Energy recovery from sewage sludge using hydrothermal processing

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ENERGY RECOVERY FROM SEWAGE SLUDGE
USING HYDROTHERMAL PROCESSING

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
2015

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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2015

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ABSTRACT

Hydrothermal conversion technology represents a more sustainable technique to convert wet sewage sludge to biofuels since prior thermal drying process is eliminated. Previously, extensive studies have been devoted to supercritical water gasification of sewage sludge for hydrogen production. However, harsh supercritical water conditions could result in severe corrosion and high operating cost. Therefore, the present study has performed comprehensive investigations on direct energy recovery from dewatered sewage sludge (DSS) using hydrothermal processing under sub- and near-critical water.

Hydrothermal carbonization (HTC) process has been successfully applied to convert DSS into hydrochars at 200 °C with prolonged residence time. Different carbonization times are adopted in order to produce hydrochars possessing better fuel properties. Uniform brown hydrochars with good grindability and nut-like smell are produced after HTC. The dehydration and decarboxylation reactions are found to be essential reaction pathways. Hydrochars possess a fuel ratio much higher than that of DSS due to higher fixed carbon and lower volatile matter. Specifically, 60% of nitrogen and sulfur can be removed while 88% of carbon is retained and higher heating values of hydrochars are 0.98-1.03 times of DSS, resulting in a cleaner solid fuel. Prolonging carbonization time could reduce the total content of surface oxygen containing functional groups and make hydrochars highly hydrophobic. On the other hand, HTC has altered patterns of main combustion decomposition from a single stage for DSS to two stages for hydrochars. The first order combustion reaction of DSS and hydrochars is verified and kinetic parameters are derived. Hydrochar obtained after 8 h of carbonization is a better fuel in terms of easier and more stable combustion.

To shorten the HTC process, hydrothermal conversion of DSS within 20 min has been conducted under various sub- and near-critical water conditions. Effects of

moisture content and CaO additive are also examined in near-critical water. Increasing temperature and pressure reduces energy recovery rate, however, more significant decarboxylation and dehydration reactions lead to production of solid fuel with high quality. The results suggest that decarboxylation reaction dominates hydrothermal conversion of DSS while intense dehydrogenation and methanation reactions initiate when approaching near-critical water. Mineralization of heteroatomic compounds and dissolution of metals or mineral elements are observed. Under higher temperature and pressure, except increased destruction of organic compounds, heavy metals or mineral elements are prone to be immobilized whereas dehalogenation is promoted. Higher moisture content favors decarboxylation and hydrolysis reactions. Nevertheless, it reduces H₂ and CH₄ yield. Introduction of CaO additive has some positive effects on H₂ yield, hydrolysis of organic compounds, and immobilization of inorganic elements. At 380 °C and Ca/C molar ratio of 0.2, H₂ yield increases almost 6-fold, resulting in 58% H₂ and 26% CH₄ in final fuel gas. However, CaO additive has detrimental effects on the calorific value of solid fraction.

Systematical co-combustion of hydrochar with different coals has been studied towards efficient utilization of hydrochar in existing co-firing power plants. Hydrochar derived under 320 °C and 12.0 MPa (SHC-320) has been screened for co-combustion with different rank coals. SHC-320 reduces activation energy of blends and alters main combustion profiles. Meanwhile, blending SHC-320 may induce greater heat loss for higher rank coals, whereas higher portion ($\geq 70\%$) of SHC-320 further improves ignition reactivity of high rank coal blends. Blending SHC-320 leads to higher heat loss to high rank coals in main co-combustion. In high temperature region, pre-exponential factor value increases with elevated Coal/SHC-320 ratios, resulting in more intense synergistic effects in blends. Under a low Coal/SHC-320 ratio (30:70), intense anti-synergistic effects occur in co-combustion with low or high rank coals. Due to distinct synergistic

interactions, co-combustion with moderate rank coal achieves the best combustion performance and highest burn out efficiency among blends.

The fate of nitrogen during hydrothermal conversion of DSS has been investigated and a novel system integrating hydrothermal deamination and air stripping has been successfully developed to effectively remove and recover nitrogen from DSS for the first time. The overall nitrogen transformation reactions and conversion pathways have been elucidated. In particular, three characteristic hydrothermal regimes contributing to deamination are identified. CaO has been identified as an effective and economical catalyst to accelerate hydrothermal deamination. It can not only accelerate deamination of stable protein-N, pyrrole-N, and pyridine-N, but also favor transformations of protein-N and quaternary-N to nitrile-N and pyridine-N, respectively. The coupled air stripping process demonstrates good performance to remove and recover ammonia from liquid fraction via ammonium sulfate. Based on an ideal scale-up, 51.93 kg N could be removed and 37.27 kg N would be recovered from 1 tonne dry mass of this DSS containing 60.12 kg N.

To conclude, this study gives a better understanding on direct energy recovery from DSS using hydrothermal conversion under sub- and near-critical water. Under very low temperature, HTC could convert DSS to an alternative solid fuel from the perspectives of fuel characteristics and combustion performance. A holistic understanding of reaction chemistry contributes to the design of hydrothermal conversion of DSS under mild conditions. These findings also offer valuable insights into co-combustion scenario for sludge derived solid fuel with coals and effective strategy for N control during sustainable DSS management in future applications.

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LIST OF IMPORTANT SYMBOLS AND NOMENCLATURE

k	Rate constant
α	Thermal conversion fraction
E	Activation energy
A	Pre-exponential factor
R	Universal gas constant
β	Heating rate
n	Order of reaction
$f(\alpha)$	General expression of the reaction mechanism
S	Comprehensive combustibility index
MC_e	Approximate equilibrium moisture content
SR	Solid residues recovery rate
LR	Liquid residues recovery rate
RE	Recovered energy as hydrochar
ERR	Energy recovery rate as hydrochar
TG	Weight loss
DTG	Rate of weight loss
$M_{\text{TRm-N}}$	Total N mass removed from dewatered sewage sludge
$E_{\text{H-N}}$	N removal efficiency during hydrothermal conversion
$E_{\text{S-NH}_4^+}$	Ammonium removal efficiency via air stripping process
$M_{\text{TRc-N}}$	Total mass of recovered N via $(\text{NH}_4)_2\text{SO}_4$
$R_{\text{TRc-N}}$	Overall N recovery rate via $(\text{NH}_4)_2\text{SO}_4$

LIST OF IMPORTANT ABBREVIATIONS

APR	Aqueous phase reforming
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halender
CAPR	Catalytic aqueous phase reforming
CGE	Carbon gasification efficiency
CHG	Catalytic hydrothermal gasification
COD	Chemical oxygen demand
FC	Fixed carbon
FE-SEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatograph
GC/MS	Gas chromatograph/Mass spectrometry
GE	Gasification efficiency
HHV	Higher heating value
HGE	Hydrogen gasification efficiency
HO	Heavy oil
HPLC	High performance liquid chromatography
HRTEM	High resolution transmission electron microscopy
HTC	Hydrothermal carbonization/conversion
ICP-OES	Inductively coupled plasma optical emission spectrometer
LHV	Lower heating value
PHY	Potential hydrogen yield
SCW	Supercritical water
SCWG	Supercritical water gasification
SCWO	Supercritical water oxidation
TDN	Total dissolved nitrogen
TOC	Total organic carbon
TGA	Thermogravimetric analysis

VM	Volatile matter
WGS	Water-gas shift reaction
WWTPs	Wastewater treatment plants
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

CHAPTER 1 INTRODUCTION

1.1 Background

Sewage sludge is a semi-solid residue generated from wastewater treatment plants (WWTPs). Wastewater treatment system is generally integrated with a series of physical, chemical, and biological treatment units. After anaerobic digestion, the sludge is subjected to conventional mechanical dewatering which can reduce the moisture content to around 80 wt.%. Sewage sludge is rich in organic matter and nutrients (such as nitrogen and phosphorus) and mainly composed of proteins (~40%), lipids (10–25%), carbohydrates (14%), lignin and ash (30–50%) ADDIN EN.CITE (. Depending on the characteristics of wastewater sources and wastewater treatment process, heavy metals (i.e. Cd, Cr, Cu, Zn, Pb, Ni, and As), pathogens or other microbiological pollutants, persistent organic pollutants (POPs) (i.e. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins, pesticides, nonyl phenol, and linear alkyl sulfonates, etc.) (Rulkens, 2008) can be entrained in sewage sludge, posing potential risks to environment and human health if it is not appropriately treated.

Due to urbanization and increasingly stringent regulations for the quality of discharged water, the sludge generation from WWTPs is soaring worldwide. At present, the annual production of dry sludge in European Union is more than 10.96 million tons (Kelessidis and Stasinakis, 2012) and sludge production in China is estimated to reach 6 million dry tons per year (Liu, F. et al., 2012). Moreover, the cost used for sludge treatment represents almost 50% of the total capital cost of wastewater treatment process (Campbell, 2000). Therefore, a wide variety of sludge treatment technologies have been implemented, including three main categories, landfill disposal, land application, and incineration.

Landfill disposal not only occupies plenty of land but also generates a large volume of landfill leachates and gases resulting from the high moisture and organic matter contents in sewage sludge. The landfill leachates and gases can incur pollutions to surrounding water, air, and soil. Sometimes, the landfill site may even collapse due to insufficient strength of sludge. Moreover, metabolites in the leachates can be more toxic than its precursors (Kamler and Soria, 2012). Composting is a prominent technology for land application. However, the odour control is problematic both in the processing stage and storage areas (Campbell, 2000). Oleszczuk (2008) reported composting could significantly increase the toxicity of sewage sludge, which may be associated with the increased mobility and bioavailability of metabolites (Kamler and Soria, 2012). On the other hand, the market for composted sludge is a prerequisite. Thus, suitable revenue for the composting facilities is required and more outlets for the final compost should be developed (Campbell, 2000). Given migrations of heavy metals and organic pollutants, it may not be advisable to use sewage sludge derived compost for land application. Furthermore, due to the high calorific value in sludge (i.e. higher heating values for dry sewage sludge before and after digestion around 23 MJ/kg and 8.5–17 MJ/kg, respectively), energy recovery from sludge has attracted great attention recently (Fonts et al., 2012). The potential energy in sludge could be recovered using either biological or thermochemical processes. In particular, incineration can dramatically reduce the sludge volume. Nonetheless, before being fed into incinerator, the moisture content of sludge should be lowered down to 35% during pre-drying step, leading to high energy consumption (Kamler and Soria, 2012).

To eliminate prior energy-intensive drying process, hydrothermal conversion technology has been introduced to recover energy from wet biomass waste. Recently, direct supercritical water gasification of sewage sludge has been

extensively investigated, however, most of the research work is focused on the activated sludge with solid content less 5 wt.%, which will not be suitable for practical treatment. Moreover, gas yield decreased with increasing solid sludge concentration, whereas char/coke in solid residues increased to 10% as a result of severe carbonization (Xu, Z. R. et al., 2012). Therefore, the present study contributes to an in-depth investigation on hydrothermal conversion of dewatered sewage sludge under mild conditions (i.e. sub- and near-critical water). Besides, combustion of derived clean solid fuel and transformation of N-containing compounds in sewage sludge are elucidated.

1.2 Objectives

In this study, hydrothermal processing technology has been applied to directly recover energy from dewatered sewage sludge (DSS) under sub- and near-critical water conditions towards sustainable sludge treatment and utilization. The schematic research framework is shown in Figure 1.1 and the specific objectives are summarized as follows.

Objective 1 is to investigate the effect of residence time on physicochemical properties (e.g. fuel characteristics and surface properties) and combustion behavior of hydrochar solid fuel obtained from hydrothermal carbonization of DSS under a very low temperature (Chapter 3).

Objective 2 is to determine the effects of reaction conditions (i.e. temperature and pressure, moisture content) and calcium oxide additive on hydrothermal conversion of DSS under sub- and near-critical water conditions (Chapter 4).

Objective 3 is to screen hydrochar of superior fuel quality for co-combustion of different rank coals, which could benefit strategy design of co-combustion based on existing co-firing power plants (Chapter 5).

Objective 4 is to understand the fate of nitrogen during hydrothermal conversion of DSS and develop a system to efficiently remove and recover N from DSS in order to reduce considerable emissions of N-containing pollutants during re-utilization of sludge derived fuel (Chapter 6).

Figure 1.1 Schematic research framework.

1.3 Organization of the thesis

The thesis consists of seven chapters. **Chapter 1** gives a brief introduction that incorporates the research background information, scope and objectives, and the structure of this thesis. **Chapter 2** exhibits a comprehensive literature review on hydrothermal conversion and gasification processes, including (1) effects of operating conditions, oxidants and intermediates; (2) hydrothermal conversion of biomass model compounds and sewage sludge for hydrogen production; and (3) catalytic hydrothermal gasification. **Chapter 3** presents the conversion of DSS

to clean solid fuel using hydrothermal carbonization under a low temperature with prolonged residence times. The fuel characteristics and combustion behavior of hydrochars produced are systematically investigated. **Chapter 4** discusses the effects of reaction conditions (i.e. temperature and pressure, moisture content) and calcium oxide additive on hydrothermal conversion of DSS under sub- and near-critical water conditions. Specifically, evolution of gas products, distribution of solid and liquid products, fuel characteristics of solid products and corresponding energy recovery rates, and water characteristics of liquid products are extensively examined. **Chapter 5** describes the co-combustion performance of DSS derived hydrochars with different rank coals. Effect of subcritical water on combustion profiles and characteristics of hydrochars are discussed. Three Chinese coals of different ranks are blended with selected hydrochars of superior fuel quality under various blending scenarios. Synergistic and anti-synergistic effects are investigated to benefit co-combustion design in existing co-firing power plants. **Chapter 6** elucidates the fate of nitrogen during hydrothermal conversion of DSS and demonstrates a novel system integrating hydrothermal deamination and air stripping processes to significantly remove N from DSS and efficiently recover the N as ammonium sulfate. Effects of temperature/pressure and calcium oxide additive on hydrothermal deamination are discussed in details. The nitrogen transformation reactions and conversion pathways during hydrothermal deamination are proposed and detailed elaborated. Performances of air stripping process and this hybrid system are evaluated in terms of ammonium removal efficiency and overall N recovery rate. **Chapter 7** summarizes the main findings throughout this thesis and provides some recommendations for future study.

CHAPTER 2 LITERATURE REVIEW*

Hydrothermal conversion is a thermochemical process to reform biomass in hot compressed water. Under elevated temperature and pressure, specifically when exceeding the critical point (374.3 °C and 22.1 MPa) of water, the density, static dielectric constant and ion dissociation constant of water drop drastically, which can accelerate the reaction rate substantially (Akiya and Savage, 2002). Due to those superior properties of hot pressurized water, it acts as a non-polar solvent and benign reactant with high diffusivity, excellent transport properties and solubility. Consequently, hydrothermal conversion technology has been widely applied for fuels and chemicals recovery from wet biomass and organic waste with high moisture content in the last two decades. As shown in Figure 2.1a, hydrothermal conversion can be divided into (1) hydrothermal carbonization (180–250 °C) for hydrochar production (Funke and Ziegler, 2010; He et al., 2013), (2) hydrothermal liquefaction (about 200–370 °C, with pressures between 4 and 20 MPa) for heavy oil production and (3) hydrothermal gasification (near-critical temperatures up to about 500 °C) (Peterson et al., 2008) to generate hydrogen rich gas under various conditions. From the perspectives of fossil energy shortage and environmental impacts, renewable hydrogen recovery from readily available wet biomass using hydrothermal gasification is desired in the long run. Kruse (Kruse, 2008) summarized previous research work relating to supercritical water gasification (SCWG) of biomass without heterogeneous catalysts whereas Elliott (2008), Guo et al. (2010b) and Azadi et al. (2011) reviewed catalytic sub- and supercritical water gasification of biomass for hydrogen production. In recent years, more efforts have been made to explore strategies to enhance hydrogen yield and carbon gasification efficiency during

* This chapter is written based on my review article “Hydrothermal gasification of sewage sludge and model compounds for renewable hydrogen production: A review”, *Renewable and Sustainable Energy Reviews* (2014).

hydrothermal conversion of biomass or wastes. Up-to-date information and comprehensive summary are imperative to highlight technical and economic feasibility of hydrothermal gasification technology for wet biomass waste management system, especially sewage sludge, algae, and food wastes. This review covers three main parts: (1) effects of operating conditions, oxidants and intermediates on the hydrothermal gasification efficiency; (2) hydrothermal conversion and gasification of biomass model compounds and sewage sludge for hydrogen production; and (3) updates of catalytic hydrothermal gasification. Based on abovementioned aspects, perspectives relating to hydrothermal gasification of sewage sludge are presented.

2.1 Hydrothermal conversion technology

During conventional steam reforming of biomass to produce desired light gases, tar and char as well as higher hydrocarbons are greatly formed (Antal et al., 2000). In 1985, Modell (1985) initiated the SCWG process of maple wood sawdust without char formation. The mechanism of SCWG of biomass was described as a process involving hydrolysis of biomass in supercritical water (SCW) followed by further gasification of the produced aqueous oligomers (Azadi et al., 2011; Minowa et al., 1998). Since SCWG of biomass is regarded as a high-pressure steam reforming, pre-drying could be avoided. Due to high solubility of water under SCW conditions, intermediates derived from biomass decomposition can be dissolved. As a consequence, remarkably reduced tar and coke formation can be expected in SCWG compared to classical gasification process (Guo et al., 2010b; Kruse et al., 2003). Contrasting to the high temperature of conventional gasification (e.g. $> 800\text{ }^{\circ}\text{C}$), SCWG of biomass materials is typically conducted at temperatures lower than $600\text{ }^{\circ}\text{C}$ (Azadi et al., 2012). Table 2.1 summarizes the advantages and assessment criteria of SCWG. Though SCWG of biomass is a complex process, the involved chemical reactions can be described by reactions

(1) – (5) in Table 2.2 (Guo et al., 2007).

2.1.1 Role of water

Under normal temperature and pressure, water can exist in the form of ice, liquid, and vapor. When the temperature and pressure are elevated to above the critical point (374.3 °C and 22.1 MPa), water goes into supercritical state, where the gas and liquid phase become miscible (Figure 2.1a) (Shanableh, 1990).

Figure 2.1b illustrates the physical properties of water as the temperature increases under constant pressure 25.3 MPa. Water density decreases with the increase of temperature and a drastic decrease is observed at the critical temperature, resulting in broken hydrogen bonds in water. As a consequence, dielectric constant of water decreases from approximately 80 (at normal temperature and pressure) to 5 (at critical point) (Guo et al., 2010b). Dielectric constant is used to measure the polarity and solubility of the fluid. Lower dielectric constant reflects the high solubility of organic solvent and the low solubility of inorganic compounds (Zhang, 2011). Due to these unique properties, SCW has been regarded as an attractive reaction medium.

Figure 2.1 Hydrothermal conversion options (a) and physical properties of water in subcritical, near-critical, and supercritical conditions at 25.3 MPa (b) (adapted from Kruse (2008); Peterson et al. (2008); Zhang, L. et al. (2010b)).

2.1.1.1 Acid/base catalysis and source of free-radicals

Below the critical point, ion product of water increases with elevated temperature by three orders of magnitude from $K_w = 10^{-14} \text{ mol}^2/\text{L}^2$ at 25 °C to $K_w \approx 10^{-11} \text{ mol}^2/\text{L}^2$ at 300 °C. Above this temperature, K_w decreases drastically to $10^{-20} \text{ mol}^2/\text{L}^2$ at 380 °C (Möller et al., 2011). In subcritical water, ionic reactions are generally reinforced because of the higher concentrations of H^+ and OH^- . Because of high water density in subcritical water, hydrolysis is more preferable. Thus, high molecular weight compounds can be hydrolyzed to smaller fragments and dissolved into water for further oxidation and gasification (He et al., 2008) as a result of the acid/base catalysis of subcritical water. Water in hydrothermal conditions not only acts as reaction medium and reactant, but also as acid/base catalysts. The chemistry of acid/base catalysis and oxidation reactions for selective conversion of biomass to value-added products under hydrothermal conditions is given in a detailed review (Jin and Enomoto, 2011). Besides, water was regarded as a catalyst in SCW for hydrogen production from formic acid degradation via decarboxylation and dehydration in reactions (2.6) and (2.7) (Sinağ et al., 2004).

In contrast to hydrolysis, free-radical reactions are favorable in low water density so that free-radical reactions dominate under high temperatures. Free-radical mechanism is composed of generation of radicals and fast free-radical reactions (Guo et al., 2010b). Hydroxyl radical, known as the most effective oxidant, is of great importance in supercritical water oxidation (SCWO). Reactions (2.8) – (2.13) which can form OH radicals significantly contribute to overall kinetics. Because the formed H_2O_2 in reaction (2.13) can subsequently generate two OH radicals, the less reactive oxidant hydroperoxyl radical (HO_2) can effectively generate three OH radicals in the presence of water (Akiya and Savage, 2002).

Table 2.1 Some major advantages and assessment criteria of SCWG for hydrogen production.

Advantages (Kruse et al., 2005; Resende, 2009; Yong and Matsumura, 2012)	Assessment criteria (Lu et al., 2012)
Energy-intensive prior drying is not required.	Gas yield (i.e. total gas yield, H ₂ yield, CH ₄ yield)
Pressurized H ₂ rich fuel gas is more convenient for further applications.	Molar fraction of product gas
Rapid and effective conversion reduced tar can be achieved.	Gasification efficiency (GE)
Gas cleaning process is avoided and heteroatoms (N, S, and halogens) containing substances are left in liquid phase.	Carbon gasification efficiency (CGE)
Compact SCWG batch or continuous reactor can save space.	Hydrogen gasification efficiency (HGE)
Inorganic elements in feedstocks in solid residues or liquid phase can be further recovered.	Potential hydrogen yield (PHY)

Moreover, the delocalization of π -electrons by substitution of hydroxyl groups makes benzene rings readily cleaved to form small molecular weight compounds. In addition, heteroatoms can be also removed from the precursors at the same time. Ogunsola and Berkowitz (1995) reported H radicals donated by SCW reinforced saturation of heterocyclic rings, which subsequently opened to form hydrocarbons, sulfides, and NH₃. Thus rupture of $-C-S=$ and $-C-N=$ bonds in heterocyclic ring by SCW hydrolysis can eliminate more N and S than pyrolysis and common hydrolysis.

2.1.1.2 Reactant and source of hydrogen

Apart from the role of water in acid/base catalysis, hydrolysis, and free-radical reactions, water also plays a critical role in hydrogen production as a catalyst and reactant. Park and Tomiyasu (2003) investigated SCWG of organic compounds in D₂O using RuO₂ as the catalyst. The CD₄ and D₂ in the gas products indicated all the H atoms originated from water. Kruse (2008) summarized the hydrogen and methane formation from glucose in reactions (2.14) and (2.15). It can be deduced from the equations that H₂ formation is water dependent while CH₄ formation is water independent. Actually, Kruse et al. (2003) reported that the hydrogen originating from water in SCWG could be as high as 50%.

Table 2.2 Summary of chemical reactions involved in Chapter 2 (Akiya and Savage, 2002; Gadhe and Gupta, 2005; Gadhe and Gupta, 2007; Guo et al., 2007; Kruse, 2008; Sinađ et al., 2004; Sinađ et al., 2003; Susanti et al., 2012; Zhang, L. et al., 2011b).

Reaction type	Stoichiometric reaction equation	Reaction number
Simplified overall reaction of SCWG	$\text{CH}_x\text{O}_y + (2 - y)\text{H}_2\text{O} \rightarrow \text{CO}_2 + (2 - y + x / 2)\text{H}_2$	(2.1)
Steam reforming	$\text{CH}_x\text{O}_y + (1 - y)\text{H}_2\text{O} \rightarrow \text{CO} + (1 - y + x / 2)\text{H}_2$	(2.2)
Water-gas shift reaction	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2, \Delta H_{298\text{K}} = -41.0 \text{ kJ / mol}$	(2.3)
Methanation of CO	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}, \Delta H_{298\text{K}} = -206.2 \text{ kJ / mol}$	(2.4)
Methanation of CO ₂	$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}, \Delta H_{298\text{K}} = -165.0 \text{ kJ / mol}$	(2.5)
Decarboxylation	$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$	(2.6)
Dehydration	$\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$	(2.7)
Formation pathways of OH radicals	$\text{H}_2\text{O} + \text{M} \rightleftharpoons \text{OH} + \text{H} + \text{M}, (\text{M represents a collision partner})$	(2.8)
	$\text{H}_2\text{O} + \text{H} \rightleftharpoons \text{OH} + \text{H}_2$	(2.9)

Hydrogen formation route

Methane formation route

Overall reaction for SCWG of glucose

Methanol decomposition

Catalytic mechanism of K_2CO_3 in SCWG

2.1.2 Effect of temperature, pressure, and residence time

Both of ionic and free-radical reactions occur in hydrothermal environment but they are dependent on the properties of water under various temperatures and pressures. Due to the high ion product of water, ionic reactions dominate below critical point of water (Güngören Madenoğlu et al., 2013). Above the critical point, free-radical reactions are favored with hydrogen as the typical product (Promdej and Matsumura, 2011). The reaction mechanism is shifted from ionic reactions in the subcritical water to the free-radical reactions in SCW region (Matsumura et al., 2005). Since the free-radical reactions are not affected by the properties of water, such as dielectric constant and ion product, the Arrhenius behavior is expected. However, as a result of the change of dielectric constant or ion product, the ionic reaction deviated from Arrhenius behavior (Promdej and Matsumura, 2011).

In reactions (2.14) and (2.15), hydrogen formation is endothermic while CH_4 formation is slightly exothermic. According to the Le Chatelier principle, hydrogen formation is more favorable at high temperatures while CH_4 formation is preferred at high pressures (Kruse, 2008). In SCWG of corn cob and sodium carboxymethylcellulose (CMC), influences of experimental parameters on hydrogen yield exhibited the order of temperature > pressure > feedstock concentration > residence time (Lu et al., 2012). As the residence time increased, hydrogen yield and CGE increased while CO yield decreased. Longer residence time can realize complete gasification of biomass which is expected within seconds when temperature is above 600 °C (Kamler and Soria, 2012).

In Figure 2.2, the yields of hydrogen and CO_2 increased with elevated temperature ranging from 480 to 750 °C under 28 MPa, especially above 660 °C

(Lee et al., 2002). However, the yield of CO gradually built up to a maximum value at 660 °C and decreased afterwards, which was supposed to be associated with the consumption of CO in water-gas shift reaction. Subsequently, Güngören Madenoğlu et al. (2013) investigated simultaneous effects of temperature and pressure on hydrothermal gasification of glucose under 400–600 °C and 20–42.5 MPa within one hour. They found that CGE increased with the increasing temperature and decreased with increasing pressure. Compared to the effect of pressure, temperature plays a more important role in gas composition, which could be explained by the drastic decrease of dielectric constant of water at higher temperature but only a slight increase of that with increased pressure. Decreased yields of H₂ as well as CO₂ and increased yield of CH₄ with increasing pressure under a constant temperature were attributed to methanation reaction. Overall, yields of H₂, CH₄, and CO₂ increased at higher temperatures.

Figure 2.2 Effect of temperature on (a) gas yield and (b) gasification efficiency in SCWG of glucose at 28 MPa and a 30 s residence time (adapted from Basu (2010); Lee et al. (2002)).

In the catalytic hydropyrolysis of glucose at 500 °C and 30 MPa, where glucose was used as model compound for cellulosic biomass, Sinağ et al. (2004) demonstrated that the heating rate has a considerable influence on intermediates and products (Figure 2.3). As the heating rate increased, yields of gas and formic acid increased while the yield of furfural decreased. Based on the assumption that

formic acid was an intermediate of water-gas shift, higher gas yield may be associated with high yield of formic acid which suggested a higher water-gas shift activity. Furfural was suggested to be formed under subcritical conditions and may polymerize to form tar which was regarded as undesirable by-product. Therefore, slow heating rate decreased hydrogen yield due to the formation of coke/char (Matsumura et al., 2005).

2.1.3 Effect of oxidants on partial oxidative gasification

The addition of oxidants can improve the CGE. However, hydrogen yield cannot be constantly enhanced without limitation. Lu et al. (2012) reported the hydrogen yield during gasification of corn cob and CMC decreased with the addition of KMnO_4 while that in glucose gasification increased initially and then decreased with the increase of H_2O_2 concentrations.

Due to competing pathways between gasification and oxidation reactions, oxidant concentration is an important parameter to optimize hydrogen production in SCWG (Guo et al., 2010a). Hydrogen yield was enhanced in partial oxidative SCWG of n-hexadecane by introduction of O_2 with O/C of 1.0 whereas the H_2/CO_2 ratio was decreased which may result from H_2 combustion with excess O_2 (Watanabe et al., 2003). It is worth noting that SCWG reaction is an endothermic reaction while oxidation is an exothermic process. Guo et al. (2010a) reported that a small amount of oxidant accelerated hydrogen production but excess oxidant may result in combustion of H_2 and CO. Therefore, an appropriate amount of oxidants should be determined to improve gasification efficiency and hydrogen yield in SCWG of specific feedstock.

Figure 2.3 Effects of heating rate and catalysts on products distribution of supercritical water gasification of glucose (adapted from Sinağ et al. (2004)).

2.1.4 Effect of by-products/intermediates

Though tar and coke are reduced in SCWG compared to conventional pyrolysis, coke formation is commonly observed, especially during the heating up, causing reduction of the CGE (Müller and Vogel, 2012).

Onwudili and Williams (2009) presented the simplified mechanistic scheme of hydrothermal gasification of biomass in Figure 2.4 and pointed out that the conversion of hydrolysis products is critical during hydrothermal gasification. Because of the competition between dehydration route and gasification route, tar and char can be formed when water soluble products were dehydrated rather than retaining the hydrolysis products and converting them to hydrogen through gasification.

Figure 2.4 Mechanistic scheme of hydrothermal gasification process (adapted from Onwudili and Williams (2009)).

Therefore, tar and coke formation has been investigated during the degradation of glucose, cellulose, and other carbohydrates under hydrothermal conditions. 5-hydroxymethylfurfural (5-HMF) was confirmed to be an intermediate for the coke formation in SCWG of glucose under 300–400 °C and 25 MPa (Chuntanapum and Matsumura, 2010). Müller and Vogel (2012) examined tar and coke formation in hydrothermal processing of glycerol in a temperature range of 300–430 °C at 30 MPa. They found that coke was formed in subcritical temperatures (especially under 350–370 °C) with longer residence time while phenols and hydroquinone can be ruled out as the precursors of coke formation.

Acetic acid was the most refractory intermediate in SCW, which was reported to be stable above 600 °C (Susanti et al., 2012). During SCWG of glucose above 740 °C, only acetic acid in liquid effluents was detected whereas 42 compounds were found at 600 °C in the absence of catalysts. Phenol can also be very stable in SCWG. Guo et al. (2012) reported SCWG of methanol was significantly

retarded by acetic acid and phenol. Although acetic acid inhibited HGE, decarboxylation of HAc to CH₄ and CO₂ resulted in a great increase of CGE.

2.2 Hydrothermal conversion and gasification of biomass model compounds

2.2.1 Hydrogen production

Hydrogen is widely used in ammonia and methanol syntheses, fuel cells, hydrotreating and hydrogenation processes (Azadi et al., 2012). Due to lower cost of fossil fuels, coal gasification is currently the most important industrial hydrogen production process. To lessen the dependence on fossil fuels, hydrothermal gasification of wet organic waste has been developed to generate hydrogen by maintaining water in the slurry feedstocks via exerting increased pressure. Aqueous phase reforming (APR) is a process typically conducted under 175–265 °C and 3.4–5.6 MPa (de Vlieger et al., 2012b). Cortright et al. (2002) demonstrated APR of oxygenated hydrocarbons (i.e. sugars and alcohols) to generate hydrogen rich fuel gas using platinum-based catalysts. Using a high throughput batch reactor, Huber et al. (2003) discovered a non-precious metal catalyst, which was prepared by adding Sn to Raney-Ni catalysts, to significantly suppress the rate of methane formation while retaining the rate of hydrogen production. However, the hydrothermal stability of Raney-NiSn is a major concern when employed in SCW.

In order to make APR commercially viable, increased reaction rates are desired by increasing the temperature to near-critical or supercritical conditions. Meanwhile, as the objective of SCWG is hydrogen production, the increased temperature may also increase the undesired alkanes formation, thereby decreasing hydrogen yield (de Vlieger et al., 2012b). Hence, effective catalysts for selective hydrogen production under SCWG of biomass are required.

Hydrogen is generated from reforming reactions via C–C cleavage followed by water-gas shift while alkanes are mainly formed via C–O cleavage followed by hydrogenation. Effective catalysts should possess high activities in C–C cleavage and water-gas shift with suppressed C–O cleavage (Davda et al., 2005). The catalytic hydrothermal gasification process for hydrogen production will be discussed in details in Section 2.3.

2.2.2 Hydrogen production from biomass model compounds

Recently, many researchers have used lignocellulosic biomass and biomass model compounds as feedstocks in hydrothermal gasification for hydrogen production. These studies provided fundamental information on application experience and mechanism of hydrothermal gasification process. However, the main organic compounds in sewage sludge are carbohydrates, proteins, lipids, and lignin, which can be decomposed to a mixture of furfurals, alcohols, carboxylic acids, aldehydes, amino acids, fatty acids, benzenes, and phenols under hydrothermal conditions (Figure 2.5). It is necessary to understand hydrothermal decomposition and gasification of simple model compounds before discussing the feasibility and performance of hydrothermal gasification of sewage sludge for hydrogen production. Furthermore, control strategies to maximize hydrogen yield and selectivity may be applicable for sewage sludge.

2.2.2.1 Carbohydrates

Cellulose and hemicellulose are carbohydrates in biomass. Since products distribution from hydrothermal conversion of glucose are almost the same as that of cellulose, glucose is proved to be the primary hydrolysis product of cellulose (Kruse, 2008). Thus, glucose is widely used as a biomass model compound in SCWG. The decomposition pathways of glucose and fructose under 300–400 °C and 25–40 MPa with a residence time of 0.02–0.2 s are depicted in Figure 2.6

Figure 2.5 Main organic components in sewage sludge and corresponding hydrolysis monomers under hydrothermal conditions.

(Kabyemela et al., 1999). The products from glucose decomposition were fructose (from isomerization), 1,6-anhydroglucose (from dehydration), erythrose and glyceraldehyde (from C–C bond cleavage). Reverse aldol condensation and double bond rule were responsible for the C–C bond cleavage. Knežević et al. (2009, 2010) also conducted hydrothermal conversion of glucose under 300–350 °C with longer residence time ranging from 10 s to 10 d. Water production predominated in the first 5 min whereas gas and char were favored afterwards. Water and solvent soluble products formed a polymerized oily component with lower oxygen content than glucose, leading to a 50% increase in energy density. The overall theoretical reaction for SCWG of glucose is summarized in reaction (2.16). Susanti et al. (2012) investigated the non-catalytic SCWG of glucose at 600–767 °C with residence time of 15–60 s. The maximum hydrogen yield of 11.5 mol H₂/mol glucose could be achieved at 767 °C and 25 MPa with the glucose concentration of 1.8 wt.%, which was quite close to the theoretical value of 12 mol H₂/mol glucose in reaction (2.16).

Figure 2.6 Reaction pathways of glucose in sub- and supercritical water
(adapted from Kabyemela et al. (1999)).

The rapid hydrolysis of cellulose to glucose and oligomers is the first reaction step of phyto biomass (Kruse and Gawlik, 2003). However, hydrolysis of cellulose is changed from heterogeneous on the cellulose crystal surface to homogeneous above the critical point of water (Resende, 2009). The conversion rate of hydrolysis products under subcritical conditions was faster than hydrolysis of cellulose, while hydrolysis of cellulose under supercritical conditions was more than one order of magnitude faster than decomposition of hydrolysis products of cellulose. Thus, higher hydrolysis products yield was found in supercritical water than in SCW (Sasaki et al., 1998). A simplified reaction scheme of cellulose is shown in Figure 2.7. High ion product of water in subcritical water resulted in more furfural production and low gas yield. The furfural could be either dissolved or polymerized to form coke. On the other hand, gas yield increased under supercritical water because of the free-radical reactions. Based on non-catalytic gasification of cellulose in SCW (Resende et al., 2007),

cellulose loading and water density are two effective variables controlling the gas product selectivity. At 500 °C and 0.08 g/m³ water density, CH₄/H₂ molar ratio decreased remarkably from 18.93 to 0.76 when the cellulose loading was increased from 5 to 33.3 wt.%.

Figure 2.7 Interactions of cellulose and proteins in hydrothermal gasification (adapted from Kruse et al. (2007)).

Hemicellulose is a copolymer composed of pentose, hexose, and uronic acid units (Pińkowska et al., 2011). Xylan is used as a model substance for hemicellulose in SCW. Similar to decompositions of glucose and fructose in SCW, retro-aldol condensation and dehydration contributed to the overall reaction rate (Matsumura et al., 2006). Strategies for SCWG of cellulose can be applied for hemicellulose.

2.2.2.2 Lignin

Carrier et al. (2012) have reported that carbohydrates produced five carbon-containing compounds (cyclopentanones, furfurals and cyclopentenones), while six carbon-containing compounds (phenols, guaiacols, benzene) were derived from lignin under sub- and supercritical conditions (Figure 2.8). High lignin

content had an adverse effect (Yoshida and Matsumura, 2001) whereas high alkali salts had a positive effect (Kruse et al., 2000) on the hydrogen yield in SCWG. The interactions between lignin and intermediates from cellulose/xylan decreased hydrogen yield via hydrogen donation. Moreover, cellulose generates higher hydrogen during SCWG, while lignin is prone to produce more CH₄. CH₄ fraction was increased as the water density increased by manipulating the pressures during SCWG of alkylphenols (model compounds of lignin) catalyzed by Ru/ γ -Al₂O₃ (Sato et al., 2003). Resende et al. (2008; 2007) investigated the non-catalytic SCWG of cellulose and lignin in quartz capillary reactors with a concentration of 9 wt.% and 0.08 g/cm³ water density at 600 °C. Comparison of gas compositions in syngas from cellulose and lignin showed that CH₄/H₂ ratio increased with higher lignin loading but decreased with higher cellulose loading. Interestingly, CH₄ and CO₂ were the major products in non-catalytic SCWG of lignin. More CH₄ formation was probably related to the cleavage of methyl in lignin structure whereas less methyl substituents are contained in cellulose. The higher CO₂ yield in cellulose than lignin may be attributed to 49 wt.% O in cellulose and only 27 wt.% O in lignin.

Figure 2.8 Degradation pathways of lignin, holocellulose and cellulose in sub- and supercritical water (adapted from Carrier et al. (2012)).

2.2.2.3 Phenols

Phenols, which originate from lignin and carbohydrates in biomass, are rather inert in SCWG. As a result, the degradation of phenols becomes problematic for complete gasification of biomass and thus it has attracted extensive research attention (Kruse, 2008). A small amount of phenol can significantly diminish hydrogen yield and gasification efficiency of glucose even under 24 MPa and 400–550 °C (Weiss-Hortala et al., 2010). Similar to proteins (Kruse et al., 2005; Kruse et al., 2007), this negative effect on SCWG may be attributed to the role of phenol as a free radical scavenger.

