CATALYTIC SUPERCRITICAL WATER GASIFICATION OF SEWAGE SLUDGE/SECONDARY PULP/PAPER-MILL SLUDGE FOR HYDROGEN PRODUCTION

By

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A thesis submitted to the Department of Civil Engineering
in conformity with the requirement for
the degree of Doctor of Philosophy

Queen’s University
Kingston, Ontario, Canada
April, 2011

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Abstract

Supercritical water gasification (SCWG) is an innovative hydrothermal technique, employing supercritical water (SCW, T≥374°C, P≥22.1 MPa) as the reaction media, to convert wet biomass or aqueous organic waste directly into hydrogen (H₂)-rich synthetic gas (syngas). In the first stage of this research, a secondary pulp/paper-mill sludge (SPP, provide by AbitibiBowater Thunder Bay Operations) was gasified at temperatures of 400-550°C for 20 to 120 min in a high-pressure batch reactor for H₂ production. The highest H₂ yield achieved was 14.5 mol H₂/kg SPP (on a dry basis) at 550°C for 60 min. In addition, SPP exhibited higher H₂-generation potential than sewage sludges, likely attributed to its higher pH and higher volatile matter and alkali salt contents. In the second stage, a novel two-step process for sludge treatment was established. The first step involved the co-liquefaction of SPP with waste newspaper in a batch reactor at varying mixing ratios, aimed at converting the organic carbons in the feedstocks into valuable bio-crude and water-soluble products. The highest heavy oil (HO) yield (26.9 wt%) was obtained at 300°C for 20 min with a SPP-to-newspaper ratio of 1:2. This co-liquefaction process transformed 39.1% of the carbon into HOs, where 16.3% of the carbon still remained in the aqueous waste. Next, an innovative Ru₀.₁Ni¹₀/γ-Al₂O₃ catalyst (10 wt% Ni, Ru-to-Ni molar ratio=0.1), with long-term stability and high selectivity for H₂ production, was developed for the SCWG of 50 g/L glucose, where no deactivation was observed after 33 h on stream at 700°C, 24 MPa and a WHSV (weight hourly space velocity) of 6 h⁻¹. The H₂ yield was maintained at ~50 mol/kg feedstock. The addition of small amounts of Ru to Ni¹₀/γ-Al₂O₃ was found to be effective in enhancing Ni
dispersion and increasing the reducibility of NiO. Finally, the Ru\textsubscript{0.1}Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} catalyst together with an activated carbon (AC) supported catalyst (Ru\textsubscript{0.1}Ni\textsubscript{10}/AC) were utilized for treating the aqueous by-product from sludge-newspaper co-liquefaction using a continuous down-flow tubular reactor. More than 90% of the carbon in the waste was destroyed at 700\degree C with the highest H\textsubscript{2} yield of 71.2 mol/kg carbon noted using Ru\textsubscript{0.1}Ni\textsubscript{10}/AC.
Co-Authorship

Chapters 2 through 8 included in this thesis have been accepted/submitted for publication in peer-reviewed scientific journals. The presented work was carried out by Linghong Zhang, with the assistance of the following co-authors, who provided valuable comments, suggestions and revisions to the manuscripts for publication.

- Chapter 2: Chunbao (Charles) Xu and Pascale Champagne

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• Chapter 7: Chunbao (Charles) Xu and Pascale Champagne
  o Manuscript submitted to the journal of *Applied Catalysis B: Environmental*, Elsevier.

• Chapter 8: Pascale Champagne and Chunbao (Charles) Xu
  o Manuscript submitted to the journal of *Bioresource Technology*, Elsevier.
Acknowledgements

I would first like to express my sincere appreciation and gratitude to my supervisors, Dr. Pascale Champagne and Dr. Charles Xu, for their unceasing and invaluable encouragement, guidance and advice during my Ph.D. studies at Queen’s and Lakehead Universities. It has been a great honour for me to be their student. Their scientific intuition and enthusiasm have inspired and enriched my growth. Their originality and critical thinking have triggered and nourished my intellectual maturity. They have always been available to advise me, give me support and guidance. Their involvement made this thesis possible.

