other biomass composition remained in sludge. In general, higher initial temperature of primary degradation region and shift of initial rates increased for DTG profiles to higher temperatures could be observed indicated the extracted components from sludge started to degrade at low temperature. Rates of degradation, DTG of the apparent peak 1 at low temperature region of 200-300°C also gradually reduced. Mass% in db at 500°C and 950°C increased as removal of extractives reduced the organic contents in solvent extracted residues. These observations agreed well with the direct analysis of TGA-DTG for extractives. Differences between sludge, EER and EFR were comparable to the thermal degradation characteristics of EE and WE for CsP, CsS, and CsY. Summations of the mass loss curves of solvent extracted residues with corresponding extractives were also highly similar to mass loss behaviours of sludge.

EE extracted from sludge degraded into mostly volatile compounds within primary degradation region at 200-500°C and formed small amounts of char residues. WE formed large amounts of char residues and showed significant secondary degradation at 500-950°C. These results were comparable to lipids and carbohydrates model compounds respectively but relatively higher formation of char residues observed for extractives from sludge. TGA mass loss curves of the extractives were highly similar for CsP, CsS and CsY respectively but DTG profiles of EE and WE showed that multiple apparent peaks could be observed with qualitative similarity (temperature of apparent peaks) and quantitative variations (degradation rates) for extractives extracted from different types of sludge. DTG profiles also showed that the thermal stability for EE of CsY higher than CsS and

followed by CsP with maximum degradation at around 320°C and 250°C respectively. TGA data also supported the observations where approximately 60% (CsP), 50% (CsS) and 40% (CsY) mass loss recorded at 300°C. These results suggested that hydrophobic materials remained in sludge were more difficult to be thermally degraded after anaerobic digestion. DTG profiles of WE showed different characteristics. WE of CsS and CsY degraded similarly at lower temperature with maximum degradation rates at around 200-220°C as compared to CsP at 270°C. However, more volatile compounds were formed from pyrolysis of CsP-WE due to significant secondary degradation at higher temperature. In contrast to extractions by water and ethanol where targeted components were isolated in mild treatment conditions with other compounds remained as solids, alkaline hydrolysis and acid digestion removed the others with targeted compounds remained as solids by using harsh treatment conditions. As illustrated by AH-Cellulose and AD-Lignin, significant alterations of thermal degradation behaviours could be observed before and after alkaline and acid treatments. For AHR and ADR of CsP, CsS and CsY, degradations occurred over a broad temperature region of 200-500°C. AHR degraded similarly to AH-Cellulose where alkaline treatment shifted the initial degradation of cellulose to lower temperature and broadened the temperature region of primary degradation. TGA analysis of ADR for CsP showed significant amount of adsorbed moisture and volatiles compounds that released at low temperature. As supported by TGA-FTIR analysis and data obtained for AD-Lignin, H₂O and SO₂ released at low temperature could be considered as interfering residues. After deducting the interfering components, ADR of all sludge samples tested were showing similar characteristics with low degradation rates over broad temperature region and comparable to lignin.

Based on the thermochemical characteristics recorded in Table 8.6, significant differences among isolated components (EE, WE, AHR and ADR) from sludge and high similarity among the solid residues remained as waste mixtures (sludge, EER and EFR) could be observed. These observations suggested that the waste mixtures with complex organic composition could not be easily distinguished while characteristics of components isolated in respective categories could be determined. Therefore, biomass composition analysis in this study could help to reduce the

complexity of direct thermal analysis of waste mixtures such as sludge. Thermal analysis of isolated biomass components from sludge also suggested that multiple categories of sludge biomass components degraded within similar and overlapping temperature regions and multiple compounds degraded within a single category of biomass composition. However, components within the same category showed higher similarity in thermochemical characteristics. Therefore development of multiple-steps kinetics model with TGA-DTG deconvolution analysis could be more accurate with clearer physical meaning if these techniques applied on isolated components from sludge (Nowicki and Ledakowicz, 2014).

Figure 8.4: Sludge, EER and EFR analysis. (a) TGA and (b) DTG of CsP. (c) TGA and (d) DTG of CsS. (e) TGA and (f) DTG of CsY calculated in dry sludge basis.

Table 8.4: TGA-DTG analysis of sludge biomass composition.

Biomass composition	Sample label	Initial Temp °C	Maximum degradation		Terminate Temp °C	Mass% in db		Volatiles released in relative%	
			Temp °C	Rate %/min		500°C	950°C	100-500°C	500-950°C
Sludge	CsP	167.3	274.6	-3.09	557.0	46.36	38.53	87.26	12.74
	CsS	179.8	341.5	-5.02	567.6	45.69	38.15	87.81	12.19
	CsY	173.0	316.8	-2.31	538.4	58.30	49.95	83.32	16.68
EER	CsP	172.8	319.2	-2.71	543.1	53.22	44.98	85.02	14.98
	CsS	176.9	345.7	-5.70	567.6	45.01	38.21	88.99	11.01
	CsY	169.6	315.5	-2.20	549.9	60.84	52.25	82.01	17.99
EFR	CsP	181.5	321.2	-2.79	554.3	55.28	46.85	84.14	15.86
	CsS	186.9	345.6	-6.10	554.6	46.49	39.94	89.09	10.91
	CsY	182.7	321.7	-2.20	577.3	62.75	54.08	81.12	18.88
EE	CsP	176.0	256.5	-9.24	394.0	4.99	3.16	98.11	1.89
	CsS	165.2	259.5	-5.57	435.7	7.31	5.24	97.82	2.18
	CsY	181.4	321.3	-7.24	455.8	7.58	6.34	98.68	1.32
WE	CsP	164.4	273.7	-3.48	453.4	42.44	26.74	78.57	21.43
	CsS	143.8	201.6	-4.76	408.3	40.88	31.40	86.17	13.83
	CsY	163.4	221.7	-4.62	418.3	42.80	31.42	83.41	16.59
AHR	CsP	238.5	440.6	-0.42	518.0	89.94	84.22	63.75	36.25
	CsS	234.7	442.3	-0.63	497.1	87.92	82.76	70.07	29.93
	CsY	251.1	453.9	-0.48	525.4	76.20	72.26	85.80	14.20
ADR	CsP	140.6	232.0	-6.83	608.1	48.03	35.58	80.67	19.33
	CsS	202.6	325.7	-1.49	528.5	70.42	65.83	86.57	13.43
	CsY	207.4	422.4	-1.05	528.7	90.37	85.06	64.46	35.54

Table 8.5: Thermal degradation stages of sludge biomass composition.