Higher dry matter loading can increase phenol yield and therefore hinder the complete SCWG of biomass (Kruse et al., 2003). By adding KOH, more than 99% gasification rate of pyrocatechol was obtained at 700 °C in 1 min (2000). In addition, introducing a small amount of oxidants in SCWG is another effective way to achieve nearly complete conversion. Xu et al. (2011) reported a maximum hydrogen yield of 0.245 mol/mol phenol with molar ratio of 46.2% was obtained at 500 °C when an oxidation coefficient (oxidant added/oxidant needed for complete oxidation) of 0.6 within 3 min was employed in the presence of Na_2CO_3 . Guan et al. (2011a; 2011b) investigated the partial oxidative gasification of phenol in SCW and proposed the following reactions pathways (Figure 2.9): (1) phenol oxidation, (2) acid oxidation, (3) acid gasification, and (4) gaseous products interconversion. Based on the abovementioned mechanism, the derived kinetic model fitted the experimental data very well in terms of predominant reactions and gaseous products distribution. Complete decomposition of phenol cannot be achieved but lower concentrations of oxygen could enhance the acid gasification and water-gas shift by inhibiting the oxidation process.

Figure 2.9 The pathways of partial oxidation of phenol (adapted from Guan et al. (2011a)).

2.2.2.4 Proteins and amino acids

As proteins account for a large portion in sewage sludge, it is essential to understand the decomposition of proteins or amino acids in hydrothermal conditions. Subcritical water technology is considered as an effective method to extract amino acids from proteinaceous waste via the hydrolysis of proteins. Sato et al. (2004) investigated the behavior of five selected amino acids (alanine, leucine, phenylalanine, serine, and aspartic acid) in hydrothermal conditions under 200–430 °C at 20 MPa. The overall decomposition of amino acids followed first order reaction. Two main reaction pathways of these amino acids were identified: (1) decarboxylation to produce carbonic acid and amines; and (2) deamination to produce ammonia and organic acids as in the case of aspartic acid. In addition, interconversion of amino acids from hydrolysis of proteins may take place. Under saturated subcritical water, the transformation and decomposition of amino acids may be easier due to the decreased overall stability in the mixed amino acids (Abdelmoez et al., 2007). Klingler et al. (2007) demonstrated model compounds of proteins (i.e. alanine and glycine) could be hydrothermally converted into value-added amines under 250–450 °C and 34 MPa with a

residence time of 2.5–35 s.

Apart from subcritical water hydrolysis, SCWG of proteins or amino acids are widely explored. DiLeo et al. (2008) claimed that glycine is more resistant than phenol in SCWG. After SCWG of glycine more than 1 h, glycine was significantly retained in the liquid phase. The CO was found to be the major product gas. Kruse et al. (2005) found that SCWG of protein-containing biomass resulted in an unexpected low gas yield even under a high concentration of alkali salts. Subsequently, Kruse et al. (2007) carried out a comparative hydrothermal gasification of model phyto mass (i.e. glucose + potassium salts) and model zoo mass (i.e. glucose + potassium salts + alanine) to investigate the influence of proteins on product gas composition. It was reported that the addition of alanine into glucose/ KHCO_3 decreased gas yield and increased the CO yield as well as dissolved organic carbon (DOC) in liquid solution. It is assumed that Maillard reaction occurred in the presence of proteins, which resulted from the interaction of degradation products of carbohydrates and proteins. The nitrogen containing compounds from interactions of amines and aldose sugars via Maillard reaction can further form free radical scavengers. The free radical scavenger is a stable free radical which is not reactive enough to start a free radical chain reaction. However, it can interact with reactive free radicals, thereby reducing the free radicals numbers and inhibiting overall free radical reaction chain. Consequently, the gas yield was reduced while DOC content was increased due to the addition of alanine. The influence of proteins on hydrothermal gasification of carbohydrates is shown in Figure 2.7. As biomass may contain both proteins and salts, increased gas yield resulting from salts catalysis can compensate the negative effect of proteins on gas yield to some extent (Kruse et al., 2007).

2.2.2.5 Alcohols

Alcohols can be formed under hydrothermal conditions (Azadi et al., 2012). Methanol, glycerol, and ethylene glycol are three typical model compounds used in SCWG for hydrogen production. Methanol is the simplest compound for reforming in SCW. Methanol reforming was conducted at 27.6 MPa and 700 °C to produce H₂, CH₄, CO, and CO₂, which was catalyzed by the reactor wall (Gadhe and Gupta, 2005). The results suggested that methanation reactions were favored under high pressures, long residence time, and low steam/carbon ratio. Ni-Cu in the tubular reactor can minimize the CH₄ production. The main reactions in methanol reforming, including methanol decomposition, water-gas shift reaction, and methanation (Gadhe and Gupta, 2007) can be found in Table 2.2.

Due to the complicated functional groups and ring-structure in 5-HMF formed during hydrothermal gasification of glucose, glycerol becomes a simpler and better model compound. Besides, glycerol could partly represent glycerolipids (Azadi et al., 2013). Bühler et al. (2002) investigated hydrothermal decomposition of glycerol in near- and supercritical water under 349–475 °C and 25, 35, or 45 MPa within 32–165 s using a tubular reactor. The main products were methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, CO, CO₂, and H₂. Qadariyah et al. (2011) recently reported the degradation of glycerol in a batch reactor under 200–400 °C and 30 MPa with a reaction time of 20–60 min. They claimed that acetaldehyde and allyl alcohol were only formed in subcritical water and SCW, respectively. Acrolein can be formed in both conditions. The highest glycerol conversion rate of 99.92% can be obtained. SCWG of glycerol for hydrogen production has also been carried out (Azadi et al., 2013; Byrd et al., 2008; May et al., 2010). Compared with other sewage sludge model compounds (i.e. glucose, glycine, lauric acid, and humic

acid), glycerol showed the highest carbon conversion in Raney nickel catalyzed SCWG (Azadi et al., 2013). In the presence of Ru/Al₂O₃, H₂ with low CH₄ and CO was produced at 700–800 °C in a tubular fixed-bed flow reactor within 5 s (Byrd et al., 2008). Complete conversion of glycerol was obtained under 510 and 550 °C with 1 wt.% Ru/ZrO₂, but the complete gasification was not possible as acetic acid and acetaldehyde were difficult to be gasified. The carbon deposits from polymerization of high concentration of acetic acid also reduced hydrogen yield (May et al., 2010).

de Vlieger et al. (2012a) carried out catalytic reforming of ethylene glycol in SCW under 450 °C and 25 MPa using Ir, Pt, and Ni based mono- and bi-metallic catalysts. High Pt loading exhibited highest hydrogen yield while low Pt loading had an adverse effect on hydrogen selectivity and catalyst stability. The primary liquid by-products were methanol, ethanol, and acetic acid (de Vlieger et al., 2012b). The Pt-Ni/Al₂O₃ was suggested to improve hydrogen yield by inhibiting CH₄ production and acetic acid. Since acetic acid was associated with the hydroxylation of the Al₂O₃ support, suppressed acetic acid could prolong the lifetime of catalysts.

2.2.2.6 Lipids

SCWG of oleic acid (C₁₈H₃₄O₂, a model compound for lipids) was conducted at 28 MPa with three temperature levels of 400, 450, and 500 °C (Youssef et al., 2011). At 400 °C, long chain fatty acids were formed via hydrolysis of oleic acid but saturated acids were resistant to hydrolysis below 300 °C. As temperature increased, hydrogen yield increased with the primary liquid products of aromatic and cyclo-compounds formed at 450 °C, but heptanoic and hexanoic acids, cresol, and ketones formed at 500 °C. It was speculated that hydrogen was produced from dehydrogenation processes and water-gas shift. The Diels-Alder cyclization

was responsible for cyclo-compounds formation.

2.2.3 Effect of feedstock nature

Performance of SCWG is closely associated with type and concentration of feedstocks. A wide variety of biomasses, such as lignocellulosic woody biomass, chicken manure, food wastes, fermentation residues, sewage sludge, and algae have been successfully gasified in SCW (Azadi and Farnood, 2011). Conventional lignocellulosic biomass consists of cellulose (38–50%), hemicellulose (25–32%), and lignin (15–25%) (Kumar, 2010). Cellulose and hemicellulose are carbohydrates whereas lignin is a complex compound with high molecular weight and composed of three highly cross-linked phenylpropane units of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol via ether bonds (C–O–C) and C–C bonds (Amen-Chen et al., 2001; Fang et al., 2008). On the other hand, sewage sludge is typically consisted of proteins (40%), lipids (10–25%), carbohydrates (14%), lignin and ash (30–50%) (Goto et al., 1999), and less heavy metals, pathogens or other microbiological pollutants, and POPs. The sewage sludge varies from different sources and processes. For example, the digested sludge contains considerable but recalcitrant organic matter, including lignin compounds (Zhang, L. et al., 2010a). In comparison to sludge from WWTPs, Zhang, L. et al. (2010a) reported that the secondary pulp/paper-mill sludge (SSP) produced high hydrogen yield. Apart from the higher contents of volatile matter and alkali salts therein, a better performance of hydrogen production may also be associated with the high pH value of SSP. Even though some constituents contained in real biomass are similar with pure model compounds, SCWG process may be significantly different due to interactions of different constituents. The existence of sulfur and other minerals can even lead to catalyst deactivation in catalytic hydrothermal gasification process (Azadi and Farnood, 2011).

As the concentration of feedstock increases, carbonaceous deposits from undesired side reactions can lead to a decrease of the hydrogen selectivity in the reforming of glucose (Davda et al., 2005). According to studies of supercritical water partial oxidative gasification under 650 °C and 25 MPa (Jin et al., 2010), the fraction of H₂ decreased from 29.3 to 10.14% and the yield of hydrogen decreased from 8.939 to 1.933 mol/kg when concentrations of glucose was increased from 10 to 24%. This may be associated with limited reaction rates of hydrolysis and water-gas shift. Muangrat et al. (2010) reported that yields of CO, CO₂, CH₄, and C₂–C₄ increased, whereas the hydrogen yield reduced as the feed concentration increased in partial oxidative gasification of food-based biomass. Under this context, it is imperative to gain more insights into relationships between the gas evolution profile and chemical composition of biomass material.

2.3 Catalytic hydrothermal gasification

It is of particular interest to integrate catalytic process into thermochemical biomass conversion process to improve the yield and quality of gas or liquid fuels (Huber et al., 2006). Introduction of catalysts (either homogeneous or heterogeneous) in hydrothermal gasification could achieve good gasification performance under mild temperatures and pressures, lowering the operating cost and equipment investment. Therefore, latest applications of homogeneous and heterogeneous catalysts in hydrothermal gasification are discussed herein.

2.3.1 Homogeneous catalysts

The catalytic effect of alkali salts in improving the water-gas shift has been widely reported in literature. Muangrat et al. (2010) conducted partial oxidative gasification of food-based biomass, including glucose, molasses, and rice bran, with the aid of H₂O₂ in alkali hydrothermal conditions. The tar/oil and char were not found because of the presence of alkali. It was addressed that NaOH had a

positive effect on the hydrogen yield via water-gas shift. By examining cellulose decomposition under catalytic hydrothermal conditions at temperatures from 200 to 350 °C, Minowa et al. (1998) verified the important role of alkali materials (i.e. sodium carbonate) in inhibiting char formation from oil. The addition of alkali salts also increased the H₂ and CO₂ yields but decreased the CO yield (Güngören Madenoğlu et al., 2011; Matsumura et al., 2005). The catalytic effect of the alkali salts can be explained by the improvement of water-gas shift reaction resulting from the formation of formate salt in the presence of alkali salts (Smağ et al., 2003). Smağ et al. (2003) proposed the catalytic mechanism of K₂CO₃ in SCWG in reactions (2.18) – (2.22). Besides, alkali salts can accelerate C–C bond splitting to increase hydrogen production (Güngören Madenoğlu et al., 2013). Recently, Trona (Na₂CO₃·NaHCO₃·2H₂O) was proved to be an economical natural mineral catalyst as effective as K₂CO₃, and it increased the hydrogen yield by seven-fold in SCWG of acorn under 600 °C and 35 MPa (Güngören Madenoğlu et al., 2011).

Apart from aforementioned studies, Onwudili and Williams (2009) also investigated the role of sodium hydroxide in promoting hydrogen production from hydrothermal gasification of glucose and other biomass materials from 200 °C and 2 MPa to 450 °C and 34 MPa at a constant water content. Two different processes for hydrogen formation were proposed: (1) hydrogen gas produced via water gas shift using the CO released from decarbonylation of hydroxylated carbonyl compounds; and (2) hydrogen gas released from the reaction of sodium carboxylate with water. The removal of CO₂ as sodium carbonate or bicarbonate improved the formation of hydrogen gas.

In practice, the trade-off between yield and purity of hydrogen still exists. He and Chen (2012) proposed a one-step sorption-enhanced steam reforming procedure

to improve hydrogen yield and selectivity using dolomite as CO₂ acceptor. Guo et al. (2007) found hydrogen yield in SCWG of cellulose in the presence of Ca(OH)₂ was almost twice of that without catalyst and very low concentrations of CO₂ and CO could be achieved because of CO₂ capture by Ca(OH)₂. The overall SCWG of cellulose with Ca(OH)₂ is described in reaction (2.23).

Though alkali catalysts are effective to promote hydrogen yield, issues pertaining to corrosion, plugging, and fouling may be induced by them (Guo et al., 2010b). In order to achieve a high hydrogen yield with minimized detrimental effects, the optimal alkali content in feedstock is essential.

2.3.2 Heterogeneous catalysts

Compared to homogeneous catalysts, heterogeneous catalysts present higher hydrogen selectivity, CGE, as well as easier recyclability (Guo et al., 2010b). In the past decades, catalytic hydrothermal gasification (CHG) has been extensively explored. Table 2.3 lists studies on CHG of model compounds and real biomass for hydrogen rich gas production using various heterogeneous catalysts in recent years.

2.3.2.1 Nickel catalysts

Due to relatively low cost of nickel catalysts, nickel based catalysts have been extensively applied in petrochemical industries. Cortright et al. (2002) developed APR to convert carbohydrates into H₂ and gaseous alkanes at a low temperature and medium pressure. Resende and Savage (2010) quantified the catalytic effect of metals, including nickel, iron, copper, zinc, and zirconium wires, ruthenium powder, and Raney nickel slurry, on SCWG of cellulose and lignin in quartz reactors. A measurable increase of gas yield can be achieved when using a catalyst surface area to biomass weight ratio higher than 15 mm² /mg. Nickel and copper with a loading ratio of 5.0 wt.% was proved to obtain higher gas yield.

Moreover, nickel with a loading ratio of 1.0 wt.% gave the highest hydrogen yield while copper exhibited no background hydrogen formation in the absence of biomass feedstock under SCWG conditions. The presence of metals had little influence on CH₄ yield. The oxidation of metals is commonly found under hydrothermal conditions. Only nickel and copper can remain reduced in the metallic form among base metals and nickel can be active in numerous formulations whereas the effective lifetimes rely on the support materials (Elliott, 2008). On the contrary, nickel oxide hardly exhibits any catalytic activity.

Raney nickel catalysts are prepared by leaching out aluminum from Ni-Al alloy with concentrated sodium hydroxide to form Ni catalyst with a spongy structure (Azadi and Farnood, 2011). Fresh Raney nickel possesses a specific surface area ranging from 50 to 100 m²/g, which is far higher than that of metal powder and wire catalysts, i.e. <<1 m²/g. In addition, Raney nickel exhibited beneficial hydrogen yield in near-critical water gasification (Azadi et al., 2009). It has been noted that hydrogen selectivity may be enhanced by increasing the metal loading due to the high sensitivity of methanation reaction to metal dispersion. Due to preparation methods, a considerable amount of hydrogen may be stored in Raney nickel, which can be one order of magnitude higher than that chemisorbed on catalyst surface. Under hydrothermal conditions, the release of stored hydrogen as well as that from partial oxidation of nickel by water may cause misleading results of anomalously higher hydrogen in final gas yield (Azadi and Farnood, 2011). Therefore, the examination of background hydrogen formation from catalysts is essential before conducting CHG.

Alkali or alkaline earth metals, such as Na, K, Ca, Mg, Ru, are proved effective to enhance metal dispersion and retard Ni sintering, thus they were previously used as promoters to reduce coke formation in CH₄ reforming with CO₂. Azadi

et al. (2012) summarized the addition of alkali metal (i.e. K, Na, Cs) enhanced the hydrogen selectivity and carbon conversion of Ni/ α -Al₂O₃ while Sn decreased the catalytic activity. Lu et al. (2013) studied the effect of Ce loading in Ni-based catalyst (i.e. Ni/CeO₂/Al₂O₃) on catalytic activity and carbon deposition in SCWG of glucose at 400 °C and 24.5 MPa. Because of the lattice oxygen on the surface of CeO₂, carbon deposition on the catalyst was inhibited and thus catalytic activity was enhanced by adding CeO₂. On the other hand, the surface area of catalysts decreased after the increase of Ce loading, thereby reducing the catalytic activity. As a result, the maximum hydrogen yield and selectivity can be observed at a Ce loading of 8.46 wt.% among the range of 1.22 to 10.83 wt.%. However, noble metal catalysts are found to be very active in SCWG even with a low loading, particularly, ruthenium is more resistant than nickel against oxidation and hydrothermal sintering (Azadi and Farnood, 2011; Elliott et al., 2006).

2.3.2.2 Noble metal catalysts

In the presence of Pt-Ni/Al₂O₃ or Pt/Al₂O₃, de Vlieger et al. (2012b) examined the effects of intermediates, i.e. methanol, ethanol, and acetic acid, on hydrogen selectivity and catalyst stability during the reforming of ethylene glycol. They proposed that higher hydrogen yields resulted from high dehydrogenation activity of Pt-Ni/Al₂O₃ by inhibiting the formation of methane and acetic acid. However, the acetic acid affected the hydroxylation of Al₂O₃ support and caused the migration and coverage of metal particles by Al(OH)₃, thereby deactivating the Pt based catalysts.

Byrd et al. (2008) investigated hydrogen production from SCWG of glycerol with concentration varied from 5 to 40% over Ru/Al₂O₃, 7 mol H₂/mol glycerol could be obtained with diluted feed concentration at 800 °C. Later, Zhang, L. et al.

(2011a) reported Mg and Ru could also be effective promoters for Ni/ γ -Al₂O₃ catalyst to suppress coke and tar formation in SCWG. In the catalytic SCWG of glucose at 700 °C and 24 MPa, the addition of 0.1NiRu/ γ - Al₂O₃ was proved effective in promoting the water-gas shift reaction (Zhang, L. et al., 2011b). It enhanced hydrogen yield by 5-fold to 53.8 mol/kg glucose and decreased the contents of CH₄ and CO from 11.8 vol.% and 28.1 vol.% to 2.9 vol.% and 1.2 vol.%, respectively. The reduction of CH₄ may result from enhanced steam-methane reforming in reaction (24). Moreover, yields of tar and char were significantly suppressed to 0.08% and 0.5%, respectively. Based on the electronic structure calculation and isotopic experiments, Peterson et al. (2012) claimed Ru-based catalysts served for facile interchange of hydrogen atoms between adsorbates and catalyst surface in SCWG.

Table 2.3 Summary of catalytic hydrothermal gasification of model compounds and real biomass for hydrogen rich gas production using various heterogeneous catalysts.

Feedstock	Experimental condition	Reactor type	Catalyst	Experimental results and remarks	Reference
Cellulose, sawdust	500 °C, 27 MPa, 20 min	Stainless steel 316L 140 mL high-pressure autoclave	Ru/C, Pd/C, CeO ₂ particles, nano-CeO ₂ , nano-(CeZr) _x O ₂	The catalytic activity was Ru/C > Pd/C > nano-(CeZr) _x O ₂ > nano-CeO ₂ > CeO ₂ particles; By adding sodium carboxymethylcellulose, the 10 wt.% cellulose or sawdust can be completely gasified.	(Hao et al., 2005)
Lignin	400 °C, 37.1 MPa, water density 0.5	Stainless steel 316 tube bomb	Ru/TiO ₂ , Ru/γ-Al ₂ O ₃ , Ru/C	The initial catalytic activity was high and in the order of Ru/TiO ₂ >	(Osada et al., 2006)

	g/cm ³	reactor		<p>Ru/γ-Al₂O₃ > Ru/C; Ru/C and Ru/γ-Al₂O₃ gradually lost high lignin gasification activities which can be ascribed to decreased surface area and dissolution of ruthenium active sites resulting from phase change of γ-Al₂O₃.</p>	
Methanol	700 °C, 27.6 MPa, < 1 min	Stainless steel 316 tubular reactor	Copper nanoparticles continuously generated from cupric acetate in	In-situ generated copper nanoparticles were highly active in SCWG of methanol in 15 s; The reactor was suitable for sulfur- containing feedstock as sulfur can	(Gadhe and Gupta, 2007)

			feedstock	be removed out by forming Cu ₂ S	
				in the continuous flow reactor.	
Glycerol	700-800 °C, < 5 s	Tubular fixed-bed flow reactor	Ru/Al ₂ O ₃	Ruthenium exhibited high activity for C-C bond cleavage for H ₂ rich gas formation; H ₂ decreased whereas CH ₄ increased as the glycerol concentration was increased to 40%; Short residence time reduced CH ₄ production.	(Byrd et al., 2008)
Polyethylene glycol	390 °C, 24 MPa, 60-300 s	Continuous reactor, Inconel 625	Ni/ZrO ₂	Catalytic activity was 5%Co15%Ni/ZrO ₂ > 5%W15%Ni/ZrO ₂ > 5%Ni/ZrO ₂ >	(Yan et al., 2009)

15%Co/ZrO₂ > ZrO₂ > 15%W

/ZrO₂ > NiO/ZrO₂; ZrO₂ can

suppress methanation reaction and

Ni/ZrO₂ inhibited toxic

intermediates production.

Glucose,	450 °C, 47.1 MPa,	Batch reactor,	RuO ₂	RuO ₂ achieved complete SCWG	(Yamamura et
cellulose,	60 min	Inconel 625,		of cellulose into H ₂ , CH ₄ , and	al., 2009)
sewage		10.8 cm ³		CO ₂ ; RuO ₂ can be deactivated by	
sludge				sulfur compounds.	
Cellulose	SCWG at 400-525	Capillary	Nickel, iron,	All the tested metal (except	(Resende and
and lignin	°C, 10 and 15 min,	quartz reactor	copper, zinc,	copper) produced H ₂ from SCW in	Savage, 2010)
	water density 0.05-		zirconium wires,	the absence of biomass; Catalysts	

	0.18 g/cm ³		ruthenium powder, surface area/biomass weight ratio and Raney nickel was critical in increasing gas yields; 40-50% energy content in cellulose and lignin could be recovered in gas when using nickel wires; Ruthenium powder presented low activity.	
Glucose	600 °C, 24 MPa, WHSV 3.0 and 6.0 h ⁻¹	Continuous-flow tubular reactor	Ni, Ru, Cu and Co supported on γ -Al ₂ O ₃ , ZrO ₂ , and Activated carbon (AC)	Ru and Ni supported on γ -Al ₂ O ₃ showed highest activity and H ₂ selectivity among catalysts investigated; Ni based catalytic activity on support materials for (Zhang, L. et al., 2011a)

H₂ production was γ -Al₂O₃ >

ZrO₂ > AC; Ru and Mg effectively

promoted Ni/ γ -Al₂O₃ by

suppressing coke and tar

formation.

Oleic acid	400-500 °C, 28	Batch reactor,	Ru/Al ₂ O ₃ , Ru/AC,	Catalytic activity for H ₂	(Youssef et al., 2011)
	MPa, 30 min	Hastelloy C-	Pt/AC, Pd/AC,	production was pelletized	
		276, 600 mL	Ni/SiO ₂ -Al ₂ O ₃	Ru/Al ₂ O ₃ > powder Ni/SiO ₂ -	
				Al ₂ O ₃ > powder Pt/AC > granular	
				Ru/AC > powder Pd/AC; Ni/SiO ₂ -	
				Al ₂ O ₃ and Ru/Al ₂ O ₃ achieved 96%	
				and 86% COD reduction	

efficiency, respectively;

Ruthenium favored the methane

formation at the cost of consuming

H₂; Significant deactivation of

Ru/Al₂O₃ and Ru/C were

observed.

Glucose	380 °C, 23 MPa, 15 min	Batch reactor, Stainless steel, 50 mL	Nickel supported on α -Al ₂ O ₃ , carbon nanotubes (CNTs), MgO, SiO ₂ , Y ₂ O ₃ , hydrotalcite,	At 5% Ni loading, carbon conversion followed the order: α -Al ₂ O ₃ , CNT, and MgO > SiO ₂ , Y ₂ O ₃ , hydrotalcite, YSZ, and TiO ₂ ; Different γ -Al ₂ O ₃ supports showed a wide range of catalytic activities	(Azadi et al., 2012)
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			yttria-stabilized zirconia (YSZ), TiO ₂ , γ -Al ₂ O ₃ , zeolites, molecular sieves, CeO ₂ , ZrO ₂	and may not be practically used in SCWG. Increased Ni loading of Ni/ α -Al ₂ O ₃ resulted in an increasing H ₂ selectivity; K, Ca, Cs promoted while Sn decreased the catalytic activity of Ni/ α -Al ₂ O ₃ .	
Water solubles from biomass pyrolysis	350 °C, 20 MPa, LHSV 45 h ⁻¹	Continuous fixed-bed reactor	Ni/C, Ni-Pt/C	Impregnation of Pt into Ni/C improved carbon conversion to higher than 99.9%.	(Idesh et al., 2012)

Ethylene glycol	450 °C, 25 MPa, WHSV 5.9 and 17.8 h ⁻¹	Continuous reactor	Pt-Ni/Al ₂ O ₃ , Pt/Al ₂ O ₃	<p>Pt-Ni bimetallic catalyst enhanced H₂ yield with two-fold higher activity than monometallic Pt catalyst. Addition of Ni prevented sintering of Pt particles.</p> <p>Acetic acid deactivated Pt/Al₂O₃ and Pt-Ni/Al₂O₃ through the hydroxylation of Al₂O₃ support and re-deposition of Al(OH)_x on catalytic Pt sites.</p>	(de Vlieger et al., 2012a)
Ethylene glycol,	450 °C, 25 MPa, 6 h, 2mL/min	Continuous reactor	Pt/CNT	Pt/CNT was a stable and effective catalyst for SCWG of ethylene	(de Vlieger et al., 2012)

Acetic acid				glycol and acetic acid.	
Glucose	400 °C, 24.5 MPa	140 mL	Ni/CeO ₂ /Al ₂ O ₃	Addition of Ni/CeO ₂ /Al ₂ O ₃	(Lu et al.,
		stainless steel		increased H ₂ yield and selectivity	2013)
		autoclave		dramatically due to the role of	
				CeO ₂ in inhibiting carbon	
				formation by increasing Ni	
				dispersion and reacting with	
				deposited carbon.	

2.3.2.3 Screening of catalysts

According to the reaction pathways for CHG of carbohydrates in Figure 2.10, a desired catalyst should exhibit high rates of C–C cleavage and water-gas shift, low rates of C–O cleavage or methanation, and good hydrothermal stability to obtain a higher hydrogen selectivity (Azadi et al., 2012; Davda et al., 2005). Depending on the operation conditions in reforming processes, critical issues associated with catalyst stability include carbon deposition, steaming/oxidation of catalyst, metal sintering, and support degradation (Elliott et al., 1993; Mirodatos et al., 1987).

Figure 2.10 Reaction pathways for catalytic hydrothermal gasification of carbohydrates for hydrogen production (adapted from Azadi et al. (2012); Cortright et al. (2002)).

2.3.2.4 Support materials

Support materials were reported as stable in near-critical and supercritical water, including carbon, such as activated carbon (Elliott et al., 1993; Lee and Ihm, 2009) and carbon nanotube (Azadi et al., 2010), α - Al_2O_3 , rutile TiO_2 , and monoclinic ZrO_2 while all forms of alumina, except α - Al_2O_3 , could react to form boehmite γ - $\text{AlO}(\text{OH})$ (Elliott et al., 2006; Elliott et al., 1993) or α - Al_2O_3 (Osada

et al., 2006). When exposed to SCW for few minutes, α -Al₂O₃ became more crystalline without phase changing (Azadi and Farnood, 2011). However, Zhang et al. (2011a) reported γ -Al₂O₃ was partially transformed to α -Al₂O₃ only in spend Ru/ γ -Al₂O₃ catalyst. Osada et al. (2006) evaluated the stability of various supported Ru catalysts in catalytic gasification of lignin and the order of sequence in initial activity (i.e. Ru/TiO₂ > Ru/ γ -Al₂O₃ > Ru/C) was observed. Zhang et al. (2011a) found the effect of support materials on activity in hydrogen formation followed the order of γ -Al₂O₃ > ZrO₂ > activated carbon, though ZrO₂ exhibited higher stability than γ -Al₂O₃ in SCWG. Carbon nanotube (CNT) is a promising catalyst support material for SCWG of biomass waste (de Vlieger et al., 2012). CNTs are reported to be very stable materials with crystalline nature and open structure, which can enhance the mass transfer and decrease the possibility of coke blockage.

2.3.2.5 Deactivation of catalysts

Char formation has been observed in decomposition of cellulose, glucose, and sugars under sub- and supercritical water. Promoters are often incorporated into nickel based catalysts to prevent carbon deposition. It is the encapsulating carbon rather than the filamentous carbon that should be responsible for the deactivation of catalysts (Cunha et al., 2009; Mattos et al., 2012). Because of nucleic growth of filaments, metal particles can be lifted off the support and thus remain the accessibility to reactants. Compared with nickel, Ni-Cu alloys are more effective for formation of filamentous carbons, in which Cu can inhibit the formation of encapsulating carbon and enhance the stability of Raney-Ni in the methane decomposition at 600 °C (Cunha et al., 2009). Kim et al. (2012) identified that alkyl substituted C5 ring hydrocarbons were responsible for the formation of polycyclic aromatic hydrocarbon which could result in coke formation during decomposition of methylcyclohexane in SCW. During methanol reforming at 700 °C and 27.6 MPa (Gadhe and Gupta, 2007), Cu can be significantly deactivated

by sulfur through the reaction (2.25).

2.4 Sewage sludge treatment using SCW

Because of the high organic matter and water content in sewage sludge, SCWG is an emerging technology suitable for sewage sludge treatment and energy recovery. SCWO is an oxidation process closely related to SCWG, which functions as “wet incineration” in hydrothermal conditions by using strong oxidants (e.g. H_2O_2 , O_2 , and KMnO_4) to completely destruct organic matter in SCW. SCWO was originally developed more than 30 years ago at Massachusetts Institute of Technology for NASA (Kamler and Soria, 2012). Various applications of SCWO have been implemented in defense industry. For instance, the U.S. Navy designed a shipboard SCWO plant to destroy the Navy excess hazardous materials, while the U.S. Army and U.S. Air Force used SCWO for destruction of obsolete nerve gas, biological weapons and other munitions (Crooker et al., 2000; Kamler and Soria, 2012).

2.4.1 Feasibility of SCWG of sewage sludge for hydrogen rich fuel gas

Xu, D. H. et al. (2012) demonstrated the first SCWO pilot plant in China with a treatment capacity of 125 kg/h for sewage sludge harmless treatment. The SCWO showed particular advantages over incineration of sewage sludge in terms of lower operating cost and harmless treatment products. It was pointed out that more byproducts income could further reduce the operating cost. Therefore, optimization of hydrogen yield from SCWG of sewage sludge is of great interest to facilitate the commercialization of this technology.

Meanwhile, Xu, Z. R. et al. (2012) investigated the potential feasibility of direct SCWG of sewage sludge with moisture contents ranging from 76.2 to 94.4 wt.%. However, as the moisture content decreased, total gas yield decreased with a substantial reduction of CO_2 yield and slight reduction of H_2 and CH_4 . It was proved that carbonization process was accelerated in lower moisture content and

thus the obvious reduction of CO₂ yield can be ascribed to the carbon transformation into coke therein. Guo et al. (2007) claimed that higher reaction temperature was required for high concentration feedstocks to achieve complete gasification in SCWG of sludge.

Table 2.4 summarizes the SCWG of sewage sludge with and without catalysts in terms of gaseous composition, carbon/hydrogen gasification rate and hydrogen yield. Most of the studies were focused on the activated sludge with solid content less 5 wt. %, which exhibited hydrogen yield 15.49 mol/kg dry sludge (Chen et al., 2013a) but may not be economical for practical treatment of the huge volume of sewage sludge. The hydrogen production from SCWG is only of significance in industrial application when a solid concentration of sewage sludge higher than 15% is applied. However, for those SCWG of dewatered sludge or digested sludge with solid loading higher than 8 wt.%, the hydrogen yield is limited with lower CGE. In fact, Zhang et al. (2011b) proposed a combined hydrothermal liquefaction of simulated biomass waste and catalytic SCWG of aqueous products from hydrothermal liquefaction to harvest heavy oil and hydrogen rich gas simultaneously. Recently, a pre-liquefaction process of sewage sludge and wood sawdust in subcritical water was found to enhance H₂ and CH₄ yield (Onwudili and Williams, 2013a; Sawai et al., 2013). Since the majority of organic compounds in sewage sludge can be hydrolyzed and dissolved in near-critical water, a two-stage hydrothermal gasification process could be feasible. In the first stage, near-critical water gasification process can hydrolyze the majority of organic compounds in sewage sludge into water soluble products and generate a part of hydrogen. In the subsequent stage, the CHG of aqueous products is employed to generate more hydrogen, where catalysts can be easily recovered via solid-liquid separation thereafter.

Table 2.4 Supercritical water gasification of sewage sludge for hydrogen production with and without catalysts.

Feedstock ^a	T	P	Time and	Reactor	Catalysts	H ₂	CH ₄	CO ₂	CO	Remarks	References
	(°C)	(MPa)	Flow rate	type		(%)	(%)	(%)	(%)		
Digested sewage sludge (2.1 wt.%) + corn starch (5.1 wt.%)	650	28	1.23-1.88 h; 2.0 g/min	Continuous	Coconut shell activated carbon	42	17	39	1	100% CGR ^b	(Xu and Antal, 1998)
Sewage sludge (0.23 wt.%)	450	33	2 h	Batch	- K ₂ CO ₃	49 47	17 15	31 37	3 1	55% CGR 85% CGR	(Schmieder et al., 2000)
Sewage sludge (3.2 wt.%)	450	47.1	2 h	Batch	RuO ₂	56	37	7	-	CGR 11 (%) HGR ^c 23.1	(Yamamura et al., 2009)

										(%)	
Primary sewage sludge (2.8 wt.%)	500	37	1 h	Batch	-	32.3	11.7	48.4	7.6	~2.5 mol H ₂ /kg dry sludge	(Zhang, L. et al., 2010a)
Secondary sewage sludge (4.5 wt.%)					-	20	15.5	55.3	9.2	~1 mol H ₂ /kg dry sludge	
Digested sewage sludge (2.8 wt.%)					-	20	13.6	55	11.4		
Activated sludge (3 wt.%)	380	23	15 min	Batch	-	16	9	69	6	10	(Afif et al., 2011)
					Raney nickel (1.5 g/g feed)	46	25	29	0.1	CGR (%)	58

					Raney nickel (1.8 g/g feed)	36	36	28	0		69	
Dewatered sewage sludge (15.2 wt.%)	400	24.5	1 h	Batch	-	33.1	21.1	44.3	1.5	~1.1 mol H ₂ /kg dry sludge		(Xu, Z. R. et al., 2012)
Digested sewage sludge (8.9 wt.%)	450	25	25 min	Batch	-	~30	~25	~40	~5	~29% CGR; ~3.9 mol H ₂ /kg dry sludge		(Chen et al., 2013b)
Digested sewage sludge (2 wt.%) + CMC (2 wt.%)	540	25	Water flow rate 125	Continuous	-	43.6	-	-	-	H ₂ yield (mol/kg	9.26	(Chen et al., 2013a)
					0.5 wt.% K ₂ CO ₃	52.2	-	-	-		13.98	

Digested sewage						g/min;	-	17.7	-	-	-	dry	1.89
sludge (10 wt.%)						Slurry	0.5 wt. %	26.6	-	-	-	sludge)	2.74
+ CMC (2 wt.%)						flow rate	K ₂ CO ₃						
						25 g/min							
Sewage sludge	450	34	1 h	Batch	2 g NaOH			66.4	17.7	4.64	3.85	74% TOC	(Onwudili et
(2.5 wt.% ^d)					3 g NaOH			76.1	17.8	-	-	removed	al., 2013)

^a: The weight percentage refers to the solid concentration in the feedstock calculated on dry basis. ^b: Carbon gasification rate. ^c: Hydrogen gasification rate. ^d: Calculated as grams TOC per gram liquid sewage sludge sample, assuming the density of liquid sample was 1 g/mL.

2.4.2 Technical and economic evaluation

SCWG is regarded as an emerging technology for sewage sludge treatment as well as hydrogen production. Gasafi et al. (2008) determined the cost of hydrogen production and revenues from sewage sludge disposal using the total annual revenue requirement method. As it can be seen in Figure 2.11, when sewage sludge revenue exceeds 211 €/t dry matter, SCWG is competitive for hydrogen production from natural gas reforming (6.82 €/GJ) while SCWG is comparable to electrolysis (26.82 €/GJ) if the revenue can exceed 62 €/t dry matter. Though SCWG is suitable for hydrogen production of biomass, Calzavara et al. (2005) claimed that technological improvements (i.e. reactor engineering and catalysts) are indispensable for industrial scale-up. Importantly, combustion of methane should be taken into consideration. Due to the great amount of non-reactant water, overall energy efficiencies are 15% and 50% based on LHVs of $H_2 + CO$ and $H_2 + CO + CH_4$, respectively, under the classical recovery efficiency of 80%.

Figure 2.11 Hydrogen production costs vs. sewage sludge revenues, base case (solid line) and learning case (dotted line) (adapted from Gasafi et al. (2008)).

2.5 Limitations and solutions

The review highlights that hydrothermal gasification is a promising technology for hydrogen rich fuel gas production from sewage sludge or other biomass wastes. Nevertheless, three key problems concerning corrosion, plugging and high operating cost still exist, making some commercial scale SCWO of sewage sludge plants inactive (Xu, D. H. et al., 2012). Due to harsh hydrothermal conditions, issues pertaining to hydrothermal gasification must be addressed to make this technology economically and practically feasible in industrial applications. The challenges associated with corrosion, high operating cost, reactor plugging and catalyst deactivation are discussed as follows.

At elevated temperatures and pressures, water can be highly acidic, basic, oxidizing, or reducing in specific hydrothermal conditions. Generally, stainless steel and nickel based alloys are used reactor materials in hydrothermal decomposition. During SCWG of glucose (Sinağ et al., 2004), Ni, Cr, and Mo, which are the constituents of reactor wall, can be detected in the solid phase as a result of corrosion, indicating corrosion of the reactor wall. In addition, heteroatoms in sewage sludge can form corrosive acids in hydrothermal environment. A comprehensive review pertaining to corrosion issues under hydrothermal conditions can be found elsewhere (Kritzer, 2004). Both equipment-based and process-based approaches could be applied for corrosion control. Though hastelloy reactor is highly corrosion-resistant, the high construction cost may be uneconomical. Acceptable corrosion control can be achieved via combination of proper corrosion-resistant materials, chemical control, process control, and mechanical design (Marrone and Hong, 2009).

The severe hydrothermal conditions may hinder wider applications to some extent. Moreover, to achieve complete destruction of biomass with maximum gasification rate, feedstock concentrations less than 5% are generally used, which

could be further increase the operating cost. A series of pre-treatment, chemical conditioning, and CHG should be employed in future investigations to run the hydrothermal gasification under economically reasonable feedstock concentrations and milder temperatures/pressures.

Inorganic alkali salts can be used as homogeneous catalysts in CHG. On the contrary, due to decreased solubility of inorganic compounds, the precipitated salts may cause plugging in the continuous reactor. Besides, high temperatures and pressures can result in metal sintering and phase change of support materials, which shorten the lifetime of catalysts. Sulfur poisoning and coke deposition can also deactivate catalysts. To mitigate these three key issues, the two-stage hydrothermal gasification concept proposed in Section 2.4.1 could be a promising strategy to handle sewage sludge with high solid loading by incorporating catalytic process in the second stage.