I would also acknowledge the contributions of AbitibiBowater Thunder Bay Operations and Thunder Bay Water Pollution Control Plant, who kindly provided pulp/paper-mill sludge and sewage sludge for my lab experiments. Without their assistance, my Ph.D. research would not have even been commenced.

The financial support from the Ontario Ministry of Energy, Ontario Centers of Excellence (OCE), Natural Sciences and Engineering Research Council of Canada (NSERC), Ontario Ministry of Research and Innovation, is greatly acknowledged, as well the financial contributions of Queen’s and Lakehead Universities. These sources of funding enabled me to turn my research ideas into reality and offered me opportunities to present my work at international academic conferences.
Very special thanks also go to all the past and present group members in the Green Energy Laboratory at Lakehead University who have contributed greatly to my personal and professional time in Thunder Bay. I would like to acknowledge Dr. Zhongshun Yuan, Dr. Hanning Li, Dr. Hui Chen, and Dr. Mingcun Wang for their precious advice and consistent help in my research and my life; Mr. Kailash Bhatia for his valuable assistance in building up my reactor and fixing my lab equipments; Ms. Shuna Cheng and Mr. Yun Yang for their friendship, advice and collaboration; Mr. Matthew Wishman for his help with some of the laboratory work during the summer, 2009.

I am thankful to Mr. Keith Pringnitz at Lakehead University for conducting CNH elemental analysis on my samples and for training me on the operation of the XRD instrument, to Ms. Joanne Joncas at Lakehead University for performing ICP analyses, to Ms. Paula Whitley at Queen’s University for analyzing the TOC contents in my aqueous samples, and to Mr. Md. Zakir Hossain at the University of Western Ontario for conducting TPR experiments on my catalysts.

I am indebted to the faculty and staff in the Department of Civil Engineering, Queen’s University and the Faculty of Engineering, Lakehead University, in particular Ms. Maxine Wilson, who helped me a lot during my Ph.D. studies.

It was a great pleasure to share my Ph.D. studies and life with wonderful people such as Ms. Ami Wang, Ms. Chenxi Li, Ms. Heather Lossing, Ms. Weijue Gao, Mr. Guo Li, Ms. Carolynne Wilks, etc. “No road is long with good company.” Their consistent love and support made my life more joyful, hopeful and meaningful.
Next, I gratefully appreciate the unconditional and never-ending support and encouragement from my parents. I love you Mom and Dad.

Last, but not least, I owe my deepest gratitude to my dear husband, Victor. Thank you for staying with me all the time. Your love, support and encouragement are always the spiritual power for me to overcome all the obstacles in my life. Thank you.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling Fluidized Bed</td>
</tr>
<tr>
<td>CFB</td>
<td>Circulating Fluidized Bed</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>DS</td>
<td>Dewatered Sewage Sludge</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative Thermogravimetry</td>
</tr>
<tr>
<td>ETVS</td>
<td>Entwässern, Trocknen, Vergasen, Strom erzeugen</td>
</tr>
<tr>
<td>FC</td>
<td>Fixed Carbon</td>
</tr>
<tr>
<td>FOG</td>
<td>Fat, Oil and Grease</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas Chromatography/Mass Spectrometry</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher Heating Value</td>
</tr>
<tr>
<td>HO</td>
<td>Heavy Oil</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-Performance Liquid Chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma-Optical Emission Spectrometer</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower Heating Value</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal Solid Waste</td>
</tr>
<tr>
<td>PACs</td>
<td>Polycyclic Aromatic Compounds</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PCBs</td>
<td>Polychlorinated Biphenyls</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>PS</td>
<td>Primary Sewage Sludge</td>
</tr>
<tr>
<td>RAW</td>
<td>Real Aqueous Waste</td>
</tr>
<tr>
<td>SAW</td>
<td>Simulated Aqueous Waste</td>
</tr>
<tr>
<td>SCW</td>
<td>Supercritical Water</td>
</tr>
<tr>
<td>SCWG</td>
<td>Supercritical Water Gasification</td>
</tr>
<tr>
<td>SCWO</td>
<td>Supercritical Water Oxidation</td>
</tr>
<tr>
<td>SPP</td>
<td>Secondary Pulp/Paper-Mill Sludge</td>
</tr>
<tr>
<td>SR</td>
<td>Solid Residue</td>
</tr>
<tr>
<td>SS</td>
<td>Secondary Sewage Sludge</td>
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<tr>
<td>TCDs</td>
<td>Thermal Conductivity Detectors</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analyzer</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TPR</td>
<td>Temperature-Programmed Reduction</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solid</td>
</tr>
<tr>
<td>USEPA</td>
<td>US Environmental Protection Agency</td>
</tr>
<tr>
<td>VFA</td>
<td>Volatile Fatty Acids</td>
</tr>
<tr>
<td>VM</td>
<td>Volatile Matter</td>
</tr>
<tr>
<td>WEO</td>
<td>Wet Electrolytic Oxidation</td>
</tr>
<tr>
<td>WHSV</td>
<td>Weight Hourly Space Velocity</td>
</tr>
<tr>
<td>WSPs</td>
<td>Water-Soluble Products</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
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</table>
Chapter 1
General Introduction