Biomass composition	Sample label	Thermal degradation stages, T (°C) and R (%/min) at 10K/min									
		Initial stage		Apparent peak 1		Apparent peak 2		Apparent peak 3		Terminate stage	
		T	R	T	R	T	R	T	R	T	R
Sludge	CsP	167.3	-0.20	274.6	-3.09	313.0	-2.95	426.3	-1.20	557.0	-0.20
	CsS	179.8	-0.20	272.4	-2.27	341.5	-5.02	436.1	-1.00	567.6	-0.20
	CsY	173.0	-0.20	280.3	-2.20	316.8	-2.31	426.6	-1.06	538.4	-0.20
EER	CsP	172.8	-0.20	270.6	-2.58	319.2	-2.71	417.1	-1.16	543.1	-0.20
	CsS	176.9	-0.20	280.5	-2.34	345.7	-5.70	396.0	-1.00	567.6	-0.20
	CsY	169.6	-0.20	282.5	-2.07	315.5	-2.20	404.4	-1.13	549.9	-0.20
EFR	CsP	181.5	-0.20	282.5	-2.45	321.2	-2.79	388.5	-1.27	554.3	-0.20
	CsS	186.9	-0.20	281.6	-2.09	345.6	-6.10	393.6	-1.02	554.6	-0.20
	CsY	182.7	-0.20	279.8	-1.91	321.7	-2.20	405.2	-1.13	577.3	-0.20
EE	CsP	176.0	-1.00	256.5	-9.24	336.1	-3.89	467.9	-1.39	394.0	-1.00
	CsS	165.2	-1.00	259.5	-5.57	330.1	-4.81	439.2	-0.98	435.7	-1.00
	CsY	181.4	-1.00	264.6	-4.10	321.3	-7.24	425.3	-1.51	455.8	-1.00
WE	CsP	164.4	-1.00	204.9	-2.18	273.7	-3.48	376.0	-1.49	453.4	-1.00
	CsS	143.8	-1.00	201.6	-4.76	287.2	-2.29	-	-	408.3	-1.00
	CsY	163.4	-1.00	221.7	-4.62	-	-	-	-	418.3	-1.00
AHR	CsP	238.5	-0.20	-	-	320.9	-0.37	440.6	-0.42	518.0	-0.20
	CsS	234.7	-0.20	-	-	319.1	-0.59	442.3	-0.63	497.1	-0.20
	CsY	251.1	-0.20	-	-	330.3	-0.31	453.9	-0.48	525.4	-0.20
ADR	CsP	140.6	-0.20	232.0	-6.83	-	-	468.9	-0.88	608.1	-0.20
	CsS	202.6	-0.20	286.6	-1.37	325.7	-1.49	410.6	-1.16	528.5	-0.20
	CsY	207.4	-0.20	-	-	330.4	-1.04	422.4	-1.05	528.7	-0.20

Table 8.6: Thermochemical characteristics of sludge biomass composition.

Biomass composition	Sample label	VM	Char residues	IM	Ash ₉₅₀	FR	FC	VM/FC or VM/FR ratio
Sludge	CsP	61.47	38.53	18.17	-	20.36	-	3.02
	CsS	61.85	38.15	17.18	-	20.97	-	2.95
	CsY	50.05	49.95	31.33	-	18.62	-	2.69
EER	CsP	55.02	44.98	20.66	-	24.32	-	2.26
	CsS	61.79	38.21	19.73	-	18.48	-	3.34
	CsY	47.75	52.25	32.50	-	19.75	-	2.42
EFR	CsP	53.15	46.85	24.66	-	22.19	-	2.40
	CsS	60.06	39.94	20.79	-	19.16	-	3.14
	CsY	45.92	54.08	34.93	-	19.15	-	2.40
EE	CsP	96.84	3.16	0.00	-	3.16	-	30.66
	CsS	94.76	5.24	0.00	-	5.24	-	18.09
	CsY	93.66	6.34	0.00	-	6.34	-	14.78
WE	CsP	73.26	26.74	0.00	-	26.74	-	2.74
	CsS	68.60	31.40	0.00	-	31.40	-	2.19
	CsY	68.58	31.42	0.00	-	31.42	-	2.18
AHR	CsP	15.78	84.22	-	80.46	-	3.76	4.20
	CsS	17.24	82.76	-	77.54	-	5.22	3.31
	CsY	14.94	85.06	-	87.08	-	-	-
ADR	CsP	64.42	35.58	-	59.02	-	-	-
	CsS	34.17	65.83	-	35.92	-	29.90	1.14
	CsY	27.74	72.26	-	59.08	-	13.18	2.11

Figure 8.5: CsP, CsS and CsY extractives analysis. (a) TGA (b) DTG of EE. (c) TGA (d) DTG of WE in dry basis.

Figure 8.6: CsP, CsS and CsY residues analysis. (a) TGA (b) DTG of AHR. (c) TGA (d) DTG of ADR in dry basis.

8.3.3. Synthetic sludge analysis

CsY sludge was selected as reference waste sample. Synthetic sludge was formed based on data from biomass composition analysis and model compounds selected. TGA-DTG data of model compounds and CsY biomass components were used in simulations and comparisons to provide supporting information for synthetic sludge formation. Results calculated in icf basis were illustrated in Figure 8.7, 8.8 and 8.9. Three types of lipids were selected to represent EE extracted from sludge included phospholipids, sterol and glycerol lipids. Simulation of thermal degradation behaviours of lipids mixture was carried out based on the superposition principle with the measured data of individual model compounds illustrated in Figure 8.7. The approximate proportions of asolectin, cholesterol and glyceryl tripalmitate were adjusted to be comparable to TGA-DTG data of EE from CsY. Results of simulation showed that acceptable representation of complex waste mixture could be achieved with deviations observed. CsY-EE thermally degraded in slightly broader temperature region and lower degradation rates as compared to the lipids mixture simulated suggested that EE from sludge consisted more diverse components that degraded at different temperatures. Mass of volatile matters and fixed residues remained of EE agreed well with simulated data. Lipids with lower and higher thermal stability than selected model compounds could be considered if further improvements needed to form the synthetic mixture of EE from sludge. Since EE could be easily isolated from sludge, further kinetics modelling and compositional study could also be carried out directly with EE samples.

Lipids, simple sugars, proteins, cellulose, and lignin were separately quantified based on the sequential extraction and isolation procedures, therefore polysaccharides and hemicellulose were suggested as the main components in the residual organics. Three types of carbohydrate polymers were selected to represent OOM in sludge included starch, glycogen and xylan. Starch and glycogen were common storage polysaccharides while xylan was generally used as model compounds for hemicellulose in thermal analysis. For WE, proteins, AHR and ADR of sludge, only one model compounds selected to represent each category of biomass components. Sucrose, whey isolates, cellulose and lignin were selected. Main components of EFR remained after extractions were proteins, cellulose, lignin

and polysaccharides. Therefore these four groups of model compounds were used for simulation and compared to TGA-DTG data of EFR illustrated in Figure 8.8. Similar to simulation of EE in sludge, acceptable representation with deviations could be observed. Since the compounds presence in EFR were more diverse and complex than model compounds selected, thermal degradation of EFR were distributed at different temperatures with lower degradation rates. WE, AHR and ADR were compared to sucrose, cellulose and lignin directly in icf as illustrated in Figure 8.9. WE consisted of hydrophilic materials with slightly lower thermal stability than sucrose. These compounds could be simple organic alcohol, acids and amines. Further chemical compounds identification could help to improve the representation of WE similar to model compounds mixture formed for EE. For simplicity and the aim for proof of concept instead of optimisation, sucrose was selected to form synthetic sludge in this study. AHR and cellulose degraded differently during pyrolysis. The differences were similar to AH-Cellulose and cellulose where solid residues after alkaline hydrolysis treatment were degraded over broader temperature region at lower degradation rates. Therefore TGA-DTG of AHR could not directly represent its initial thermal degradation behaviours in sludge as expected. ADR showed highly similar behaviours with lignin before 400°C but more thermally stable compounds presence in ADR that degraded at temperature around 400-500°C.