CHAPTER 3 Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: Hydrochar fuel characteristics and combustion behavior*

3.1 Introduction

The treatment of sewage sludge (SS) produced from wastewater treatment plants is still an important global issue due to its high moisture content and poor dewaterability. At present, SS has attracted great attention as a promising feedstock for the production of renewable biofuels (Yoshida and Antal, 2009). Pyrolysis-based concept is the main stream of research in converting SS into energy carriers (Park and Jang, 2011; Shao et al., 2007) and adsorption materials (Li, W. H. et al., 2011). As an alternative, the hydrothermal treatment technology is developed to harness energy from SS in the presence of water to avoid the energy-intensive prior drying. The desired products mainly depend on the hydrothermal conditions. Previous studies on hydrothermal processing focused on the production of heavy oil through hydrothermal liquefaction at 250-380 °C (Xu and Lancaster, 2008) and enhanced H₂ yield using catalytic hydrothermal gasification under 380 °C and 23 MPa (Afif et al., 2011). It is not until recently that the hydrothermal carbonization (HTC) regains great attention as a promising technology for efficient wet biomass conversion to biocarbons, although it has been used to simulate natural coalification for over a century (Funke and Ziegler, 2010).

HTC is defined as a thermochemical process used to convert organic feedstock into carbonaceous product (hydrochar) in the presence of water under moderate

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temperatures (180-250 °C) and pressures (2-10 MPa) (Mumme et al., 2011). After HTC, the hydrochars obtained exhibit moderate calorific value, high aromaticity structures and mesoporous textures. In addition, hydrochars are biologically sterilized due to thermal treatment (Park et al., 2011) whereas aqueous by-product can be efficiently separated from hydrochars. Consequently, HTC extends the potential feedstocks for hydrochar production to biomass materials with high moisture content (Libra et al., 2011).

Currently, many biomass substrates, including cellulose (Sevilla and Fuertes, 2009), microalgae (Chisti and Yan, 2011; Heilmann et al., 2011a), anaerobically digested maize silage (Mumme et al., 2011), municipal solid waste (Berge et al., 2011; Jin et al., 2013; Lu et al., 2011), distiller's grains (Heilmann et al., 2011b), and black liquor (Kang, S. M. et al., 2012), have been applied in HTC to gain fuels or materials. Previously, Yoshida et al. (2009) carbonized SS with moisture content up to 30% in order to produce biochar for land utilization. According to heavy metals elution results, the biochar could be acceptable for land use. In another study, Park et al. (2011) enhanced the stability and dispersibility of coal-sludge-water slurry using SS hydrothermally pretreated at 200 °C. More recently, Meng et al. (2012) examined the hydrothermal dewatering and drying of SS at 160-200 °C. Their experimental results showed that the moisture content of treated SS was reduced to less than 20% with an evaporation rate of four times higher than untreated SS.

In general, carbohydrates and proteins comprise the main organic components in SS whereas lignin accounts for only a small amount. Carbohydrates and proteins can be hydrothermally decomposed at above 180 °C while lignin is degraded at 280-500 °C (Inoue et al., 1997; Ramsurn et al., 2011). During HTC, two distinct phases, i.e. solid and liquid, are formed. The evolved gas is small and mainly consists of carbon dioxide (Berge et al., 2011). However, an immiscible liquid-

phase was observed during HTC of municipal waste streams at 250 °C (Berge et al., 2011), which indicated that hydrothermal liquefaction occurred and lower carbonization temperature was desired. In addition, carbonization time can also affect the products of HTC. Zhang et al. (2008) showed that prolonged liquefaction time did not promote liquefaction process while it could raise the yield of residues. Therefore, in this study, an HTC process using stainless steel Teflon-lined reactor under lower temperature and different carbonization times was employed to recover solid fuel from SS with minimized liquefaction and corrosion issues.

The main purpose of this study was to develop an HTC process that can be applied to convert SS to an alternative clean fuel. The specific objectives were to: (1) investigate the fuel characteristics of hydrochars; (2) interpret the formation pathways of hydrochars; (3) discuss the effect of carbonization time on the characteristics of hydrochars; and (4) analyze the combustion behavior of hydrochars and evaluate the feasibility of hydrochars as alternative clean fuels.

3.2 Materials and methods

3.2.1 Materials

Dewatered SS was collected from Ulu Pandan Water Reclamation Plant in Singapore. The sludge was derived from treatment of domestic wastewater followed by anaerobic digestion and thickened to approximately 85.7 wt.% moisture content. The SS was stored at 4 °C and used as received in HTC experiments. With regard to the characterization of samples, the SS was air-dried for two weeks and ground into fine powders. The air-dried sludge powders (here labeled as DS) were sealed in a dry glass bottle.

3.2.2 HTC experiments

HTC experiments were conducted in a non-stirred 125 mL stainless steel Teflon-

lined reactor (Parr Instrument Co., USA). Since the stainless steel surface can be easily attacked by halogen and sulfur in feedstocks under hot-compressed water (Kritzer, 2004), Teflon-liner was employed to avoid the corrosion of stainless steel reactor wall. In each batch experiment, approximately 10.3 g of the dewatered SS was loaded into the vessel and sealed. The reactor was placed in a muffle furnace and heated up to 200 °C under autogenous pressure. When the pre-set temperature was reached, five carbonization times of 4, 6, 8, 10, and 12 h were maintained, respectively. After the desired carbonization time elapsed, the reactor was removed from the furnace and placed in a 4 °C cold room to quench the reactor rapidly.

After hydrothermal carbonization process, the liquid was poured out of the vessel since the dewaterability of SS was greatly enhanced. The liquid was collected in a sampling vial and weighed to determine the weight of liquid phase. The remaining solid/liquid mixture was washed out of the vessel into a beaker. Then, the solid product was washed with distilled water for several times and separated using a vacuum filtration apparatus through microfiltration filter paper. Finally, the solid product was collected in a beaker. The suspended solid in the beaker was oven-dried at 105 °C overnight and weighed to obtain the weight of hydrochars. The hydrochars were marked as HC-4, HC-6, HC-8, HC-10, and HC-12 in accordance with carbonization time. All the experiments were carried out in triplicate. Hydrochar yield and corresponding approximate equilibrium moisture content were calculated using the following equations.

$$\text{Hydrochar yield (\%)} = \frac{\text{Hydrochar weight}}{\text{Dry sludge weight}} \times 100\% \quad (3.1)$$

$$MC_e = \frac{W_1 - W_2}{W_0} \times 100\% \quad (3.2)$$

where MC_e is the approximate equilibrium moisture content, W_1 is the weight of moisture in the loaded sludge, W_2 is the weight of liquid phase, and W_0 is the

weight of the loaded sludge.

3.2.3 Solid fuel characterization

3.2.3.1 Chemical and physical properties analyses

Test methods for ash and volatile matter (VM) were performed based on ASTM D3174 and D3175, respectively. The fixed carbon (FC) percentage was determined by difference. The elemental compositions of the raw sludge and hydrochars were determined using elemental analyzer (vario EL cube CHNOS, Germany). The higher heating values (HHVs) of the samples were measured by IKA C2000 BASIC bomb calorimeter. The FTIR spectra were obtained using a Perkin Elmer spectrum GX FTIR spectrometer. Briefly, hydrochars were ground into fine particles and mixed with KBr powders in order to prepare pellets. Samples were scanned from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} . A constant sample to KBr ratio of 2 mg: 280 mg was used to compare corresponding intensities of functional groups in samples semi-quantitatively. The background was subtracted from the spectra of samples. Surface morphologies of the raw sludge and hydrochars derived at different carbonization times were examined by JEOL JSM-7600F Field Emission Scanning Electron Microscope (FE-SEM).

3.2.3.2 Surface properties analyses

Zeta potential measurements were conducted to investigate the surface charge of hydrochars. Zeta potential values were measured at $25\text{ }^{\circ}\text{C}$ under pH values ranging from 2 to 7 using Malvern Zeta Sizer Nano Series, which was equipped with a rectangular electrophoresis cell. The pH value of solution was adjusted by titrating $0.05\text{ M H}_2\text{SO}_4$ into 0.1 M NaOH bulk solution. Then, 20 mL solution was added into a flask containing 0.01 g sample to make a $0.05\text{ wt. \%}$ suspension. The surface oxygen containing functional groups are mainly composed of carboxylic ($-\text{COOH}$), lactone ($-\text{C=O}$), and phenolic ($-\text{OH}$). Boehm titration method was used to determine the amount of oxygenated surface groups with

different alkali solutions (Liu et al., 2010). The principle of Boehm titration method is based on the assumption that NaOH neutralizes carboxyl, lactone and phenolic groups, Na_2CO_3 neutralizes carboxyl and lactone, and NaHCO_3 neutralizes only carboxyl groups. A series of suspension tests were prepared by mixing 0.1 g raw sludge or hydrochars in a conical flask with 1 M NaOH, 1 M NaHCO_3 , and 0.05 M Na_2CO_3 , respectively. After that, the flasks were sealed and shaken for 24 h under the room temperature. The suspensions were then filtered and further titrated with 0.05 M H_2SO_4 using compact titrator (Mettler Toledo G20). Contact angle (θ) was used to estimate the wettability of raw sludge and hydrochars following the procedure described by Yu et al. (2012). Approximately 100 mg of powders was pelletized into a 13 mm disc under 10 MPa for 15 min by Perkin Elmer hydraulic press. A 2 μL uniform drop of distilled water was deposited on the surface of the sample disc at the room temperature. The process was recorded by a VCA OPTIMA XE (AST products, Billerica, MA) system which was equipped with a high-resolution video camera and powerful lens system for fine image focus. The droplet image was captured and the contact angle was calculated by Sessile Drop method using AutoFAST imaging software.

3.2.4 Combustion behavior analysis

3.2.4.1 Thermogravimetric analysis (TGA)

TGA is believed to be an effective way to analyze combustion behavior (Lu et al., 2011). In this study, it was used to determine combustion kinetics of raw sludge and hydrochars. TGA was carried out by Perkin Elmer Thermogravimetric Analyzer TGA 7 in an atmospheric pressure with a flow rate of air fixed at 20 mL/min. The weight loss (TG) and the rate of weight loss (DTG) of samples were recorded continuously under non-isothermal conditions with a temperature range of 30 °C to 900 °C at a heating rate of 10 °C/min. These dynamic experimental runs were conducted by placing 9 mg of samples on the same TG pan (Lu et al., 2011).

Three characteristic temperatures, i.e. ignition temperature (T_i), maximum combustion rate temperature (T_m) and burn out temperature (T_b), were determined using the TG-DTG curves. T_i refers to the temperature at which fuels start to burn while T_m corresponds to DTG peak temperature. T_b refers to the temperature at which the rate of weight loss diminishes to 1 wt.%/min at the end of the combustion profile. Particularly, two points should be identified to determine T_i . The first one is the intersection point A of TG curve and the vertical line passing through the DTG peak, and the second one is point B where devolatilization begins. Then, point C can be derived by crossing the tangent to TG curve at A with the horizontal tangent to B. T_i is the corresponding temperature of point C (Wang et al., 2009).

3.2.4.2 Calculation of kinetic parameters

The reaction kinetics of combustion process is expressed by the decomposition rate of samples given by:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (3.3)$$

$$f(\alpha) = (1 - \alpha)^n \quad (3.4)$$

$$\alpha = (m_i - m) / (m_i - m_f) \quad (3.5)$$

where α is the thermal conversion fraction of samples at time t , which was obtained from TG-DTG data; m_i , m , and m_f refer to the initial, instantaneous, and final mass of samples, respectively; $f(\alpha)$ is a general expression of the reaction mechanism; n is the order of reaction; and rate constant k is given by Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (3.6)$$

where E and A represent the activation energy (kJ mol^{-1}) and the pre-exponential factor (min^{-1}) of the reaction, respectively; R is the universal gas constant $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; T is the absolute temperature (K).

In this non-isothermal combustion investigation, a constant heating rate $\beta = dT/dt = 10\text{ }^{\circ}\text{C/min}$ was adopted. Therefore, a combined and rearranged form of equations (3.3) and (3.6) is written as:

$$\frac{d\alpha}{f(\alpha)} = A \exp\left(-\frac{E}{RT}\right) dt = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (3.7)$$

Integrating equation (3.7) becomes:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{T_0}^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (3.8)$$

Coats-Redfern approximation method is widely used to analyze the kinetic parameters of non-isothermal combustion process (Coats and Redfern, 1964; Shao et al., 2007; Wang et al., 2012). Thus, equation (3.8) is transformed following Coats-Redfern method, giving:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \quad (3.9)$$

Given the temperature range and activation energies in this study, $RT/E \ll 1$ and $1 - RT/E \approx 1$. Hence, the kinetic mechanism equation of combustion process incorporating the order of reaction is described below:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (3.10)$$

$$\text{For } n = 1, \quad G(\alpha) = -\ln(1-\alpha), \quad \ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (3.11)$$

$$\text{For } n \neq 1, \quad G(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}, \quad \ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (3.12)$$

According to the kinetic mechanism equations, the plot of $\ln [G(\alpha)/T^2]$ versus $1/T$ will present a straight line when an appropriate reaction order is selected. Then kinetic parameters can be derived from the plot. The activation energy E is determined by the slope while the pre-exponential factor A is calculated from the intercept of this straight line.

3.2.4.3 Calculation of comprehensive combustibility index

Comprehensive combustibility index (S) (Wang et al., 2009; Wang et al., 2012) was used to evaluate the combustion reactivity of samples.

$$S = \frac{(dw/dt)_{\max} (dw/dt)_{\text{mean}}}{T_i^2 T_b} \quad (3.13)$$

where $(dw/dt)_{\max}$ and $(dw/dt)_{\text{mean}}$ represent the maximum and mean rates of weight loss (wt.%/min), respectively; T_i and T_b are the ignition and burnout temperature ($^{\circ}\text{C}$), respectively.

3.3 Results and discussion

3.3.1 Characteristics of hydrochars

After HTC, SS was converted into brown solid chars with a nut-like smell. The produced hydrochars were uniform in composition and could be easily ground into powders. The physical appearance implies that hydrochars could be moulded into high density pellets as solid fuel.

3.3.1.1 Physico-chemical properties analyses

The proximate analysis of hydrochars is presented in Table 3.1. The volatile matter (VM) of hydrochars decreased with carbonization time while the loss of VM was partly compensated by the increase of fixed carbon (FC). After 10 h of HTC, VM reduced to around 45% and FC increased to 8%, suggesting that the carbonization process became stable. In addition, the ash content increased significantly from 28.60% to 46% due to the excess loss of VM and retained minerals in hydrochars. The increased FC was attributed to the devolatilization of VM and the mass conversion during HTC. However, according to the mass balance, the loss of VM was higher than the increased FC. This indicates that VM was also converted into other products, such as CO_2 or liquid (Berge et al., 2011; Kang, S. et al., 2012).

Table 3.1 Chemical compositions and fuel characteristics of DS and hydrochars.

		DS	HC-4	HC-6	HC-8	HC-10	HC-12
Proximate analysis (wt.%, db)	Ash	28.60	43.89	44.39	44.67	46.58	46.69
	VM	69.98	50.64	50.25	48.76	45.42	45.00
	FC	1.42	5.47	5.35	6.56	8.00	8.31
Fuel ratio	FC/VM	0.02	0.11	0.11	0.13	0.18	0.18
Ultimate analysis (wt.%, db)	C	36.7	33.3	33.2	32.6	32.5	32.5
	H	6.4	4.4	4.3	4.2	4.1	4.1
	O	35.9	18.5	17.8	17.6	17.4	16.9
	N	5.5	2.1	2.1	2.2	2.2	2.2
	S	9.5	3.8	3.8	3.8	3.8	3.9
Atomic ratio	H/C	2.10	1.60	1.55	1.53	1.53	1.53
	O/C	0.73	0.42	0.40	0.41	0.41	0.39
HHV (MJ/kg)		14.67	15.09	14.72	14.37	14.45	14.74
HHV _{daf} (MJ/kg)		24.12	28.40	27.55	26.95	27.93	28.52

Notes:

(1) VM-volatile matter; FC- fixed carbon; db-dry basis; daf-dry ash-free basis; HHV-higher heating value.

(2) The pH value of the aqueous phase generated from HTC under 4, 6, 8, 10, and 12 h of carbonization, was 6.9, 7.0, 7.1, 7.2, and 7.6, respectively.

The fuel ratio (FC/VM) ranks the hydrochars as an alternative coal fuel. Since FC increased and VM decreased with carbonization time, the fuel ratio gradually increased from 0.02 to 0.18 after 10 h of HTC. This reveals that the rank of hydrochars was greatly improved via HTC.

Higher heating values (HHVs) and elemental analysis of hydrochars are also presented in Table 3.1. The HHVs were around 15 MJ/kg, comparable to calorific value of lignite (16.3 MJ/kg). Furthermore, the elemental composition demonstrates that O and H contents in HC-12 were reduced by approximately 50% and 35%, respectively. Since C content was retained by 88%, HHV_{daf} was increased by at least 11%. As shown in Table 3.1, H/C and O/C atomic ratios diminished from 2.1 and 0.73 to 1.53 and 0.39, respectively. The evolution of H/C and O/C atomic ratios can be visualized by the Van Krevelen diagram in Figure 3.1 in order to depict reaction pathways, including dehydration, decarboxylation, and demethanation (Van Krevelen, 1950). Following the reaction pathways of raw sludge to hydrochars, it is obvious that dehydration and decarboxylation were the essential reaction pathways in HTC of SS while the demethanation pathway was negligible. For comparison, H/C vs. O/C atomic ratios of four typical coals, i.e. anthracite, bituminous, sub-bituminous, and lignite, were also plotted in Van Krevelen diagram. Since H/C and O/C atomic ratios of lignite are generally 0.8-1.3 and 0.2-0.38, respectively (Park and Jang, 2011), hydrochars were approaching the region of lignite as shown in the diagram. In this regard, the coal band of hydrochars was comparable to lignite, which is a low rank coal. Thus, co-combustion of blended hydrochars and coal can achieve good performance due to the good compatibility of hydrochars with lignite.

Since HHVs depend on elemental composition of samples, the variations of HHVs after HTC can be explained by different evolutions of hydrochars composition.

Figure 3.1 Van Krevelen diagram for raw sludge and hydrochars. Four typical coals, i.e. anthracite, bituminous, sub-bituminous, and lignite, are shown for comparison.

Channiwala and Parikh (2002) have developed a unified correlation to predict HHV of solid fuel expressed by elemental composition:

$$\text{HHV} = 0.349C + 1.1783H + 0.1005S - 0.1034O - 0.0015N - 0.0211A \text{ (MJ/kg)} \quad (3.14)$$

where C, H, S, O, N and A represent the mass percentages on dry basis of carbon, hydrogen, sulfur, oxygen, nitrogen and ash contents of fuels, respectively.

Comparing the predicted HHV from the formula with the measured HHV, it was found that the predicted method was quite precise with a relative error of less than 6%. Therefore, the HHVs of raw sludge and hydrochars can be measured based on their elemental composition. Besides, the derivation of higher ash content with longer carbonization time reduced the HHVs of hydrochars. Given different evolutions of components and elemental compositions in hydrochars,

the HHVs of hydrochars slightly fluctuated with carbonization time, which were 0.98-1.03 times (energy content by weight) of DS.

3.3.1.2 Removal of nitrogen and sulfur

Regarding the nitrogen content, 40% remained in the hydrochars while 60% was released into gases and liquid phase. Longer carbonization time did not improve the removal efficiency. The majority of nitrogen in SS originates from proteins, so it is reasonable that nitrogen content decreased in hydrochars since proteins are degraded above 150 °C. Previously, Inoue et al. (1997) investigated the behavior of nitrogen during hydrothermal liquefaction of dewatered SS with temperatures ranging from 150 to 350 °C. They found that the organic-N was decomposed to NH_4^+ -N with the increase of reaction temperature whereas carboxylic acids were decomposed into CO_2 or CO. That also explained the slightly increased pH values of the liquid phase in Table 3.1.

Similar to nitrogen, sulfur content was removed by 60% in hydrochars. Longer carbonization time had no significant effect on desulfurization. The desulfurization of SS during HTC follows the same principle as coal desulfurization in subcritical conditions described by Ramsurn et al. (2011). Moreover, additional sulfur can cause catalyst poisoning during hydrothermal gasification (Afif et al., 2011). In this regard, HTC can convert SS to hydrochars with less sulfur and nitrogen, which is a more valuable feedstock for thermochemical process.

3.3.1.3 Evolution of functional groups in hydrochars

The FTIR spectra of raw sludge and hydrochars with different carbonization times are presented in Figure 3.2. As indicated in Figure 3.2, the FTIR spectra are assigned into six regions representing the main identification peaks. It seems that there was no significant difference in FTIR spectra of hydrochars.

Figure 3.2 FTIR spectra of DS and hydrochars produced at various carbonization times. 1: -OH stretching; 2: aliphatic -CH_x stretching; 3: -C=O; 4: aromatic ring C=C stretching; 5: ethers C-O-R; 6: aromatic nucleus -CH.

According to identification peaks (Francioso et al., 2010; Li, M. et al., 2011; Liu et al., 2010; Mursito et al., 2010; Özçimen and Ersoy-Meriçboyu, 2010; Yang et al., 2007):

- (i) The band at 3400 cm⁻¹ was attributed to -OH stretching vibration in hydroxyl or carboxyl groups. As shown in Figure 3.2, this peak of hydrochars became less intense compared to that of raw sludge. It is probably related to the dehydration of raw sludge during HTC.
- (ii) Intensities of bands between 3000-2800 cm⁻¹, associated with aliphatic carbon -CH_x stretching vibration, showed no prominent fluctuation. More specifically, asymmetric and symmetric -C-H stretching of methylene groups were identified at 2925 cm⁻¹ and 2850 cm⁻¹ (de Oliveira Silva et al., 2012), respectively.
- (iii) Remarkable reduction of the relative intensity of hydrochars was observed at 1645 cm⁻¹ and 1540 cm⁻¹. The band at 1645 cm⁻¹ implied the stretching

vibration of -C=O in ketone and amide groups (de Oliveira Silva et al., 2012) whereas the peak at 1540 cm^{-1} was attributed to asymmetric stretching of -C=O in carboxylic groups (Li, M. et al., 2011). This indicates that decarboxylation reactions occurred, which was consistent with carbon content change in elemental analysis revealing the release of carbon in the form of CO_2 .

(iv) The peak at 1455 cm^{-1} was assigned to the -C=C stretching in aromatic ring carbons which slightly increased after HTC. In addition, the increase peak at 910 cm^{-1} was attributed to the out-of-plane bending vibration in aromatic nucleus -CH structure, which suggests the occurrence of aromatization (Kang, S. et al., 2012), such as aldol condensation (Li, M. et al., 2011). These bands changes reveal that high carbon aromaticity was obtained during HTC of SS. These findings are in agreement with a previous study by Mursito et al. (2010).

(v) The drastic increase of relative intensity at 1030 cm^{-1} was due to -C-O-R in aliphatic ethers and alcohol -C-O stretching (Li, M. et al., 2011; Özçimen and Ersoy-Meriçboyu, 2010). However, the peak at 1030 cm^{-1} may also be assigned to -Si-O stretching, which reveals the presence of SiO_2 (Yuan et al., 2011). The high ash content verified the mineral compounds were retained during the HTC process.

3.3.1.4 Formation pathways of hydrochars

Figure 3.3 presents the influence of carbonization time on the hydrochar yield and equilibrium moisture content. There was a gradual increase of the hydrochar yield by prolonging the carbonization process. After 12 h of HTC, a maximum hydrochar yield of 60.4% was derived while the approximate equilibrium moisture content was reduced to 46.4%. The decreased moisture contents in hydrochars were in accordance with hydrothermal drying of sludge (Meng et al., 2012).

Figure 3.3 Effect of carbonization time on hydrochar yields and approximate equilibrium moisture contents.

According to previous studies on hydrochar formation mechanisms (Dinjus et al., 2011; Falco et al., 2011; Kang, S. et al., 2012; Karayildirim et al., 2008; Kruse et al., 2007; Yao et al., 2007; Zhang et al., 2012), the carbonaceous particles can be obtained via two main reaction pathways: (1) direct solid-solid conversion of biomass materials (named “char”) which undergoes devolatilization, condensation, dehydration and decarboxylation; and (2) polymerization of dissolved intermediates degraded from the original biomass (termed “coke”). Briefly, carbohydrates in SS were hydrolyzed to glucose or fructose which was converted to 5-hydroxymethylfurfural (HMF) via dehydration under the HTC condition. The derived HMF was polymerized to primary particles followed by aggregation to form carbonaceous spheres (coke) (Zhang et al., 2012). The coke accumulated along with longer carbonization time while a part of the HMF was dissolved in the liquid phase. Simultaneously, amino acids derived from hydrolysis of proteins in SS subsequently interacted with sugars to form N-containing ring compounds via Maillard reaction (Kruse et al., 2007). The brown color and characteristic odor of hydrochars were the evidences of Maillard reaction. Based on the aforementioned pathways, hydrochars formation pathways

during HTC of SS are proposed in Figure 3.4.

Figure 3.4 Schematic hydrochar formation pathways during HTC of SS.

3.3.2 Surface properties of hydrochars

3.3.2.1 Effect of carbonization time on the morphologies of hydrochars

SEM images were used to study surface morphology evolutions from raw sludge to hydrochars under different carbonization times. In Figure 3.5A, DS exhibited clustered aggregates without pores or pathways, thus water is difficult to flow out of sludge matrix. However, the morphologies of hydrochars changed significantly as can be seen in Figure 3.5B to F. By increasing the carbonization time, the fragmentation and porosity of hydrochars increased. That was caused by the release of volatile gases during devolatilization and chemical bond decomposition of sludge matrix. Remarkable biomass fibers were observed in zoomed images of Figure 3.5C and D. This implies that lignin was only partially carbonized because of its high thermal stability. However, less sphere-like microparticles were observed adhering to mesoporous texture compared with hydrochars from HTC of corn stover (Fuentes et al., 2010). These microspheres are mainly derived from the degradation of cellulose (Sevilla and Fuentes, 2009) whereas SS contains less cellulose components than phyto biomass. Overall, it could be concluded that HTC induced mesoporous texture and the degree of porosity accelerated with the carbonization time. The increased porosity can contribute to easier drying of produced hydrochars at an ambient temperature.

Figure 3.5 SEM images of DS and hydrochars. A:DS; B:HC-4; C:HC-6; D:HC-8; E:HC-10; F:HC-12.

3.3.2.2 Effect of carbonization time on zeta potential values of hydrochars

Figure 3.6 shows the effect of different pH values on zeta potential values of hydrochars. The zeta potential value decreased with increasing pH value until it reached a plateau. The zeta potential is generated from protonation and deprotonation of polar functional groups, such as carboxyl and hydroxyl groups, on the surfaces of solid particles (Hunter, 1981; Yuan et al., 2011). The negative zeta potential with increasing pH suggests the increase of negative charges on the surfaces of samples. This tendency was attributed to the dissociation of carboxyl and hydroxyl groups at higher pH values. In addition, minimum zeta potential

value of hydrochars was at pH 5 while it was at pH 6 for raw sludge. This change was attributed to the evolution of functional groups on the surface. Lower pH could inhibit the dissociation of carboxyl and hydroxyl groups whereas it may facilitate the amide group. Though carboxyl and hydroxyl groups were reduced, the lactone groups were increased accompanied by forming more amide groups therein. At pH lower than 3, the zeta potential value became positive since the dissociation of carboxyl and hydroxyl functional groups were greatly inhibited. However, the complex evolution of the functional groups under different carbonization times makes it unclear to predict the dominant functional groups in each HTC process.

Figure 3.6 The zeta potential vs. pH curves of DS and hydrochars from HTC under different carbonization times.

3.3.2.3 Relationship between PZCs and functional groups

Point of zero charge (PZC) is defined as the pH value when the zeta potential value is zero (Yu et al., 2012). As shown in Table 3.2, the PZCs of hydrochars

were higher than 2.7 of raw sludge. Since less amount of H^+ is required to neutralize the negative charge electrolyzed from carboxyl and phenolic hydroxyl, the increase of PZC indicates the reduction of carboxyl and phenolic hydroxyl functional groups. As shown in Table 3.2, contents of these two groups continuously dropped as carbonization time increased. After 12 h of carbonization, -COOH and -OH decreased from 4.29 mmol/g to 3.46 mmol/g and from 0.51 mmol/g to 0.21 mmol/g, respectively. Concurrently, the content of lactone (-C=O) group increased, which probably originated from the conversion of carboxyl (-COOH) group. Due to oxygen loss in the form of CO_2 and H_2O , the total content of oxygen containing functional groups reduced to 4.21 mmol/g.

The PZCs are also used to classify the rank of hydrochars as coals. Hydrophobicity of coals is consistent with high PZCs (Yu et al., 2012). Since the oxygen containing functional groups are hydrophilic, oxygen functional groups should be reduced to make hydrochars hydrophobic. In this regard, the increase of PZC and decrease of oxygen containing functional groups with carbonization time significantly upgrade the rank of hydrochars.

3.3.2.4 Effect of carbonization time on wetting properties of hydrochars

In Table 3.2, contact angles of hydrochars discs slightly increased from 86° to 91° with carbonization time, revealing the hydrophobic tendency of solid surfaces.

Compared to raw sludge, the contact angles of hydrochars are lower in spite of the conversion of oxygen functional groups. It is believed that the contact angle is not only affected by the surface chemistry but also the surface roughness of sample discs (Wenzel, 1948). Since hydrochar powders were more uniform and homogeneous than raw sludge particles, the compactability was thus significantly improved. After the water droplet standing for 20 minutes, it was gradually absorbed into raw sludge disc and finally disappeared. On the contrary, the

droplets on hydrochars discs remained standing without wetting the surface. Moreover, a smooth hydrochar disc surface was retained after the droplet was wiped off. In conclusion, the higher initial contact angle of raw sludge may result from its poor grindability as well as compactability and the high hydrophobicity of hydrochars makes them suitable for solid fuel.

Table 3.2 Surface properties of DS and hydrochars.

	Acid surface functional groups				PZC	Contact angle (°)
	(mmol/g dry mass)					
	Carboxyl	Phenolic	Lactone	Total		
	(-COOH)	hydroxyl (-OH)	(-C=O)			
DS	4.11	0.63	0.22	4.95	2.7	98
HC-4	4.29	0.51	0.29	5.09	2.8	86
HC-6	4.19	0.55	0.37	5.11	3.1	89
HC-8	4.10	0.50	0.39	5.00	3.1	89
HC-10	3.87	0.38	0.41	4.66	3.0	90
HC-12	3.46	0.21	0.53	4.21	3.0	91

3.3.3 Consideration of combustion behaviors of DS and hydrochars

3.3.3.1 Effect of HTC on combustion profiles

(1) Patterns of main decomposition

Combustion profiles of raw sludge and hydrochars are illustrated in Figure 3.7. For a better evaluation of the different combustion behaviors, the entire combustion profile was divided into several stages depending on the rate of weight loss in the DTG curve, i.e. stage D is the dehydration process, stage E is the devolatilization and combustion phase, stage F is the char combustion phase

and the last stage is the burnout phase. These temperature ranges are shown in Table 3.3.

Figure 3.7 TG-DTG curves for combustion profiles of DS and hydrochars.

(a):DS; (b):HC-4; (c):HC-6; (d):HC-8; (e):HC-10; (f):HC-12.

For air-dried raw sludge, stage D exhibited a high peak due to the higher moisture content. Only above 195 °C, the stage E began to be pronounced. Due to the low FC and high VM in raw sludge, the char combustion stage F was accomplished along with devolatilization and combustion, resulting in a sharper peak and wider covering range of stage E. For hydrochars, the VM decreased whereas FC increased. Thus, stage E and F became distinct due to the compensation effect of FC and VM contents. The DTG curve of HC-4 exhibited minor fluctuations at the transition period between stage E and F. It probably indicates that raw sludge was not thoroughly carbonized because hydrochars still contained about 50% VM. For HC-6, the transition part disappeared, suggesting that hydrochars become more stable thereafter. Subsequently, the VM content further reduced towards a thorough carbonization process, thus stage E became gentle. The continuous increase of FC content in hydrochars with carbonization time was

reflected from the higher peak of HC-12 in contrast with that of HC-4 at stage F.

Generally, devolatilization of biomass materials occurs at relatively low temperatures while char combustion initiates at higher temperatures (Biagini and Tognotti, 2006; Xu and Sheng, 2011). As shown in the DTG curve of raw sludge, the overall decomposition was governed by a single stage in the temperature range of 200-550 °C with a slight left “shoulder” observed at 310 °C. It was attributed to the abundant volatile matter in raw sludge. Furthermore, the devolatilization of raw sludge increased drastically after the dehydration stage D (70-195 °C) and reached the peak at 325 °C. But for the hydrochars, two obvious peaks were found in the DTG curves. The first decomposition stage which was mostly related to depolymerization reactions occurred between 150 °C and 350 °C whereas the second stage took place in the temperature range of 350-550 °C for the further degradation of VM and char combustion. The two-stage combustion of hydrochars was similar to hydrothermally treated MSW reported by Muthuraman et al. (2010a).

(2) Residues

It is noticeable that residues in Table 3.3 were much higher than ash contents in proximate analysis, which was previously mentioned by Wang et al. (2009). Because of the exothermic reaction of combustion process and the cylindrical shape of the burning chamber, it may result in uneven heating and insufficient air for the fuel combustion at the bottom part. Therefore, longer time is required to reach complete combustion until the ash content approximates to that in proximate analysis.

(3) The shift of characteristic temperatures

T_i , T_m , and T_b are shown in Table 3.3. T_i is a critical parameter to minimize fire and explosion when using biochar as solid fuel (Xu and Sheng, 2011). After HTC, T_i increased gradually along with the residence time with a maximum increase within 20 °C. It implies the higher difficulty of ignition with carbonization time

in HTC process. Biagini and Tognotti (2006) reported that the devolatilization of coals required higher temperatures because of the lower volatile matter compared to biomass materials. The increase of T_i can be explained by the decrease of VM in hydrochars. Because of less VM, the hydrochars became less reactive. However, although the VM content reduced greatly during HTC, the increase of T_i did not exceed 20 °C. This may be attributed to higher ash contents in hydrochars since inorganic matter in hydrochars can have a significant catalysis effect on combustion reactivity (Várhegyi et al., 2012; Xu and Sheng, 2011). Apart from the increase of T_i , T_m and T_b also showed apparent increase. Especially, T_m was increased by almost 100 °C. Therefore, it needs longer reaction time to achieve the maximum decomposition rate after HTC.

Table 3.3 Combustion stages, characteristic temperatures and residues of DS and hydrochars.

	Dehydration	Devolatilization	Char	Characteristic			Residues (%)
	-stage D	and combustion	combustion	temperatures (°C)			
	(°C)	-stage E (°C)	-stage F (°C)	T_i	T_m	T_b	
DS	~195	195-590		267.3	325.0	464.0	37.5
HC-4	~100	150-255	300-590	267.3	372.3	478.5	56.5
HC-6	~100	150-350	350-590	271.3	417.6	476.2	51.3
HC-8	~100	150-350	350-590	277.5	423.8	482.8	50.3
HC-10	~100	150-350	350-590	277.5	427.8	483.1	51.0
HC-12	~100	150-350	350-590	285.9	427.9	488.1	51.3

3.3.3.2 Kinetic parameters analysis

The determination of kinetic parameters is of great importance for a better understanding of combustion behaviors of raw sludge and hydrochars. Activation

energy and pre-exponential factor are two crucial kinetic parameters to evaluate the difficulty and intensity of combustion reactions for fuels. Since TG-DTG curves displayed evident differences during devolatilization and char combustion stages, the data corresponding to different combustion stages were screened and the kinetic parameters of each stage were determined using linear regression method independently.

According to the fitting results of linear regression using different kinetic mechanism equations, the first order combustion reaction was proved to be the best function model which gave a correlation coefficient ranging from 0.9825 to 0.9986.

Table 3.4 summarizes the derived kinetic parameters for specific temperature ranges calculated from the first order kinetic mechanism equation. It is obvious that E and A values of DS were much higher than hydrochars, which were 37.64 kJ mol⁻¹ and 167.50 min⁻¹, respectively. It reveals that DS was difficult to be burnt while the burning range was short as described by Wang et al. (2009). For both temperature ranges of hydrochars, E and A values were much lower than DS. During the first temperature range, E and A values showed a decrease trend with carbonization time whereas they increased during the second temperature range. Given these two trends, HC-8 was turned out to be a good fuel in terms of easy and stable combustion.

Table 3.4 Combustion kinetic parameters of DS and hydrochars for different temperature ranges.

Sample	Temperature range (°C)	E (kJ mol ⁻¹)	A (min ⁻¹)	n	R^2
DS	250-450	37.64	167.50	1	0.9908
HC-4	170-250	27.94	13.96	1	0.9986
	320-500	21.25	1.93	1	0.9912
HC-6	200-350	27.23	7.02	1	0.9825
	350-500	33.56	31.45	1	0.9966
HC-8	200-350	25.43	4.51	1	0.9852
	350-500	34.32	34.87	1	0.9965
HC-10	200-350	25.83	4.94	1	0.9850
	350-500	33.92	31.89	1	0.9969
HC-12	200-350	24.57	3.53	1	0.9888
	350-500	34.27	32.60	1	0.9961

3.3.3.3 Evaluation of combustion performance

S values for DS and hydrochars were calculated in Table 3.5. Because of the high VM in DS, $(dw/dt)_{\max}$ of DS was much higher than hydrochars and S was thus greater. However, the high VM may cause unstable flame and combustion, thereby leading to large heat loss. Thus, the combustion of hydrochars is speculated to be less violent and the flame is more stable.

Table 3.5 Comprehensive combustibility index (S) for DS and hydrochars.

	$(dw/dt)_{\text{mean}}$	$(dw/dt)_{\text{max}}$	$S \times 10^8$
DS	0.718	3.772	8.173
HC-4	0.500	1.735	2.539
HC-6	0.560	2.170	3.465
HC-8	0.572	2.221	3.415
HC-10	0.563	2.116	3.203
HC-12	0.560	2.099	2.945

In this regard, the combustion performance of DS may not be good enough though it presented a high S value. Comparing S values of hydrochars, HC-6 and HC-8 performed the best with S values around 3.4×10^{-8} , which indicates a relatively good combustion performance. Moreover, the increase of T_b can result in a long combustion process. Hence, HTC process can convert raw sludge into solid fuel with a more stable flame but longer combustion process.

3.4 Conclusions

Hydrothermal carbonization (HTC) process was used to convert sewage sludge (SS) into hydrochars at 200 °C in a Teflon-lined batch reactor. Thus, hydrothermal liquefaction and corrosions of reactor wall were minimized. The elimination of prior drying makes HTC a promising technology to directly recover energy from SS. After HTC of SS, uniform brown hydrochars with good grindability and nut-like smell were produced. As a consequence of higher fixed carbon (FC) and lower volatile matter (VM), hydrochars possessed a fuel ratio high up to 0.18 which was much higher than 0.02 of raw sludge. Despite the VM loss and higher ash content, carbon was retained by 88% and the HHVs of hydrochars were 0.98-1.03 times of raw sludge. Moreover, 60% of nitrogen and

sulfur was removed, resulting in a cleaner solid fuel. The decrease of O/C and H/C atomic ratios suggested that dehydration and decarboxylation reactions were the essential reaction pathways during HTC of SS. As the carbonization time was prolonged, total content of surface oxygen containing functional groups reduced to 4.21 mmol/g, making hydrochars highly hydrophobic. The yield and properties of hydrochars became relatively stable after 6 h of carbonization. In terms of the main combustion decomposition, HTC altered patterns of DTG curves from a single stage (195-590 °C) for raw sludge to two stages (150-350 °C and 350-590 °C) for hydrochars. The first order combustion reaction of raw sludge and hydrochars was derived. E and A values of raw sludge (i.e. 37.64 kJ mol⁻¹ and 167.50 min⁻¹, respectively) were much higher than hydrochars. Therefore, HTC can convert SS to an alternative solid fuel from the perspectives of fuel characteristics and combustion performance.