1.1 Background information

Due to the depletion of fossil fuels and the ever increasing impact of the greenhouse effect caused by fossil fuel combustion, scientists have been seeking for other energy sources which are more sustainable, green and efficient. As the only alternative energy source containing fixed carbon, bio-energy, extracted from biomass, has been gaining great attention as it is renewable, clean and readily available [1,2]. In contrast to petrochemical sources, biomass refers to organic materials derived from recently living flora and fauna, with stored chemical energy initially captured through photosynthesis [3]. Biomass covers a variety of materials, from plant and plant-derived materials (e.g., energy crops, agricultural and forest residues) to various organic wastes, such as food processing waste, organic components of municipal solid waste and sludges from municipal and industrial sources [2,3].

As a special bio-energy source, sludge is a liquid or semisolid liquid resulting from wastewater treatment plants. On the one hand, sludge is generally considered to be detrimental to the environment because of the presence of microorganisms (e.g., pathogens, parasites, etc.), heavy metals (e.g., Zn, Pb, Cu, Cd and As) and a number of biodegradable and recalcitrant organic compounds [4-9]. However, on the other hand, sludge is a potential energy source with energy contents ranging between 9 and 29 MJ/kg of total suspended solid [9]. Therefore, it would be of great significance to find an
approach that is not only able to destroy or stabilize the harmful components of sludge but also able to convert the stored chemical energy into usable forms of bio-fuels.

Direct combustion/incineration, pyrolysis and gasification are commonly used thermo-chemical processes for bio-energy production from traditional biomass feedstock such as woody plants and agricultural residues [10]. However, in comparison to these types of feedstocks, sludge has an extremely high water content (>90 wt%) [9], and hence an energy-and-capital-intensive drying process is typically required before its treatment via the abovementioned approaches. In fact, there are three processes that can convert sludge directly into bio-fuels, eliminating the pre-drying step: anaerobic digestion, direct liquefaction and supercritical water gasification (SCWG). Direct liquefaction is primarily aimed at the production of bio-crude [11] while anaerobic digestion and SCWG are more targeted for generating gaseous fuels such as methane (CH₄) and hydrogen (H₂) [12,13]. In comparison to anaerobic digestion, a biological process that takes several days, weeks or months, SCWG requires much less processing time (e.g., a few minutes or even seconds) [14]. Moreover, SCWG is able to destroy lignin compounds, which are recalcitrant to anaerobic digestion [15]. Last but not least, as the target product from SCWG, H₂ has higher energy content than CH₄ (on a mass basis), the major component of biogas produced via anaerobic digestion. For these reasons, the energy recovery from sludge via SCWG is of particular interest.