Based on the simulations of model compounds and comparison to TGA-DTG of biomass components of CsY sludge, it could be concluded that acceptable representation of sludge thermal degradation behaviours with proper selection of model compounds was achieved. Therefore, all the selected model compounds were mixed physically and manually to form synthetic sludge for further analysis. The composition of CsY and synthetic sludge were showed in Table 8.7. Thermochemical characteristics of synthetic sludge were calculated and compared to direct measurements of CsY. Results in Table 8.8 showed that good agreements achieved except with the overestimation of C contents and underestimation of S contents as discussed in simulations study in Chapter 7.

FTIR analysis was carried out for CsY sludge, synthetic sludge formed from mixture of model compounds and synthetic sludge mixed with ash residues of CsY sludge. Results were showed in Table 8.9 and Figure 8.10. In general, peaks identified on FTIR spectra of all three samples were highly comparable indicated similar functional groups and compounds could be presence. FTIR spectra also showed that mixing of organic model compounds with inorganic ash residues could significantly reduced the resolution of peaks on the spectra.

Inorganic bounded O-H groups with wavenumber of 3700 and 3620 cm^{-1} could only be observed in CsY but not in synthetic sludge as residual moisture remained in sludge after drying at 105°C were removed by combustion at 550°C as discussed in Chapter 4. Broad peaks at 3600-3100 cm^{-1} contributed by O-H and N-H functional groups suggested presence of alcohols, acids, amides and amines. Multiple peaks showed at 3100-2600 cm^{-1} were caused by C-H groups of unsaturated hydrocarbons and aromatics at 3076 cm^{-1} and saturated hydrocarbons, ethers, and lipids at 2925 and 2855 cm^{-1} . C=O functional groups could be observed for aldehydes, ketones, carboxylic acids, and esters at 1710 cm^{-1} . C=O and N-H groups for amides and proteins observed at 1635 cm^{-1} and 1535 cm^{-1} . Multiple peaks showed at 1450-1350 cm^{-1} could be attributed to C-H groups for saturated hydrocarbon, ethers, and lipids at 1445 cm^{-1} and O-H groups for acids and alcohols at 1415 cm^{-1} . Peak at 1375 cm^{-1} could be caused by C-N groups of primary amides, S-O groups of sulphur organic compounds and O-H groups of alcohols and polysaccharides. Peak at 1314 cm^{-1} could be caused by C-N groups of amines, S-O groups of sulphur organic compounds and O=C-O groups of carboxylic acids and esters.

Broad peaks and multiple narrow peaks could be observed in the region of 1250–950 cm^{-1} for FTIR spectra of CsY and synthetic sludge respectively. 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 the inorganic components presence, peaks at 1080 and 1008 cm^{-1} were corresponding to the inorganic functional groups in phosphates, silicates, sulphates, and clay minerals. In the region of 850–600 cm^{-1} , multiple peaks could be identified for minerals and silicates at 797 cm^{-1} , for carbonates and nitrates at 779 cm^{-1} , amides, amines and halogenated compounds at 750 cm^{-1} , aromatics and alcohols at 694 cm^{-1} and sulphates at 668 cm^{-1} .

Table 8.7: Formation of synthetic sludge for CsY.

CsY		Synthetic sludge		
Composition	Mass% in icf	Model compounds	Mass% in icf	
EE	5.50	Asolectin	2.61	5.13
		Cholesterols	2.03	
		Glyceryl tripalmitate	0.49	
WE	10.19	Sucrose	9.95	9.95
Proteins	41.65	Whey Isolates	40.17	40.17
AHR	7.30	Cellulose	6.30	6.30
ADR	15.31	Lignin	15.32	15.32
OOM	20.05	Starch	9.19	23.32
		Glycogen	6.93	
		Xylan	7.20	

Table 8.8: Thermochemical characteristics of CsY and synthetic sludge.

Thermochemical characteristics	Data in icf		Bias error	
	CsY	Synthetic sludge	ϵ_{bias}	%
Heat capacity, Cp	1.78	1.86	-0.07	-4.19
Heating value, HHV	21.16	21.41	-0.25	-1.18
Heat of pyrolysis	60.96	67.00	-6.04	-9.91
Volatile matter, VM	74.51	73.89	0.62	0.83
Fixed residues, FR	25.49	26.30	-0.81	-3.18
VM/FR ratio	2.90	2.81	0.09	3.13
Carbon, C	46.02	52.96	-6.94	-15.09
Hydrogen, H	6.92	6.92	0.00	0.00
Nitrogen, N	7.28	7.00	0.28	3.87
Sulphur, S	6.72	0.38	6.34	94.32
Oxygen, O	33.07	32.93	0.14	0.43

Figure 8.7: (a) TGA (b) DTG of simulation of lipids model compounds and compared to (c) TGA (d) DTG of CsY-EE in icf basis.

Figure 8.8: (a) TGA (b) DTG of simulation of model compounds and compared to (c) TGA (d) DTG of CsY-EFR in icf basis.

Figure 8.9: Comparison analysis in icf basis. (a) TGA (b) DTG of WE, (c) TGA (d) DTG of AHR and (e) TGA (f) DTG of ADR with respective model compounds.

Table 8.9: Peaks identification of FTIR spectra for synthetic sludge analysis.

Wavenumber regions	Peaks identification of FTIR spectra		
	CsY	Synthetic sludge	Synthetic sludge with ash
3700 - 3600	3700, 3621	-	-
3600 - 3100	-	3559, 3381	-
	3284	3322	3280
3100 - 2600	3076, 2971, 2925	2971, 2940, 2914	2971, 2940, 2914
	2875, 2853	2855	2855
1800 -1400	1710, 1635	1710, 1633	1710, 1632
	1535	1535	1535
	1518, 1445	1512, 1460	1512, 1452
1400 - 1300	1415, 1375	1427, 1367	1426, 1374
	1314	1344, 1322	-
1300 -900	1220	1277, 1237, 1208	1277, 1203
	1158	1161, 1116, 1104	-
	1030, 1008	1066, 1049, 1004	1075, 1023
	913	988, 942, 908	-
900 - 600	-	866, 849	-
	797, 778	-	797
	750	731	-
	694, 668	680, 650	673

Figure 8.10: FTIR spectra of CsY and synthetic sludge with/without ash residues.

Thermal degradation behaviours of synthetic sludge with/without ash residues were determined and compared to CsY sludge and simulation calculated based on TGA-DTG data of individual model compounds selected. Results were summarised in Table 8.10, 8.11, 8.12 and illustrated on Figure 8.11 in db and vb. Synthetic sludge formed and the simulation calculated showed comparable characteristics suggested that superposition principle could be applied for thermal degradation behaviours analysis with minimal deviations and interaction effects observed. Slightly higher char residues formed for synthetic sludge at 29.60 mass% as compared to calculated simulation at 27.08 mass% in db while almost completely overlapping mass loss curves could be observed in vb. Synthetic sludge with ash residues and CsY also showed comparable mass loss curves suggested acceptable representation of real waste sample with mixture of selected model compounds. VM/FR ratios of four TGA-DTG data ranged from 2.52-2.90 suggested high similarities in distribution of volatiles and solid residues. Compare to synthetic sludge without ash residues, relatively lower release of volatiles in primary degradation region of 100-500°C could be observed for synthetic sludge mixed with ash residues caused by thermal degradation of inorganics at higher temperature. DTG profiles showed that CsY thermally degraded with relatively lower maximum degradation rates at around 300-320°C and higher degradation rates at temperature around 400-500°C. Significant mass loss also observed at secondary degradation region of 500-950°C caused by decomposition of inorganics and secondary char degradation reactions. These observations illustrated the highly complex and diverse composition presence in real wastes mixture as compared to synthetic sludge formed.