CHAPTER 4 Development of low temperature hydrothermal conversion of dewatered sewage sludge: Effects of reaction conditions and calcium oxide additive*

4.1 Introduction

The management and disposal of sewage sludge (SS) generated from wastewater treatment plants is problematic due to high moisture content and pollutants (e.g. pathogens, heavy metals, and persistent organic pollutants) together with unpleasant smells therein (He et al., 2014a). Nevertheless, SS is rich in organic matter and nutrients, and thus it is regarded as an alternative energy source. In order to efficiently harness energy from SS with great volume reduction, thermochemical conversions (e.g. gasification and pyrolysis) have been extensively investigated (Fonts et al., 2012; Manara and Zabaniotou, 2012). Among them, hydrothermal conversion (HTC) technology represents a more sustainable technique to convert wet SS to biofuels since prior thermal drying process is eliminated under high temperature (200-600 °C) and high pressure (5-40 MPa) conditions (Chen et al., 2013b; Peterson et al., 2008).

Currently, research is widely focused on supercritical water gasification (SCWG) of SS for H₂ rich gas production (Chen et al., 2013b; Xu, Z. R. et al., 2012; Zhang, L. et al., 2010a), hydrothermal liquefaction of SS to generate bio-oil (Leng et al., 2014; Xu and Lancaster, 2008; Zhai et al., 2014), and hydrothermal carbonization for hydrochar solid fuels production (Chen et al., 2013b). Most of the research is application oriented and thus only certain aspects were considered. For instance, the effect of moisture content on direct SCWG of SS has been explored (Xu, Z.

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R. et al., 2012). Fuel characteristics and combustion behavior of solid hydrochars, removal of N or S precursors, as well as NO emissions during combustion after hydrothermal carbonization were investigated towards cleaner solid fuel production (Chen et al., 2013b; Zhao et al., 2013). In addition, transformation behaviors and environmental risk of heavy metals in solids have been extensively discussed for land application (Leng et al., 2014; Shi et al., 2013; Zhai et al., 2014). Moreover, simultaneous extraction, decomposition, and stabilization processes during HTC could result in mineralization and migration of inorganic elements in SS (Shi et al., 2014). Although heavy metals tended to be accumulated and redistributed in solid residues after sub- and supercritical water (SCW) treatment (Shi et al., 2013; Zhai et al., 2014), the distribution of heavy metals in liquid phase is also of great importance for post-treatment and reclamation of the processing effluents.

Apart from heterocyclic N and S precursors, trace amounts of halogenated substances and/or perfluorinated compounds (PFCs) can be found in SS during wastewater treatment. It has been reported that a typical cyclic perfluoroalkyl surfactant was efficiently decomposed in sub- and SCW in the presence of iron catalyst (Hori et al., 2012). Besides, desulfurization of organic sulfides was found in SCW via free-radical reactions (Patwardhan et al., 2013). Hwang et al. (2012) indicated that chlorine in precursors could be converted into soluble chloride compound after subcritical water treatment. Yet little effort has been devoted to the destruction of the heteroatomic compounds during HTC of SS. Calcium oxide additive has been used to facilitate water-gas shift reaction (WGS) to increase hydrogen yield during SCWG of lignite (Cheng et al., 2007) as well as catechol and starch (Youssef et al., 2012), and catalytic aqueous phase reforming of glycerol (He et al., 2015b). Furthermore, Ca(OH)_2 was found to inhibit toxic pollutants formation during hydrothermal gasification of biomass waste (Yildiz Bircan et al., 2011). These results indicated that Ca-based alkaline could be

economical conditioner for effective HTC of SS.

More recently, subcritical water treatment of SS under lower temperature hydrothermal condition (200-380 °C, 2-22 MPa) has attracted great attention due to its lower energy consumption and safer operation. However, the gasification process (i.e. gas yield and H₂ purity) for SS under this range has not been well studied. Moreover, characteristics of liquid products are unspecified, especially the behavior of heteroatomic compounds, heavy metals, mineral elements and their interactions. Moreover, little attention has been paid to the effects of Ca-based alkaline on products distribution and migration of heteroatoms (such as nitrogen, sulfur, chlorine, and fluorine) which are essential information to make this promising technology commercially viable.

In order to conceptualize the reaction chemistry in HTC of SS under low temperature and pressure, effects of operating conditions and moisture content on evolution characteristics of gas, solid, and liquid products were examined in this study. Furthermore, CaO additive was employed in near-critical water to act as CO₂ absorber via carbonation. The reaction chemistry was systematically interpreted in terms of products distribution and environmental pollutants migration.

4.2 Experimental section

4.2.1 Materials

Dewatered anaerobically digested sewage sludge (DSS) with a moisture content of 82.5 wt.% was collected from Ulu Pandan Water Reclamation Plant, Singapore. Before being used as feedstocks in low temperature/pressure HTC process, DSS sample was kept at 4 °C. The main characteristics of DSS are shown in Table 4.1.

4.2.2 HTC procedures

HTC experiments were carried out in a 1 L stainless steel (SS 316L) fixed-head

Table 4.1 Characteristics of DSS.

Moisture content	HHV	Ultimate analysis (wt.%, daf)					Proximate analysis (wt.%, db)			Fuel ratio	
(wt.%)	(MJ/kg, db)	C	H	N	S	O ^a	VM	FC	Ash	FC/VM	
82.5	17.97	39.9	6.2	6.0	5.6	20.5	69.0	9.2	21.8	0.13	
Metal and mineral elements (wt.%, db)											
K	Na	Mg	Ca	Fe	Al	P	Cr	Cu	Zn	Pb	Ni
0.224	0.084	0.322	1.247	1.584	1.537	1.300	0.0043	0.1175	0.1001	0.005	0.0089

db, on dry basis; daf, dry and ash-free basis; VM, volatile matter; FC, fixed carbon; HHV, higher heating value.

^a Calculated by difference on dry and ash-free basis.

Table 4.2 Experimental conditions for HTC of DSS and corresponding C or N mass balance.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17
Moisture content (wt.%)	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	82.5	85	90	92	95
DSS (g)	182	182	182	182	182	182	182	182	182	182	182	182	182	151	95	74	45.5
DI water (g)	0	0	0	0	0	0	0	0	0	0	0	0	0	25.5	71.5	89	113
Ca/C molar ratio	-	-	-	-	-	-	-	-	-	-	0.05	0.10	0.20	-	-	-	-
Reaction temperature (°C)	200	220	240	260	280	300	320	340	360	380	380	380	380	380	380	380	380
Reaction pressure (MPa)	2.0	2.6	3.8	5.0	7.0	9.3	12.0	15.5	19.4	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
Reaction time (min)	20																
C balance	1.02	0.89	0.94	0.92	0.93	0.91	0.88	0.86	0.79	0.75	0.86	0.83	0.88	0.79	0.85	0.72	0.80
N balance	1.40	1.17	1.28	1.15	1.14	1.13	1.05	0.98	0.99	1.00	1.16	1.09	1.06	1.10	1.16	1.30	1.56

batch autoclave reactor (Parr Instrument Co., USA) with a maximum operating temperature and pressure of 500 °C and 35 MPa, respectively. Detailed configuration of the HTC system has been described elsewhere (He et al., 2014c). Three sets of experimental runs were conducted as shown in Table 2. For set 1 (Run 1 – 10), various operating temperatures and pressures were employed. Typically, 182 g of DSS containing approximately 150 g of water was loaded into the reactor vessel and sealed. Under stirring at 500 rpm, the vessel was heated up to the temperature and pressure in Table 4.2. After 20 min reaction time, the heating mantle was removed and the vessel was quenched rapidly to room temperature via internal cooling water circulator. Gaseous products were gently released to Tedlar gas bags through the gas outlet valve for further analysis. Subsequently, the vessel was opened for solid and liquid products separation and collection. Liquid products were filtered through 0.45 µm PTFE membranes and kept in glass vials at 4 °C before analysis. The solid residues were carefully collected and oven dried at 105 °C overnight. The overall schematic procedure is depicted in Figure 4.1. The dry solids were ground into less than 0.5 mm fine powders and termed hydrochars hereinafter. The hydrochars were denoted as HC-T, where T stands for the reaction temperature.

For set 2 (Run 11 – 13), the feedstocks were 182 g of DSS and a specific amount of CaO (see Table 2). This set of experiments was conducted under 380 °C and 22.0 MPa for 20 min. The solid residues were denoted as SR-Ca-X, where X indicates Ca/C molar ratio.

For set 3 (Run 14 – 17), various deionized (DI) water amounts were fed into original DSS to prepare SS feedstocks with different moisture contents. The total amount of water in these SS samples was 150 g to achieve the same pressure of 22.0 MPa under 380 °C. Hydrochars were recovered following the same

procedure after 20 min reaction at 380 °C and 22.0 MPa, which were denoted as HC-85, HC-90, HC-92, and HC-95 according to various moisture contents.

4.2.3 Products analyses

4.2.3.1 Gas products

The gaseous products were analyzed by an Agilent Gas Chromatograph described elsewhere (He et al., 2015b). Hydrogen, carbon dioxide, methane, nitrogen, and carbon monoxide were detected as major compounds in gaseous products. Initial ambient air in the headspace of vessel was calibrated as 820 mL by GilAir Plus air pump. However, the nitrogen gas actually originated from the headspace air in the reactor based on the calculations of total nitrogen gas volume before and after HTC. Gas yield was determined by the wet gas meter.

4.2.3.2 Liquid products

Total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), and total dissolved nitrogen (TDN) concentrations in liquid products were determined using TOC/TN analyzer (multi N/C 2100, Analytik Jena). In addition, chemical oxygen demand (COD) and ammonium (NH_4^+ -N) were measured using corresponding HACH test kits and HACH DR 2800 spectrophotometer. The pH values were measured by Mettler Toledo pH meter (SevenGo Duo SG23). Concentrations of major anions (i.e. F^- , Cl^- , and SO_4^{2-}) were analyzed by Dionex ICS 1100 ion chromatography. Concentrations of total dissolved heavy metals and mineral elements were measured using PerkinElmer Optima 2000 DV inductively coupled plasma optical emission spectrometer (ICP-OES).

4.2.3.3 Solid products

Ultimate analysis was performed to determine elemental compositions of DSS and solid residues using vario EL CHNS elemental analyzer. Higher heating values (HHVs) of all oven dried solid samples were determined by bomb

calorimeter (IKA C2000 BASIC). Proximate analysis was used to investigate transformations of organic matter during HTC. Specifically, ash content in DSS and solid residues was determined according to ASTM D3174 and VM content was measured by STA 449 F3 Jupiter Simultaneous TG-DTA/DSC Apparatus (NETZSCH-Gerätebau GmbH) based on ASTM D3175-11. The fixed carbon (FC) content was derived by difference.

4.2.4 HTC performance evaluation

HTC performance was assessed in terms of solid residues recovery rate (SR), liquid residues recovery rate (LR), recovered energy as hydrochar (RE), and energy recovery rate as hydrochar (ERR) based on following equations.

$$SR (\%) = (S_1 + S_2) / W_0 \times 100 \quad (4.1)$$

$$LR (\%) = (L_1 + L_2) / V_0 \times 100 \quad (4.2)$$

$$RE \text{ (MJ/kg Dry SS)} = SR \times HHV_S / 100 \quad (4.3)$$

$$ERR (\%) = RE / HHV_{DSS} \times 100 \quad (4.4)$$

where S_1 , S_2 , and W_0 are the dry weights of solid residues and feedstocks in Figure 4.1, respectively; L_1 , L_2 , and V_0 are the volumes of liquid residues and moisture in feedstocks in Figure 4.1, respectively; HHV_S and HHV_{DSS} represent higher heating values of solid residues and DSS, respectively.

Figure 4.1 Schematic procedure for HTC of DSS and products collection.

4.3 Results and discussion

4.3.1 Evolution of gas products

4.3.1.1 Effect of operating temperature/ pressure

Figure 4.2 illustrates the influence of operating temperature/pressure on gas yield and composition. Overall, the total gas production increased progressively from 1596.3 to 2861.8 mL when temperature and pressure were increased from 200 °C and 2.0 MPa to 360 °C and 19.4 MPa, respectively. Interestingly, it dropped suddenly to 2379.2 mL at 380 °C and 22.0 MPa, which was mainly ascribed to the great reduction of CO₂ yield which was in good agreement with total gas production. Under subcritical water condition, CO₂ was the major gas component

(> 90%) due to predominant decarboxylation reaction throughout HTC. Formation of H₂ and CH₄ initiated at 260 °C and 280 °C, respectively, but only became obvious from 360 °C, revealing that dehydrogenation/demethanation occurred and became intense with the increased temperature. CO fraction increased to ca. 3% when the temperature was above 260 °C, which might be associated with increased decarbonylation reaction. At 380 °C, H₂ and CH₄ yield achieved 0.14 and 0.24 mol/(kg organic matter), respectively, which were nearly twice of those at 360 °C. The reduced CO₂ and increased CH₄ yields imply that methanation reaction was facilitated, leading to a distinct decrease of total gas yield. Nevertheless, H₂ and CH₄ fractions increased to 3.7% and 6.5%, respectively, while CO₂ fraction decreased to 84.1%. The significant difference in total gas and H₂ yields suggested that H₂ generation was favorable above critical point of water. In this case, CO tended to form, which was 5.8% at 380 °C and 22.0 MPa.

4.3.1.2 Effect of CaO

As depicted in Figure 4.2, gas production decreased from 1765.8 to 698.5 mL as Ca/C molar ratio increased from 0.05 to 0.2. It seems that gas production declined substantially when Ca/C molar ratio was 0.1 but dropped slightly afterwards. At Ca/C molar ratio of 0.05, H₂ and CH₄ yields did not change too much but CO₂ and CO yields decreased by 26.7% and 40% to 2.65 and 0.15 mol/(kg organic matter), respectively. When Ca/C ratio was 0.1, H₂ yield nearly doubled to 0.25 mol/(kg organic matter) while CO₂ decreased significantly to 0.62 mol/(kg organic matter). Nonetheless, CO yield increased slightly. Thus, H₂ and CH₄ fractions were 18.2% and 22.2%, respectively, whereas CO₂ and CO accounted for 45.3% and 14.3%, respectively. When Ca/C molar ratio was 0.2, H₂ yield grew almost 6-fold to 0.72 mol/(kg organic matter). In contrast, CO₂ yield was only 0.01 mol/(kg organic matter) and its composition in gas product was

negligible. A relatively constant CO yield made up 15.9% whereas H₂ and CH₄ were 58% and 26%, respectively. It has been pointed out that CaO acts as in-situ CO₂ absorber via carbonation and thus promotes WGS towards H₂ rich gas production (He et al., 2015b; Onwudili and Williams, 2013b) Hence, it can be concluded that CaO additive could accomplish simultaneous carbon sequestration and H₂ yield enhancement during HTC of SS but CO yield (decarbonylation reaction) was not greatly affected.

Figure 4.2 Effects of various operating temperature/pressure and Ca/C molar ratios on (a) gas yield as well as total gas volume and (b) gas composition during HTC of DSS.

4.3.1.3 Effect of moisture content

The effect of moisture content in SS (82.5 to 95 wt.%) on gas yield and composition is described in Figure 4.3. Since less organic matter was fed in the reactor with the increase of moisture content, the total gas production presented a decreasing trend from 2379.2 to 743.0 mL but CO₂ yield increased. More specifically, it reached 4.97 mol/(kg organic matter) at moisture content of SS of 95 wt.%, indicating significant decarboxylation reaction occurred under very high moisture content. Furthermore, the reduction of CO₂ under lower moisture

content could also be ascribed to the preferable carbonization reaction of carbonaceous substances (Xu, Z. R. et al., 2012). Generally, the total gas yield slightly decreased around 4.20 mol/(kg organic matter) with the increased moisture content. Interestingly, it increased dramatically to 5.33 mol/(kg organic matter) at moisture content of 95 wt.% as a result of favorable hydrolysis and decarboxylation reactions. Different from results under SCWG reported by Xu, Z. R. et al. (2012), H₂, CH₄, and CO yields generally decreased with the increase of moisture content in this study. Accordingly, when the moisture content was elevated from 82.5 to 95 wt.%, CO₂ fraction increased from 84.1 to 93.3% while H₂, CH₄, and CO fractions declined gradually to 2.5%, 2.0%, and 2.1%, respectively. Hence, under low temperature HTC, it is advisable to directly employ DSS as feedstock for more H₂ and CH₄ production.

Figure 4.3 Effect of moisture content of DSS on (a) gas yield well as total gas volume and (b) gas composition during HTC of DSS. Operating conditions: 380 °C and 22 MPa for 20 min in the absence of CaO with an initial 820 mL ambient air in the headspace.

4.3.2 Distribution of solid and liquid products

4.3.2.1 Effect of operating temperature/ pressure

Figure 4.4a presents the influence of operating temperature/pressure on recovery rates of liquid and solid products. LR (> 85 vol.%) were found to be higher than SRs (< 70 wt.%), which was due to the dissolution and decomposition of organic matter during HTC. Under relatively low temperatures (i.e. 200 and 220 °C), liquid residues showed dark brownish color. Since low temperature favored the liquefaction of SS (Zhai et al., 2014), bio-oil in aqueous phase could not be effectively separated. In this study, the vacuum filtration process for aqueous samples derived at 200 and 220 °C was more difficult than that for the rest samples, and thus more aqueous phase was lost, causing LR of ca. 87 vol.%. When the temperature was higher than 240 °C, an extremely high LR (> 96 vol.%) was obtained. Especially, between 280 and 320 °C, LR was higher than 99 vol.%, suggesting that dehydration reaction was favorable. At 340 to 380 °C, LRs were reduced by ca. 2 vol.%. This might be associated with WGS which promotes H_2 generation when the condition approaches the critical point. In contrast, SRs decreased from 66.56 to 43.11 wt.% with increased temperature/pressure. SRs and HHVs of solid products in Table 3 were combined to calculate RE values during HTC. The trend of RE value was consistent with that of SRs. HC-200 exhibited the highest RE value of 12.6 MJ/kg Dry SS, while RE values were between 10.2 and 11.1 MJ/kg Dry SS for hydrochars derived at temperature ranging from 220 to 340 °C. When temperature increased further, RE values dropped to about 8.5 MJ/kg Dry SS. Although high temperature/pressure had detrimental effects on REs, fuel quality and water characteristics of processing effluents are crucial parameters to be taken into consideration in HTC design.

Figure 4.4 Liquid and solid residues recovery rates, recovered energy as hydrochar (MJ/kg DSS) under (a) various operating temperature/pressure as well as Ca/C molar ratios and (b) different moisture contents of DSS during HTC process.

4.3.2.2 Effect of CaO

In comparison with HTC at 380 °C, LR increased to 99.2 vol.% after addition of 3.08 g CaO, which implies that small amount of CaO could greatly improve dehydration reaction. When Ca/C molar ratio was elevated to 0.2, there was a slight decrease of LRs as water could be reacted in facilitated WGS as discussed in Section 4.3.1. With more inorganic CaO addition, SR presented a continuous increase while RE value decreased from 8.2 to 5.5 MJ/kg Dry SS. CaO significantly improved H₂ yield and captured carbon to mitigate CO₂ emissions, however, inorganic residues could also greatly reduce calorific values of solid products.

4.3.2.3 Effect of moisture content

The effect of moisture content on LRs and SRs is presented in Figure 4.4b. With the increase of moisture content from 82.5 to 95 wt.%, LR firstly increased to 98.3 vol.% for moisture content of 90 wt.% and then declined to 93.3 vol.% for moisture content of 95 wt.%. This variation of LR was probably ascribed to better carbonization performance (e.g. deoxygenation and dehydration) at relatively

high moisture content. But when it was higher than 90 wt.%, more organic matter could be dissolved and decomposed into small molecules and liquefaction of these intermediates tended to form viscous bio-oil. Thus liquid phase may get lost within the membrane filters during vacuum separation. Similar tendency was observed for SRs. Particularly, SRs for HC-85 and HC-90 were higher (45.4 and 45.7 wt.%, respectively) but SRs for HC-92 and HC-95 (35 and 37.3 wt.%, respectively) were lower than 43.1 wt.% for original DSS. This phenomenon could be reflected by gas evolution. For instance, distinct CO₂ released at 95 wt.%. Due to these effects, RE values were generally higher (around 8.8 MJ/kg Dry SS) for HC-85 and HC-90 while the value was even lower than 6.3 MJ/kg Dry SS for HC-92 and HC-95.

4.3.3 Fuel characteristics of solid products and ERR

Tables 4.3 summarizes fuel characteristics of solid products under different reaction conditions and CaO amounts during HTC in terms of proximate analysis, fuel ratio, ultimate analysis, HHV, and ERR.

4.3.3.1 Effect of operating temperature/ pressure

During HTC, VM component of organic matter in DSS was partially dissolved and contributed to the formation of additional FC via carbonization (Chen et al., 2013b). Thus VM decreased to 12.86% while FC increased to 47.03% until the temperature/pressure reached 320 °C and 12.0 MPa. Interestingly, VM (42.03%) was much higher than FC (16.80%) in HC-340, indicating VM may not be transformed to FC but form heavy oil which subsequently deposited on the surfaces of hydrochars. It has been reported that highest heavy oil yield was obtained at 350 °C during hydrothermal processing of SS (Xu and Lancaster, 2008). For HC-360 and HC-380, the evolution of VM and FC mainly relied on the transformation degree of heavy oil to FC and carbon-containing light gases. Based on the variations of FC and VM, fuel ratio reached a peak value of 3.66 at

Table 4.3 Fuel characteristics of solid products derived from HTC of DSS.

	Proximate analysis (wt.%, db)			Fuel ratio	Ultimate analysis (wt.%, db)					HHV (MJ/kg)	ERR (%)
	Ash	VM	FC		C	H	N	S	O ^a		
HC-200	32.76	55.55	11.69	0.21	41.83	5.49	5.15	4.19	10.58	19.00	70.37
HC-220	35.82	51.82	12.36	0.24	41.43	5.09	4.48	4.04	9.14	18.52	58.89
HC-240	38.88	49.60	11.52	0.23	41.57	5.07	4.10	4.11	6.27	18.66	61.29
HC-260	37.78	47.06	15.16	0.32	43.92	5.03	3.92	4.04	5.30	19.43	60.42
HC-280	38.72	37.68	23.60	0.63	44.56	5.13	3.82	3.88	3.89	20.24	61.52
HC-300	38.80	18.24	42.96	2.36	44.48	5.03	3.73	3.94	4.03	20.30	60.31
HC-320	40.11	12.86	47.03	3.66	43.74	4.86	3.56	3.73	4.00	20.35	58.30
HC-340	41.17	42.03	16.80	0.40	44.38	4.83	3.52	3.68	2.42	20.23	56.73
HC-360	44.23	18.88	36.89	1.95	42.87	4.50	3.29	3.55	1.57	19.24	47.73
HC-380	43.20	38.25	18.55	0.48	42.99	4.46	3.22	3.56	2.57	19.58	46.96
SR-Ca-0.05	56.10	42.03	-	-	34.43	3.75	1.95	3.67	-	14.91	45.33
SR-Ca-0.1	65.70	43.00	-	-	29.35	2.91	1.33	3.30	-	11.64	39.06
SR-Ca-0.2	76.80	43.27	-	-	22.90	1.89	0.78	2.66	-	7.31	30.82
HC-85	43.80	40.12	16.08	0.40	42.79	4.46	3.09	3.93	1.93	19.56	49.40
HC-90	44.40	42.53	13.07	0.31	42.19	4.65	2.72	4.00	2.05	19.23	48.90
HC-92	47.90	39.72	12.38	0.31	37.65	4.21	2.38	4.01	3.86	17.96	34.98
HC-95	50.90	40.38	8.72	0.22	37.01	4.18	2.26	4.00	1.65	16.69	34.64

db, on dry basis; VM, volatile matter; FC, fixed carbon; Fuel ratio, FC/VM ; HHV, higher heating value.

^a Calculated by difference on dry ash-free basis. -: Not applicable. The formation of CaCO₃ via carbonation after addition of CaO increased VM in corresponding solid products due to CaCO₃ decomposition under high temperature in proximate analysis. Moreover, in ultimate analysis, decomposition of inorganic CaCO₃ affected accurate O calculation.

320 °C. Afterwards, due to loss of VM into gases and less FC formation, fuel ratio was only 0.48 for HC-380. Besides, with the weight loss into gas and liquid products, the inert ash component presented a continuous increase to ca. 44%.

Ultimate analysis results showed the elemental composition changes in solids, which reflected the predominant reactions in HTC process. With increased temperature/pressure, H, N, S, and O contents were reduced from 6.2%, 6.04%, 5.62%, and 20.5% for DSS to 4.46%, 3.22%, 3.56%, and 2.57% for HC-380, respectively. C contents for all solid products were higher than that in DSS (39.88%). Good carbonization performance was obtained at 320 °C, giving a C content of ca. 44%. Because of improved gasification in near-critical water (e.g. 360 °C/19.4 MPa and 380 °C/22.0 MPa), C content for HC-360 and HC-380 slightly declined. It is also noted that N and S contents leveled off after reduction rates of about 47% and 37%, respectively. This reveals that more active H radicals were necessary to break down $-C-S=$ and $-C-N=$ bonds in heterocyclic rings in SCW (Ogunsola and Berkowitz, 1995), especially for DSS with complex composition. Alternatively, catalysts or additives may help to further eliminate recalcitrant heterocyclic sulfur and nitrogen precursor in solids.

The evolution of elemental compositions resulted in elevated HHVs of solids which were 1.03-1.13 times higher than that (17.97 MJ/kg) of DSS. Since intensive decarboxylation and dehydration reactions but less vigorous dehydrogenation and demethanation reactions took place, HC-320 exhibited superior fuel quality with highest fuel ratio (3.66) and HHV (20.35 MJ/kg). Additionally, ERR decreased to 46.96% with elevated reaction temperature/pressure and was below 60% when exceeding 320 °C and 12.0 MPa.

4.3.3.2 Effect of CaO

Adding CaO could definitely increase the ash content in solids. VM increased by 5% to 43% because the formed CaCO_3 via carbonation could be released in ultimate analysis. Thus FC could not be calculated due to an overlap of CaCO_3 between ash and VM. C, H, and N contents were reduced when Ca/C molar ratio increased from 0.05 to 0.2. According to gas yields in Figure 4.2, the reduced C content was likely to be released as CH_4 in gas products and dissolved organic carbon in liquid phase. Low H content (1.89%) in solid residue was derived because CaO additive facilitated H_2 yield. Importantly, N content was further reduced to 0.78% for SR-Ca-0.2, whereas S was removed slightly. This suggests that CaO was more effective to reduce N than S, which could be related with OH^- ions catalyzed hydrolysis of nitrile-N and amide-N under basic hydrothermal condition (Akimoto et al., 2002). The detailed mechanism is still under investigation. As the Ca/C molar ratio increased from 0.05 to 0.2, HHV decreased to 7.31 MJ/kg and EER was 30.82%. Solid residues with high CaO addition could be suitable for landfilling disposal.

4.3.3.3 Effect of moisture content

As shown in Table 4.3, moisture content had greater influence on FC than VM in hydrochars. When the moisture content increased from 82.5 to 95 wt.%, FC declined progressively from 18.55% to 8.72%. Nevertheless, VM remained constant around 40%, leading to decreased fuel ratio to 0.22. This implies that lower moisture content favored carbonization because VM was converted to FC except gasification. On the other hand, gasification mainly resulted from decomposition of FC and became more intense under higher moisture content of SS feedstock. As a consequence of greatly reduced FC, ash content was 50.90% which was even higher compared to HC-380. Unlike relatively high S content (4%), C, H, and N contents exhibited a decreasing trend. Since protein nitrogen

accounted for the majority of nitrogen functionality (Liu et al., 2015; Tian et al., 2013), it is postulated that hydrolysis of N-containing compounds was preferential in high water condition. In contrast, S-containing compounds were more temperature sensitive and mainly removed through cleavages of bonds in heterocyclic rings (e.g. $-C-S=$) due to higher activation energy of reactants under higher temperature/pressure. Promoted hydrolysis of organic matter with elevated moisture content caused a decreasing HHV while ERR was significantly reduced. Especially, HHV of hydrochars could be even lower than that of DSS (17.97 MJ/kg) when moisture content exceeded 92 wt.%.

4.3.4 Water characteristics of liquid products

The influence of reaction conditions and CaO additive was discussed herein in terms of wastewater parameters (i.e. TOC, COD, pH, NH_4^+ -N and TDN), mineralization of heteroatomic compounds, and extraction or solubility of heavy metals as well as mineral elements.

4.3.4.1 Evolution profiles of TOC, COD, pH, NH_4^+ -N and TDN

(1) Effect of operating temperature/ pressure

As presented in Figure 4.5a and b, TOC and COD decreased from 24.07 and 63.9 g/L to 12.51 to 30.4 g/L, respectively, by increasing temperature/pressure, while IC was accumulated from 0.48 to 3.67 g/L. This suggests that gasification was faster than hydrolysis and dissolution of organic substances while carbon underwent gradual mineralization. The pH value decreased from 8.6 to 8.3 at 240 °C but fluctuated around 8.3 thereafter, which may result from IC variation and/or other acidic substances dissolution. TDN generally showed a downward trend while NH_4^+ -N increased from 4020 to 7980 mg/L with elevated temperature due to deamination (Chen et al., 2014). Reduced TDN and N in solids could lead to N-containing gas but it was negligible in final gas products according to gas analysis. Overall, NH_4^+ -N release was divided into three stages, i.e. steady

Figure 4.5 Effects of various operating temperature/pressure as well as Ca/C molar ratios (a, b, and c), and moisture content of DSS (d, e, and f) on water characteristics of liquid products during HTC process. Operating conditions for different moisture contents of DSS: 380 °C and 22 MPa for 20 min in the absence of CaO with an initial 820 mL ambient air in the headspace.

increase from 4020 to 5380 mg/L at 200 to 240 °C, being constant around 6400 mg/L between 260 and 320 °C, and continuous increase from 7200 to 7980 mg/L at 340 to 380 °C.

(2) Effect of CaO

Adding CaO created an alkaline hydrothermal condition with pH value soaring from 8 to 10. The increased alkalinity promoted solubility of organic compounds and caused a drastic increase of TC, TOC, and COD to 23.37, 18.63, and 55.80 g/L, respectively. Since gasification was also enhanced, TOC and COD dropped to 16.61 and 49.4 g/L, respectively. The increased IC was probably due to improved mineralization of organic carbon at Ca/C molar ratio of 0.2. Moreover, the addition of CaO led to sharp increase of TDN to above 12000 mg/L regardless of CaO amount. On the other hand, NH_4^+ increased gradually from 8540 to 9960 mg/L as the Ca/C molar ratio was elevated from 0.05 to 0.2. The TDN increase could be due to catalyzed hydrolysis N-containing compounds in SS under alkaline condition (Liu et al., 2015), whereas the continuous release of NH_4^+ could be attributed to the increased Ca^{2+} ion concentration which facilitated deamination of amines.

(3) Effect of moisture content

TC, TOC, IC, and COD demonstrated an obvious diminishing trend from 16.18, 12.51, 3.67, and 31.4 g/L at moisture content of 82.5 wt.% to 7.6, 5.63, 1.97, and 11 g/L at moisture content of 95 wt.%, respectively (Figure 4.5d and e). Even though hydrolysis could be favored, dilution effect dominated these evolutions under higher moisture content, while pH value increased from 8.12 to 8.46 as well. In Figure 4.5f, NH_4^+ and TDN decreased from 7980 and 10040 mg/L to 3660 and 4860 mg/L with increasing moisture content. However, NH_4^+/TDN ratio initially decreased but increased to ca. 75% at moisture content of 95 wt.%, implying that improved hydrolysis outweighed dilution effect.

4.3.4.2 Mineralization behavior of heteroatomic compounds

Effects of reaction condition and CaO on concentrations of major anions detected in liquid products were illustrated in Table 4.4. When the reaction temperature

increased from 200 to 380 °C, F⁻ concentration accumulated from 109.08 to 584.05 mg/L. Particularly, F⁻ concentration was almost 2- fold compared to that at 360 °C, which indicated SCW was powerful to crack C–F bonds (Hori et al., 2012). Because of metal oxides (including iron) in DSS, this result could be in relation to enhanced mineralization of PFCs via radical reactions in SCW. When Ca/C molar ratio increased from 0.05 to 0.2, free F⁻ concentration reduced from 473.12 to 216.14 mg/L, which may result from F⁻ fixation by calcium to form CaF₂ (Wang et al., 2013).

SO₄²⁻ concentration presented a highest value of 1249.48 mg/L at 200 °C (Table 4.4). Subsequently, it slightly decreased and fluctuated around 1000 mg/L. Alif et al. (2013) found that S-containing organic compounds were extracted at low temperatures and decomposed at high temperatures. Furthermore, they claimed that alkali promoted destruction of S-containing organic compounds into inorganic forms (e.g. SO₄²⁻ and S²⁻) which could be trapped as precipitants (i.e. CaSO₄ and CaS) after addition of CaO. Thus, SO₄²⁻ concentration decreased sharply with the increase of Ca/C molar ratio. Unlike evolutions of F⁻ and SO₄²⁻ anions, Cl⁻ concentration was relatively stable between 172.86 and 217.53 mg/L along the temperature/pressure applied. It is speculated that further dechlorination of organic chlorine compounds in DSS was limited under current hydrothermal conditions. After adding CaO, Cl⁻ concentration decreased to 114.65 mg/L, which might be captured by calcium, such as hydrocalumite (Ca₈Al₄(OH)₂₄(CO₃)(Cl) (H₂O)_{9.6}) as suggested by Bayuseno et al. (2009). Due to dilution effect, F⁻, Cl⁻, and SO₄²⁻ concentrations decreased to 130.81, 30.33, and 289.99 mg/L, respectively, when moisture content was 95 wt. %.

4.3.4.3 Solubility and immobilization behaviors of heavy metals and mineral elements

Table 4.4 presents heavy metals and mineral elements concentrations in the liquid phase after HTC. Cu and Pb concentrations remained constant, however, the concentrations of Cr, Zn, Ni, Ca, Al, Fe, and P decreased to various degrees during heating up from 200 to 380 °C. Especially, Ni was not detectable after 260 °C, showing the best immobilization performance. Higher temperature/pressure had positive effects on Cr precipitation (from 1.12 mg/L at 200 °C to 0.78 mg/L at 380 °C) within 20 min, which was consistent with results by Zou et al. (2013). It has been reported that metals were readily transformed into dissolved ions under hydrothermal conditions and metal sulfide took place after cooling down (Liang et al., 2012). Higher temperature increased zinc ion diffusion and subsequent hydrothermal sulfidation in the form of ZnS, thereby achieving better stabilization of Zn (Liang et al., 2012). Additionally, significantly dissolved Ca, Al, Fe, and P could interact with each other to form more stable structures which was similar to the effect of CaO additive.

Upon addition of CaO, increased OH^- concentration facilitated dissolution of AlPO_4 to release PO_4^{3-} which subsequently reacted with Ca^{2+} to precipitate as $\text{Ca}_3(\text{PO}_4)_2$ (Shi et al., 2014; Yildiz Bircan et al., 2011). Moreover, it was deduced that dissolved PO_4^{3-} may react with CaF_2 to form $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (Wang et al., 2013). These could be corroborated by the reduced Ca^{2+} , TP, and F^- concentrations as Ca/C molar ratio increased from 0.05 to 0.2. However, increased Fe and Pb at Ca/C molar ratio of 0.05 may be due to increased solubility and decomposition of organic compounds to release more Fe and Pb. Similar decreasing trend of Pb, Al, and Fe ion concentrations with increasing Ca/C molar ratio was observed. In the complex system under near-critical water condition, CaO tended to go through solid-solid reactions with other components (e.g. silicon (Si) and

Table 4.4 Major anions concentration (mg/L), heavy metal and mineral elements concentration (mg/L) in liquid phase products after HTC of DSS.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 15	Run 16	Run 17
F ⁻	109.08	137.22	145.68	144.12	164.33	192.14	206.99	288.58	306.80	584.05	473.12	462.72	216.14	325.15	200.65	170.49	130.81
Cl ⁻	180.04	172.86	179.80	183.24	180.52	187.94	182.44	217.53	175.38	215.29	157.82	132.22	114.65	110.04	62.34	49.82	30.33
SO ₄ ²⁻	1249.48	1138.44	1004.86	931.56	886.04	1010.47	1022.15	904.51	1021.54	1014.69	689.64	577.79	268.53	715.49	685.71	638.03	289.99
Cr	1.12	0.88	0.82	0.84	0.8	0.8	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.60	0.60	0.50	0.40
Cu	0.5	0.66	0.42	0.52	0.5	0.5	0.48	0.48	0.52	0.54	0.58	0.70	0.76	0.50	0.50	0.50	0.50
Zn	12.46	11.52	9.82	8.32	9.08	8.56	9.66	9.52	8.78	9.24	7.64	8.10	8.18	8.76	8.32	8.20	8.08
Pb	0.2	0.26	0.22	0.28	0.22	0.24	0.24	0.22	0.24	0.22	0.38	0.34	0.14	0.18	0.12	0.12	0.08
Ni	0.92	0.82	0.52	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca	74.46	49.56	50.24	77.88	77.1	63.34	30.56	20.9	25.66	36.02	20.9	16.48	15.6	38.74	45.76	54.96	58.7
Al	7.74	4.50	9.20	7.84	5.15	5.96	4.82	6.63	1.78	5.40	1.80	1.40	0.80	5.00	4.60	4.60	4.40
Fe	56.12	26.96	5.36	1.24	0.88	0.84	0.74	0.26	0.28	0.18	1.16	0.64	0.36	-	-	-	-
TP	246.0	229.2	225.4	194.8	191.4	191.0	188.4	126.3	91.6	89.4	30.2	20.8	16.0	86.4	71.4	65.8	62.0

-: Under detection limit (50 ppb).

aluminum (Al)) in the ash of DSS (Zhang, R. et al., 2010). Thus complex inorganic compounds, such as $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (mayenite), $\text{Ca}(\text{Al},\text{Si})_2\text{O}_4$ (yoshiokaite), $\text{CaFe}_3\text{SiO}_8\text{OH}$ (ilvaite) (Wang et al., 2013), $\text{Ca}_8\text{Al}_4(\text{OH})_{24}(\text{CO}_3)(\text{Cl})(\text{H}_2\text{O})_{9.6}$ (hydrocalumite), $\text{Ca}_3(\text{Al},\text{Fe})_2(\text{Si},\text{P})_3\text{O}_{12}$ (garnet), $(\text{Ca},\text{Na})_2(\text{Mg},\text{Fe},\text{Si},\text{Al})_3\text{O}_7$ (gehlenite) (Bayuseno et al., 2009), could be formed. Zn concentration decreased in alkaline hydrothermal condition while it increased slightly with CaO amount. Cr and Cu were not affected too much and Ni was not detected. Hence, under high hydrothermal temperature, an appropriate amount of CaO enhanced immobilization of heavy metals and mineral elements for further recovery.