Supercritical water gasification is an innovative technique that occurs in supercritical water (T≥374°C, P≥22.1MPa) to convert wet biomass material (e.g., sludge) into H₂-rich syngas with reduced tar and coke/char formation [16,17]. The major chemical reactions
that take place during biomass SCWG are steam reforming (Eq. 1.1), water-gas shift (Eq. 1.2) and methanation (Eq. 1.3) reactions [15,18]:

\[
\begin{align*}
\text{CH}_x\text{O}_y + (1 - y)\text{H}_2\text{O} &\leftrightarrow \text{CO} + (1 - y + \frac{x}{2})\text{H}_2 & (1.1) \\
\text{CO} + \text{H}_2\text{O} &\leftrightarrow \text{CO}_2 + \text{H}_2 & (1.2) \\
\text{CO} + 3\text{H}_2 &\leftrightarrow \text{CH}_4 + \text{H}_2\text{O} & (1.3)
\end{align*}
\]

Eq. 1.1 is endothermic [15,18] and therefore an increased temperature would favour the formation of H\(_2\) gas. However, raising reaction temperature will also increase energy consumptions and the operating cost incurred by equipment maintenance. To solve this problem, catalysts can be employed as to enhance the H\(_2\) yield without increasing reaction temperature as they are effective in promoting the C-C and C-O bonds breakage and the water-gas shift reaction (Eq. 1.2) [17]. Alkalis [17,19], activated carbon (AC) [17,20] and metal oxide supported transition metal catalysts are the three main categories of catalysts for biomass SCWG [17]. However, metal oxide supported transition metal catalysts are more advantageous than alkalis and AC in terms of their ease of recyclability and higher selectivity for H\(_2\) generation [17,21]. Examples of supported transition metal catalysts that have been tested for the application of biomass SCWG are Ru/Al\(_2\)O\(_3\) [22], Ni/zeolite [23] and Ru/TiO\(_2\) [24]. Although these catalysts exhibited catalytic effects for the SCWG of model compounds such as cellulose, glycerol and lignin, none of them have been applied for the gasification of sludge. Moreover, few studies have been conducted on the investigation of the long-term stability of catalysts developed for SCWG. In fact, catalysts could be easily deactivated by a number of factors, such as coke deposition [25],
dissolution or structural change of the support material [24], and poisoning of the surface metal by the formation of metal-sulphur compounds [26]. As such, it is always of great importance to develop a novel catalyst that is more active, more economical and more stable.

In addition to the investigation of catalyst, another experimental challenge associated with sludge SCWG, especially utilizing a flow type of a reactor, is the pumping system. It is known that sludge is a slurry and is therefore difficult to deliver to the reactor system. To overcome this pumping issue, Xu and Antal [13] have tried mixing the sewage sludge with corn starch paste and utilized a cement pump. In this approach, a sludge sample with high solids concentration (i.e. 7.69 wt%) was successfully delivered to the reactor. However, cement pumps are not always readily available. In addition, the utilization of starch paste also makes this method difficult to operate.

1.2 Scope and objectives

The objectives of this thesis were:

- **Objective 1**: to understand the fundamentals and development of various processes (biological and thermo-chemical) for sludge treatment, in particular SCWG, with the purpose of establishing a better hydrothermal process for treating and recovering energy from sludge.
• **Objective 2:** to investigate the potential of different sources of sludge (e.g., sewage sludge and paper sludge) for the production of H₂ via SCWG and to explore the effects of variables such as temperature, reaction time, feedstock solid concentration on the yields of gas, heavy oil, solid residue and water-soluble products from sludge SCWG.

• **Objective 3:** to develop a novel catalyst for H₂ production from biomass via SCWG. This catalyst is expected to be effective in promoting H₂-generation reactions and minimizing the formation of coke and tar with long-term stability.

• **Objective 4:** to design a new hydrothermal process for the treatment of sludge that could solve the pumping problem and to investigate the feasibility and overall energy recovery efficiency of the proposed method.

These four abovementioned objectives are complementary to each other; starting with the collection of relevant background information (Objective 1), followed by fundamental investigations (Objective 2) and development of new techniques (Objective 3), and finally ending with a practical application (Objective 4).

### 1.3 Organization of the thesis

This thesis is composed of nine chapters. Chapter 1 is a general introduction that presents the background information, objectives, as well as the structure of this thesis. Chapters 2
through 8 are seven separate manuscripts that have been either submitted or accepted for publication in peer-reviewed scientific journals.

Chapter 2 presents a comprehensive review on a number of traditional and advanced biological and thermo-chemical approaches for sludge management, with the emphasis on their suitabilities for bio-energy recovery. In addition, the advantages, disadvantages and challenges associated with each technique are discussed. This chapter concludes with the recommendation of the most efficient approaches for organic compound destruction and energy recovery from sludge.