Table 8.10: Thermal analysis of CsY and synthetic sludge.

Sample Label	Volatile matters	Char residues	Inorganic matters	Fixed residues	VM/FR Ratio
CsY Sludge	50.05	49.95	31.33	18.62	2.69
Synthetic Sludge	70.40	29.60	1.64	27.96	2.52
Simulation	72.92	27.08	1.64	25.44	2.87
Synthetic Sludge with CsY ash	47.03	52.97	36.78	16.19	2.90

Table 8.11: TGA-DTG analysis of CsY and synthetic sludge.

Sample Label	Initial Temp °C	Maximum degradation		Terminate Temp °C	Mass% in db		Volatiles released in relative%	
		Temp °C	Rate %/min		500°C	950°C	100-500°C	500-950°C
CsY Sludge	173.0	316.8	-2.31	538.4	58.30	49.95	83.32	16.68
Synthetic Sludge	169.9	307.1	-5.72	552.6	34.84	29.60	92.56	7.44
Simulation	169.6	298.3	-7.63	559.3	31.76	27.08	93.58	6.42
Synthetic Sludge with CsY ash	192.8	305.1	-3.58	522.3	58.88	52.97	87.44	12.56

Table 8.12: Thermal degradation stages of CsY and synthetic sludge.

Sample Label	Thermal degradation stages, T (°C) and R (%/min) at 10K/min									
	Initial stage		Apparent peak 1		Apparent peak 2		Apparent peak 3		Terminate stage	
	T	R	T	R	T	R	T	R	T	R
CsY Sludge	173.0	-0.20	280.3	-2.20	316.8	-2.31	426.6	-1.06	538.4	-0.20
Synthetic Sludge	169.9	-0.20	224.8	-3.13	307.1	-5.72	406.9	-1.11	552.6	-0.20
Simulation	169.6	-0.20	237.0	-1.94	298.3	-7.63	410.6	-1.16	559.3	-0.20
Synthetic Sludge with CsY ash	192.8	-0.20	219.8	-1.60	305.1	-3.58	405.0	-0.83	522.3	-0.20

Figure 8.11: CsY and synthetic sludge analysis. (a) TGA (b) DTG in dry basis and (c) TGA (d) DTG in volatile basis.

8.3.4. TGA-DTG analysis and kinetics study

Results of multiple heating rates TGA-DTG analysis of synthetic sludge were showed in Table 8.13 and 8.14. TGA-DTG plots of synthetic sludge were illustrated in Figure 8.12 and compared to CsY as illustrated in Figure 8.13. Results of kinetics analysis of synthetic sludge compared to CsY were showed in Table 8.15 and Figure 8.14. Impacts of heating rates within the range of 5-25 K/min used in this study on TGA-DTG of synthetic sludge were compared to data for CsY recorded in Chapter 5 and high similarity could be observed. Similar to CsY, thermal degradation of synthetic sludge could be generally divided into primary and secondary degradations where majority of the volatile compounds released during primary degradations at low temperature region of 100-500°C with high mass loss rate and continuous decomposition occurred during secondary degradations at high temperature region of 500-950°C with low mass loss rate. Mass% in db recorded at 500°C and 950°C and relative% of volatiles released in both primary and secondary degradation regions remained generally consistent with random deviations at different heating rates for both CsY and synthetic sludge.

Based on the multiple heating rates TGA, highly similar and poorly separated mass loss curves from 100°C to 950°C could be observed for CsY at different heating rates were used while improved separation could be observed for synthetic sludge. Poor separation of mass loss curves for sludge indicated that heat transfer conditions less affected thermal degradation of sludge samples as compared to other biomass feedstock (Urban and Antal Jr, 1982) and could be caused by following reasons. (a) Random errors among the mass loss data caused by heterogeneity in composition and therefore resulted in less significant shift of TGA curves to higher temperature at higher heating rates. (b) High activation energy for sludge degradation reactions therefore highly sensitive to the temperature and less affected by the heating rates used. Separation of mass loss curves of synthetic sludge improved as compared to CsY indicated that well controlled and simplified composition reduced the random errors caused by heterogeneity in real wastes mixture since comparable activation energy measured for synthetic sludge and CsY as showed in the results of kinetics study. Variations in sludge composition and mass of char residues formed at different heating rates also caused random crossing

on mass loss curves as observed for all sludge samples collected and comparable to previous study (Urban and Antal Jr, 1982). This issue also reduced for synthetic sludge. Based on multiple heating rates DTG of sludge, heterogeneity of composition in sludge observed as DTG profiles plotted randomly varied at different heating rates. Improved consistency could be observed for synthetic sludge. Shifts of initialization and terminating temperatures for primary degradation region, peaks at maximum degradation rate and other apparent peaks to slightly higher temperatures and degradation rates could be found in DTG profiles for both samples when higher heating rates were used. Higher heating rates also caused the thermal degradation of samples occurred in much shorter time intervals and therefore slightly lower resolution for the three apparent peaks observed at around 220-280°C, 300-320°C and 400-420°C.

Activation energy, E in kJ/mol of CsY and synthetic sludge determined by Friedman and Ozawa-Flynn-Wall (OFW) analysis were highly similar indicating acceptable representation of complex wastes mixture with selected model compounds on thermal degradation behaviours study. In average, E values calculated for synthetic sludge were slightly lower than CsY by 5.04% and 3.10% while SD_m of E values calculated reduced significantly by 62.78% and 67.63% for Friedman and OFW analysis respectively. As illustrated in Figure 8.13, E data of both samples were closely similar at conversion below 0.50 and started to deviate at higher conversion degree when standard deviations for E of CsY increased significantly. These observations suggested that synthetic sludge showed comparable thermal degradation kinetics while reduced significantly the random errors of measurements and calculations.

Table 8.13: Multiple heating rates TGA-DTG analysis of synthetic sludge.

Heating rate K/min	Initial Temp °C	Maximum degradation		Terminate Temp °C	Mass% in db		Volatiles released in relative%		VM/FR Ratio
		Temp °C	Rate %/min		500°C	950°C	100-500°C	500-950°C	
5	173.6	293.3	-2.70	541.4	35.94	29.40	90.73	9.27	2.40
10	177.7	303.5	-5.52	564.3	36.72	30.08	90.50	9.50	2.32
15	181.7	309.4	-8.09	577.9	36.54	28.55	88.81	11.19	2.50
20	180.6	312.3	-12.21	600.2	35.62	25.69	86.63	13.37	2.89
25	171.6	315.0	-15.32	626.1	34.77	26.69	88.98	11.02	2.75
Mean ±SD	177.0 ±4.4	306.7 ±8.6		582.0 ±32.6	35.92 ±0.78	28.08 ±1.84	89.13 ±1.64	10.87 ±1.64	2.57 ±0.24

Table 8.14: Thermal degradation stages of synthetic sludge.