4.4 Conclusions

Decarboxylation dominated HTC of DSS while intense dehydrogenation and methanation reactions initiated at 380 °C and Ca/C molar ratio of 0.2, thereby producing H_2 and CH_4 rich fuel gas. High moisture content favored decarboxylation and hydrolysis reactions. Despite the highest RE value at 200 °C, HHVs of hydrochars were 1.03-1.13 times higher than that of DSS. High temperature/pressure reduced TOC and COD but improved dehalogenation. Adding CaO had positive effects on deamination and immobilization of inorganic elements and anions. The holistic understanding of reaction chemistry could benefit the design of HTC for sustainable DSS utilization.

CHAPTER 5 Utilization of sewage sludge derived hydrochars towards efficient co-combustion with different rank coals: Effects of subcritical water conversion and blending scenarios*

5.1 Introduction

With the rapid urbanization and increasingly stringent regulations on the quality of effluents, sewage sludge (SS) generation from wastewater treatment plants is soaring globally (Cao and Pawłowski, 2012). In general, SS is rich in nutrients (nitrogen, phosphorus, and potassium) and organic matter which is mainly composed of proteins, carbohydrates, small amount of lipids and lignin. Thus, SS could be considered as biomass with higher heating value (HHV) comparable to lignite. Nevertheless, pollutants present in SS, for instance, heavy metals, pathogens and persistent organic pollutants, may endanger environment and human health. Thus, appropriate treatment and efficient utilization of SS is imperative. Given the refractory pollutants and desirable calorific value in SS, thermochemical processes (i.e. pyrolysis, gasification and combustion) have been widely applied as efficient technologies for final disposal and energy recovery from SS (Manara and Zabaniotou, 2012). However, high moisture content (approximately 70–80 wt.%) in dewatered sewage sludge (DSS) hindered its further utilization as solid fuels. Because of a huge amount of vicinal and bound water therein and relatively high latent heat of water, conventional mechanical and thermal drying are energy-intensive (He et al., 2014b). More recently, some novel energy-saving drying technologies have been developed, such as solvent aided dewatering (He et al., 2014b), combined hydrothermal pretreatment and convective drying (Zhao et al., 2014).

* This chapter is written based on my article “Utilization of Sewage-Sludge-Derived Hydrochars toward Efficient Cocombustion with Different-Rank Coals: Effects of Subcritical Water Conversion and Blending Scenarios”, *Energy & Fuels* (2014).

In order to reduce coal consumption by substituting certain amount of coal with SS, co-combustion of SS and coals has been explored (Magdziarz and Wilk, 2013). However, fuel characteristics between SS and coals are quite different (Park and Jang, 2011) and high volatile matter (VM) in SS could result in unstable flame. Thus, co-combustion performance of dried SS and coals may be considerably affected (Parshetti et al., 2013b). The presence of high nitrogen and sulfur contents in SS may cause high emissions of NO_x and SO_x , which could increase the cost for flue gas cleaning. Hence, it is essential to upgrade fuel quality of SS to meet requirements for co-firing purpose based on current infrastructures (Liu and Balasubramanian, 2013). Hydrothermal carbonization of SS has been applied to produce solid fuels of better quality, termed hydrochar, for energy generation without prior drying (He et al., 2013; Parshetti et al., 2013b; Zhao et al., 2013). Apart from the upgraded HHV and fuel ratio for hydrochar via dehydration and decarboxylation, it is also found that N and S precursors in hydrochar could be significantly reduced during hydrothermal carbonization (He et al., 2013). Moreover, quality of emissions from combustion of sewage sludge derived hydrochars (SHCs) can be further improved. Parshetti et al. (2013b) reported that emissions of CO and CH_4 were mitigated through co-combustion of SHC and low rank coal. During the combustion of hydrothermally pretreated sludge, as a result of transformation of protein structure via hydrothermal treatment, interaction between NO and NH_3 was facilitated and thus NO emissions could be reduced (Zhao et al., 2013). These leading research results suggest that there is a great potential to utilize SHC for existing co-firing infrastructures towards lower coal consumption and better management of SS.

Nonetheless, existence of interactions between different solid fuels during co-combustion could lead to variations of fuel reactivity and burn out characteristics

since co-combustion performance may not necessarily demonstrate synergistic interactions or simple additive behaviors as expected (Idris et al., 2012). Thus, extensive research regarding interaction effects during co-combustion has been conducted, such as co-combustion of SS and coals (Magdziarz and Wilk, 2013; Otero et al., 2007), co-combustion of biomass or pretreated biomass and coals (Gil et al., 2010; Muthuraman et al., 2010b). In particular, Parshetti et al. (2013b) studied co-combustion of low rank Indonesian coal and SHC with a blending ratio ranging from 10% to 30%. Increasing the amount of SHC addition improved combustion reactivity of blends. Besides, Liu, Z. et al. (2012) concluded that synergistic interaction between hydrochar and low rank coals was more intense than that with high rank coals due to their similar fuel characteristics. But in order to enhance combustion reactivity, SHC of better fuel quality is desired. From the perspective of considerable coal consumption reduction, greater SHC blending ratio in co-firing is more economically viable. To date, limited information and systematic research is available pertaining to fuel characteristics and combustion behavior evolutions of SHCs derived from different hydrothermal conditions and co-combustion performance with different rank coals.

Therefore, it is meaningful to screen SHC of good fuel quality for co-combustion with different coals at a wide range of blending ratio before designing co-combustion scenarios. To fill up this research gap, the main objectives of this study are to (1) investigate fuel characteristics and combustion behaviors of SHCs prepared under various hydrothermal conditions to screen the best SHC for co-combustion; (2) compare combustion behaviors of three different rank coals with SHCs; (3) analyze the co-combustion behaviors for selected SHC and three different rank coals with a wide range of Coal/SHC blending ratio; and (4) interpret interaction effects during co-combustion process.

5.2 Experimental section

5.2.1 Materials

Dewatered sewage sludge (DSS) was collected from Ulu Pandan Water Reclamation Plant in Singapore. After anaerobic digestion and dewatering process, the generated DSS possessed 82.5 wt.% of water. The DSS sample was stored in a 4 °C cold room and used directly as feedstock to prepare hydrochar solid fuels using hydrothermal conversion (HTC). Three different rank coals (i.e. Hongshaquan coal, Shuicheng lignite, and Shaerhu coal) originated from China, which were designated as Coal-1, Coal-2, and Coal-3, respectively. Prior to characterization, all the DSS, hydrochars, and coal samples were oven dried at 105 °C overnight and ground into less than 0.5 mm fine powders using a rotary mill. These samples were sealed in dry polypropylene centrifuge tubes and stored in a dry cabinet.

5.2.2 HTC experiments

HTC of DSS was conducted in a 1.0 liter stainless steel (SS 316L) fixed-head batch reactor (Parr 4577 model) which was equipped with magnetic drive stirrer, external electric heating mantle and PID controller (Parr Instrument Co., USA). The reactor was designed to withstand a maximum operating temperature and pressure of 500 °C and 35 MPa, respectively. The temperature was precisely controlled by a J-type thermocouple. The pressure was autogenously generated by the water in DSS under corresponding temperature and shown both in analogue gauge and digital indicator. Based on records from preliminary experiments, 150 g of deionized water could generate a pressure of 22.0 MPa at 380 °C which reached near-critical water condition. In each batch experiment run, 182 g of DSS, which contained approximately 150 g of water, was loaded into the reactor vessel and sealed. Subsequently, the vessel was heated up to pre-set temperature and corresponding pressure using the electric heating mantle under

a stirring speed of 500 rpm. Following the above procedure, six hydrothermal conversion conditions were applied, i.e. 220 °C and 2.6 MPa, 260 °C and 5.0 MPa, 300 °C and 9.3 MPa, 320 °C and 12.0 MPa, 340 °C and 15.5 MPa, 380 °C and 22.0 MPa. After a reaction time of 20 min under desired temperatures and pressures, the heating mantle was removed. The vessel was firstly cooled by a standing fan. When the temperature was below 200 °C, an additional internal cooling coil was then employed to quench the vessel rapidly to room temperature via cooling water circulator.

After depressurization, the vessel was opened for solid and liquid products separation and collection. Liquid products were filtered through 0.45 µm PTFE membrane filters and kept in glass vials at 4 °C for further analysis. The solid residues were carefully collected and oven dried at 105 °C for 12 h. The dry solids were ground into less than 0.5 mm fine powders and termed hydrochars hereinafter. The SHCs were designated as SHC-220, SHC-260, SHC-300, SHC-320, SHC-340, and SHC-380, respectively. The number indicates the reaction temperature.

5.2.3 Characterization of samples

For proximate analysis, ash content determination was carried out based on ASTM D3174 and VM content was measured by STA 449 F3 Jupiter Simultaneous TG-DTA/DSC Apparatus (NETZSCH-Gerätebau GmbH) according to ASTM D7582-10. The fixed carbon (FC) percentage was then calculated by difference. Moreover, fuel ratio, which is expressed as the ratio of FC to VM, represents fuel properties of solid fuels and high rank coals generally exhibit high fuel ratio (Kurose et al., 2004; Park and Jang, 2011). In this study, the fuel ratio was used to present the evolution of FC and VM during HTC and reflect the solid fuel quality of derived hydrochars for co-firing applications.

Elemental compositions (i.e. carbon, hydrogen, nitrogen, and sulfur) of DSS, hydrochars, and coals were determined by vario EL CHNS elemental analyzer. The higher heating values (HHVs) of all the solid fuel samples were measured through IKA C2000 BASIC bomb calorimeter. Table 1 summarizes basic fuel characteristics of DSS, sewage sludge derived hydrochars, and three different rank coals.

5.2.4 Preparation of hydrochar and coal blends

Given the highest HHV (20.35 MJ/kg), greatest fuel ratio (3.66) and relatively low N and S contents in SHC-320, the hydrochar and coal blends were prepared by thoroughly mixing the hydrochars derived from sewage sludge under 320 °C and 12.0 MPa with the three Chinese coals. Different blending ratios of Coal:SHC-320, i.e. 30:70, 50:50 and 70:30, were selected. According to these blending ratios, coal and hydrochars were loaded into beakers and well dispersed in water using magnetic stirring bar at 650 rpm for 24 h under room temperature. Afterwards, the mixtures were oven dried at 105 °C for 24 h and ground into fine powders for subsequent combustion behavior analysis. In order to easily identify different blends, these hydrochar and coal blends were designated as 30C70HC-1, 50C50HC-1, 70C30HC-1, 30C70HC-2, 50C50HC-2, 70C30HC-2, 30C70HC-3, 50C50HC-3, and 70C30HC-3, respectively. Specifically, “C” represents coal sample and the number before “C” was the blending ratio (%) of coal, while “HC” represents SHC-320 sample and the number before “HC” was the blending ratio (%) of SHC-320. The number after “-” stands for different rank coals (i.e. “1” represents Coal-1, “2” represents Coal-2, and “3” represents Coal-3).

5.2.5 Combustion characteristics analyses

5.2.5.1 Thermogravimetric analysis (TGA)

In this study, combustion behaviors of solid fuel samples were analyzed by Perkin

Elmer TGA7 Thermogravimetric Analyzer based on the widely used TGA method. Combustion experiments were performed according to the procedure described in our previous study (He et al., 2013). In each run, 9 mg of samples were loaded into TG pan and heated from 30 to 900 °C at a heating rate of 10 °C/min with a fixed air flow rate of 20 mL/min under an atmospheric pressure. The weight loss (TG) and the rate of weight loss (DTG) of each sample under the non-isothermal condition were recorded dynamically and used for evaluation of combustion performance and kinetics analysis of different solid fuel samples. Repeated combustion runs of samples were conducted to verify the reproducibility of experimental results and ensure that the deviations were less than 5%.

5.2.5.2 Kinetics analysis

In general, reaction kinetics during combustion process can be expressed according to the decomposition rate of solid fuels described previously (He et al., 2013; Liu, Z. et al., 2012):

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (5.1)$$

$$\alpha = (m_i - m) / (m_i - m_f) \quad (5.2)$$

$$f(\alpha) = (1 - \alpha)^n \quad (5.3)$$

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (5.4)$$

$$\beta = dT/dt \quad (5.5)$$

where α is the thermal conversion fraction of solid fuels at time t ; m_i , m , and m_f refer to the initial, instantaneous, and final mass of solid fuels, respectively; $f(\alpha)$ represents a general expression of the combustion mechanism; n is the order of reaction; k is the rate constant which can be derived by Arrhenius equation (5.4); E and A represent the activation energy (kJ mol^{-1}) and the pre-exponential factor (min^{-1}) of the reaction, respectively; R is the universal gas constant 8.314 J K^{-1}

mol^{-1} ; T is the absolute temperature (K); β denotes a constant heating rate ($10^\circ\text{C}/\text{min}$) in the present non-isothermal combustion study.

A series of combination and rearrangement of equations (5.1) – (5.5) gives:

$$\frac{d\alpha}{f(\alpha)} = A \exp\left(-\frac{E}{RT}\right) dt = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (5.6)$$

Equation (5.6) is integrated and becomes:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{T_0}^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (5.7)$$

Equation (5.7) is then transformed based on Coats-Redfern approximation method (Coats and Redfern, 1964) for kinetic parameters analysis in non-isothermal combustion process (Gil et al., 2010), giving:

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \quad (5.8)$$

Since $RT/E \ll 1$ and $1 - RT/E \approx 1$ in this study, the kinetic mechanism equation of combustion process can be described as shown in equation (5.9) (He et al., 2013):

$$\ln\left[\frac{G(\alpha)}{T^2}\right] = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (5.9)$$

When an appropriate n is selected, a straight line can be obtained by plotting $\ln [G(\alpha)/T^2]$ vs. $1/T$. Hence, E and A can be determined from the slop and intercept of this line, respectively.

5.2.5.3 Evaluation of combustion performance

Three characteristic temperatures, i.e. ignition temperature (T_i , $^\circ\text{C}$), maximum combustion rate temperature (T_m , $^\circ\text{C}$), and burn out temperature (T_b , $^\circ\text{C}$), were derived from TG-DTG data. Three points, i.e. point A, B, and C in all the figures, were identified following a previously described procedure (He et al., 2013; Liu, Z. et al., 2012; Wang et al., 2009).

According to characteristic temperatures and representative weight loss rates in combustion profiles, comprehensive combustibility index (S) was calculated to evaluate overall combustion reactivity of solid fuels (He et al., 2013).

$$S = \frac{(dw/dt)_{\max} (dw/dt)_{\text{mean}}}{T_i^2 T_b} \quad (5.10)$$

where $(dw/dt)_{\max}$ and $(dw/dt)_{\text{mean}}$ are the maximum and mean rates of weight loss (wt.%/min), respectively.

5.2.5.4 Deviation between experimental and theoretical combustion profiles

To investigate interaction phenomenon of hydrochars and coals during their co-combustion, theoretical TG and DTG curves were calculated by taking account of individual mass fraction, weight loss, and rate of weight loss of SHC-320 and coals as follows (Kastanaki et al., 2002; Xie and Ma, 2013).

$$(TG)_{\text{cal}} = x_1 (TG)_{\text{hydrochar}} + x_2 (TG)_{\text{coal}} \quad (5.11)$$

$$(dw/dt)_{\text{cal}} = x_1 (dw/dt)_{\text{hydrochar}} + x_2 (dw/dt)_{\text{coal}} \quad (5.12)$$

where $(TG)_{\text{hydrochar}}$ and $(TG)_{\text{coal}}$ are normalized weight losses derived from TG curves of independent combustion of SHC-320 and coals, respectively; $(dw/dt)_{\text{hydrochar}}$ and $(dw/dt)_{\text{coal}}$ are normalized rates of weight loss derived from DTG curves of independent combustion of SHC-320 and coals, respectively; x_1 and x_2 are the mass fractions of SHC-320 and coals in blends, respectively.

Deviations of maximum weight loss rates and residues between experimental and calculated curves can quantify whether synergistic interaction occurred after addition of hydrochars into coals. The deviations were determined according to equation (5.13).

$$\text{Deviation (\%)} = (\text{Experimental value} - \text{Calculated value}) / \text{Calculated value} \times 100 \quad (5.13)$$

5.3 Results and discussion

5.3.1 Physicochemical properties of DSS, hydrochars, and coals

5.3.1.1 Effects of HTC on fuel characteristics of hydrochars

In Table 5.1, DSS consisted of 69.01% of VM, 9.19% of FC, and 21.80% of ash, leading to a low fuel ratio (FC/VM) of 0.13. The high N and S contents (6.04% and 5.62%, respectively) imply significant pollutants emissions when DSS is directly utilized as solid fuels. The high S content may originate from enriched alkyl surfactant and perfluorooctane sulfonate compounds in DSS. High O content (20.46%) could be detrimental to the calorific value of DSS. Consequently, HHV and lower heating value (LHV) of DSS were 17.97 MJ/kg and 16.61 MJ/kg, respectively.

Table 5.1 Characteristics of dewatered sewage sludge, sewage sludge derived hydrochars, and three different rank coals.

Sample	Proximate analysis (wt.%, db)			Fuel ratio	Ultimate analysis (wt.%, db)					Calorific analysis ((MJ/kg, db)	
	Ash	VM	FC	FC/VM	C	H	N	S	O ^a	HHV	LHV ^b
DSS	21.80	69.01	9.19	0.13	39.88	6.20	6.04	5.62	20.46	17.97	16.61
SHC-220	35.82	51.82	12.36	0.24	41.43	5.09	4.48	4.04	9.14	18.52	17.40
SHC-260	37.78	47.06	15.16	0.32	43.92	5.03	3.92	4.04	5.30	19.43	18.32
SHC-300	38.80	18.24	42.96	2.36	44.48	5.03	3.73	3.94	4.03	20.30	19.19
SHC-320	40.11	12.86	47.03	3.66	43.74	4.86	3.56	3.73	4.00	20.35	19.28
SHC-340	41.17	42.03	16.80	0.40	44.38	4.83	3.52	3.68	2.42	20.23	19.17
SHC-380	43.20	38.25	18.55	0.48	42.99	4.46	3.22	3.56	2.57	19.58	18.60
Coal-1	3.36	31.11	65.54	2.11	71.96	4.54	0.76	2.02	17.36	28.85	27.86
Coal-2	17.22	48.95	33.84	0.69	50.34	5.37	0.98	2.98	23.11	22.63	21.45
Coal-3	9.93	32.66	57.41	1.76	62.77	3.66	0.64	2.52	20.48	24.37	23.57

db, dry basis.

VM, volatile matter; FC, fixed carbon; HHV, higher heating value; LHV, lower heating value.

^a Calculated by difference on dry ash-free basis.

^b Calculated by the formula: $LHV_{dry} (MJ/kg) = HHV_{dry} (MJ/kg) - 2.4418 \times (9 \times H_{dry}/100) (MJ/kg)$.

The VM content of DSS decreased significantly after HTC. The DSS had a VM content of 69.01% which decreased to 12.86% in SHC-320 with the increased temperature and pressure. The loss of VM was converted into FC and gaseous products via dehydration and decarboxylation reactions (He et al., 2013), thus FC of hydrochars increased progressively from 9.19% in DSS to 47.03% in SHC-320. Due to increased generation and deposition of light volatile organic molecules on the surface of hydrochars (He et al., 2013; Liu and Zhang, 2008), VM in hydrochars produced from severe hydrothermal treatment (i.e. 340 °C and 15.5 MPa, 380 °C and 22.0 MPa) was at least three times higher than that of SHC-320. However, further degradation and transformation of these volatile molecules in hydrochars tended to be obvious under even higher temperature and pressure. Compared with SHC-340, VM decreased from 42.03% to 38.25% in SHC-380 while slight increase (1.75%) of FC in SHC-380 may be associated with the partial conversion of VM. Furthermore, the excess loss of VM and retained minerals resulted in a constant increase of ash content (ca. 40%) in hydrochars during all the HTC conditions. Accordingly, fuel ratio increased from 0.13 for DSS to 3.66 for SHC-320 and decreased to around 0.40 afterwards.

Based on ultimate analysis results, H, N, S, and O contents in hydrochars declined as the temperature and pressure increased. Particularly, within a reaction time of 20 min under 380 °C and 22.0 MPa, the removal efficiency of N, S, and O contents reached 47%, 37%, and 87.4%, respectively. On the other hand, C content increased to around 43% to various extents. Due to the remarkable removal of O contents and increased C contents, calorific values of hydrochars were increased by 1.03 to 1.13 times. Taking into account of evolutions of three components (i.e. ash, VM, and FC) and elemental compositions in hydrochars, SHC-320 exhibited highest HHV and LHV of 20.35 MJ/kg and 19.28 MJ/kg,

respectively. Hence, from the perspectives of superior fuel characteristics compared with DSS and other hydrochars, SHC-320 was selected as sewage sludge derived solid fuel for co-combustion with coals.

5.3.1.2 Fuel characteristics of different rank coals

Coal samples showed great difference in components and elemental compositions compared to DSS and hydrochars. As shown in Table 5.1, FC contents in coals were 3.68 to 7.13 times higher than that in DSS whereas VM contents were generally lower than 69.01% in DSS. Coal-1 and Coal-2 presented highest FC (65.54%) and VM (48.95%), respectively. Fuel ratios of the three different rank coals were 2.11, 0.69, and 1.76 for Coal-1, Coal-2, and Coal-3, respectively. Ash contents in coals were typically lower than 20% and Coal-1 contained only 3.36% ash. C contents (50.34–71.96%) in coals were much higher than 39.88% in DSS while H, N, and S contents were relatively lower. Especially, N and S contents in all coal samples were less than 1% and 3%, respectively. In addition, O content was around 20%, which was comparable to that in DSS but much higher than hydrochars. Because of higher C but lower ash contents, HHVs of coals were higher than 17.97 MJ/kg of DSS, which were 28.85 MJ/kg, 22.63 MJ/kg, and 24.37 MJ/kg for Coal-1, Coal-2, and Coal-3, respectively. Overall, coal rank followed the order of Coal-1 > Coal-3 > Coal-2 in terms of these fuel characteristics.

5.3.2 Effects of HTC on combustion profiles and characteristics of hydrochars

To investigate combustion behaviors of DSS and hydrochars, the entire decomposition profiles were characterized according to evident rates of weight loss in DTG curves. As described by He et al. (2013), combustion process generally consisted of dehydration stage D, devolatilization and combustion stage E, char combustion stage F, and burn out stage.

Previously, a two-stage decomposition kinetics was proposed to assess combustion of biomass (Gil et al., 2010; Liu et al., 2002). However, taking into account of delayed combustion of heavy VM and FC in solid fuels, a modified two-stage combustion scheme was employed to describe the combustion process in the present study as follows.

where E_1 and A_1 represent activation energy and pre-exponential factor in the first combustion stage, respectively; E_2 and A_2 represent activation energy and pre-exponential factor in the second combustion stage, respectively.

Subsequently, the kinetics analysis of individual combustion stage was examined separately through Arrhenius equation by selecting an appropriate reaction order.

5.3.2.1 Combustion of DSS

As shown in Figure 5.1, stage D (30 to 100 °C) was the initial water evaporation stage and two distinct decomposition stages (stage E and F) governed the intense combustion process of DSS. Unlike a single combustion profile (250 to 450 °C) of DSS in our previous study (He et al., 2013), the two-stage combustion profile was associated with noticeable FC content (9.19%) of DSS in this study. As summarized in Table 2, the first combustion stage E was extended from 150 to 370 °C while the second combustion stage F was from 390 to 550 °C, which was similar to main combustion process of microalgae under comparable conditions as reported by Tahmasebi et al. (2013). Two pronounced peaks were observed at 277.1 °C and 483.7 °C. Peak temperatures at 277.1 °C and 320.5 °C during stage E may be related to the step-wise decomposition of carbohydrates (180–270 °C), proteins and lipids (320–450 °C) (López-González et al., 2014; Magdziarz and

Werle, 2014; Tahmasebi et al., 2013) while peak temperature around 483.7 °C could be ascribed to residual lignin decomposition and char/FC oxidation (Parshetti et al., 2013a; Vamvuka and Sfakiotakis, 2011). Moreover, weight loss in stage E (39.9%) was higher than that in stage F (27.7%), suggesting more light VM in DSS. T_i is associated with release rate of heat from early combustion of light VM in DSS. T_i is associated with release rate of heat from early combustion of light VM (Vamvuka and Sfakiotakis, 2011). As a result, T_i was only 207.7 °C and maximum weight loss was at 278.8 °C, which were quite close. However, high T_b (514.9 °C) led to a prolonged combustion process of 30.7 min. The water evolution and small amount releases of methane and carbon dioxide could be responsible for the first peak, whereas intensive decompositions of aromatic or heterocyclic hydrocarbons led to significant emissions of hydrogen, methane, and carbon dioxide in the second peak due to the abundant VM and O contents (López-González et al., 2014; Magdziarz and Werle, 2014). Nevertheless, further investigations are necessary to gain more insights into gas evolutions.

Figure 5.1 TG and DTG curves for combustion of DSS.

5.3.2.2 Combustion of hydrochars

Figure 5.2 illustrates combustion profiles of different hydrochars. Dehydration stage D of hydrochars was less obvious with the increases of temperature and

pressure, which should be relevant to more hydrophobic characteristic of hydrochars (He et al., 2013). Besides, the peak of stage E became less intense while that of stage F tended to be sharper. Weight loss in stage E decreased to 22.5% for SHC-220 but that in stage F increased to 37.0%. The combustion kinetics of SHC-260 in Table 3 indicated there may be an overlap of stage E and F, causing a board stage F (200–550 °C) with a great mass loss of 57.6%. As shown in Table 5.2, weight loss in stage F decreased from 49.2% for SHC-300 to 40.9% for SHC-380 due to accelerated de-polymerization and re-polymerization of heavy VM in subcritical water (Liu and Li, 2014). On the other hand, during HTC of sludge, formation of water soluble oil was favored at lower temperatures while increased temperature led to higher water insoluble heavy oil (HO) yield (Xu and Lancaster, 2008). HO was mainly composed of long-chain carboxylic acids, phenolic compounds and derivatives. Since the hydrochars in this study were not extracted with solvent, HO could be entrained. These small amounts of light volatile compounds contributed to slight increase of weight loss in stage E from 6.6% for SHC-300 to 8.9% for SHC-380. One apparent peak was observed around 200 °C. An increasing trend of residues agreed with previous discussion.

Figure 5.2 TG and DTG curves for combustion of hydrochars derived under different temperatures and pressures.

Because of reduced VM and elevated FC in hydrochars, T_i exhibited a remarkable increase of 70 to 108 °C as the temperature and pressure increased. Low T_i may cause potential fire hazard (Liu, Z. et al., 2012; Muthuraman et al., 2010a). In this regard, hydrochars demonstrated advantages in safe handling and storage over DSS. Though VM contents in SHC-340 and SHC-380 were much higher than lowest VM in SHC-320, T_i values of the former hydrochars were even higher, suggesting that a high VM does not necessary give lower T_i . Further, T_m also increased drastically to around 420 °C to different extents for hydrochars. There was a minor decrease of T_b within 10 °C for hydrochars derived under HTC temperature lower than 320 °C. On the contrary, T_b increased to 517.8 °C and 557.7 °C for SHC-340 and SHC-380, respectively. The noticeable decrease of FC and relatively high ash contents should be responsible for the difficult combustion. In particular, an evident shoulder in stage F for SHC-380 appeared at high temperature (470–550 °C). Main combustion was shortened to approximately 20 min. But combustion of SHC-380 lasted 24.2 min, which was the highest among SHCs. Therefore, in terms of safer T_i , higher heat release in a higher temperature region, and slightly decreased T_b during the shortened combustion profile, the performance of SHC-320 outweighed other SHCs.

Table 5.2 Combustion stages, weight loss during main combustion stage, characteristic temperatures, total burnout time and residues after combustion.

Sample	Stage D	Stage E	Stage F	Weight loss (%)		Residues (%)	Characteristic temperatures			t_b (min)
				Stage E	Stage F		T_i (°C)	T_m (°C)	T_b (°C)	
DSS	~100	150–370	390–550	39.9	27.7	21.4	207.7	278.8	514.9	30.7
SHC-220	~100	200–350	350–550	22.5	37.0	34.2	277.1	431.2	506.9	23.0
SHC-260	~100		200–550		57.6	36.8	301.4	428.3	501.1	20.0
SHC-300	~100	150–260	270–550	6.6	49.2	39.6	301.4	405.4	507.9	20.7
SHC-320	~100	150–260	300–550	7.7	46.4	38.4	301.4	413.5	506.0	20.5
SHC-340	~100	150–270	300–550	8.7	46.0	39.3	312.6	426.3	517.8	20.5
SHC-380	~100	150–270	300–550	8.9	40.9	42.9	315.9	417.9	557.7	24.2
Coal-1	~100		410–550		75.2	2.7	409.8	473.0	543.3	13.4
30C70HC-1	~100	205–280	350–550	4.1	47.8	28.2	348.2	439.0	597.5	24.9
50C50HC-1	~100	200–280	410–550	3.1	47.7	20.5	406.4	526.3	593.9	18.8
70C30HC-1	~100		410–550		58.8	12.9	429.1	518.9	587.1	15.8
Coal-2	~100		290–520		68.5	14.6	288.4	373.1	487.3	19.9
30C70HC-2	~100	200–270	300–520	4.5	51.2	32.6	299.7	401.6	535.8	23.6
50C50HC-2	~100	220–300	300–520	4.7	54.9	26.6	298.2	352.4	538.7	24.1
70C30HC-2	~100		250–520		64.9	23.1	309.5	346.6	526.3	21.7
Coal-3	~100		350–520		71.6	5.7	367.6	403.8	501.0	13.3
30C70HC-3	~100	200–270	340–550	4.5	50.8	29.2	345.0	421.1	539.5	19.5
50C50HC-3	~100	200–270	340–550	3.0	56.8	22.8	374.2	429.6	546.9	17.3
70C30HC-3	~100		370–520		57.3	15.1	375.7	427.3	518.6	14.3

t_b : burn out time, which initializes from the time corresponding to T_i till the time corresponding to T_b .

5.3.3 Combustion profiles for different rank coals

As shown in Figure 5.3, main combustion of coals was only characterized by stage F. This suggests that decomposition of VM during coal combustion requires a higher temperature as FC, resulting in a remarkable weight loss and simultaneous oxidation of heavy VM and FC (Tahmasebi et al., 2013; Zhang et al., 2013) within a narrow stage F at high temperatures. Furthermore, higher rank coal exhibited narrower stage F and greater weight loss or heat release. In Table 5.2, the width of temperature range followed the order of Coal-1 (410–550 °C) < Coal-3 (350–520 °C) < Coal-2 (290–520 °C) while the weight loss was Coal-1 (75.2%) > Coal-3 (71.6%) > Coal-2 (68.5%). Overall, T_i , T_m and T_b increased as rank of coal became higher. The relatively lower rank Coal-2 showed T_i and T_m of 288.4 °C and 373.1 °C, respectively, which were more comparable to those of SHC-320. Typically, t_b of coals was lower than DSS and hydrochars. Interestingly, t_b of SHC-320 (20.5 min) and lower rank Coal-2 (19.9 min) was similar. Thus, a more compatible co-combustion of the two fuels was anticipated. Compared to DSS and hydrochars, burn out stage of the three coals presented some fluctuations, especially for Coal-2 which produced the highest residues (14.6%), which could be attributed to decomposition of inorganic salts or metal carbonates therein at 550 to 750 °C.

Figure 5.3 TG and DTG curves for combustion of three different rank coals.

5.3.4 Effects of hydrochar on co-combustion with different rank coals

5.3.4.1 Effects of coal/hydrochar blending ratios and different characteristics of coals

(1) Patterns of combustion profiles

According to co-combustion profiles in Figure 5.4 and combustion kinetics data in Table 3, lower supplement coal of 30% and 50% resulted in a two-stage combustion (stage E and F) while there was only one distinct stage F at a high Coal/SHC-320 ratio (70:30). Nonetheless, weight loss in stage E was less than 5%. Except Coal-2, this mass loss was inclined to be slightly lower when Coal/SHC-320 ratio was elevated to 50:50. In contrast, weight loss in stage F showed an upward trend as Coal/SHC-320 blending ratio varied from 30:70 to 70:30. In addition, compared to weight loss in stage F for individual coal, this value for Coal/SHC-320 blended fuels declined drastically as the coal rank increased. Specifically, the value of Coal-2/SHC-320 retained 74.7 to 94.7% of weight loss value in lower rank Coal-2, which was higher than those of Coal-3/SHC-320 (70.9 to 80.0%) and Coal-1/SHC-320 (63.5 to 78.2%). This reveals that heat loss may be larger during co-combustion of SHC-320 with higher rank coals. Stage F in DTG curves for different coal bended fuels in Figure 5.4 was closely examined. In Figure 5.4a, d and e, in addition to the peak at T_m , there was at least one more sub-peak in stage F when low coal percentages of 30% and 50% were employed. This phenomenon may be attributed to less significant synergistic effects resulting from either apparently different or similar characteristics between two individual fuels. Since the proportion of coals was less, the combustions of coals cannot affect that of hydrochar too much. Meanwhile, though hydrochar made up of the majority in blends, it may be inadequate to alter combustion patterns of coals.

Figure 5.4 TG and DTG curves for co-combustion of SHC-320 with different rank coals at three blending ratios.

So components in Coal-1 or Coal-2 and SHC-320 may be combusted independently (Parshetti et al., 2013b). Some combustibles may overlap, thereby exhibiting several sub-peaks in DTG curves. For the rest, especially Coal-3/SCH-320, VM and FC components may interact with each other, promoting a combined and short stage F. Yet Coal-3/SHC-320 at all blending ratios showed only one sharp peak in stage F, which may be associated with intense synergistic effects. In spite of this, there was a small shoulder at high temperatures. Besides, residues increased to approximately 30% when Coal/SHC-320 blending ratio decreased to 30:70.

(2) Evolutions of characteristic temperatures

(i) Generally, T_i increased with coal blending ratio. For low Coal:SHC-320 blending ratio (30:70), T_i was 348.2 °C, 299.7 °C, 345.0 °C for 30C70HC-1, 30C70HC-2, 30C70HC-3, respectively, which fell between T_i values of SCH-320

and individual coals. Because T_i for Coal-2 was lower than that for SHC-320 and SHC-320 dominated the blends, T_i for 30C70HC-2 was higher than lower rank Coal-2. Meanwhile, T_i values for the other two blended fuels were lower compared to their respective coals due to their inherent relatively high T_i (> 350 °C). On the other hand, high blending ratio resulted in a higher T_i for their blends. Hence, when blended with higher rank coals, ignition performance could be improved in the presence of high proportion of SHC-320 but inhibited when smaller amount ($\leq 30\%$) of SHC-320 was introduced. (ii) With the increase of coal/hydrochar blending ratio, T_m of blended fuels was shifted to lower temperature (ca. 350 °C) for lower rank Coal-2 due to higher VM therein but was at higher temperature for higher rank Coal-1 (ca. 520 °C) and Coal-3 (ca. 425 °C). Interestingly, after introduction of 70% of SHC-320, T_m displayed opposite evolutions, which was decreased to 439 °C for 30C70HC-1 but increased to 401.6 °C for 30C70HC-2. This was mainly related to the predominant role of SHC-320 in blends, resulting in a T_m close to that of SHC-320. Due to prominent intrinsic characteristics of the two coals, their blends exhibited opposite behaviors. (iii) T_b of all blends increased dramatically by ca. 20 to 50 °C to different extents, thereby extending t_b up to 24.9 min for 30C70HC-1. Although Coal-2 and SHC-320 presented similar t_b , t_b of their blends was obviously greater. Under the same blending ratio, it is worth noting that t_b for combustion of SHC-320 with high rank Coal-1 and low rank Coal-2 was longer than that of moderate rank Coal-2. Thus, a shorter combustion process may be expected for blends of SHC-320 with moderate rank coals.

5.3.4.2 Analysis and comparison of kinetic parameters

Two important kinetic parameters, i.e. activation energy (E) and pre-exponential factor (A), were determined to obtain in-depth insights into combustion behaviors of DSS, hydrochars, coals, and respective blends. Based on the two-stage

combustion scheme proposed in Section 5.3.2 and different combustion stages in TG-DTG curves, data derived from individual stages were carefully screened and applied for kinetics analysis through linear regression by selecting the most suitable reaction order. As shown in Table 5.3, the first-order oxidative mechanism was the best fitting and reliable model with correlation coefficient (R^2) ranging from 0.9501 to 0.9973, which agreed with claims from combustions of DSS, hydrochars, and hydrochar-lignite blends (Chen, Yunan et al., 2013; Liu, Z. et al., 2012; Parshetti et al., 2013a; Parshetti et al., 2013b). Moreover, kinetic parameters derived from TG-DTG curves under constant heating rate and iso-conversional method were in good agreement in qualitative terms (Liao and Ma, 2010). Thus, kinetics data were interpreted for comparison below.

DSS showed lower E_1 and A_1 (18.12 kJ mol⁻¹ and 1.43 min⁻¹, respectively) under the first combustion stage but higher E_2 and A_2 (32.31 kJ mol⁻¹ and 26.14 min⁻¹, respectively) during the second combustion stage. After HTC, E_1 for hydrochars increased by 8.31–16.37 kJ mol⁻¹ to around 30 kJ mol⁻¹, confirming better reactivity of DSS than hydrochars at low temperatures. Particularly, E_1 for SHC-220 and SHC-320 was relatively lower (26.43 and 28.98 kJ mol⁻¹, respectively) while E_1 for SHC-340 was the highest (34.49 kJ mol⁻¹), which was in relation to their T_i values. This reflects that SHC-220 and SHC-320 may be more reactive to ignite than other hydrochars. Interestingly, excluding SHC-380, E_2 values for all the other hydrochars were similar to that of DSS, suggesting comparable energies to oxidize char and FC. Compared with DSS, A_1 for hydrochars increased while A_2 decreased slightly due to compensation effects. The lowest E_2 (27.61 kJ mol⁻¹) and A_2 (6.60 min⁻¹) values for SHC-380 could be mainly attributed to the lower concentrations of heavy VM and FC therein as A is closely related to concentrations of reactants based on Collision Theory (Goldfarb and Liu, 2013).

Table 5.3 Combustion kinetic parameters of DSS, hydrochars, three different rank coals and their respective blends with hydrochar derived under 320 °C and 12.0 MPa for 20 min.