Heating rate, K/min	Thermal degradation stages of synthetic sludge, T (°C) and R (%/min)									
	Initial stage		Apparent peak 1		Apparent peak 2		Apparent peak 3		Terminate stage	
	T	R	T	R	T	R	T	R	T	R
5	173.6	-0.10	220.9	-0.96	293.3	-2.70	416.8	-0.55	541.4	-0.10
10	177.7	-0.20	231.5	-2.03	303.5	-5.52	413.7	-1.10	564.3	-0.20
15	181.7	-0.30	245.6	-3.89	309.4	-8.09	432.1	-1.65	577.9	-0.30
20	180.6	-0.40	243.0	-5.28	312.3	-12.21	424.6	-2.20	600.2	-0.40
25	171.6	-0.50	250.9	-8.42	315.0	-15.32	414.6	-2.75	626.1	-0.50
Mean ±SD, Temp °C	177.0 ±4.4		238.4 ±12.1		306.7 ±8.6		420.4 ±7.9		582.0 ±32.6

Figure 8.12: Multiple heating rates analysis of synthetic sludge. (a) TGA (b) DTG on temperature and (c) TGA (d) DTG on time.

Figure 8.13: Multiple heating rates data of CsY. (a) TGA (b) DTG on temperature in $^{\circ}\text{C}$ and (c) TGA and (d) DTG on time in minutes.

Table 8.15: Comparison study for activation energy of CsY and synthetic sludge by Friedman and Ozawa-Flynn-Wall analysis.

Conversion in vb	Activation energy, E in kJ/mol							
	Synthetic sludge				CsY			
	Freidman analysis		OFW analysis		Freidman analysis		OFW analysis	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	209.2	26.4	170.5	17.2	203.0	69.1	168.9	58.0
0.25	205.2	23.8	171.7	15.1	208.7	71.1	177.5	55.8
0.30	201.7	22.3	172.0	14.1	207.2	72.0	180.7	55.8
0.35	196.5	21.3	171.8	13.4	207.2	70.4	183.7	55.3
0.40	191.2	21.7	170.6	13.3	206.0	74.9	183.3	56.1
0.45	189.2	23.6	169.5	14.0	204.7	85.2	182.1	61.4
0.50	191.3	28.2	169.8	15.9	194.2	103.6	176.0	72.1
0.55	196.0	36.5	171.7	20.1	154.1	118.4	150.5	86.0
0.60	198.3	48.4	174.9	27.4	148.2	107.4	137.9	90.0
0.65	186.3	64.6	173.8	38.3	174.1	108.3	150.9	97.2
0.70	153.7	84.5	155.0	52.7	217.5	115.5	184.6	106.0
0.75	122.6	91.4	124.3	68.0	265.2	162.2	221.7	133.7
0.80	111.3	71.5	117.3	66.9	86.5	357.1	82.6	237.0
Mean $\pm$ SD	180.9 $\pm$ 31.5	43.4 $\pm$ 25.8	162.5 $\pm$ 19.2	29.0 $\pm$ 20.7	190.5 $\pm$ 42.8	116.6 $\pm$ 77.2	167.7 $\pm$ 32.9	89.6 $\pm$ 50.6

Figure 8.14: Mean data and standard deviations for activation energy of CsY and synthetic sludge determined by (a) Friedman and (b) Ozawa-Flynn-Wall analysis.

8.3.5. Products evolution analysis

Based on all spectra collected, products released during thermal degradation sludge biomass composition from CsP, CsS and CsY were highly comparable with slight variations among the components respectively which agreed well with results from TGA-DTG analysis. Selected TGA-FTIR spectra of biomass components from CsY

sludge and related model compounds in primary degradation region were illustrated on Figure 8.15 and 8.16. Distinct characteristics of volatiles released according to reaction temperatures and types of samples could be observed in TGA-FTIR spectra collected. Main functional groups detected in TGA-FTIR system included O-H, N-H, C-O, C-H, H-C≡N and C=C groups. Gaseous compounds identified were methane (CH₄), carbon dioxide (CO₂), carbon monoxide (CO), water vapour (H₂O), ammonia (NH₃), hydrogen cyanide (HCN), and carbonyl sulphide (COS).

Broad and multiple apparent peaks at 3032-2876cm⁻¹ observed for CsY-EE comparable to lipids model compounds indicated presence of C-H functional groups from different compounds with diverse chemical structures. Peaks for CH₄ at 3016cm⁻¹ and C=C groups at 950cm⁻¹ were also identified in EE and lipids. C-O groups at 1032cm⁻¹ identified in EE and asolectin. For WE and sucrose, comparable peaks at 3016cm⁻¹ for CH₄, 2359cm⁻¹ for CO₂, 2173cm⁻¹ for CO, 1541cm⁻¹ for H₂O and 1176cm⁻¹ for C-O groups were observed. However additional peaks at 966cm⁻¹ for NH₃, 712cm⁻¹ for HCN and 2066cm⁻¹ for COS could also be observed during pyrolysis WE because of highly complex composition with nitrogen and sulphur containing compounds as suggested in biomass composition analysis in Chapter 6. Therefore, representation of WE could be improved with additional nitrogen and sulphur model compounds based on further analysis on compounds identification of WE. With more than 40% in icf of proteins in EFR, TGA-FTIR spectra showed high similarity to whey isolates in peaks identified suggested compatibility of model compound to represent proteins mixture in sludge. However, relative absorbance for NH₃ and HCN were significantly lower because of volatiles contribution on CO₂, CO, H₂O and CH₄ from other sludge components such as cellulose, xylan, polysaccharides and lignin. Thermal degradation of model compounds for lignocellulosic biomass also showed gas evolution characteristics comparable to previous pyrolysis research where hemicellulose released higher yield of CO₂, cellulose produced relatively more CO while lignin generated significant amount of CH₄ (Yang et al., 2007). 1176cm⁻¹ for C-O groups were also detected at low temperature for both EFR and glycogen. For AHR and ADR, mainly C-H, CH₄, CO₂, CO and H₂O were identified with relatively low absorbance because of low organic contents and low degradation rates in wide temperature

region. C=O groups at 1792cm^{-1} and C-O groups at 1107cm^{-1} were identified in cellulose probably caused by condensable volatile compounds but not identified in AHR. Strong CH_4 peak at 3016cm^{-1} and C-O groups at 1033cm^{-1} were identified for lignin. In general, products released during pyrolysis for model compounds were comparable to sludge biomass components with deviations observed caused by complex composition in sludge. TGA-FTIR spectra of sludge biomass components also showed improved resolutions and peaks identification when compared to direct analysis on sludge.

Figure 8.15: TGA-FTIR spectra for pyrolysis of (a) CsY-EE, (b) asolectin, (c) cholesterol, (d) glyceryl tripalmitate, (e) CsY-WE and (f) sucrose.

Figure 8.16: TGA-FTIR spectra for pyrolysis of (a) CsY-EFR, (b) whey isolates, (c) glycogen, (d) cellulose, (e) xylan and (f) lignin.

TGA-FTIR spectra of CsY and synthetic sludge were showed in Figure 8.17. Qualitative and semi-quantitative comparison on FTIR spectra for synthetic sludge and CsY showed highly similar characteristics. Ten selected peaks identified in TGA-FTIR spectra at (a) 3032 cm^{-1} (C=C-H), (b) 3016 cm^{-1} (CH_4), (c) 2974 cm^{-1} (C-H), (d) 2359 cm^{-1} (CO_2), (e) 2173 cm^{-1} (CO), (f) 1541 cm^{-1} (H_2O), (g) 1176 cm^{-1} (C-O), (h) 966 cm^{-1} (Ammonia), (i) 951 cm^{-1} (C=C) and (j) 712 cm^{-1} (HCN) were compared in Figure 8.18. Absorbance measured were normalised to the mass of organic matters presence in the CsY and synthetic sludge samples respectively. At low temperature of around 200°C , only water vapour and carbon dioxide were significantly detected and accompanied by small amounts of carbon monoxide, ammonia and C-O containing compounds for both synthetic sludge and CsY

comparable to the findings in Chapter 5 and previous study (Hernández et al., 2013). All ten identified peaks could be clearly observed when temperature elevated to about 250°C agreed well with the first apparent peak showed in DTG profiles. Absorbance of C=C functional groups and HCN increased significantly from about 200°C and reached plateau at around 300°C for both samples and further increased at above 400°C for CsY. Release of water vapours gradually increased as temperature elevated to 500°C. Release of water vapour during pyrolysis could be caused by dehydration of organic components (Conesa et al., 1998). Dehydration of hydrated inorganic compounds in sludge could also contribute to the release of water vapour as suggested by comparison made for the FTIR spectra of sludge samples and char solids. Peaks identified in solids FTIR spectra at 3700cm⁻¹ corresponding to O-H functional groups for inorganic compounds reduced in absorbance as temperature increased and diminished from the solids residues collected after pyrolysis at 500°C. Since synthetic sludge consisted of insignificant amount of inorganics, the release of H₂O was lower than CsY. CO₂, CO, C-O functional groups and NH₃ detection reached maximum at temperature region from 300°C to 400°C corresponding to the second apparent peak in DTG profiles. Synthetic sludge released more CO at lower temperature than CsY agreed well with the relatively higher degradation rates in DTG profiles at 280-320°C. 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 recalcitrant organic matters, non-biodegradable materials and char residues decomposed (Biagini et al., 2006). In general, TGA-FTIR results of synthetic sludge and CsY were highly similar by qualitative comparison and comparable with slight variations in semi-quantitative comparison.

Figure 8.17: TGA-FTIR spectra for pyrolysis of (a) CsY and (b) synthetic sludge.

Figure 8.18: Peaks identified on TGA-FTIR spectra of CsY and synthetic sludge pyrolysis. (a) 3032 cm⁻¹ (C=C-H), (b) 3016 cm⁻¹ (CH₄), (c) 2974 cm⁻¹ (C-H), (d) 2359 cm⁻¹ (CO₂), (e) 2173 cm⁻¹ (CO), (f) 1541 cm⁻¹ (H₂O), (g) 1176 cm⁻¹ (C-O), (h) 966 cm⁻¹ (Ammonia), (i) 951 cm⁻¹ (C=C) and (j) 712 cm⁻¹ (HCN).

8.4. Conclusions

Model compounds were characterised based on thermal degradation behaviours and products evolution. Results showed distinctive characteristics for different categories of biomass composition. Similarities and variations were also observed among components within the category. Simulations were also carried out successfully based on data measured for individual components indicated applicability of superposition principle and suggested potential benefits to construct a library database for common organic compounds to be used as a reference tool. Thermal degradation behaviours and products evolution analysis provided important information on characteristics of isolated sludge biomass components. By comparing the results obtained for sludge to model compounds selected, compatibility of model compounds to represent sludge biomass components was determined and discussed based on categorisation proposed in this thesis. In general, acceptable representation was achieved with discrepancy identified for further improvement on biomass composition analysis and model compounds selection. Synthetic sludge was formed and analysed. Reduced random errors on multiple heating rates TGA-DTG data and improved consistency (SD_m reduced by 65.20% in average) in kinetics study could be observed by using synthetic sludge as compared to real waste sample collected. Comparable products evolution observed on TGA-FTIR spectra of volatiles released for CsY and synthetic sludge also supported the applicability of synthetic sludge. Hence, synthetic sludge was formed with acceptable representation to collected real waste sample based on biomass composition analytical procedure and model compounds selection method proposed. Formation of synthetic sludge provided an alternative tool to analyse and understand thermochemical characteristics of sludge with reduced heterogeneity and random errors. Individual components in sludge could be studied separately for more precise and comprehensive understanding of conversion sludge in thermochemical systems. Synthetic sludge with modifiable composition could be used as research tool for complex modelling and performance study since the characteristics of feedstock could be manipulated as a control parameter.

9. Conclusions and Recommendations

This thesis reported a comprehensive analytical study of sludge for application in thermochemical conversion processes. Significant findings were summarised and recommendations for future work were suggested in this chapter.

- Sludge generated from Water Reclamation Plants in Singapore could be classified as suitable feedstock for thermochemical conversion processes.
- Qualitative similarities and quantitative variations were observed for 14 different sludge samples collected based on type, plant and batch categorisation in the aspects of thermochemical characteristics, thermal degradation behaviours, products evolution, pyrolysis yield distributions, organic and inorganic composition.
- Presence of comparable main components with varying amounts in sludge as a waste mixture and caused difficulties to directly identify distinctive impacts of sludge composition on thermal treatment system.

Characterisation study for advanced thermochemical conversion processes

- Comprehensive characterisation determined and compared thermochemical properties of sludge collected at various stages (P, S, R, D and Y) and generated from different sources of wastewater and plants (U, C, J and K).
- Oxidation of inorganic components during ash forming and quantification analysis caused significant deviations on oxygen contents determination ($O_{\text{Difference}}/O_{\text{Total}} = 0.68 \pm 0.11$), char residues analysis ($FC = 10.51 \pm 3.32\%$ and $FR = 18.71 \pm 3.47\%$) and inorganic contents ($IM = 19.65 \pm 8.44\%$, $TI = 22.42 \pm 9.28\%$ and $Ash_{950} = 27.86 \pm 9.50\%$) for sludge.
- Alternative parameters included fixed residues (FR), inorganic matters (IM) and total inorganic contents (TI) and bases for comparison included inorganic matters free basis (imf) and total inorganic contents free basis (icf) were proposed for better estimation, reliable comparison and improved understanding on thermochemical characteristics of sludge.

- Different parameters and quantification methods should be applied for incineration, pyrolysis and gasification respectively due to differences in operating conditions and reacting environments.

Thermal degradation behaviours and products evolution analysis

- Complementary results obtained by analytical and experimental pyrolysis provided comprehensive understanding on thermal degradation behaviours and products evolution from sludge.
- Poorly separated TGA mass loss curves, random variations of DTG degradation rate profiles and varying of char residues formation suggested heterogeneity in composition of sludge significantly affected thermal degradation behaviours observed.
- For all the sludge samples analysed, primary degradation could be observed at 150-500°C and secondary degradation found to be occurring at 500-950°C.
- Components in sludge were thermally degraded at different temperature regions with varying degradation rates, products evolution and competitive reactions included formation of char and carbonization of volatiles therefore resulted in the variations of apparent activation energy, volatile compounds released and pyrolysis yield distributions.
- Thermal degradation behaviours and products evolution of sludge found to be determined by operating conditions and feedstock characteristics.
- Understanding on reaction mechanisms and modelling of sludge in thermochemical conversion systems would need to consider both operating conditions and feedstock characteristics in detail.