Sample	Temperature range (°C)	E (kJ mol ⁻¹)	A (min ⁻¹)	n	R^2
DSS	150–370	18.12	1.43	1	0.9873
	390–550	32.31	26.14	1	0.9501
SHC-220	200–350	26.43	6.59	1	0.9911
	350–550	32.29	23.58	1	0.9883
SHC-260	200–550	29.97	13.86	1	0.9942
SHC-300	150–260	30.53	18.11	1	0.9920
	270–550	32.13	20.58	1	0.9952
SHC-320	150–260	28.98	14.50	1	0.9957
	300–550	32.60	22.70	1	0.9927
SHC-340	150–270	34.49	59.59	1	0.9899
	300–550	33.60	25.68	1	0.9894
SHC-380	150–270	31.62	33.86	1	0.9821
	300–550	27.61	6.60	1	0.9910
Coal-1	410–550	87.60	2.22×10^5	1	0.9953
30C70HC-1	205–280	13.66	0.10	1	0.9973
	350–550	37.69	25.80	1	0.9911
50C50HC-1	200–280	8.84	0.02	1	0.9923
	410–550	50.03	205.24	1	0.9809
70C30HC-1	410–550	61.74	1653.08	1	0.9798
Coal-2	290–520	39.07	101.81	1	0.9919
30C70HC-2	200–270	42.82	218.33	1	0.9942
	300–520	38.69	61.21	1	0.9962
50C50HC-2	220–300	13.20	0.10	1	0.9964
	300–520	38.06	52.44	1	0.9963
70C30HC-2	250–520	45.84	222.23	1	0.9796
Coal-3	350–520	62.22	5092.79	1	0.9893
30C70HC-3	200–270	12.97	0.14	1	0.9900
	340–550	40.11	72.19	1	0.9923
50C50HC-3	200–270	4.35	0.01	1	0.9915
	340–550	44.37	140.07	1	0.9860
70C30HC-3	370–520	58.35	2115.05	1	0.9909

Higher rank coal presented greater activation energy and pre-exponential factor,

which followed the order of Coal-1 ($87.60 \text{ kJ mol}^{-1}$ and $2.22 \times 10^5 \text{ min}^{-1}$) > Coal-3 ($62.22 \text{ kJ mol}^{-1}$ and 5092.79 min^{-1}) > Coal-2 ($39.07 \text{ kJ mol}^{-1}$ and 101.81 min^{-1}). However, E values for coal blends in all combustion stages were lower than their respective coals. E_1 decreased with the elevated percentages of coals, suggesting the decrease of activation energy to initiate decomposition of coal blended fuels (Goldfarb and Liu, 2013). On the other hand, E_2 gradually increased (37.69 to $61.74 \text{ kJ mol}^{-1}$ for Coal-1/SHC-320; 38.69 to $45.84 \text{ kJ mol}^{-1}$ for Coal-2/SHC-320; 40.11 to $58.35 \text{ kJ mol}^{-1}$ for Coal-3/SHC-320) as percentages of coals increased from 30% to 70%, pointing out that higher energy was required to overcome barriers resulting from ring-opening, depolymerization, recondensation and repolymerization (Gai et al., 2013). Similar trend was observed for A values. As percentages of coals were elevated to 70%, A_2 increased drastically to 1653.08 min^{-1} , 222.23 min^{-1} and 2114.05 min^{-1} for 70C30HC-1, 70C30HC-2 and 70C30HC-3, respectively, whereas A_1 was approaching 0.

5.3.4.3 Evaluation of combustion performance

Table 5.4 illustrates $(dw/dt)_{\text{mean}}$, $(dw/dt)_{\text{max}}$, and S values for DSS, hydrochars, coals, and Coal/SHC-320 blends. DSS exhibited greatest S (11.63×10^{-8}) among all solid fuels, including three coals. This was primarily contributed by lowest T_i as $(dw/dt)_{\text{mean}}$ ($0.90 \text{ wt. \%/min}$) and $(dw/dt)_{\text{max}}$ ($2.87 \text{ wt. \%/min}$) for DSS were far lower than $(dw/dt)_{\text{mean}}$ ($1.12 \text{ wt. \%/min}$) and $(dw/dt)_{\text{max}}$ ($7.58 \text{ wt. \%/min}$) for highest rank Coal-1, respectively. Since low T_i ($< 220 \text{ }^\circ\text{C}$) could pose fire hazard, especially during co-milling of DSS and coals, it is not advisable to directly utilize DSS as solid fuels. SHC-220 and SHC-320 presented higher S value around 5×10^{-8} among hydrochars. Similarly, despite relatively lower $(dw/dt)_{\text{mean}}$ ($0.98 \text{ wt. \%/min}$) and $(dw/dt)_{\text{max}}$ ($4.54 \text{ wt. \%/min}$), lower rank Coal-2 possessed a higher S (10.98×10^{-8}) than Coal-1 (9.30×10^{-8}) and Coal-3 (10.85×10^{-8}). With the increase of coal blending percentage, $(dw/dt)_{\text{mean}}$, $(dw/dt)_{\text{max}}$, and S increased.

Unexpectedly, 70C30HC-3 showed higher $(dw/dt)_{\max}$ than 70C30HC-1 although this value for Coal-3 was much lower than that for Coal-1, suggesting that more intense synergistic effects may occur during main combustion. Overall, higher coal percentages of 50% and 70% provided higher S and blends of SHC-320 with moderate rank Coal-3 gave the highest S value compared to other blends.

Table 5.4 Comprehensive combustibility index for DSS, hydrochars, three different rank coals and their respective blends with hydrochar derived under 320 °C and 12.0 MPa for 20 min.

Sample	$(dw/dt)_{\text{mean}}$	$(dw/dt)_{\text{max}}$	$S \times 10^8$
DSS	0.90	2.87	11.63
SHC-220	0.76	2.83	5.53
SHC-260	0.73	2.99	4.79
SHC-300	0.69	3.04	4.55
SHC-320	0.71	3.26	5.04
SHC-340	0.70	3.44	4.76
SHC-380	0.66	2.61	3.10
Coal-1	1.12	7.58	9.30
30C70HC-1	0.82	3.40	3.85
50C50HC-1	0.91	4.79	4.44
70C30HC-1	1.00	6.07	5.62
Coal-2	0.98	4.54	10.98
30C70HC-2	0.77	3.07	4.91
50C50HC-2	0.84	3.22	5.65
70C30HC-2	0.88	4.50	7.85
Coal-3	1.08	6.80	10.85
30C70HC-3	0.81	4.53	5.71
50C50HC-3	0.89	5.29	6.15
70C30HC-3	0.97	6.24	8.27

5.3.5 Interactions between hydrochar and coals during their co-combustion

Figure 5.5 depicts the comparisons of experimental and calculated TG and DTG curves for co-combustion of SHC-320 and different rank coals. The experimental curves always deviated from corresponding calculated curves. Compared with

calculated DTG curves, T_m in experimental DTG curves was shifted to higher temperatures for SHC-320 blended with higher rank Coal-1 and Coal-3, but moved towards to lower temperatures for blends with lower rank Coal-2. In addition, through careful examinations on TG-DTG curves in Figure 5.5, more remarkable interactions were observed under high temperatures than low temperature region, which coincided with previous findings (Xie and Ma, 2013). In Table 5.5, corresponding characteristic parameters at high temperatures, such as T_m , $(dw/dt)_{\max}$ and residues contents, were obtained from experimental and calculated TG-DTG curves. Moreover, deviations between experimental and calculated data were determined for quantitative comparisons.

The results in Table 5.5 suggest that both positive and negative interactions between different coals and hydrochars took place during co-combustion. Briefly, “+” $(dw/dt)_{\max}$ deviation implies that higher $(dw/dt)_{\max}$ can be expected and heat loss could be less, while “+” residues deviation reveals that there are greater combustion difficulties and thus more incomplete combustions occurs during co-combustion. In this regard, “+” $(dw/dt)_{\max}$ and “-” residues deviations present the most favorable synergistic effects, which is desired during co-combustion of coal/hydrochar blends. Conversely, “-” $(dw/dt)_{\max}$ and “+” residues deviations indicate the highest anti-synergistic effects, which should be avoided when designing co-combustion scenarios. Synergistic effect index values were defined and marked accordingly.

On the whole, deviations for $(dw/dt)_{\max}$ varied significantly while those for residues were within $\pm 7\%$. 50C50HC-1, 70C30HC-1 and 70C30HC-3 presented most intense synergistic effects while 30C70HC-1, 30C70HC-2 and 50C50HC-2 showed highest anti-synergistic effects. Compared with calculated values,

Figure 5.5 Comparisons of experimental and calculated TG and DTG curves for co-combustion of SHC-320 and different rank coals at three blending ratios. Coal-1 and SHC-320: (a) TG curves and (b) DTG curves; Coal-2 and SHC-320: (c) TG curves and (d) DTG curves; Coal-3 and SHC-320: (e) TG curves and (f) DTG curves.

experimental $(dw/dt)_{\max}$ for 30C70HC-2 decreased dramatically by 10.5% with an increase of 4.2% in residues, indicating that high hydrochar blending ratio (70%) in low rank coal inhibited co-combustion. Despite obvious enhancement in $(dw/dt)_{\max}$ for 70C30HC-2, 30C70HC-3 and 50C50HC-3, incomplete co-combustion may lead to more residues. Among these three blends, 70C30HC-2

was the most apparent one and demonstrated +17.5% $(dw/dt)_{\max}$ and +6.5% residues deviations. It is noted that the higher synergistic effect index values were consistent with corresponding high A_2 in high temperature region, implying that synergistic interaction may be triggered increased A_2 as a result of high concentration of reactants (Xu et al., 2014).

Table 5.5 Deviations of maximum weight loss rates and residues of experimental curves from calculated curves and corresponding synergistic effect index values.

Calculated sample	T_m (°C)	$(dw/dt)_{\max}$	Residues (%)	Deviation (%)		Synergistic effect index ^c
				$(dw/dt)_{\max}$ ^a	Residues ^b	
30C70HC-1	450.0	3.51	27.71	-3.1	+1.8	1
50C50HC-1	460.0	4.59	20.56	+4.4	-0.3	4
70C30HC-1	470.0	5.76	13.4	+5.4	-3.7	4
30C70HC-2	410.0	3.43	31.3	-10.5	+4.2	1
50C50HC-2	410.0	3.56	26.5	-9.6	+0.4	1
70C30HC-2	370.0	3.83	21.7	+17.5	+6.5	3
30C70HC-3	410.0	4.26	28.6	+6.3	+2.1	3
50C50HC-3	410.0	4.95	22.1	+6.9	+3.2	3
70C30HC-3	400.0	5.65	15.4	+10.4	-1.9	4

^a: “+” and “-” denote positive and negative interactions in co-combustion of blends, respectively.

^b: “+” and “-” denote negative and positive interactions in co-combustion of blends, respectively.

^c: Higher index value denotes greater synergistic effect. Specifically, “4” and “1” indicate most intense synergistic and anti-synergistic effects, respectively.

Based on the claims that more significant synergistic interactions occurred between biomass/biomass derived hydrochars and low rank coals than high rank coals (Liu, Z. et al., 2012; Moon et al., 2013), results in this study suggest both synergistic and anti-synergistic interactions can take place depending on blending ratios as well as intrinsic fuel characteristics of hydrochars and coals. Hence, coal

rank and blending ratio are crucial criteria to be determined before co-combustion with SHC solid fuels. To conclude, for high rank coals, higher coal percentage ($\geq 50\%$) in blends would achieve more synergistic interactions while low blending ratio ($\leq 30\%$) may cause severe anti-synergistic interactions. For low rank coals, high coal percentage ($\geq 70\%$) may induce positive interactions but more incomplete combustion, whereas coal percentage less than 50% may not benefit co-combustion. Introduction of moderate rank coals with a wide blending ratio range can facilitate synergistic interactions.

5.4 Conclusions

Dewatered sewage sludge (DSS) was directly converted to hydrochars under various subcritical water conditions. The fuel characteristics of hydrochar derived under 320 °C and 12.0 MPa (SHC-320) outweighed DSS and other hydrochars in terms of highest calorific value, safer T_i , higher heat release in a higher temperature region, and slightly decreased T_b during the shortened combustion process. Introduction of SHC-320 lowered activation energy to initiate main decomposition of coal blends. Moreover, lower amount of SHC-320 led to a two-stage main co-combustion while large portion ($\geq 70\%$) of SHC-320 improved ignition reactivity of high rank coal blends. During main co-combustion, blending SHC-320 resulted in higher heat loss to high rank coals. Intense synergistic effects were attributed to higher pre-exponential factor values in the second co-combustion stage. Under low Coal/SHC-320 ratio (30:70), highest anti-synergistic effects occurred when blending SHC-320 with low or high rank coal, whereas co-combustion with moderate rank was impacted synergistically, thereby exhibiting highest combustion performance and burn out efficiency among blends.

CHAPTER 6 Fate of nitrogen during hydrothermal conversion of dewatered sewage sludge and efficient nitrogen recovery using a coupled air stripping process*

6.1 Introduction

Sound management and utilization of sewage sludge (SS) generated from wastewater treatment plants is problematic due to its high moisture content (ca. 80 wt.% even after dewatering) and environmental hazards (He et al., 2014a). Thermochemical conversion is an effective approach to achieve significant volume reduction of SS with potential benefit of energy recovery (Zhang et al., 2014). Particularly, many studies (He et al., 2014a; He et al., 2013; He et al., 2014c; Yu et al., 2014; Zhao et al., 2013) have shown that hydrothermal conversion (HTC) is a promising technology for SS treatment and utilization due to avoidance of in-depth dewatering and production of biofuels with superior fuel quality. Recently, nutrient reclamation using HTC has attracted increasing attentions (Blöcher et al., 2012; Heilmann et al., 2014; Tyagi and Lo, 2013). Since phosphorus was mainly accumulated in the solid fraction after HTC, Heilmann et al. (2014) recovered phosphorus from animal manures via calcium phosphate using combined HTC and subsequent acid/base extractions of solid products. Although N is not as valuable as P (estimated prices for N and P about US\$1.3 and US\$2.6 per kg, respectively) (Tyagi and Lo, 2013), the environmental impact caused by NO_x emissions from combustion of solid residues derived from HTC is worth noting. This issue becomes more critical for SS with high N content that mainly originates from proteins (He et al., 2014a; Liu et al., 2015; Zhang et al., 2014). Therefore, it is important to develop an appropriate HTC process for N

* This chapter is written based on my article “Effective nitrogen removal and recovery from dewatered sewage sludge using a novel integrated system of accelerated hydrothermal deamination and air stripping”, *Environmental Science & Technology* (2015).

recovery from SS before its final utilization and a better understanding of N transformation during HTC is a prerequisite.

Previously, effects of temperature and heating rate on nitrogen transformation and migration behaviors in pyrolysis of SS have been extensively explored (Cao et al., 2013; Shao et al., 2007; Tian et al., 2014; Tian et al., 2013; Zhang et al., 2014). Along the temperature, the entire pyrolysis of SS was divided into four temperature regions, including dehydration, intermediates formation, intermediates decomposition, and final char production (Shao et al., 2007). NH_3 and HCN gases were the major nitrogenous gas emitted from pyrolysis of SS (Zhang et al., 2014). The initial deamination of labile proteins was responsible for NH_3 released between 300 and 500 °C. When the temperature increased from 500 to 800 °C, considerable NH_3 and HCN gases were generated and above 80% of these gases was contributed by thermal cracking of N-containing intermediates (i.e. amine-N, heterocyclic-N, and nitrile-N) (Tian et al., 2013). Unlike pyrolysis, hydrothermal degradation of nitrogenous compounds led to several forms of inorganic nitrogen ions (e.g. NH_4^+ -N, CN^- -N, NO_2^- -N, and NO_3^- -N) except for complicated organic by-products (Oliviero et al., 2003; Oulego et al., 2012). Chen, Yunan et al. (2013) pointed out that N-containing compounds in SS were converted to concentrated ammonium in liquid by-product under supercritical water (SCW). Most of N in algal protein was transformed into ammonium via hydrothermal reactions (Chen et al., 2014). Unfortunately, the detailed transformation pathways of nitrogenous species were not elaborated. Besides, SCW hydrolysis can eliminate more N than pyrolysis and common hydrolysis due to reinforced saturation of heterocyclic rings induced by H radicals (Ogunsola and Berkowitz, 1995). Thus, it is imperative to get mechanistic insights into hydrothermal decomposition pathways of N-containing compounds in order to effectively remove N from SS. Moreover, the concentrated ammonium

in liquid by-product could benefit downstream N recovery using an efficient ammonia stripping process. The stripping process has demonstrated high performances to recover ammonia as ammonium sulfate from digested slurries of animal manures and pretreated source-separated urine (Ledda et al., 2013; Liu et al., 2014).

Since lime is widely used in sludge conditioning and stabilization processes (Liu et al., 2013), it is of crucial interest to investigate the effect of Ca-based additive on nitrogen transformation during HTC of SS. In previous literature, $\text{Ca}(\text{OH})_2$ is revealed to inhibit the formation of toxic pollutants during hydrothermal gasification of biomass waste (Yildiz Bircan et al., 2011). Extra addition of $\text{Ca}(\text{OH})_2$ could also reduce emissions of perfluorocarbons from fluorine mineralization in sludge thermal treatment (Wang et al., 2013). During pyrolysis of SS, CaO is found to improve NH_3 formation and hinder HCN generation via enhanced conversion of HCN to NH_3 and accelerated deamination of proteins or other N-containing organic compounds (Liu et al., 2015). Moreover, the formed CaC_x upon the addition of CaO may capture NH_3 and further lead to reduction of NO_x precursors. On the other hand, in catalytic hydrothermal gasification, CaO additive significantly facilitated hydrogen yield and selectivity via promoted water-gas shift reaction and inhibited methanation (He et al., 2015b; Onwudili and Williams, 2013b). These findings imply that Ca-based additives may be economical conditioners for effective HTC and deamination. Nonetheless, the effect of CaO additive on nitrogen transformation during HTC of SS has not been investigated.

In this context, objectives of this study are to understand the fate of nitrogen during hydrothermal conversion of SS and develop a system to efficiently remove and recovery N from SS. Specifically, the effect of temperature and pressure on

deamination performance and transformation behavior of N-containing compounds in HTC was examined. Moreover, the role of CaO additive was investigated in terms of nitrogen species conversion and distribution. An optimized air stripping process was employed to recover the ammonium nitrogen in liquid products. Based on the data gathered from these two processes, the overall nitrogen removal and recovery efficiencies from SS using this integrated system were evaluated. The results can offer an alternative strategy towards efficient N recovery from sustainable SS management with mitigated emissions of NO_x precursors.

6.2 Materials and methods

6.2.1 Characteristics of SS

Dewatered anaerobically digested sewage sludge (DSS) with a moisture content of 82.5% was obtained from Ulu Pandan Water Reclamation Plant in Singapore and directly used as feedstock in HTC process. The DSS sample contained a volatile matter (VM) content of 69.0%, a fixed carbon (FC) content of 9.2%, and an ash content of 21.8% on dry basis. Prior to characterization, DSS sample was oven dried at 105 °C for 12 h and ground into fine powders less than 0.5 mm. The elemental composition (i.e. carbon, hydrogen, oxygen, nitrogen, and sulfur), VM, FC and ash contents were analyzed following previous procedures (He et al., 2013; He et al., 2014c). Since metals could catalyze nitrogen transformation in HTC, elemental composition of the ash component in DSS was determined on a PW2400 X-ray fluorescence system and normalized by their oxide forms. Protein in DSS was determined by the Kjeldahl method with a factor of 6.25. Lipid was determined using the Soxhlet extraction method (Gai et al., 2013). The main physicochemical characteristics of DSS are described in Table 6.1.

6.2.2 Experimental procedures

6.2.2.1 HTC of DSS

HTC of DSS experiments were performed using a 1.0 L stainless steel (SS 316L) fixed-head batch autoclave reactor (Parr Instrument Co., USA) shown in Figure 6.1a. The detailed configuration and procedure have been described elsewhere (He et al., 2014c). In brief, 182 g of DSS containing approximately 150 g of water was loaded into the reactor vessel and sealed. Under stirring at 500 rpm, the vessel was heated up to the pre-set temperature (200-380 °C) and corresponding pressure (2.0-22.0 MPa) (Appendix B Text S1), which was followed by maintaining the temperature for 20 min. Subsequently, the heating mantle was removed and the vessel was rapidly cooled to room temperature using an internal cooling water circulator. After depressurization, solid and liquid products were collected and well separated. The liquid products were filtered through 0.45 µm PTFE membrane filters. The total volume of liquid phase and the dry weight of solid phase were determined to calculate residual N mass in the liquid and solid residues following a previous procedure (He et al., 2015a). The liquid samples were stored in glass vials at 4 °C before analysis. On the other hand, the solid residues oven-dried at 105 °C for 12 h were weighed and ground into fine powders less than 0.5 mm for further characterization. The solid residues were denoted as SR-T, where T stands for the reaction temperature.

In another set of experimental runs, in addition to 182 g of DSS, various amounts of CaO additive (i.e. 3.08, 6.20, and 12.37 g CaO which corresponded to Ca/(C in dry DSS) molar ratio of 0.05, 0.1, and 0.2, respectively) were introduced during HTC under 380 °C and 22.0 MPa for 20 min. The solid residues were denoted as SR-380-X, where X stands for Ca/C molar ratio.

Table 6.1 Main physicochemical characteristics of DSS.

Ultimate analysis (wt.%, db)					Proximate analysis (wt.%, db)			Composition analysis (wt.%, daf)			
C	H	N	S	O	VM	FC	Ash	Protein	Lipid	Carbohydrates and lignin	
39.9	6.2	6.0	5.6	29.1	69.0	9.2	21.8	34.1	12.3	22.6	
Ash analysis (Expressed as wt.% of basic metal oxide forms)											
SiO ₂	P ₂ O ₅	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	TiO ₂	CuO	ZnO	Cr ₂ O ₃	MnO
5.73	5.24	3.2	2.96	2.90	0.67	0.38	0.37	0.15	0.10	0.07	0.02

db, dry basis; daf, dry and ash-free basis.

6.2.2.2 Air stripping process

Ammonium rich solutions prepared from HTC were subjected to batch air stripping experiments using an air stripping setup demonstrated in Figure 6.1b. The detailed configuration of this setup has been described elsewhere (Liu et al., 2014). In a typical batch experimental run, a 100 mL aqueous feedstock was manually fed into a vertical acrylate stripping column with an inner diameter of 4 cm, a height of 1.8 m, and a thickness of 3 mm from the top end. The column was sealed by rubber stoppers at two ends and jacketed by an outer column which was filled with sufficient warm water circulated by an external water bath and a water pump to maintain a certain stripping temperature. Air was supplied by an air pump with an adjustable air flow meter and distributed through an air diffuser equipped at the bottom of the stripping column. The ammonia was stripped out along the column and released from the top of the column which was connected to a tank with 200 mL 1.5 M sulfuric acid (H_2SO_4) absorption solution for ammonia recovery as ammonium sulfate. To prevent solution foam formed in stripping process from entering the downstream N recovery system, a sponge defoamer was applied right before the top rubber stopper. From the perspectives of efficient ammonia recovery and economical operating cost, the pH value of feedstock was pre-adjusted to 10.0 ($\text{p}K_a$ value for NH_3 is 9.25 at 25 °C) by 10 M NaOH and the stripping process was continuously performed at 55 °C for 24 h with a fixed air flow rate of 0.5 L/min according to previous results (Liu et al., 2014). Particularly, 5:1 is the maximum air to liquid volume ratio per minute that could be employed to maintain a smooth operation of the existing system to avoid severe foam formation at the top part. All these batch experiments were repeated by three times and mean values of these results were reported as final results.

Figure 6.1 Schematic diagrams of (a) hydrothermal conversion system and (b) air stripping setup.

6.2.3 Analysis methodology

Total dissolved nitrogen (TDN) concentrations in liquid products were measured using TOC/TN analyzer (multi N/C 2100, Analytik Jena). The ammonium (NH_4^+ -N), nitrite (NO_2^- -N), nitrate (NO_3^- -N), and cyanide (CN^- -N) concentrations were measured using HACH test kits and HACH DR 2800 spectrophotometer. Total dissolved organic nitrogen (DON) concentrations were calculated by the difference of TDN and total inorganic nitrogen species concentrations. Elemental compositions (i.e. carbon, hydrogen, oxygen, nitrogen, and sulfur) of DSS and solid residues were determined by vario EL CHNOS elemental analyzer (refer to Section 4.3.3). All the measurement results were statistically analyzed at a 95% confidence level using OriginPro Version 9.1 and mean values were reported.

X-ray photoelectron spectroscopy (XPS) analysis experiments were carried out on a Thermo Scientific ESCALAB 250 spectrometer equipped with Al K α X-ray radiation source ($h\nu = 1486.6$ eV) at a 20 eV pass energy, a 0.1 eV energy step and 0.1 s dwelling time. N 1s XPS spectra of all sludge and solid powder samples were recorded under identical conditions and the binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. The spectra were fitted using

least-squares method based on Gauss-Lorentzian shapes using XPSPEAK 4.1. The area values of fitting peaks reflected the relative contents of different N-containing compounds and the peak area intensities were normalized according to the total nitrogen contents in samples for semiquantitative comparisons.

In order to determine the evolution of CaO additive in solid residues after HTC, thermogravimetric analysis (TGA) of solid samples was conducted by a Perkin Elmer TGA7 analyzer according to our previous study (He et al., 2013). Briefly, 9 mg of samples were loaded and heated from 30 to 900 °C at a heating rate of 10 °C/min with an air flow rate of 20 mL/min under atmospheric pressure. X-ray diffraction (XRD) patterns of these solid samples were recorded over a 2θ range from 10° to 80° using a Bruker D8 Advance X-ray diffractometer equipped with Cu-K α X-ray radiation source operated at 40 kV and 40 mA.

6.2.4 Calculations of nitrogen removal and recovery efficiencies

In this study, the nitrogen originating from DSS was significantly removed via accelerated hydrothermal deamination and ammonium rich solutions obtained subsequently went through optimized air stripping process to scrub ammonia with H₂SO₄. In order to quantify the performance of this novel system, the removed nitrogen mass and nitrogen removal efficiency in HTC, the NH₄⁺-N removal efficiency and total recovered NH₄⁺-N via air stripping process, and the overall N recovery rate are calculated according to the equations defined below.

$$M_{\text{TRm-N}} = M_{\text{DSS-N}} - M_{\text{SR-N}} \quad (6.1)$$

$$E_{\text{H-N}} = \frac{M_{\text{TRm-N}}}{M_{\text{DSS-N}}} \quad (6.2)$$

$$E_{\text{S-NH}_4^+} = \frac{M_{\text{LF-NH}_4^+} - M_{\text{LR-NH}_4^+}}{M_{\text{LF-NH}_4^+}} \quad (6.3)$$

$$M_{\text{TRc-N}} = V_{\text{RL}} \times M_{\text{R-N}} \quad (6.4)$$

$$R_{\text{TRc-N}} = \frac{M_{\text{TRc-N}}}{M_{\text{DSS-N}}} \quad (6.5)$$

where $M_{\text{TRm-N}}$ and $E_{\text{H-N}}$ are the total N mass removed from DSS and the N removal efficiency during HTC, respectively; $M_{\text{DSS-N}}$ and $M_{\text{SR-N}}$ are total N mass in DSS and solid residues, respectively; $E_{\text{S-NH}_4^+}$ is NH_4^+ removal efficiency in air stripping process along with stripping time; $M_{\text{LF-NH}_4^+}$ and $M_{\text{LR-NH}_4^+}$ are total NH_4^+ mass in the liquid feedstock and the residual liquid in air stripping process, respectively; $M_{\text{TRc-N}}$ and $M_{\text{R-N}}$ are the total mass of recovered N via $(\text{NH}_4)_2\text{SO}_4$ and the mass of recovered N per 100 mL liquid feedstock after 24 h of air stripping, respectively; V_{RL} is the volume of liquid product recovered from HTC; $R_{\text{TRc-N}}$ is the overall N recovery rate via $(\text{NH}_4)_2\text{SO}_4$ after 24 h of air stripping.

6.3 Results and discussion

6.3.1 Nitrogen species distribution in liquid and solid residues

According to nitrogen loss and balance during HTC of DSS (Table 6.2), it can be referred that the N-containing compounds were mainly partitioned in solid and liquid fractions while N-containing gas was negligible (He et al., 2015a). Understanding of nitrogen transformations in solid and liquid fractions could offer a mechanistic insight into N removal from DSS. Hence, effects of different temperature/pressure and CaO additive on the nitrogen species distribution in the liquid fraction and total residual N content in the solid fraction were examined (Figure 6.2).

Figure 6.2 (a) Nitrogen species distribution in liquid residues and (b) total nitrogen content in solid residues and corresponding nitrogen removal efficiency. The numbers marked in Figure 6.2a corresponded to $\text{CN}^-\text{-N}$ concentrations in liquid residues.

6.3.1.1 Effect of temperature and pressure

The TDN concentration showed a downward trend as the temperature and pressure increased to 340 °C and 15.5 MPa after which TDN concentration increased to ca. 10000 mg/L at 380 °C and 22.0 MPa (Figure 6.2a). The decrease of TDN concentration, from 12110 mg/L at 200 °C and 2.0 MPa to 8940 mg/L at 340 °C and 15.5 MPa, was probably associated with higher yield of liquid fraction. The evolutions of liquid and solid fractions have been comprehensively discussed in our previous study (He et al., 2015a). Nonetheless, the higher temperature and pressure (above 340 °C and 15.5 MPa) could result in dramatic cracking or dissolution of N-containing compounds in the solid fraction. Thus, TDN in the liquid fraction increased with elevated temperature and pressure afterwards. Besides, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{CN}^-\text{-N}$ were inorganic-N species present in the liquid fraction, while $\text{NO}_2^-\text{-N}$ was not detected. As a consequence of increasing temperature and pressure, the nitrogen species distribution in the liquid fraction was greatly altered. $\text{NO}_3^-\text{-N}$ and $\text{CN}^-\text{-N}$ decreased progressively to a low

concentration level of 42.3 and 0.4 mg/L, respectively, whereas NH_4^+ -N and DON were the predominant nitrogen species in all liquid residues. The degradation of cyanide in subcritical water was mainly ascribed to nonradical hydrolysis reaction rather than oxidation (Oulego et al., 2012). Different from cyanide, NH_4^+ -N was resistant to degradation and could only be selectively oxidized towards molecular nitrogen in the presence of catalysts during wet air oxidation (Lee, 2003; Oliviero et al., 2003).

Overall, the evolution profile of distribution for NH_4^+ -N and DON species in the liquid fraction exhibited a distinct three-stage transformation throughout HTC. At the first stage (below 260 °C), NH_4^+ -N increased steadily from 4020 to 6660 mg/L, while DON decreased from 7843.2 to 3265.2 mg/L as the temperature and pressure increased from 200 °C and 2.0 MPa to 260 °C and 5.0 MPa. It has been reported that rapid degradation of protein in SS to liquid fraction initiated above 150 °C and DON was decomposed to NH_4^+ -N with increased temperature within this stage (Inoue et al., 1997). At the second stage (260-320 °C), the NH_4^+ -N and DON slightly fluctuated around 6400 and 3500 mg/L, respectively. This explains that the labile organic N-containing compounds were almost decomposed below 260 °C but the rest was stable and difficult to crack below 320 °C. At the third stage (340-380 °C), NH_4^+ -N concentration increased to 7980 mg/L at 380 °C, which accounted for ca. 80% of TDN. In contrast, the 65% DON at 200 °C dropped considerably to 20% at 380 °C with a concentration of 2017.3 mg/L.

On the other hand, the total N mass in solid residue was gradually reduced and the N removal efficiency increased accordingly with elevated temperature and pressure (Figure 6.2b). At the beginning, 43.0% of N was removed at 200 °C and 2.0 MPa, retaining 1096.9 mg total N in the solid fraction. Interestingly, N removal efficiency increased sharply to 57.4% at 220 °C and 2.6 MPa, however,

the increase tended to be gentle afterwards. This evolution indicates that the majority of labile N-containing substances may be decomposed and released into liquid fraction at 220 °C, whereas hydrolysis and cracking of rest stable N-containing functionalities were temperature and pressure dependent. It is similar to the temperature dependent transformation of nitrogen during pyrolysis (Zhang et al., 2014). Consequently, total N mass in solid fraction declined by 76.9% to 444.2 mg at 380 °C and 22.0 MPa.

6.3.1.2 Effect of CaO

The introduction of CaO at 380 °C and 22.0 MPa resulted in a remarkable increase (ca. 23%) of TDN in liquid fraction to above 12000 mg/L, revealing the catalysis role of CaO in promoting hydrolysis or cracking of N-containing compounds. Both of NH_4^+ -N and DON increased substantially, however, NO_3^- -N and CN^- -N levelled off. Additionally, as the Ca/C molar ratio was raised from 0.05 to 0.2, NH_4^+ -N increased to 9960 mg/L at the expense of reduction of DON, leading to 83.0% NH_4^+ -N and 16.8% DON in final liquid residue. This high NH_4^+ -N content could benefit the downstream N recovery. Although HCN may be hydrolyzed to form NH_4^+ by CaO catalysis (Cao et al., 2015; Liu et al., 2015; Ohtsuka et al., 1997), increased NH_4^+ mainly originated from other nitrogen sources instead of HCN because the increased conversion to NH_4^+ was much higher than decreased CN^- (Figure 6.2a). Therefore, the highest N removal efficiency of 86.4% in solid residue was obtained and the total N mass was as low as 262.2 mg.

6.3.2 Evolution of nitrogen functionalities in solid residues during HTC

N 1s XPS spectra were used to investigate the evolution of nitrogen functionalities in solid residues with various temperature/pressure and CaO amounts during HTC (refer to Appendix B Text S2 and Figure 6.3). The total nitrogen content of DSS was 6.0 wt.% which is higher than that of most sludge

previously reported (Liu et al., 2015; Tian et al., 2014). It may be related to the significant amount of protein (34.1 wt.%) therein, thus it becomes more meaningful to remove and recover N from DSS. All the peaks for nitrogen functionalities were assigned (Table 6.3) based on literature (Kelemen et al., 2002; Tian et al., 2013).

The deconvolution results (Table 6.3) demonstrate that the nitrogen in DSS was primarily composed of protein-N (90.25%), inorganic-N (7.45%), and pyridine-N (2.30%). At 260 °C and 5.0 MPa, inorganic-N in solid fraction was completely dissolved or hydrolyzed in the form of NH_4^+ -N/ NO_3^- -N and protein-N content declined sharply to 54.5%, whereas the pyridine-N content significantly increased by 8.1%. As the temperature increased to 300 °C, the pyridine-N content increased to 13.8%, which was accompanied by a continuous decrease of protein-N content to 47.9%. It is also noticed that the protein-N content only slightly increased to 49.0% while the pyridine-N content decreased to 9.3% at 340 °C and 15.5 MPa, indicating the occurrence of distinct cracking for pyridine-N substances. Nevertheless, from 300 to 340 °C, the obvious increase of NH_4^+ -N concentration could be attributed to the cracking of pyridine-N in both solid and liquid fractions as there was a significant decrease of DON in Figure 6.2a. Thus N removal efficiency from DSS in Figure 6.2b did not increase remarkably. It is also deduced that the labile protein-N was almost decomposed to form NH_4^+ -N (Cao et al., 2015), retaining stable protein-N which requires higher activation energy to decompose in solid fraction. The protein-N content was reduced to 18.5% while the pyridine-N content climbed to 25.2% at 380 °C and 22.0 MPa. The formation of more heterocyclic-N species (i.e. pyrrole-N and quaternary-N) in solid residue was found as well. These results may be due to the sequential cyclization and ring condensation of N-containing intermediates through Diels-Alder reaction (Tian et al., 2013; Zhang, B. et al., 2011). Zhang et al. (2011)

claimed that the Diels-Alder reaction followed by dehydrogenation led to the formation of polycyclic aromatic hydrocarbons and H₂ production. Drastic increase of H₂ yield in the present study (refer to Section 4.3.1) verified this hypothesis. It was also reported that most of the amide nitrogen initially in peat was converted into pyrrolic and pyridinic heterocyclic structures upon pyrolysis (Kelemen et al., 2002). Although the evolution of nitrogen functionalities during HTC was similar to pyrolysis, the applied temperature was much lower than that in pyrolysis because of radicals promoted hydrolysis in SCW (He et al., 2014a; Ogunsola and Berkowitz, 1995).

After the addition of CaO, the protein-N and quaternary-N were completely decomposed and transformed. With the increase of Ca/C molar ratio to 0.2, the pyridine-N and pyrrole-N contents were gradually reduced to 9.1% and 0.5%, respectively. Initially, 3.5% nitrile-N was produced. Since Ca-based additive may accelerate more formation of free radicals (Yuan et al., 2015), this result could be related to the CaO catalyzed cracking of amine-N intermediates derived from decomposition of proteins in DSS (Tian et al., 2014; Tian et al., 2013). However, nitrile-N decreased slightly to 3.3% at Ca/C molar ratio of 0.2, suggesting further hydrolysis of nitrile-N. Previous studies (Barbosa and van Santen, 2000; Ghaffar and Parkins, 2000; Ma et al., 2009) concluded that the hydrolysis of nitriles could proceed in two consecutive steps involving hydrolysis of nitriles to amides followed by subsequent hydrolysis of amides to carboxylic acids and ammonia. It is noted that pH value for aqueous solution after HTC built up with the increase of CaO amount (refer to Section 4.3.4). Thus, the increased alkalinity could accelerate the hydrolysis of amides to ammonium (Oulego et al., 2012), which was in accordance with our results.

Figure 6.3 Evolution of N 1s XPS spectra for (a) DSS and solid residues derived from HTC of DSS under various reaction conditions: (b) 260 °C and 5.0 MPa; (c) 300 °C and 9.3 MPa; (d) 340 °C and 15.5 MPa; (e) 380 °C and 22.0 MPa; (f) 380 °C and 22.0 MPa with a Ca/C molar ratio of 0.1; (g) 380 °C and 22.0 MPa with a Ca/C molar ratio of 0.2.

Table 6.2 Total nitrogen mass in liquid and solid fractions, nitrogen loss and balance during HTC of DSS.

Experimental run	Residual N in solid residues (g)	Total N in liquid residues (g)	Error for N loss ^a (g)	N balance
200	1.0969	1.5913	-0.7644	1.40
220	0.8192	1.4216	-0.3170	1.16
240	0.7745	1.6767	-0.5274	1.27
260	0.7011	1.4944	-0.2717	1.14
280	0.6678	1.5172	-0.2613	1.14
300	0.6371	1.5246	-0.2380	1.12
320	0.5866	1.4140	-0.0768	1.04
340	0.5677	1.3106	+0.0454	0.98
360	0.4693	1.4295	+0.0249	0.99
380	0.4442	1.4689	+0.0107	0.99
380-0.05	0.3737	1.8421	-0.2921	1.15
380-0.1	0.3050	1.7828	-0.1641	1.09
380-0.2	0.2622	1.7744	-0.1129	1.06

^a Positive sign indicates lost quantities of N mass in the balance.

Table 6.3 Normalized relative intensities (%) of nitrogen functionalities in DSS and solid residues derived from different reaction conditions according to N 1s XPS spectra.

	Binding energy (eV)	DSS	SR-260	SR-300	SR-340	SR-380	SR-380-0.1	SR-380-0.2
Total N (%)		100	64.90	61.75	58.28	53.31	22.02	12.91
Inorganic-N (%)	402.5	7.45	0	0	0	0	0	0
Protein-N (%)	400.0	90.25	54.53	47.92	49.00	18.51	0	0
Pyridine-N (%)	398.8	2.30	10.37	13.83	9.28	25.17	17.60	9.06
Heterocyclic-N Pyrrole-N (%)	400.3	0	0	0	0	7.58	0.88	0.54
Quaternary-N (%)	401.4	0	0	0	0	2.05	0	0
Nitrile-N (%)	399.7	0	0	0	0	0	3.54	3.31

6.3.3 Nitrogen transformation pathways during hydrothermal deamination

Because the accelerated hydrothermal deamination could generate more $\text{NH}_4^+\text{-N}$ for recovery, it is very important to figure out possible reaction routes and nitrogen conversion pathways throughout HTC. On the basis of above analysis and discussion, reaction routes involved in N transformation were proposed (Figure 6.4).

Figure 6.4 Proposed reaction routes during HTC of DSS.

The inorganic-N, including ammonium and nitrate salts, went through hydrolysis to form $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ via route 1. However, the decomposition of protein-N was not that straightforward (Tian et al., 2014). The protein-N was first

hydrolyzed to labile and stable amides through cleavage of peptide bonds (route 2). The labile amide then generated NH_4^+ -N by deamination under mild hydrothermal condition (below 340 °C and 15.5 MPa) while ring opening reaction of stable (cyclic) amide was favored under SCW (above 380 °C and 22.0 MPa) to release more NH_4^+ -N (Chen, Yunan et al., 2013). Concurrently, the cyclization of amine-N intermediates derived from thermal cracking of stable proteins could lead to the generation of heterocyclic-N compounds through route 3. Thus, pyridine-N content increased with elevated temperature and pressure. At 340 °C and 15.5 MPa, the deamination of pyridine-N was predominant, whereas the decomposition of protein-N compounds was not noticeable. Due to the dehydrogenation and subsequent cyclization of amine-N intermediates (Tian et al., 2013), the pyrrole-N compounds were formed at 380 °C and 22.0 MPa (route 3). In addition, polymerization or ring condensation reactions of pyridine-N intermediates led to the formation of more stable quaternary-N compounds (route 4). Furthermore, the addition of CaO enhanced the dehydrogenation of amine-N and induced the formation of nitrile-N (route 5). The calcium ion could also interact with stable amide to generate NH_4^+ -N accompanied by CaCO_3 precipitation via ureolysis accelerated deamination (route 6) (Cuthbert et al., 2013), causing complete decomposition of protein-N compounds. The severe and catalytic deamination of pyrrole-N and pyridine-N compounds resulted in a remarkable release of NH_4^+ -N (route 7). Hence, there was a significant and continuous reduction of pyrrole-N and pyridine-N contents with the increase of Ca/C molar ratio. Nevertheless, the quaternary-N compounds were decomposed. This may result from the catalytic cracking to form pyridine-N (route 8), thereby contributing to additional release of NH_4^+ -N. Nitrile-N slightly decreased when the amount of CaO increased further. However, NH_4^+ -N concentration increased by 16.6%, while the CN^- -N concentration remained changeless. It is postulated that consecutive hydrolysis of nitrile-N to NH_4^+ -N occurred (route 5).

Based on aforementioned reaction routes, the deamination and nitrogen conversion pathways in solid residues during HTC were clearly elucidated (Figure 6.5). Generally, three characteristic hydrothermal regimes were identified to reflect noticeable deamination processes. The majority of NH_4^+ -N released below 300 °C and 9.3 MPa was contributed by the deamination of labile protein-N compounds and hydrolysis of inorganic-N substances, remaining 61.8% of initial N in the solid residue. Substantial deamination of pyridine-N compounds led to great N removal between 300 °C/9.3 MPa and 340 °C/15.5 MPa. Next, the deamination of stable protein-N dominated when temperature and pressure were raised to 380 °C and 22.0 MPa. This could be responsible for obvious increases of pyridine-N and pyrrole-N contents. Meanwhile, stable quaternary-N compounds were derived from pyridine-N intermediates. On the other hand, the addition of CaO favored complete conversion of stable protein-N, distinct deamination of pyridine-N compounds, and slight deamination of pyrrole-N compounds. More importantly, quaternary-N compounds were completely converted to pyridine-N compounds. Increased CaO amount further facilitated the deamination of pyridine-N compounds while pyrrole-N and nitrile-N contents were less influenced with 12.9% of initial N retained in solid residue. Specifically, the N in the solid fraction consisted of 9.1% pyridine-N, 3.3% nitrile-N, and 0.5% pyrrole-N.

Figure 6.5 Possible nitrogen conversion pathways in solid residues during HTC of DSS. The numbers indicated the involved reaction routes and the thickness of conversion lines or text boxes implied the conversion degree or relative intensity of nitrogen functionalities.

TGA and XRD analyses of solid residues were used to demonstrate the transformation of CaO additive at 380 °C and 22.0 MPa (Figure 6.6 and 6.7). DTG curve for SR-380 (Figure 6.6a) showed two remarkable peaks at 220.9 and 417.9 °C which corresponded to VM and FC combustion processes, respectively (He et al., 2014c).

Figure 6.6 Thermogravimetric decomposition profiles of solid residues from HTC at 380 °C and 22.0 MPa under a fixed air flow rate of 20 mL/min: (a) without CaO; (b) Ca/C molar ratio of 0.05; (c) Ca/C molar ratio of 0.1; (d) Ca/C molar ratio of 0.2; (e) pure Ca(OH)_2 ; (f) pure CaCO_3 .

As the Ca/C molar ratio increased from 0.05 to 0.2, the VM combustion peak became gentle, implying the improved decomposition of VM by CaO. Conversely, the second peak around 430 °C became wider and more obvious but reduced sharply thereafter. Increased Ca/C molar ratio shifted the major peaks to a higher temperature (ca. 720 °C). Compared to the TG/DTG curves for pure Ca(OH)_2 and CaCO_3 (Figure 6.6e and f), it is speculated that the above

phenomenon may be due to the transformation of CaO to Ca(OH)₂ and CaCO₃. Moreover, the ureolysis accelerated deamination (Cuthbert et al., 2013) and CO₂ capture (He et al., 2015b) could be responsible for the formation of CaCO₃. The XRD patterns (Figure 6.7) confirmed that DSS contained a large amount of quartz, along with minor illite/muscovite minerals and calcium based chemicals (e.g. CaO, Ca(OH)₂, and CaSO₄) (Qian and Jiang, 2014; Wang et al., 2013). But the peaks for quartz and Ca(OH)₂ became slightly intense after HTC at 380 °C and 22.0 MPa. Besides, peaks for CaCO₃ appeared, which could be associated with carbonation of CO₂ produced. They became predominant with the increase of CaO amount. In SR-380-0.2, peaks for hematite and CaF₂ were also observed. On the whole, CaO additive was ultimately transformed to CaCO₃.

Figure 6.7 Transformation of XRD patterns for DSS and solid residues prepared from HTC at 380 °C and 22.0 MPa with various CaO amounts.

6.3.4 Performance evaluation of air stripping process and hybrid system

6.3.4.1 Nitrogen removal efficiency and recovered nitrogen mass via air stripping

Feedstocks prepared from four representative hydrothermal conditions were

selected and their air stripping results were dynamically recorded (Figure 6.8). All $E_{S-NH_4^+}$ values increased drastically to above 75% in the initial 6 h. Similar results under comparable conditions were observed in stripping of intensively hydrolyzed urine (Liu et al., 2014). After 10 h of stripping time, $E_{S-NH_4^+}$ reached 98.8%, 91.6%, 98.0%, and 90.7% for liquid feedstock prepared under 340 °C/15.5 MPa, 380 °C/22.0 MPa, 380 °C/22.0 MPa with Ca/C molar ratio of 0.05, 380 °C/22.0 MPa with Ca/C molar ratio of 0.2, respectively. This efficiency was even higher than 98% after 24 h (Figure 6.8), reflecting the excellent performance of this process. Finally, the corresponding M_{TRC-N} values for the above feedstocks were 900.8 mg, 919.6 mg, 1185.6 mg, and 1192.6 mg, respectively.

6.3.4.2 Overall nitrogen removal and recovery from DSS

The N mass flow of the hybrid system under four scenarios (i.e. S1, S2, S3, and S4) in a bench scale system was illustrated in Figure 6.9. Taking into account of total recovered solid, M_{TRm-N} for SR-340, SR-380, SR-380-0.05, and SR-380-0.2 was 1356.0 mg, 1479.5 mg, 1550.0 mg, and 1661.9 mg, respectively, in the first HTC process. Despite a relatively lower $E_{S-NH_4^+}$ for S4 in the subsequent air stripping, the corresponding M_{R-N} was the highest (808.8 mg per 100 mL liquid feedstock), giving a high M_{TRC-N} of 1192.6 mg incorporating V_{RL} value. Additionally, R_{TRC-N} value for S1, S2, S3 and S4 was 46.8%, 47.8%, 61.6%, and 62.0%, respectively. Based on the highest E_{H-N} of 86.4% and R_{TRC-N} of 62.0% in the optimal S4, 51.93 kg N could be removed and 37.27 kg N would be recovered from 1 tonne dry mass of this DSS containing 60.12 kg N according to an ideal scale-up. Nevertheless, due to the limitation of existing lab-scale air stripping setup (e.g. column diameter and height), the air to liquid volume ratio

per minute could be adjusted appropriately to shorten the stripping time while achieving a sufficient N recovery rate. Meanwhile, in order to reduce NH_4^+ -N loss in a closed system, minimization of foam formation along the column and at connection parts is another critical technical issue to be tackled in industrial applications.

Figure 6.8 Ammonium removal efficiency of four typical aqueous products prepared from HTC of DSS under different reaction conditions: (a) 340 °C and 15.5 MPa; (b) 380 °C and 22.0 MPa; (c) 380 °C and 22.0 MPa with a Ca/C molar ratio of 0.05; (d) 380 °C and 22.0 MPa with a Ca/C molar ratio of 0.2. Stripping conditions: 100 mL aqueous feedstock, an air flow rate of 0.5 L/min, a column temperature of 55 °C, 1.5 M H_2SO_4 absorption solution, and 24 h of stripping time.

Figure 6.9 Overall nitrogen recovery rate and ammonium removal efficiency under four typical scenarios using a bench scale system, and optimal removed/recovered nitrogen amounts from DSS under an ideal scale-up.

6.4 Environmental implications

Prior nitrogen removal from DSS before final utilization is crucial to reduce emissions of N-containing pollutants, but this topic has not been well studied. This study has clearly elucidated the overall nitrogen transformation reactions and conversion pathways. Based on the mechanism, a novel system integrating hydrothermal deamination and air stripping processes has been developed to significantly remove N retained in solid fraction and efficiently recover the N as ammonium sulfate. Nitrogen migration and transformation were greatly affected by temperature and pressure. Under near-critical water (i.e. 380 and 22.0 MPa), N removal efficiency achieved 76.9% and concentrated ammonium solution was obtained. CaO additive accelerated deamination via catalyzed hydrolysis and cracking, leading to 86.4% N removal efficiency. The coupled air stripping helped recover 62.0% of total N present in DSS. Therefore, this system will provide an effective strategy for N control during sustainable sludge management.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

This thesis investigates energy recovery from dewatered sewage sludge (DSS) using hydrothermal processing under sub- and near-critical water conditions. A series of experiments have been carried out to examine specific topics related to different hydrothermal conversions and downstream applications, including (1) effect of residence time on physicochemical properties and combustion behavior of hydrochar solid fuel obtained during hydrothermal carbonization (HTC), (2) effects of reaction conditions (i.e. temperature and pressure, moisture content) and calcium oxide (CaO) additive on hydrothermal conversion of DSS under sub- and near-critical water conditions, (3) screening hydrochar of superior fuel quality for co-combustion of different rank coals, and (4) understanding nitrogen transformations in hydrothermal conversion and development of a system to efficiently remove and recovery N from DSS in order to reduce considerable emissions of N-containing pollutants during re-utilization of DSS derived solid fuel. The main findings are summarized as follows.

(1) HTC process was successfully applied to convert DSS into hydrochars at 200 °C in a Teflon-lined batch reactor. Thus, hydrothermal liquefaction and corrosions of reactor wall were minimized. The elimination of prior drying makes HTC a promising technology to directly recover energy from sludge. Different carbonization times were adopted in order to produce hydrochars possessing better fuel properties. After HTC of DSS, uniform brown hydrochars with good grindability and nut-like smell were produced. As a consequence of higher fixed carbon and lower volatile matter, hydrochars possessed a fuel ratio high up to 0.18 which was much higher than 0.02 of raw sludge. Despite the VM loss and higher ash content, carbon was retained by 88% and the higher heating values (HHVs) of hydrochars were 0.98-1.03 times of DSS. Moreover, 60% of nitrogen

and sulfur was removed, resulting in a cleaner solid fuel. The decrease of O/C and H/C atomic ratios suggested that dehydration and decarboxylation reactions were the essential reaction pathways during HTC of DSS. As the carbonization time was prolonged, total content of surface oxygen containing functional groups reduced to 4.21 mmol/g, making hydrochars highly hydrophobic. The yield and properties of hydrochars became relatively stable after 6 h of carbonization. In terms of the main combustion decomposition, HTC altered patterns of DTG curves from a single stage for raw sludge to two stages for hydrochars. The first order combustion reaction of DSS and hydrochars was derived. *E* and *A* values of raw sludge were much higher than hydrochars. Hydrochar obtained after 8 h of carbonization turned out to a better fuel in terms of easier and more stable combustion. Hence, HTC can convert DSS to an alternative solid fuel from the perspectives of fuel characteristics and combustion performance.

(2) Gas, solid, liquid products evolution profiles in hydrothermal conversion of DSS within 20 min of reaction time were determined under various conditions (i.e. 200-380 °C and 2.0-22.0 MPa, moisture content ranging from 82.5 to 95 wt.%) and CaO additive amounts (i.e. Ca/C molar ratio ranging from 0.05 to 0.2).

Increasing temperature and pressure reduced energy recovery rate, however, more significant decarboxylation and dehydration reactions led to high quality hydrochar solid fuel production. Thus, in spite of the highest value of recovered energy as hydrochar at 200 °C/2.0 MPa, HHVs of hydrochars obtained under higher temperature and pressure were 1.03-1.13 times higher than that of raw sludge. The results suggest that decarboxylation reaction dominated hydrothermal conversion of SS while intense dehydrogenation and methanation reactions initiated in near-critical water. It is also found that mineralization of heteroatomic compounds and dissolution of metals or mineral elements occurred during hydrothermal conversion. Under higher temperature and pressure, heavy metals or mineral elements were prone to be immobilized. High

temperature/pressure increased destruction of organic compounds and improved dehalogenation.

Higher moisture content favored decarboxylation and hydrolysis reactions. Nevertheless, it reduced H₂ and CH₄ yield. Because of relative higher solid yield and moderate decarboxylation, moisture content at 85 and 90 wt.% gave higher values of recovered energy as hydrochar.

Introduction of CaO additive had some positive effects on H₂ yield, hydrolysis and immobilization of inorganic elements. Although decarboxylation dominated hydrothermal conversion of SS, with the increase of CaO amount, intense dehydrogenation and methanation reactions initiated at 380 °C/22.0 MPa, thereby producing H₂ and CH₄ rich fuel gas. At 380 °C and Ca/C molar ratio of 0.2, H₂ yield increased almost 6-fold, resulting in 58% H₂ and 26% CH₄ in final fuel gas. Furthermore, CaO additive not only facilitated hydrolysis and deamination of organic compounds but also accelerated further fixation of inorganic elements and anions. However, CaO additive had detrimental effects on the calorific values of solid products and thus reduced the energy recovery from solid fraction.

The holistic understanding of reaction chemistry contributes to the design of hydrothermal conversion under mild conditions for sustainable sludge utilization.

(3) Considering the highest calorific value, safer T_i , higher heat release in a higher temperature region, and slightly decreased T_b during the shortened combustion process, hydrochar derived under 320 °C and 12.0 MPa (SHC-320) was screened for systematical co-combustion with different rank coals. The results suggest that SHC-320 reduced activation energy of blends and altered main combustion profiles. Meanwhile, blending SHC-320 induced greater heat loss for higher rank coals, whereas higher portion ($\geq 70\%$) of SHC-320 further improved ignition

reactivity of high rank coal blends. During main co-combustion, blending SHC-320 resulted in higher heat loss to high rank coals. In high temperature region, pre-exponential factor value increased with elevated Coal/SHC-320 ratios, resulting in more intense synergistic effects in blends. Under a low Coal/SHC-320 ratio (30:70), intense anti-synergistic effects occurred in co-combustion with low or high rank coals. Due to distinct synergistic interactions, co-combustion with moderate rank coal achieved the best combustion performance and highest burn out efficiency among blends. These findings benefit efficient utilization of dewatered sewage sludge as hydrochar solid fuel in existing co-firing power plants.

(4) The nitrogen transformation reactions and conversion pathways during hydrothermal conversion have been proposed and detailed elaborated. A hybrid system of hydrothermal deamination and air stripping has been successfully developed to effectively remove and recover nitrogen from DSS. In particular, three characteristic hydrothermal regimes contributing to deamination were identified. Initial hydrolysis of inorganic-N and labile protein-N was responsible for ammonium (NH_4^+ -N) released below 300 °C/9.3 MPa, whereas deamination of pyridine-N dominated when being raised to 340 °C/15.5 MPa. At 380 °C and 22.0 MPa, remarkable deamination of stable protein-N occurred, which was accompanied by formation of more heterocyclic-N compounds and resulted in 76.91% N removal from DSS and 7980 mg/L NH_4^+ -N solution.

CaO has been found to be an effective additive and catalyst to accelerate hydrothermal deamination. As a result of catalytic hydrolysis and cracking, CaO additive not only accelerated deamination of stable protein-N, pyrrole-N, and pyridine-N but also favored transformations of protein-N and quaternary-N to nitrile-N and pyridine-N, respectively, leading to 86.37% total N removal

efficiency and significant release of concentrated NH_4^+ -N of 9960 mg/L for subsequent nitrogen recovery in air stripping process. Subsequently, an efficient air stripping process was coupled to remove and recover ammonia from liquid fraction via ammonium sulfate. Consequently, this system achieved an overall N recovery rate of 61.99% from original DSS. According to an ideal scale-up, 51.93 kg N could be removed and 37.27 kg N would be recovered from 1 tonne dry mass of this DSS containing 60.12 kg N. It is believed that these findings provide an effective strategy for N control and recovery during sustainable sewage sludge management in industrial applications.

7.2 Recommendations for future study

As proposed in Chapter 2, a two-stage hydrothermal gasification process could be feasible to overcome limitations (such as corrosion, high operating cost, reactor plugging and catalyst deactivation) resulting from the application of SCW. This thesis demonstrates that sub- and near-critical water can convert sewage sludge to energy carriers in forms of clean solid fuel and hydrogen/methane rich fuel gas. However, high values of TOC and COD in the liquid by-products indicate that significant organic compounds are dissolved therein. Thus there is a great potential to generate more hydrogen using catalytic hydrothermal gasification, where catalysts can be easily recycled. Based on extensive literature review, novel catalysis materials and system have been attempted to product H_2 from glycerol which is a simple model compound of alcohol. The combination of Pt-Ni bimetallic catalyst and CaO additive has been identified as an effective catalytic system for H_2 production from CAPR of glycerol. Our detailed report has been published in **Applied Catalysis B: Environmental** (He et al., 2015b) and can be found in Appendix C. Nevertheless, this catalysis system should be furthered tested and verified in real wastewater from hydrothermal conversion of sewage sludge. Operation conditions of CAPR should also be optimized in future

study.

Since dehalogenation and mineralization of heteroatomic compounds in DSS were found in hydrothermal processing, the in-depth investigation regarding evolution of POPs could be an interesting topic for future study. Besides, the fate of sulfur transformation is also an important issue to be tackled in hydrothermal processing. At current stage, it is not suitable to achieve an accurate economic evaluation based on existing lab-scale system as many assumptions should be made before the calculations. Additionally, environmental impact is another important consideration when conducting the economic evaluation. Hence, to follow up this Ph.D. study, it is imperative to perform comprehensive comparative study for life cycle assessment of hydrothermal conversion and conventional thermochemical conversion of DSS from environmental and economic perspectives in order to make this concept more industrially viable.

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APPENDIX

Appendix A. Supporting information for Chapter 3: GC/MS analysis results of sludge oil extracted from liquid products after hydrothermal carbonization of sewage sludge

The heavy oil in hydrolysate from HTC of sewage sludge was extracted with ethyl acetate. The ethyl acetate soluble phase was separated by a long needle syringe. The extracted heavy oil was then diluted in acetone and 1.5 mL sample was placed in a GC vial for qualitative analysis using a Agilent gas chromatograph/mass spectrometer (GC/MS) equipped with a HP-5MS capillary column (30 m long $\times$ 0.25 mm diameter $\times$ 0.25 μ m film thickness). Approximately 1 μ L of sample was injected into the instrument with a splitless mode. The column temperature was initially held at 40 $^{\circ}$ C for 2 min and raised to 280 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min.

Figure A.1 GC/MS spectrum of the extracted heavy oil in hydrolysate from HTC of sewage sludge at 200 $^{\circ}$ C for 6 h. The detailed information of identified compounds has been listed in Table A.1.

Table A.1 Identified compounds in the extracted heavy oil in hydrolysate from HTC of sewage sludge using GC/MS analysis with confidence level higher than 70%.

RT (min)	Compound name	Molecular Formula	Compound Structure
3.797	5-Hexen-2-one	C ₆ H ₁₀ O
	4-Penten-2-one, 3-methyl-	C ₆ H ₁₀ O
	2-Pentanone, 3-methylene-	C ₆ H ₁₀ O
	2,4-Pentanedione, 3-methyl-	C ₆ H ₁₀ O ₂
4.484	3-Penten-2-one, 4-methyl-	C ₆ H ₁₀ O
	Furan, 2-methoxy-	C ₅ H ₆ O ₂
	2-Pentene, 2,3-dimethyl-	C ₇ H ₁₄
	2H-Pyran, 3,4-dihydro-4-methyl-	C ₆ H ₁₀ O
	Cyclohexane, methyl-	C ₇ H ₁₄
5.124	2,4-Dimethyl-1-heptene	C ₉ H ₁₈
	Cyclopentane, 1,3-dimethyl-	C ₇ H ₁₄

5.251	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$
5.500	Ethylbenzene	C_8H_{10}
	p-Xylene	C_8H_{10}
	Benzene, 1,3-dimethyl-	C_8H_{10}
	Benzene, 1,2-dimethyl-	C_8H_{10}
5.642	Benzene, 1,3-dimethyl-	C_8H_{10}
	Benzene, 1,2-dimethyl-	C_8H_{10}
	p-Xylene	C_8H_{10}
6.711	2,5-Hexanedione	$C_6H_{10}O_2$
7.361	4-Piperidinone, 1-methyl-	$C_6H_{11}NO$
	pyrrolidine, 1-acetyl-	$C_6H_{11}NO$
	furan, tetrahydro-2,2,4,4-tetramethyl-	$C_8H_{16}O$
7.356	Glutarimide	$C_5H_7NO_2$
7.409	Pentanoic acid, 4-methyl-3-oxo-, ethyl ester	$C_8H_{14}O_3$

	3-Pyrrolidinol	C ₄ H ₉ NO
7.853	Decane	C ₁₀ H ₂₂
8.017	Heptane, 3,3,5-trimethyl-	C ₁₀ H ₂₂
	Heptane, 2,5,5-trimethyl-	C ₁₀ H ₂₂
	Octane, 3,3-dimethyl-	C ₁₀ H ₂₂
8.234	Hexane, 2,3,5-trimethyl-	C ₉ H ₂₀
8.604	1-Nonene	C ₉ H ₁₈
	Decane, 4-methylene-	C ₁₁ H ₂₂
9.181	2-Undecene, 4-methyl-	C ₁₂ H ₂₄
	Cyclooctane	C ₈ H ₁₆
	Heptane, 4-methylene-	C ₈ H ₁₆
	3-Heptene, 4-methyl-	C ₈ H ₁₆
9.249	2-Undecene, 4-methyl-	C ₁₂ H ₂₄
	Ethanone, 1-cyclopentyl-	C ₇ H ₁₂ O
	3-Heptene, 4-methyl-	C ₈ H ₁₆
11.021	Dodecane	C ₁₂ H ₂₆
	Tetradecane	C ₁₄ H ₃₀
	Hexadecane	C ₁₆ H ₃₄
	Undecane	C ₁₁ H ₂₄

	Decane	$C_{10}H_{22}$
11.238	Undecane, 4,8-dimethyl-	$C_{13}H_{28}$
	Heptadecane	$C_{17}H_{36}$
11.560	Undecane, 4,6-dimethyl-	$C_{13}H_{28}$
	Undecane, 5-methyl-	$C_{12}H_{26}$
	Nonane, 5-methyl-5-propyl-	$C_{13}H_{28}$
	Octane, 3,3-dimethyl-	$C_{10}H_{22}$
11.682	Dodecane, 4,6-dimethyl-	$C_{14}H_{30}$
	Dodecane, 2,6,10-trimethyl-	$C_{15}H_{32}$
	Undecane, 4,6-dimethyl-	$C_{13}H_{28}$
	Octane, 2,3,6,7-tetramethyl-	$C_{12}H_{26}$
	Dodecane, 4,6-dimethyl-	$C_{14}H_{30}$
11.783	Nonane, 2,6-dimethyl-	$C_{11}H_{24}$
	Dodecane, 4,6-dimethyl-	$C_{14}H_{30}$
11.878	Benzene, 1,3-bis[1,1-dimethylethyl-]	$C_{14}H_{22}$
12.158	1-Propanone, cyclohexyl-	$C_9H_{16}O$

12.496	3-[Butylamino] propionitrile	C ₇ H ₁₄ N ₂	
12.560	2-Acetylcyclopentanone	C ₇ H ₁₀ O ₂	
	Cyclohexane, 1,3,5-trimethyl-	C ₉ H ₁₈	
12.676	2-Acetylcyclopentanone	C ₇ H ₁₀ O ₂	
	Cyclohexane, 1-methyl-3-propyl-	C ₁₀ H ₂₀	
13.803	Tetradecane	C ₁₄ H ₃₀	
14.358	Hexadecane, 7-methyl-	C ₁₇ H ₃₆	
14.617	Decane, 2-methyl-	C ₁₁ H ₂₄	
	Dodecane	C ₁₂ H ₂₆	
14.850	Dodecane, 4,6-dimethyl-	C ₁₄ H ₃₀	
	Nonane, 2,6-dimethyl-	C ₁₁ H ₂₄	
14.966	Hexadecane	C ₁₆ H ₃₄	
	Decane, 2-methyl-	C ₁₁ H ₂₄	
15.262	Phenol, 2,4-bis[1,1-dimethylethyl]-	C ₁₄ H ₂₂ O	
15.723	Ethanone, 1-cyclopethyl-	C ₇ H ₁₄ O	
	cyclohexane, 1-ethyl-2-propyl-	C ₁₁ H ₂₂	

15.844	cyclohexane, 1,2,4-trimethyl-	C ₉ H ₁₈
16.310	Propanoic acid, 2-methyl-	C ₄ H ₈ O ₂
	Furan, 2-butyltetrahydro-	C ₈ H ₁₆ O
	Methylamine, N-[1-methylhexylidene]-	C ₈ H ₁₇ N

Appendix B. Supplementary explanations

Text S1

Temperatures ranging from 220 to 380 °C were selected and the highest temperature of 380 °C was near critical temperature of water (374.3 °C). In hydrothermal conversion process, pressure is autogenously generated by water vapor under different temperatures. Thus the water content required to approach the critical pressure of water (22.1 MPa) under 380 °C was determined to be 150 g in a 1.0 L batch reactor according to our preliminary experiments. In order to keep the same feedstock, 182 g of DSS, which contained approximately 150 g of water, was loaded into the reactor vessel. When this feedstock was employed and the reactor was heated up to a series of sub- and near-critical water ranging from 220 to 380 °C, a pressure corresponding to the pre-set temperature could be autogenously generated and recorded. Ten hydrothermal conversion conditions were attempted, i.e. 200 °C and 2.0 MPa, 220 °C and 2.6 MPa, 240 °C and 3.8 MPa, 260 °C and 5.0 MPa, 280 °C and 7.0 MPa, 300 °C and 9.3 MPa, 320 °C and 12.0 MPa, 340 °C and 15.5 MPa, 360 °C and 19.4 MPa, 380 °C and 22.0 MPa.

Text S2

In particular, protein-N content (1744.35 mg) derived from N 1s XPS spectrum of DSS was in good agreement with the N content (1745.92 mg) calculated from protein determined using the Kjeldahl method, strongly suggesting that N 1s XPS spectrum is a powerful technique to quantify the changes of nitrogen functionalities in sewage sludge.

Appendix C. Attached report on development of effective catalysis system*

C.1 Introduction

Biomass derived alternative energy carriers and chemicals are becoming increasingly important due to rapid depletion of fossil fuel and associated environmental problems. Biodiesel produced from non-food feedstocks (e.g. lignocellulosic biomass and microalgae) is regarded as a promising alternative biofuel (Mata et al., 2010). However, approximate 10 wt.% of glycerol by-product is generated during the biodiesel processing (Byrd et al., 2008). The ever increasing biodiesel production leads to excess glycerol in market, which attracts great attention to increase overall benefits during biodiesel production by re-utilizing this main by-product (Markočič et al., 2013). Unlike applications of pure glycerol in cosmetics, pharmaceuticals and chemicals, re-utilization of crude glycerol is limited by its high water content (Chakinala et al., 2013).

Direct conversion of glycerol to hydrogen rich gas via thermochemical processes has been extensively explored (Tran and Kannangara, 2013). Catalytic aqueous phase reforming (CAPR) is one of the technically feasible approaches to produce hydrogen with trace amounts of CO from oxygenated hydrocarbons derived from biomass under hydrothermal conditions of 175-265 °C (de Vlieger et al., 2012b) and 15-50 bar (Davda et al., 2005). The CAPR reaction mainly includes dehydrogenation (C-C bond cleavage) and water-gas shift (WGS) reaction of adsorbed CO (van Haasterecht et al., 2013). CAPR of glycerol to H₂ involves the following reactions (El Doukkali et al., 2012; Guo et al., 2012).

* This report is written based on my article "Sorption enhanced aqueous phase reforming of glycerol for hydrogen production over Pt-Ni supported on multi-walled carbon nanotubes", Applied Catalysis B Environmental (2015).

WGS reaction:

Methanation reactions (Chakinala et al., 2013):

Therefore, desired catalysts in CAPR process should be highly active in C-C bond cleavage and WGS reaction while C-O bond cleavage and methanation reactions should be inhibited.

Platinum supported on alumina (Pt/Al₂O₃) has been reported as active and selective catalyst in CAPR (Ciftci et al., 2012; Cortright et al., 2002; Wen et al., 2010). To increase H₂ production and selectivity, intensive studies on CAPR of glycerol (including other polyols, such as ethylene glycol) for H₂ production over Pt-based bimetallic catalysts have also been conducted, such as Pt-Re (Ciftci et al., 2014; King et al., 2010; Kunkes et al., 2008), Pt-Co (Huber et al., 2006; Wang et al., 2012), and Pt-Ni bimetallic catalysts (Chakinala et al., 2013; de Vlieger et al., 2012a; de Vlieger et al., 2012b; El Doukkali et al., 2012; Huber et al., 2006; Tran and Kannangara, 2013; Tupy et al., 2013). Alloying Pt with Re showed improved C-C bond cleavage and glycerol conversion with relatively poor H₂ selectivity (Ciftci et al., 2014; King et al., 2010; Kunkes et al., 2008). Pt-Co bimetallic catalyst reported by Wang et al. (2012) achieved a high H₂ production rate of 4.6 mmol g cat⁻¹ min⁻¹ from CAPR of ethylene glycol. Similarly, Pt-Ni exhibited higher H₂ and less alkane formation from CAPR of glycerol than Pt monometallic catalyst (de Vlieger et al., 2012a). More importantly, adding base metals (i.e. Co and Ni) into Pt catalyst can significantly reduce the usage of noble metals (Wang et al., 2012).

Apart from Pt-based catalysts, taken into account of good activity of Ni for C-C bond cleavage and that of Cu in WGS reaction, 60% of glycerol was converted

at 270 °C with high H₂ selectivity and suppressed methanation over a Ni-Cu catalyst (Tuza et al., 2013). Byrd et al. (2008) reported that glycerol with concentration up to 40 wt.% can be completely gasified to produce near-theoretical H₂ yield in the presence of Ru/Al₂O₃ in supercritical water (SCW). Nonetheless, high CH₄ yield reduced H₂ purity.

Catalyst stability in CAPR is another challenging issue (Koichumanova et al., 2013). Due to the phase transformation of γ -Al₂O₃ to boehmite [AlO(OH)], Pt/ γ -Al₂O₃ was not stable even under mild hydrothermal condition (Ciftci et al., 2012; Koichumanova et al., 2013). Besides, CAPR is a structure sensitive reaction (Lehnert and Claus, 2008). Compared to platinum nanoparticle size, structural properties and support nature exhibited more remarkable effects on catalytic performance. Through catalytic performance screening of Pt-based catalysts supported on various oxides (i.e. Al₂O₃, ZrO₂, CeO₂, and MgO) in CAPR of glycerol, Menezes et al. (2011) found that MgO demonstrated the best activity for H₂ production with low alkanes as a result of the basic nature of MgO. Due to unique properties (e.g. thermal resistance, metal dispersion, acid-base and redox properties, activity in WGS reaction, inhibition of coking and methanation) of CeO₂, CeO₂-doped Al₂O₃ was employed as support materials for Pt catalyst to enhance H₂ selectivity and carbon conversion to gas with low CH₄ yield (Rahman et al., 2013).

Due to the diffusion limitation induced by irregular porous structure of activated carbon, gaseous products cannot be removed rapidly and thus hydrogen production was inhibited (Kim et al., 2011). Kim et al. (2011) claimed that ordered mesoporous carbon was an effective carbonaceous support due to its hydrothermal stability and open mesoporous structure. The activity of supported Pt-Re catalyst followed the order of CMK-3 > activated carbon > SiO₂ > Al₂O₃ (Kim et al., 2012). Carbon nanotubes (CNTs), both single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWCNTs), have been

reported to be superior catalyst support materials for hydrothermal gasification (Azadi et al., 2009; Wang et al., 2012), even under SCW conditions (de Vlieger et al., 2012).

In addition to catalyst design, some novel processes have also been developed in order to enhance H_2 yield and selectivity. For instance, dolomite was conventionally selected as CO_2 absorber to enhance catalytic steam gasification process towards more H_2 yield with high purity via in-situ CO_2 removal and carbonation (Fermoso et al., 2012). More recently, calcium oxide has been employed to achieve high H_2 and CH_4 selectivity in supercritical water gasification of biomass (Onwudili and Williams, 2013). The WGS reaction is regarded as the rate-limiting step in CAPR reaction network of glycerol over Pt-based catalysts (Guo et al., 2012). Rapid CO_2 removal would be able to shift WGS reaction towards selective H_2 production. Along this line, MWCNTs supported Pt monometallic and Pt-based bimetallic catalysts were prepared for H_2 production in CAPR of glycerol in this study. Moreover, CaO was selected as the in-situ CO_2 absorber. The effects of alloying the second metal with Pt and introducing CaO as CO_2 acceptor on gas and liquid products yields were discussed in detail. Based on the reaction results, reaction pathways in present CAPR of glycerol were proposed.

C.2 Experimental

C.2.1 Materials

Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, >37.5% Pt basis), palladium chloride ($PdCl_2$, ReagentPlus, 99%), ruthenium (III) nitrosyl nitrate solution ($HN_4O_{10}Ru$), nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999%), copper (II) nitrate hydrate ($Cu(NO_3)_2 \cdot xH_2O$, 99.999%), concentrated nitric acid (HNO_3 , ACS reagent, 69%), glycerol ($\geq 99.5\%$), 1,2-propanediol (ACS reagent, $\geq 99.5\%$), calcium hydroxide ($Ca(OH)_2$, Reag. Ph. Eur., $\geq 96\%$), calcium carbonate ($CaCO_3$,

ReagentPlus) and calcium oxide (CaO, reagent grade) were purchased from Sigma-Aldrich. Hydroxyacetone (95%) and cobalt (II) chloride (Anhydrous, 97%) were provided by Alfa Aesar. All these chemicals were used without further purification. Deionized (DI) water produced from Millipore Milli-Q water purification system was used throughout entire experiments.

C.2.2 Catalyst preparation

MWCNTs (Shenzhen Nanotech Port Co., China) were employed as support materials during monometallic and bimetallic catalysts preparation. The pristine MWCNTs were refluxed in concentrated nitric acid at 120 °C for 4 h under stirring to remove metallic impurities and introduce oxygen-containing functional groups onto the surface of MWCNTs, thereby facilitating uniform precipitation of metal precursors (Guo et al., 2010). The functionalized MWCNTs were washed and prepared following the procedure described by Nassr et al. (2013), which were denoted as FCNTs thereafter.

Both monometallic and bimetallic platinum catalysts were prepared by incipient wetness impregnation method. Specifically, a 5 wt.% Pt supported on FCNTs catalyst was prepared by impregnating 100 mg of FCNTs with 722 μL of 20 mg/mL $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution and 30 mL DI water in a 50 mL round bottomed flask. The mixture was vigorously stirred by magnetic stirring bar at 650 rpm for 2 h at room temperature. The slurry was dried by rotary evaporator at 60 °C under 200 mbar. The Pt-FCNTs composite was further oven dried at 100 °C for 12 h. The prepared catalyst composite was pulverized into fine powders in agate mortar and reduced at 350 °C for 2 h under a H_2 flow rate of 40 mL/min. The as-synthesized catalyst with 5 wt.% Pt loading was denoted as 5Pt/CNT.

Similarly, bimetallic platinum catalysts were prepared in the presence of Pt and transition metal precursors at a fixed Pt loading of 5 wt.% and Pt to promoter

atomic ratio of 1:1 following the same procedure. These catalysts were denoted as 5Pt1.5Ni/CNT, 5Pt1.5Co/CNT, 5Pt1.6Cu/CNT, 5Pt2.7Pd/CNT, and 5Pt2.6Ru/CNT. For comparison, another two Pt to Ni atomic ratios (2:1) and (1:2) were attempted, resulting in a final Ni loading of 0.75 wt.% and 3.0 wt.%, respectively. These two catalysts were denoted as 5Pt0.75Ni/CNT and 5Pt3Ni/CNT accordingly. To determine actual metal loadings, the catalysts were digested in concentrated Aqua Regia in High Performance Microwave Digestion System (Milestone Inc.) under 200 °C for 30 min and diluted into 100 mL solution after cooling down. The dissolved metals were analyzed using PerkinElmer Optima 8300 inductively coupled plasma optical emission spectrometer (ICP-OES). The determined metal loadings were close to the theoretical values. The chemical composition and physicochemical characteristics of all these catalysts are described in Table 1.

C.2.3 Catalyst characterization

Textural characteristics of as-synthesized catalysts were measured by Quantachrome Autosorb sorption system. Prior to liquid nitrogen adsorption-desorption at -196 °C, the catalysts were degassed at 150 °C for 12 h under vacuum. Specific surface areas of catalysts were determined through multi-point Brunauer-Emmett-Teller (BET) method. Pore volume and average pore diameter were calculated using Barrett-Joyner-Halender (BJH) method based on N₂ desorption data.

Chemisorption uptakes of H₂ and CO on catalysts were conducted on Micromeritics ASAP 2020 (M+C) analyzer using static volumetric method following a modified procedure described elsewhere (Lin et al., 2012). Briefly, ca. 500 mg of as-synthesized catalyst was reduced in high-purity H₂ at 350 °C for 4 h and then evacuated for 1 h to ensure complete removal of chemisorbed species. An initial isotherm was measured under 100-600 Torr at 35 °C. Subsequently,

evacuation was carried out for 30 min at 35 °C to remove reversibly adsorbed adsorbates (H₂ and CO) on catalyst surface prior to measurement of a repetitive isotherm under the same condition. Finally, the uptakes of irreversibly chemisorbed adsorbates on catalysts were derived by the difference between the initial and repetitive isotherms.

X-ray diffraction (XRD) patterns of catalysts were determined over a 2θ range from 10° to 80° using Philips PANALYTICAL X'pert Pro powder X-ray diffractometer equipped with a graphite monochromator using Cu-K α radiation X-ray source operated at 40 kV and 30 mA. High resolution transmission electron microscopy (HRTEM) images were taken on Philips Analytical FEI Tecnai F30 electron microscope operated at an acceleration voltage of 300 kV. The catalysts were sonicated in ethanol for 5 min, deposited onto carbon coated copper grids and then dried before analysis.