Biomass composition analysis

- Biomass composition analytical procedure was developed and used to satisfactorily quantify and categorise main components presence in sludge with improved estimations for protein contents and heat capacity of sludge.

- Based on calculated mean values on inorganic contents free basis (icf), sludge samples consisted of $11.27 \pm 4.70\%$ of EE, $12.81 \pm 4.97\%$ of WE, $31.98 \pm 6.61\%$ of proteins, $5.97 \pm 2.30\%$ of AHR, $17.14 \pm 7.19\%$ of ADR, and $20.83 \pm 9.73\%$ of OOM.
- Correlation analysis identified the impacts of organic composition on physical and chemical properties of sludge.
- Characterisation of components isolated from sludge showed distinctive properties as compared to the initial sludge samples collected.

Simulation study on thermochemical properties

- Distinctive characteristics for model compounds from different categories of biomass composition were observed.
- Specific characteristics and contributions on sludge physical and chemical properties by individual biochemical components were estimated.
- Thermochemical characteristics of sludge were simulated with good agreements and expected variations as compared to the measured data.
- Acceptable representation was achieved with discrepancy identified for further improvement on biomass composition analysis and model compounds selection.

Formation of synthetic sludge

- Simulations were successfully performed based on data measured indicated applicability of superposition principle and suggested potential benefits to construct database on thermochemical characteristics and thermal degradation behaviours for organic compounds to be used as a reference tool for model compounds selection to represent complex waste mixtures.
- Components in sludge could be studied separately for more precise and comprehensive understanding of conversion in thermochemical systems.

- Reduced random errors on multiple heating rates TGA-DTG and improved consistency (SD_m reduced by 65.20% in average) in kinetics study were observed by using synthetic sludge as compared to sludge collected.
- Comparable products evolution observed on TGA-FTIR spectra of volatiles released for CsY and synthetic sludge supported the applicability of synthetic sludge with acceptable representation to collected waste sample.
- Formation of synthetic sludge provided an alternative tool to analyse and understand thermochemical characteristics of sludge with reduced heterogeneity and random errors.
- Synthetic sludge with modifiable composition could be used as research tool for complex modelling and performance study since the characteristics of feedstock could be manipulated as control parameters.

Recommendations

Recommendations for future work were made based on the findings in this study.

- Detailed components analysis for different categories of biomass composition in sludge could further improve and optimise model compounds selection to represent the biomass components in sludge.
- Thermochemical analytical study and performance analysis for main components in sludge could be carried out individually in selected thermal treatment system based on methodology developed in this study.
- Separate study of inorganic compounds degradation with primary and secondary degradation region of organics to improve kinetics parameters estimation and models development.
- Models for thermochemical systems to account for engineering parameters and feedstock composition with corresponding interactions in the system could be further developed.
- Synthetic sludge could be applied in performance study with composition considered as modifiable parameters by adjusting the recipe according to the targeted waste sludge.

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Appendix A: Supporting materials for kinetics analysis

Figure A1: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for UR

Figure A2: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for UD

Figure A3: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for CP

Figure A4: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for CS

Figure A5: $\ln(\beta \, da/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for CY

Figure A6: $\ln(\beta \, da/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for JR

Figure A7: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for JD

Figure A8: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for KR

Figure A9: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for KD

Figure A10: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for UsR

Figure A11: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for UsD

Figure A12: $\ln(\beta \, da/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for CsP

Figure A13: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for CsS

Figure A14: $\ln(\beta \, d\alpha/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) for CsY

Figure A15: $\ln(\beta \, da/dT)$ vs $1/T$ (Friedman) and $\ln\beta$ vs $1/T$ (OFW) synthetic sludge

Table A1: Activation energy of UR and UD at $0.20 < \alpha < 0.80$.

Conversion α	UR				UD			
	Friedman		OFW		Friedman		OFW	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	188.5	26.0	154.5	23.0	169.6	59.5	132.7	48.9
0.25	203.2	25.3	164.6	19.2	180.6	62.9	143.7	49.9
0.30	213.7	29.1	176.5	18.1	195.5	61.1	155.1	51.3
0.35	217.7	32.3	184.3	18.8	220.3	55.5	175.6	50.9
0.40	223.1	33.4	191.4	19.7	232.0	51.0	194.6	48.4
0.45	225.4	31.2	197.6	19.7	240.2	51.7	206.5	46.0
0.50	222.7	24.8	201.4	17.7	255.7	59.8	219.4	49.6
0.55	219.2	16.2	201.6	13.3	268.9	72.7	234.7	60.7
0.60	224.8	13.4	202.1	7.9	273.3	75.9	247.5	68.1
0.65	247.7	17.0	217.9	10.3	297.9	76.1	271.6	72.3
0.70	257.4	18.6	233.3	12.5	315.7	88.9	287.9	80.5
0.75	269.0	15.3	249.3	12.6	347.5	135.0	306.8	108.2
0.80	273.9	20.4	257.4	13.3	133.7	313.8	143.0	223.9
Mean $\pm$ SD	229.7 $\pm$ 25.2		202.4 $\pm$ 30.7		240.8 $\pm$ 61.3		209.2 $\pm$ 58.2	

Table A2: Activation energy of UsR and UsD at $0.20 < \alpha < 0.80$.

Conversion α	UsR				UsD			
	Friedman		OFW		Friedman		OFW	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	189.7	30.3	149.6	31.7	249.1	106.6	209.4	103.4
0.25	195.4	16.2	160.2	21.3	282.9	92.5	234.9	86.0
0.30	187.7	17.0	161.3	12.2	312.6	89.3	258.3	78.7
0.35	175.2	24.3	154.5	14.9	328.4	92.8	275.6	78.9
0.40	163.4	28.8	146.7	20.3	339.1	94.3	286.3	80.8
0.45	157.5	29.6	140.7	23.7	357.5	103.0	300.5	86.7
0.50	153.9	31.2	137.9	25.6	380.7	130.2	316.2	103.3
0.55	151.1	34.1	135.8	27.5	398.5	205.6	319.0	152.4
0.60	140.3	43.4	133.0	30.4	252.4	347.4	204.8	254.5
0.65	106.0	59.2	117.8	35.4	-60.7	360.8	-28.9	234.6
0.70	93.0	61.3	90.7	42.3	-192.2	308.6	-156.0	251.5
0.75	138.9	59.2	100.4	51.8	-347.8	233.6	-247.7	186.0
0.80	185.2	89.6	130.6	71.9	-243.0	75.0	-125.2	53.7
Mean $\pm$ SD	156.7 $\pm$ 31.6		135.3 $\pm$ 21.6		158.3 $\pm$ 266.6		142.1 $\pm$ 203.6	

Table A3: Activation energy of JR and JD at $0.20 < \alpha < 0.80$.

Conversion α	JR				JD			
	Friedman		OFW		Friedman		OFW	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	203.0	29.1	156.9	30.4	204.5	107.6	157.9	74.6
0.25	222.7	26.1	174.5	25.4	157.7	128.0	134.2	93.6
0.30	235.8	26.5	190.1	20.9	129.8	128.3	113.4	98.7
0.35	242.3	29.3	201.3	18.3	96.5	131.0	91.9	99.5
0.40	243.8	35.0	208.7	19.0	50.6	130.9	63.5	94.7
0.45	238.2	40.5	210.5	23.3	18.5	114.9	33.3	81.0
0.50	229.5	44.3	208.4	28.1	38.1	98.6	30.3	77.2
0.55	210.5	50.3	201.1	32.9	79.2	97.9	50.1	89.4
0.60	184.2	52.7	182.0	38.0	127.5	114.3	87.0	108.9
0.65	195.3	45.0	180.7	38.3	128.4	146.2	112.2	123.6
0.70	203.4	52.3	189.7	41.8	15.5	178.0	48.0	115.6
0.75	185.6	76.0	181.9	53.5	-74.9	95.2	-29.0	67.2
0.80	55.5	96.8	81.1	69.3	48.4	114.0	13.8	82.0
Mean $\pm$ SD	203.8 $\pm$ 49.3		182.1 $\pm$ 34.1		78.4 $\pm$ 73.3		69.7 $\pm$ 52.5	

Table A4: Activation energy of KR and KD at $0.20 < \alpha < 0.80$.

Conversion α	KR				KD			
	Friedman		OFW		Friedman		OFW	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	133.0	119.5	113.1	101.5	223.9	119.7	194.1	105.8
0.25	146.6	123.2	121.8	102.3	240.4	115.0	206.6	100.3
0.30	157.5	129.9	130.4	107.7	226.2	118.2	224.4	100.9
0.35	164.5	130.3	141.4	110.6	291.3	125.2	246.6	105.5
0.40	176.6	132.1	151.7	110.8	309.0	128.8	267.2	109.0
0.45	195.8	152.1	158.8	119.8	324.6	128.0	285.6	109.4
0.50	195.4	190.1	152.4	143.2	342.4	133.7	304.2	110.9
0.55	157.0	244.1	120.4	171.5	351.2	158.0	314.2	123.2
0.60	-57.3	288.5	-6.2	111.9	349.7	203.3	311.4	157.8
0.65	-184.0	169.9	-111.3	119.0	308.3	271.3	290.2	220.4
0.70	-145.4	124.0	-129.6	107.2	263.1	294.4	248.6	250.7
0.75	-108.6	136.6	-109.8	137.1	225.2	420.8	193.7	338.8
0.80	-68.0	183.9	-52.4	164.3	-507.5	318.6	-335.7	236.7
Mean $\pm$ SD	58.7 $\pm$ 145.3		52.4 $\pm$ 115.1		226.8 $\pm$ 225.8		211.6 $\pm$ 170.0	

Table A5: Activation energy of CP, CS and CY at $0.20 < \alpha < 0.80$.

Conversion α	CP				CS				CY			
	Friedman		OFW		Friedman		OFW		Friedman		OFW	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	176.6	37.0	149.4	30.8	131.5	43.8	112.5	24.8	358.5	142.8	309.5	128.2
0.25	177.9	36.9	150.7	27.4	132.8	41.4	113.6	28.1	411.4	134.8	347.2	119.6
0.30	182.7	36.0	154.6	25.2	136.9	35.5	117.4	28.7	464.2	135.6	395.5	116.4
0.35	185.6	35.7	159.7	24.0	139.6	30.9	122.1	27.6	491.6	135.1	430.3	114.6
0.40	184.2	36.1	162.1	23.6	139.4	30.0	125.3	26.6	515.2	124.1	455.5	105.7
0.45	184.0	37.3	163.5	24.0	135.1	30.9	126.7	25.8	563.1	118.7	489.4	99.3
0.50	186.4	45.1	164.4	27.0	127.9	38.9	125.9	25.8	676.0	135.5	568.5	108.9
0.55	189.8	61.0	165.9	35.5	111.5	49.8	121.6	27.5	936.0	247.2	775.6	193.1
0.60	186.7	80.5	163.3	50.6	69.8	73.5	107.9	31.8	1295.6	715.4	1116.9	593.3
0.65	181.3	99.9	160.4	69.8	6.1	74.6	69.1	35.2	608.6	1197.6	566.8	1053.2
0.70	175.3	105.9	158.2	86.1	17.5	51.2	45.4	30.6	-730.7	1237.1	-626.3	1108.7
0.75	183.0	112.7	167.3	96.7	60.6	35.9	45.7	31.0	-929.8	640.3	-756.8	567.8
0.80	193.3	144.7	174.4	112.7	69.0	39.5	57.7	34.3	-507.2	141.3	-328.2	112.1
Mean $\pm$ SD	183.6 $\pm$ 5.1		161.1 $\pm$ 6.8		98.3 $\pm$ 48.1		99.3 $\pm$ 32.1		319.4 $\pm$ 648.7		288.0 $\pm$ 539.5	

Table A6: Activation energy of CsP, CsS and CsY at $0.20 < \alpha < 0.80$.

Conversion α	CsP				CsS				CsY			
	Friedman		OFW		Friedman		OFW		Friedman		OFW	
	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m	Mean	SD _m
0.20	176.7	22.6	150.2	18.0	181.4	163.6	140.0	133.9	203.0	69.1	168.9	58.0
0.25	171.8	24.8	146.0	18.1	199.0	188.1	159.7	150.1	208.7	71.1	177.5	55.8
0.30	171.8	30.1	143.1	20.7	218.0	190.3	182.1	161.2	207.2	72.0	180.7	55.8
0.35	174.8	34.0	143.1	25.2	234.7	188.9	205.6	165.3	207.2	70.4	183.7	55.3
0.40	175.9	34.4	145.2	28.3	254.2	182.8	229.0	162.4	206.0	74.9	183.3	56.1
0.45	173.4	35.1	146.7	30.0	269.2	174.0	248.6	155.9	204.7	85.2	182.1	61.4
0.50	173.7	35.7	147.9	31.0	280.3	164.5	262.1	147.6	194.2	103.6	176.0	72.1
0.55	175.1	40.3	150.2	32.8	299.1	157.8	273.1	140.5	154.1	118.4	150.5	86.0
0.60	176.4	50.4	151.1	37.6	325.0	162.1	287.7	139.5	148.2	107.4	137.9	90.0
0.65	182.8	64.8	153.6	47.2	354.0	186.4	300.3	148.8	174.1	108.3	150.9	97.2
0.70	185.3	82.0	158.0	64.2	392.7	289.9	305.2	209.2	217.5	115.5	184.6	106.0
0.75	191.2	97.9	164.5	80.2	-170.3	385.1	-100.7	292.4	265.2	162.2	221.7	133.7
0.80	191.0	145.0	156.6	109.7	-79.7	307.3	-51.2	244.7	86.5	357.1	82.6	237.0
Mean $\pm$ SD	178.5 $\pm$ 6.8		150.5 $\pm$ 6.3		212.1 $\pm$ 162.2		187.8 $\pm$ 128.6		190.5 $\pm$ 42.8		167.7 $\pm$ 32.9	