C.2.4 Catalyst testing

The CAPR of glycerol was carried out in a 50 mL stainless steel micro bench reactor (Parr 4592 model) equipped with magnetic drive stirrer, PTFE liner, and PID controller (Parr Instrument Co., USA). The dead volume of the autoclave with PTFE liner was calibrated as 43 mL by GilAir Plus air pump. Typically, 15 mL of 10 wt.% glycerol stock solution, 100 mg catalysts, and a specific amount of CaO were loaded into the PTFE vessel. The reactor was purged with nitrogen gas for 5 min and pressurized to an initial N₂ pressure of 30 bar, which served as an internal standard for final gas yield calculation. Subsequently, the reactor was heated to 230 °C using an external electric heating mantle under a stirring speed of 500 rpm. After maintaining at 230 °C for 4 h, the reactor was quenched to room temperature in ice water bath rapidly. Gaseous products were gently released to Tedlar gas bags through the gas outlet valve. After depressurization, the reactor was opened for liquid products sampling and spent catalysts recovery.

The liquid products were collected and filtered through 0.45 μm PTFE membrane filters for further analysis. The spent catalysts were washed with DI water and oven dried at 100 $^{\circ}\text{C}$ overnight.

C.2.5 Products analyses

C.2.5.1 Gas products

Gaseous products were analyzed using gas chromatograph (Agilent Technologies 7890A, USA) equipped with dual thermal conductivity detectors (GC-TCD/TCD) with HayeSep Q, HayeSep C, HayeSep R, Molesieve 13X, and Molesieve 5A columns for gas separation. Hydrogen, carbon dioxide, methane, and nitrogen were detected in gaseous products.

C.2.5.2 Liquid products

A 10 μL liquid solution was injected into an UltiMate 3000 high performance liquid chromatography (HPLC) equipped with an UV-Vis detector for analysis. Liquid analytes separation was carried out by Bio-Rad Aminex HPX-87H ion exclusion column (300 mm $\times$ 7.8 mm) with a 5 mM H_2SO_4 aqueous solution as the mobile phase at a flow rate of 0.7 mL/min and column temperature of 33 $^{\circ}\text{C}$. The dissolved calcium ion concentration in liquid products was determined by ICP-OES.

C.2.6 Catalyst regeneration and recycle experiments

Thermogravimetric analysis (TGA) was performed by STA 449 F3 Jupiter Simultaneous TG-DTA/DSC Apparatus (NETZSCH-Gerätebau GmbH) under N_2 atmosphere with a fixed flow rate of 20 mL/min. The weight loss (TG) and the weight loss rate (DTG) of catalysts and standard chemicals were recorded dynamically from 50 to 900 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. TGA of 5Pt1.5Ni/CNT + 180 mg CaO after first catalytic run was conducted to determine the peak temperature of spent catalyst with pure CaCO_3 and $\text{Ca}(\text{OH})_2$ as standard chemicals. Subsequently, the spent catalysts were calcined at the peak

temperature determined by TGA under 40 mL/min of N₂ for 1 h. The calcined catalysts were reused with 180 mg fresh CaO powders in the next catalytic reaction experiment.

C.2.7 Terms and definitions for catalysts activity and selectivity evaluation

The catalysts were evaluated in terms of glycerol conversion rate, carbon conversion to gas, hydrogen gasification ratio, H₂ yield, H₂ selectivity, and CH₄ selectivity according to following equations proposed previously (King et al., 2010).

$$\text{Glycerol conversion rate (\%)} = \left(1 - \frac{\text{Moles of glycerol remaining in liquid phase}}{\text{Moles of glycerol in feedstock}}\right) \times 100$$

$$\text{Carbon conversion to gas (\%)} = \frac{\text{C atoms in gas products}}{\text{Total C atoms in feedstock}} \times 100$$

$$\text{Hydrogen gasification ratio (\%)} = \frac{\text{H atoms in gas products}}{\text{Total H atoms in feedstock}} \times 100$$

$$\text{H}_2 \text{ yield (mmol / g Glycerol)} = \frac{\text{Molecules of produced H}_2 \text{ (mmol)}}{\text{Mass of glycerol in feedstock (g)}}$$

$$\text{H}_2 \text{ selectivity (\%)} = \frac{\text{Molecules of produced H}_2}{\text{C atoms in gas products}} \times \frac{1}{n} \times 100$$

where $n=7/3$, which is the H₂/CO₂ stoichiometric reforming ratio in equation (C.1).

$$\text{CH}_4 \text{ selectivity (\%)} = \frac{\text{C atoms in produced CH}_4}{\text{Total C atoms in gas products}} \times 100$$

C.3 Results and discussion

C.3.1 Structural and physicochemical properties of catalysts

Figure C.1 depicts XRD patterns of FCNTs and all the as-synthesized catalysts. The sharp diffraction (002) of hexagonal graphite at 2θ of 25.8° that represents

graphite structure of carbon nanotubes was retained after HNO₃ oxidation, Pt monometallic and bimetallic impregnation and reduction at high temperature (Guo et al., 2010). The catalytic activity in CAPR reaction was reported to associate with metal nanoparticle size and dispersion on carbonaceous support (Kim et al., 2011). As presented in Figure C.1, 5Pt/CNT displayed noticeable diffraction peaks at 2θ of 39.9°, 46.1°, and weak signal at 67.4°, which were assigned to (111), (200) and (220) facets of Pt fcc structure, respectively (Nassr et al., 2013). After adding promoters, the characteristic diffraction peaks of Pt became less intensive, indicating the smaller metal nanoparticles after alloying with the second metal. Due to the low metal loadings of promoters, good dispersion as well as small particle size, the crystalline structures of promoters cannot be clearly identified in Figure C.1 as a result of XRD instrument detection limit (de Vlieger et al., 2012a).

Figure C.1 X-ray diffraction patterns of FCNTs and as-synthesized catalysts supported on FCNTs.

Particle size distribution histograms of 5Pt/CNT and 5Pt1.5Ni/CNT and

corresponding HRTEM images are shown in Fig. 2. Particle size distribution histograms were derived by counting 308 and 403 particles for 5Pt/CNT and 5Pt1.5Ni/CNT, resulting in an average particle size of 2.2 and 1.2 nm, respectively. After adding 1.5 wt.% of Ni, 5Pt1.5Ni/CNT presented a slightly narrower particle size distribution than 5Pt/CNT. According to the inset TEM images in Figure C.2A and B, the well dispersed Pt and Pt-Ni nanoparticles on FCNTs and the small average particle size of 1.2 nm for 5Pt1.5Ni/CNT coincided with the weak diffraction peaks in abovementioned XRD patterns. Apart from Pt-Ni alloy in Fig. 2D, Pt nanoparticles were observed elsewhere, which was in agreement with results found by de Vlieger et al. (de Vlieger et al., 2012a). Recently, the Pt-Ni alloy structure has been presumed to be formed by a Pt-rich alloy shell with a Ni-rich core near support surface resulting from negatively charged FCNTs during catalyst preparation (Nassr et al., 2013). The presence of Pt-Ni alloy may modify the electronic environment of Pt, thereby increasing binding energy of Pt4d_{5/2} and thus the Pt dispersion (El Doukkali et al., 2012). This claim was consistent with observations in XRD patterns.

The diffraction peaks of Pt for 5Pt2.6Ru/CNT and 5Pt2.7Pd/CNT were stronger than base metal promoted Pt bimetallic catalysts, which may be ascribed to higher metal loadings of noble metal promoters at a fixed atomic ratio of 1:1. Besides, the Pt (111) diffraction peaks for Pt-Ni catalysts slightly shifted to higher 2θ values, implying that smaller Ni atoms may be incorporated into Pt fcc lattice to form Pt-Ni alloy structure (Nassr et al., 2013). The alloy formation can be further evidenced by measuring the lattice spacing on HRTEM images (Purushothaman et al., 2014). The lattice spacing of Pt (111) plane in 5Pt/CNT was 0.225 nm (Figure C.2C) whereas that of well resolved (111) planes in 5Pt1.5Ni/CNT was found to be 0.220 nm (Figure C.2D). The Pt-Ni alloying was more pronounced for higher Ni loading 5Pt3Ni/CNT (Pt to Ni atomic ratio of 1:2) with broad peak at 2θ of 41.8°. 5Pt1.5Co/CNT showed similar Pt (111) diffraction peak compared to 5Pt1.5Ni/CNT, implying the formation of Pt-Co alloying as well. Huber et al.

(Huber et al., 2006) reported previously that bulk Pt-Ni or Pt-Co alloy is inclined to be formed when stoichiometric amounts of Ni or Co are introduced into Pt catalyst.

Figure C.2 Particle size distribution histograms of (A) 5Pt/CNT (Inset: TEM image of 5Pt/CNT) and (B) 5Pt1.5Ni/CNT ((Inset: TEM image of 5Pt1.5Ni/CNT); HRTEM images of (C) 5Pt/CNT and (D) 5Pt1.5Ni/CNT (Arrows indicated the lattice spacing of Pt (111) plane and Pt-Ni bimetallic cluster).

Table C.1 summaries the physicochemical properties of FCNTs support material and as-synthesized catalysts. The BET specific surface area (S_{BET}) of FCNTs was 164.6 m²/g, which was remarkably lower than that of CMK-3 (884 m²/g) (Kim et al., 2011). After impregnation of Pt, due to the formation of Pt nanoparticles on FCNTs surface, S_{BET} of 5Pt/CNT slightly increased to 174.7 m²/g while

average pore diameter decreased from 40.8 to 37.5 nm and total pore volume remained similar (around 1.65 cm³/g). Compared with 5Pt/CNT, S_{BET} (140-160 m²/g), average pore diameter (0.8-1.3 cm³/g), and total pore volume (20-37 nm) of Pt-based bimetallic catalysts all decreased. These physicochemical properties may contribute to different catalytic activities of these catalysts in the following discussion.

C.3.2 Catalyst screening experiments

C.3.2.1 Hydrogen gasification ratio, carbon conversion to gas, and glycerol conversion rate

Eight catalysts were attempted in CAPR of glycerol under experimental conditions shown in Table C.2. Although the initial pressure was 30 bar, the pressure increased and differed slightly when the temperature reached 230 °C, which was around 55 bar. After 4 h of reaction, final pressure increased to different extent due to different activities of catalysts and gas production. Figure C.3 presents activities of various catalysts in terms of glycerol conversion rate, hydrogen gasification ratio, and carbon conversion to gas. Overall, adding promoters, such as Ni, Co, and Ru, improved the glycerol conversion rate except Cu and Pd. The glycerol conversion rate over 5Pt1.6Cu/CNT was only 13.5% and hydrogen gasification ratio as well as carbon conversion to gas was less than 5%. Ni and Co significantly enhanced the glycerol conversion rate from 26.33% for 5Pt/CNT to 81.21% and 75.67% for 5Pt1.5Ni/CNT and 5Pt1.5Co/CNT, respectively. The carbon conversion to gas for 5Pt1.5Ni/CNT (15.3%) was slightly higher than that of 5Pt1.5Co/CNT (14.3%) and the hydrogen gasification ratio for 5Pt1.5Ni/CNT (7.2%) was comparable to that of 5Pt1.5Co/CNT (7.7%). Noble metal Pd and Ru promoters showed different activities of glycerol conversion rate which increased to 42.58% for 5Pt2.6Ru/CNT but declined to 20.23% for 5Pt2.6Pd/CNT. Regardless the difference in glycerol conversion rate, both hydrogen gasification ratio and carbon conversion to gas for these two

catalysts were promoted dramatically. In particular, the hydrogen gasification ratio for 5Pt2.6Pd/CNT (15.8%) and the carbon conversion to gas for 5Pt2.6Ru/CNT (15.1%) were 3.3 and 1.8 times higher than those of 5Pt/CNT, respectively.

Figure C.3 Effects of different metal promoters and CaO amounts on glycerol conversion rate, hydrogen gasification ratio, and carbon conversion to gas during catalytic aqueous phase reforming. Operating conditions: 230 °C, an initial N₂ pressure of 30 bar, 15 mL of 10 wt.% glycerol with 100 mg catalyst for 4 h reaction time.

C.3.2.2 Gas composition and yield

Figure C.4 demonstrates the evolution of gas product composition when metal promoters were varied. The gas products were mainly composed of H₂, CO₂, and a small amount of CH₄ which was less than 5%. Adding transition metals

increased the CH₄ fraction in gas products. Hydrogen accounted for 58.9% and 53.0% over 5Pt2.7Pd/CNT and 5Pt2.6Ru/CNT, respectively. Although the catalytic activity of 5Pt1.6Cu/CNT was poor, an ultimate H₂ fraction of 44.4% was slightly higher than 33.2% H₂ of 5Pt1.5Ni/CNT and 38.4% H₂ of 5Pt1.5Co/CNT, which may be mainly associated with dehydrogenation of glycerol and low activity for C-C bond cleavage in reforming reaction as summarized by Wen et al. (Wen et al., 2008) and van Haasterecht et al. (van Haasterecht et al., 2013). Wang et al. (Wang et al., 2012) has previously demonstrated that Pt-Co bimetallic catalyst supported on SWNTs was effective for hydrogen production in CAPR. In this study, 5Pt1.5Co/CNT exhibited the lowest CH₄ fraction (2.9%) among all Pt-based bimetallic catalysts other than moderate H₂ yield (177.9 $\mu\text{mol min}^{-1} \text{ g cat}^{-1}$).

Experimental gas production, hydrogen yield and corresponding hydrogen production rate during CAPR are summarized in Table C.3. In CAPR of glycerol, the stoichiometric reforming ratio of H₂/CO₂ is 2.33. However, H₂/CO₂ ratio values in Table C.3 were lower than 2.33 and the lowest H₂/CO₂ ratio was around 0.5 (for Pt-Ni bimetallic catalysts). This low H₂ concentration implied that the generated H₂ was consumed during hydrogenation of unsaturated intermediates. In addition, methanation in stoichiometric amounts also explained this phenomenon, leading to the formation of one H₂ molecule when two CO₂ molecules were produced (Wawrzetz et al., 2010). Hence, CH₄ yield over Pt-Ni bimetallic catalysts was significantly increased by a factor of around 2.5 compared to 5Pt/CNT. In contrast, noble metals promoted Pt-based bimetallic catalysts, i.e. 5Pt2.7Pd/CNT and 5Pt2.6Ru/CNT, presented higher H₂/CO₂ ratio of 1.59 and 1.21, respectively. Since CH₄ yields over these two catalysts were comparable to that over 5Pt1.5Ni/CNT, the increased H₂/CO₂ ratios should be mainly attributed to disfavored hydrogenation of unsaturated intermediates.

Figure C.4 Effects of different metal promoters and CaO amounts on gas composition during catalytic aqueous phase reforming. Operating conditions: 230 °C, an initial N₂ pressure of 30 bar, 15 mL of 10 wt.% glycerol with 100 mg catalyst for 4 h reaction time.

C.3.2.3 H₂ and CH₄ selectivity

Figure C.5 represents H₂ and CH₄ selectivity in gaseous products from CAPR of glycerol over different catalysts. Compared with H₂ selectivity (29.8%) and CH₄ selectivity (4.3%) over 5Pt/CNT catalyst, all the promoters facilitated the CH₄ formation to different extents. Under a fixed atomic ratio (1:1) of Pt to promoter, the effect of promoters on H₂ selectivity was Pd > Ru > Cu > Co > Ni and that on CH₄ selectivity followed a descending order of Pd > Cu > Ru > Ni > Co. 5Pt2.7Pd/CNT demonstrated the highest H₂ selectivity (61.5%) and CH₄ selectivity (9.9%). H₂ selectivity decreased after adding Ni and Co promoters. Although H₂ selectivity for Pt-Ni bimetallic catalysts (18.6 - 23.0%) and 5Pt1.5Co/CNT (26.8%) was poor, CH₄ selectivity showed a high level ranging from 4.7 to 7.2% due to enhanced catalytic methanation by Co and Ni because CH₄ is more thermodynamically stable than H₂ (van Haasterecht et al., 2013).

Figure C.5 Effects of different metal promoters and CaO amounts on H₂ and CH₄ selectivity during catalytic aqueous phase reforming. Operating conditions: 230 °C, an initial N₂ pressure of 30 bar, 15 mL of 10 wt.% glycerol with 100 mg catalyst for 4 h reaction time.

C.3.3 Effect of Ni loading on CAPR of glycerol

In present study, the glycerol conversion rate (81.21%) and carbon conversion to gas (15.3%) over 5Pt1.5Ni/CNT were the highest among the catalysts, which might be attributed to the synergistic effects between Pt and Ni in bimetallic catalyst through Pt-Ni alloy structure formation. In addition, compared with noble metals promoted Pt-based bimetallic catalysts, 5Pt1.5Ni/CNT exhibited moderate hydrogen gasification ratio (7.2%). Thus, Pt-Ni bimetallic catalyst was selected and the effect of Ni loading was further explored. As shown in Figure C.3, glycerol conversion rate, hydrogen gasification ratio, and carbon conversion to gas for 5Pt0.75Ni/CNT were higher than 5Pt3Ni/CNT but lower than 5Pt1.5Ni/CNT. The atomic ratio (1:1) of Pt to Ni was optimal, which closely correlated with the highest activity per surface site at atomic ratio of 1:1 as Huber et al. deduced (Huber et al., 2006). It was postulated that the excess Ni may cover

the active Pt surface sites as not all the Ni formed Pt-Ni alloy (El Doukkali et al., 2012). Furthermore, the excess Ni which was not in Pt-Ni alloy structure would be significantly deactivated during CAPR at 225 °C (Davda et al., 2003). When Ni loading was increased from 0.75 wt.% to 3 wt.%, CO₂ fraction increased gradually from 61.0% to 64.7%, while H₂ fraction decreased from 34.9% to 30.3%. CH₄ concentration remained the same. Ni was active in WGS reaction which was responsible for the improved hydrogen yield (de Vlieger et al., 2012a). In Table 3, H₂ and CO₂ yields over 5Pt1.5Ni/CNT were remarkably higher than those over 5Pt/CNT, 5Pt0.75Ni/CNT, and 5Pt3Ni/CNT, indicating that certain amounts (i.e. 1.5 wt.%) of Ni may lead to the improvement of WGS reaction as well as excess amounts of H₂ production. Interestingly, as Ni loading was increased from 0.75 wt.% to 3 wt.%, H₂ selectivity decreased from 23% to 18.6%, whereas CH₄ selectivity increased from 6.3 to 7.2%, which could be associated with the greater yield evolution of CO₂ than that of H₂ according to their definitions in Section C.2.7.

According to chemisorption data shown in Table 1, H₂ and CO uptakes increased progressively as Ni loading was elevated to equimolar amount. However, excess Ni (Pt:Ni = 1:2) reduced H₂ and CO uptakes to a lower level compared to 5Pt/CNT (Simonetti et al., 2007). CO uptakes were higher than H₂ uptakes, and the greater coverage of CO was ascribed to the stronger affinity of CO on Pt (He et al., 2005). The increased uptakes of adsorbents correlated well with higher catalytic activity and H₂ yield. In CAPR of glycerol, CO species formed from decarbonylation of aldehyde intermediates were bound on catalyst surfaces and can interact with co-adsorbed hydrogen or H₂O (Copeland et al., 2013). The increased CO uptakes promoted the reaction with H₂O via WGS reaction to generate loosely bound CO₂ which can be readily desorbed, thereby shifting the WGS reaction towards more H₂ formation. Thus, lower H₂ yield (1.59 mmol/g glycerol) of 5Pt3Ni/CNT than that of 5Pt/CNT (1.83 mmol/g glycerol) might be due to the reduced H₂ and CO uptakes.

Figure C.6 illustrates the linear correlation between hydrogen yield and chemisorption uptakes of H₂ and CO for 5Pt/CNT and Pt-Ni/CNT catalysts with varying Pt:Ni atomic ratios. The linear regression analysis followed a previously published procedure (He et al., 2013). Pearson's correlation coefficient (R) was employed to assess the linear correlation and the statistical significance of the correlation was analyzed using one-way analysis of variance method at a confidence level of 95% ($p < 0.05$). As displayed in Figure C.6, chemisorption uptakes of CO and H₂ had a remarkable positive correlation ($R = 0.998$, $p < 0.05$ and $R = 0.956$, $p < 0.05$ for CO and H₂, respectively) with hydrogen yield. Therefore, apart from C-C and C-O bond cleavages, adsorption capacities of H₂ and CO on the surface of catalysts were crucial parameters for evaluation of catalytic activity for H₂ production.

C.3.4 Effect of CaO addition on CAPR of glycerol

Compared with 5Pt2.7Pd/CNT and 5Pt2.6Ru/CNT, 5Pt1.5Ni/CNT exhibited the highest carbon conversion to gas (15.3%) but relatively lower hydrogen gasification ratio (7.2%). There was a great potential to improve hydrogen production at the expense of carbon conversion to gas via inhibited methanation and facilitated WGS reaction. Hence, CaO which served as sorbent was introduced to enhance WGS reaction (equation (C.2)) and reduce methanation reactions (equations (C.3) and (C.4)) through CO₂ capture and accelerated CO removal. Different amounts (i.e. 90 mg and 180 mg) of CaO, which corresponded to Ca/(C in glycerol feedstock solution) molar ratio of 0.1 and 0.2, were attempted. With the increasing amount of CaO, the hydrogen gasification ratio was elevated from 7.2% to 11.1%, while carbon conversion to gas was reduced from 15.3% to 10.1%. The glycerol conversion rate was also increased and achieved 94.96% when a mixture of 180 mg of CaO and 100 mg of 5Pt1.5Ni/CNT was adopted. Adding CaO in the absence of catalyst did not show any catalytic activity in the

same CAPR reaction. Glycerol conversion rate was only 2% along with negligible amounts of H_2 , CO_2 and CH_4 in gas product, revealing that CaO was not active in C-C and C-H bond cleavages of oxygenated hydrocarbons under investigated hydrothermal conditions.

Figure C.6 Relationships between hydrogen yield (mmol H_2 /g glycerol) and chemisorption uptakes (μ mol/g catalyst) of H_2 and CO for Pt/CNT and Pt-Ni/CNT catalysts with various Pt:Ni atomic ratios.

After adding CaO into 5Pt1.5Ni/CNT, gas composition changed dramatically. As depicted in Figure C.4, H_2 increased from 33.2% to 59.4%, whereas CO_2 decreased from 62.4% to 40.4%. The H_2 purity (59.4%) of 5Pt1.5Ni/CNT in the presence of 180 mg CaO was comparable to that of 5Pt2.7Pd/CNT. In addition, CaO reduced CH_4 to a significantly low level (0.2%). As the amount of CaO was increased to 180 mg, H_2 selectivity showed a pronounced increase from 21.3% to 62.6% while CH_4 selectivity declined from 6.6% to 0.5% over 5Pt1.5Ni/CNT catalyst. The increased H_2 selectivity and decreased alkane selectivity were consistent with results after adding KOH into 3%Pt-3%Re/C reported by King et al. (2010).

Consequently, acting as CO_2 acceptor, CaO not only accelerated WGS reaction

but also inhibited methanation in CAPR. Substantially low CO concentration and negligible CH₄ would benefit downstream application of H₂, e.g. proton exchange membrane fuel cells (Fermoso et al., 2012). From the perspectives of H₂ purity and yield in CAPR reaction for renewable H₂ production, the combination of 5Pt1.5Ni/CNT and CO₂ absorber can be comparable to 5Pt2.7Pd/CNT with reduced consumption of precious metal catalyst. Moreover, it does not compromise catalyst performance.

C.3.5 Reaction pathways

Hydroxyacetone, 1,2-propanediol, ethylene glycol methanol, lactic acid, and acetic acid were detected in liquid products. Based on analyses results of gas and liquid products as well as previous research work (Ciftci et al., 2014; Ciftci et al., 2012; Guo et al., 2012; King et al., 2010; Wawrzetz et al., 2010), the plausible reaction pathways under present CAPR of glycerol for hydrogen production were primarily composed of two competitive routes, i.e (1) dehydrogenation-decarboxylation (C-C bond cleavage) and (2) dehydration-hydrogenation (C-O bond cleavage). The schematic reaction pathways are proposed in Figure C.7.

In route (1), glycerol was firstly dehydrogenated to glyceraldehyde. On one hand, glyceraldehyde went through decarbonylation to generate CO and ethylene glycol via C-C bond cleavage. As King et al. (2010) reported, the dehydrogenation-decarboxylation reactions proceeded progressively to form more CO and H₂. CO was subsequently removed by WGS reaction to generate H₂ and CO₂. Methanol was formed via hydrogenolysis of ethylene glycol and decarbonylation of glycolaldehyde whereas acetic acid yielded from rearrangement of glycolaldehyde (van Haasterecht et al., 2013) and tended to be stable under CAPR, especially for 5Pt1.5Co/CNT (1.23 g/L). Adding promoters increased methanol formation to some extent. Specifically, methanol was increased from 12.75 to 69.04, 76.2, and 88.93 g/L over 5Pt3Ni/CNT,

5Pt2.7Pd/CNT and 5Pt2.6Ru/CNT, respectively. On the other hand, glyceraldehyde was partially converted to lactic acid. Due to effective deprotonation of glycerol and high catalytic activity of lactic acid formation from glyceraldehyde, base additives may significantly promote glycerol conversion rate and lactic acid selectivity (Purushothaman et al., 2014). Therefore, increased lactic acid production after adding CaO (i.e. 9.70 g/L for 180 mg CaO) may result from the basic condition. Moreover, methanol formation over 5Pt1.5Ni/CNT+180mg CaO (88.53 g/L) was increased by nearly 30% compared to 5Pt1.5Ni/CNT alone (68.20 g/L). The further increased methanol production was in agreement with high H₂ yield, which implied promoted route (1). These results may be related to the basic nature of adding CaO (Menezes et al., 2011).

Figure C.7 Possible reaction pathways of catalytic aqueous phase reforming of glycerol for hydrogen production over Pt-based bimetallic catalysts supported on carbon nanotubes at 230 °C.

Dehydration rate was faster than dehydrogenation over Pt which was regarded as a solid acid (Wawrzetz et al., 2010). In parallel route (2), glycerol was directly dehydrated to hydroxyacetone, which was a primary intermediate for the formation of 1,2-propanediol from CAPR of glycerol (Ciftci et al., 2014). The hydrogenation (C-O bond cleavage) consumed H₂ generated from dehydrogenation (C-C bond cleavage) in route (1). Adding Ni into 5Pt/CNT decreased H₂ selectivity and increased CH₄ selectivity as shown in Figure C.5. Besides, remarkable increase of hydroxyacetone and 1,2-propanediol was also

observed in Table C.4. Adding Co did not show obvious difference. Compared with Pt-Ni bimetallic catalysts, far less 1,2-propanediol was formed for 5Pt1.6Cu/CNT, 5Pt2.7Pd/CNT, and 5Pt2.6Ru/CNT, suggesting that Ni can be more active for catalyzing hydrogenation of hydroxyacetone than Cu, Pd, and Ru. Interestingly, the ratio of 1,2-propanediol to hydroxyacetone for 5Pt0.75Ni/CNT and 5Pt3Ni/CNT was significantly higher than that for 5Pt1.5Ni/CNT, indicating higher hydrogenation and H₂ consumption. However, dramatically decreased hydroxyacetone indicated that route (2) was less favored after adding CaO. The unchanged 1,2-propanediol yield may be explained by base-catalyzed dehydration of glyceraldehyde and subsequent hydrogenation of produced pyruvaldehyde (King et al., 2010).

Therefore, the high glycerol conversion over Pt-Ni bimetallic catalysts was due to the promoted dehydrogenation-decarboxylation (C-C bond cleavage) in route (1) and dehydration-hydrogenation reaction in route (2). Higher H₂ yield for 5Pt1.5Ni/CNT was associated with lower hydrogenation rate (H₂ consuming) and adding CaO further favored C-C bond cleavage over 5Pt1.5Ni/CNT towards more H₂ yield. On the other hand, 5Pt2.7Pd/CNT and 5Pt2.6Ru/CNT were active for dehydrogenation-decarboxylation (C-C bond cleavage) in route (1) but relatively inert to dehydration-hydrogenation (C-O bond cleavage and H₂ consuming) in route (2) to generate even more H₂ than that of combination of 5Pt1.5Ni/CNT and 180 mg CaO.

Apart from route (1) and (2), gaseous products inter-conversion contributed significantly to final gas yield and composition. The WGS reaction was a key step in CAPR of glycerol to generate more H₂ through reaction of removed CO with water over Pt-based catalysts (Ciftci et al., 2014; Guo et al., 2012). Besides, formed H₂ can react with co-adsorbed CO and desorbed CO₂ to form CH₄ via methanation reactions (equations (C.3) and (C.4)). As discussed in Section C.3.4, CaO can inhibit CH₄ and facilitate WGS reaction via efficient CO₂ in-situ

removal. King et al. (2010) and Ciftci et al. (2014) claimed that methane was the decomposition product of ethanol. But no distinct evidence proved that in present study. Formation pathway of methane needs further investigations.

C.3.6 Regeneration of spent catalysts and stability of recycled catalyst

Based on above discussion, combination of 5Pt1.5Ni/CNT and 180 mg CaO was identified as an effective and relatively economical catalytic system for H₂ production from CAPR of glycerol and thus catalytic stability of this mixture was investigated.

C.3.6.1 Calcium distribution in CAPR of glycerol over 5Pt1.5Ni/CNT

To mitigate catalyst deactivation caused by CaO, regeneration of spent catalyst was necessary. Figure C.8 shows TG and DTG curves of pure CaCO₃ and Ca(OH)₂ as well as spent 5Pt1.5Ni/CNT + 180 mg CaO catalyst which was recovered after first catalytic run and oven drying. Different from two peaks in DTG curves reported by Onwudili and Williams (Onwudili and Williams, 2013), the DTG curve of spent catalyst showed only one peak weight loss at 712 °C which was close to 772 °C of CaCO₃. Upon addition of CaO into glycerol solution, Ca(OH)₂ will be formed. Due to the absence of peak at 432 °C for Ca(OH)₂, it can be inferred that CO₂ was excess and thus Ca(OH)₂ was completely converted to CaCO₃ as precipitant on catalyst surface. Hence, all spent catalysts were calcined at 750 °C under N₂ for regeneration. The residual Ca²⁺ distributed in liquid products from five recycle runs was 2.16 ± 0.05 mmol, which corresponded to 121.0 ± 2.9 mg CaO. The recovered solid was around 160 mg on dry basis. Weight loss after calcination at 750 °C for 1 h was 40 mg, which was most probably in the form of CO₂. Thus, ca.10 wt.% (i.e. 20 mg in 180 mg) of added CaO remained in regenerated catalyst.

Figure C.8 Thermogravimetric decomposition profiles (A: TG curves; B: DTG curves) of spent 5Pt1.5Ni/CNT + 180 mg CaO catalyst, Ca(OH)_2 and CaCO_3 under N_2 atmosphere.

C.3.6.2 Catalytic performance of regenerated 5Pt1.5Ni/CNT in recycle experiments

After the spent 5Pt1.5Ni/CNT + 180 mg CaO catalyst was regenerated, 180 mg fresh CaO which served as sacrificial reagent was added in the next recycle experiment. Figure C.9 presents the catalytic performance of 5Pt1.5Ni/CNT and recycled 5Pt1.5Ni/CNT + 180 mg CaO in terms of gas composition, H_2 yield, and hydrogen gasification ratio. As shown in Figure C.9A, when spent 5Pt1.5Ni/CNT used in first cycle with 180 mg CaO, the fraction of H_2 was increased from 33.2% to 59.4% while the fraction of CO_2 and CH_4 was reduced from 62.4% and 4.4% to 40.4% and 0.21%, respectively. In the following four

recycle runs, fraction of H₂ tended to increase to 86.1% and the fraction of CO₂ decreased to 13.9%. More importantly, CH₄ was retarded to undetectable level. This phenomenon can be related to the accumulated residual CaO after regeneration since every time fresh 180 mg CaO was introduced with spent catalyst, which accelerated CO₂ capture. In Figure C.9B, H₂ yield and hydrogen gasification ratio over 5Pt1.5Ni/CNT + 180 mg CaO slightly decreased from 4.7 mmol H₂/g glycerol and 11.1% in the first cycle to 3.5 mmol H₂/g glycerol and 8.2% in the fifth cycle, respectively. It was noted that the accumulated CaO cannot compensate the reduced 5Pt1.5Ni/CNT activity. This further confirmed CaO alone was not active in CAPR. Even though, these catalytic activities were higher than those of fresh 5Pt1.5Ni/CNT alone which demonstrated 2.4 mmol H₂/g glycerol and 7.2% hydrogen gasification ratio. Therefore, 5Pt1.5Ni/CNT + 180 mg CaO was an effective and stable candidate for H₂ rich fuel gas production from CAPR of glycerol.

Figure C.9 Activity and stability of regenerated catalysts in five recycle experiments (A: Gas composition; B: H₂ yield and hydrogen gasification ratio).

C.4 Conclusions

Multi-walled carbon nanotubes supported Pt and Pt-based bimetallic catalysts have been investigated for H₂ production using catalytic aqueous phase reforming of glycerol. It was found that hydrogen gasification ratio and carbon

conversion to gas were significantly enhanced after promoting the Pt catalyst with transition metals. Despite moderate hydrogen gasification ratio (7.2%), nickel promoted Pt catalyst (5Pt1.5Ni/CNT) showed the highest glycerol conversion rate (81.21%) and carbon conversion to gas (15.3%). In-situ CO₂ removal by adding CaO facilitated water-gas shift reaction and inhibited methanation at the expense of carbon conversion to gas. The combination of 5Pt1.5Ni/CNT and CaO decreased CH₄ fraction and selectivity to 0.2% and 0.5%, respectively, while H₂ fraction and selectivity were increased to 59.4% and 62.6%, respectively. Reaction pathways were proposed based on the results, and it showed that the improved dehydrogenation-decarboxylation and dehydration-hydrogenation reactions led to high glycerol conversion over Pt-Ni bimetallic catalysts, and a relatively low hydrogenation rate. Moreover, the introduced CaO further facilitated C-C bond cleavage over 5Pt1.5Ni/CNT towards high H₂ yield. Pt catalysts promoted by noble metals (i.e. Pd and Ru) were active in C-C bond cleavage but slightly inert in C-O bond cleavage and H₂ consuming, thereby generating more H₂ than Pt-Ni catalyst in the presence of CaO additives. The recovered 5Pt1.5Ni/CNT + 180 mg CaO catalyst showed excellent activity and hydrothermal stability after five recycle runs.

Table C.1 Chemical composition and physical characteristics of as-synthesized catalysts.

Sample	Metal type and loading (wt. %) ^a	S_{BET} (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)	H ₂ uptake (μmol/g cat)	CO uptake (μmol/g cat)
FCNTs	-	164.6	1.68	40.8	-	-
5Pt/CNT	4.88 (Pt)	174.7	1.64	37.5	23.37	37.95
5Pt0.75Ni/CNT	4.70 (Pt), 0.74 (Ni)	158.6	1.00	25.3	27.85	44.52
5Pt1.5Ni/CNT	4.67 (Pt), 1.36 (Ni)	140.6	1.29	36.7	32.11	45.91
5Pt3Ni/CNT	4.65 (Pt), 2.75 (Ni)	153.6	0.80	20.9	20.80	34.00
5Pt1.5Co/CNT	4.74 (Pt), 1.33 (Co)	141.1	1.03	29.1	-	-
5Pt1.6Cu/CNT	4.61 (Pt), 1.57 (Cu)	136.7	1.19	34.9	-	-
5Pt2.7Pd/CNT	4.76 (Pt), 2.45 (Pd)	155.0	1.12	29.0	-	-
5Pt2.6Ru/CNT	4.68 (Pt), 2.23 (Ru)	139.5	1.22	35.1	-	-

^a Determined by ICP-OES.

Table C.2 Experimental conditions of catalytic aqueous phase reforming of glycerol for hydrogen production.

Catalyst	Experimental conditions				
	Catalyst weight (g)	Temperature (°C)	Initial pressure (bar)	Running pressure at 230 °C (bar)	Time (h)
5Pt/CNT	0.1	230	30	56 ^a /62 ^b	4
5Pt0.75Ni/CNT	0.1	230	30	54/64	4
5Pt1.5Ni/CNT	0.1	230	30	58/66	4
5Pt1.5Ni/CNT+90mg CaO	0.1	230	30	61/67	4
5Pt1.5Ni/CNT+180mg CaO	0.1	230	30	62/68	4
5Pt3Ni/CNT	0.1	230	30	57/63	4
5Pt1.5Co/CNT	0.1	230	30	54/64	4
5Pt1.6Cu/CNT	0.1	230	30	54/58	4
5Pt2.7Pd/CNT	0.1	230	30	55/69	4
5Pt2.6Ru/CNT	0.1	230	30	57/69	4

^a Pressure when reaction temperature reached 230 °C; ^b Pressure after 4 h of reaction.

Table C.3 Gas production and hydrogen production rate of catalytic aqueous phase reforming of glycerol.

Catalyst	Total gas volume (mL)	H ₂ (mL)	CO ₂ (mL)	CH ₄ (mL)	H ₂ /CO ₂	H ₂ production (mmol)	H ₂ yield (mmol/g glycerol)	H ₂ production rate ($\mu\text{mol min}^{-1} \text{ g cat}^{-1}$)
5Pt/CNT	150.2	61.6	84.8	3.8	0.73	2.75	1.83	114.6
5Pt0.75Ni/CNT	228.6	79.7	139.5	9.4	0.57	3.56	2.37	148.3
5Pt1.5Ni/CNT	245.5	81.5	153.2	10.8	0.53	3.64	2.43	151.7
5Pt1.5Ni/CNT +90mg CaO	275.8	139.2	133.4	3.2	1.04	6.21	4.14	258.8
5Pt1.5Ni/CNT +180mg CaO	267.2	158.6	108.0	0.6	1.47	7.08	4.72	295.0
5Pt3Ni/CNT	176.7	53.5	114.3	8.9	0.47	2.39	1.59	99.6
5Pt1.5Co/CNT	249.0	95.7	146.0	7.3	0.66	4.27	2.85	177.9
5Pt1.6Cu/CNT	83.0	36.8	42.3	3.9	0.87	1.64	1.1	68.3
5Pt2.7Pd/CNT	337.5	198.8	125.0	13.7	1.59	8.88	5.92	370.0
5Pt2.6Ru/CNT	344.8	182.8	151.7	10.3	1.21	8.16	5.44	340.0

Table C.4 Liquid products distribution after catalytic aqueous phase reforming of glycerol over different catalysts. Operating conditions: 230 °C, an initial N₂ pressure of 30 bar, 15 mL of 10 wt.% glycerol with 100 mg catalyst for 4 h reaction time.

Catalyst	Concentration of liquid products (g/L)						
	Glycerol	Hydroxyacetone	1,2-Propanediol	Ethylene glycol	Methanol	Lactic acid	Acetic acid
5Pt/CNT	73.67	3.90	11.79	-	12.75	0.95	0.32
5Pt0.75Ni/CNT	25.51	10.31	59.89	1.29	59.33	0.97	0.62
5Pt1.5Ni/CNT	18.79	11.24	9.65	1.27	68.20	0.91	0.58
5Pt1.5Ni/CNT+90mg CaO	11.12	0.70	10.17	1.15	85.00	7.75	0.40
5Pt1.5Ni/CNT+180mg CaO	5.04	0.46	9.26	12.25	88.53	9.70	0.40
5Pt3Ni/CNT	29.91	5.08	65.30	-	69.04	1.17	0.25
5Pt1.5Co/CNT	24.33	1.78	13.31	1.09	14.56	1.77	1.23
5Pt1.6Cu/CNT	86.50	5.93	0.47	-	30.81	0.26	0.16
5Pt2.7Pd/CNT	79.77	-	2.22	-	76.20	0.14	0.07
5Pt2.6Ru/CNT	57.42	0.17	4.30	10.61	88.93	0.23	0.23

-: Under detection limit.

C.5 References

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