In Chapter 3, the principles, reactions, applications as well as recent development of four fundamental categories of thermo-chemical processes for energy production from waste biomass materials (e.g., combustion, pyrolysis, gasification and liquefaction) are reviewed. In addition, an introduction of the characteristics of biomass and the current status of bio-energy production is included.

As the first attempt for the investigation of sludge SCWG in this thesis, Chapter 4 presents a research paper that examines the product yield dependency on a variety of experimental parameters such as reaction temperature, reaction time, feedstock concentration and the intrinsic properties of sludge. This part of the research was performed using a bench-scale batch reactor. The characterization of the gas and heavy oil products are also provided at the end of the chapter.
Chapters 5-8 collectively deal with a novel two-step hydrothermal process (Fig. 1.1), combining sludge co-liquefaction with waste newspaper and catalytic SCWG, for the treatment of sludge. The relationships of these chapters are illustrated in Fig. 1.1.

**Fig. 1.1** A proposed novel two-step hydrothermal process for sludge treatment.

Specifically, Chapter 5 focuses on converting sludge into bio-crude (heavy oil) via a co-liquefaction process with waste newspaper in hot-compressed water at various reaction temperatures, sludge-to-newspaper mixing ratios, with and without the addition of catalysts. A batch reactor is employed for this part of the work. This step aims at producing heavy oil product. However, the aqueous by-product is collected and will be further treated in Step 2.

Chapters 6 & 7 describe the development of innovative supported transition metal catalysts for biomass SCWG using glucose solutions as model compounds. Several transition metals, support materials and promoters are investigated. Moreover, long-term stability tests of the developed catalysts are performed and the fresh and spent catalysts
are characterized using various analytical methods. This part of research is conducted with a bench-scale continuous down-flow tubular reactor.

As the final application, in Chapter 8, model compounds and the aqueous by-product resulting from sludge/waste newspaper co-liquefaction as mentioned in Chapter 5 are gasified under SCW with the assistance of the catalysts developed in Chapter 6 to convert the organic compounds into H₂-rich syngas. This part of the work is also performed in a bench-scale continuous down-flow tubular reactor. A calculation of the overall energy recovery efficiency for the proposed two-step treatment process is included.

Chapter 9 concludes the entire thesis with a brief summary of the engineering contributions of this work and proposes recommendations for future work.
1.4 References


Chapter 2
Biological and Thermo-Chemical Processes for Product Recovery from Sludges: A Review

2.1 Abstract

Sludge is the residue produced from the treatment of wastewaters from domestic, industrial, or commercial sources. It is a liquid suspension that contains 0.25-12% solids, and is composed of biodegradable and recalcitrant organic compounds, as well as pathogens, heavy metals, and other inorganic constituents. Sludge can also be considered a source of nutrients and energy, because of its high phosphorus, nitrogen, and organic carbon contents. In the present paper, several biological (anaerobic digestion and composting) and thermo-chemical (combustion/incineration, pyrolysis, gasification, liquefaction, and wet oxidation) treatment processes are briefly reviewed, along with their potential for product recovery. Each of these approaches is efficient in destroying pathogens, reducing BOD levels, and degrading recalcitrant organic compounds to some extent. However, they perform differently in terms of energy and product recovery. For example, the energy restored in bio-solids is released in the form of heat during combustion/incineration, which can be recycled for power generation. Alternatively, bio-energy can also be converted into gaseous (e.g., biogas or syngas) or liquid (e.g., bio-oil) bio-fuels in the processes such as anaerobic digestion, gasification, pyrolysis, and liquefaction. These forms of bio-fuels represent potential fossil fuel substitutes with versatile applications. In addition, residues from these processes can be safely landfilled.
or be applied as fertilizers or soil amendments, depending on their nutrient, heavy metal and other contaminant contents.

2.2 Introduction

2.2.1 Sludge characteristic

Sludge is a term used to define the liquid or semisolid liquid product of wastewater treatment from domestic, industrial, or commercial sources. It contains 0.25-12% by weight of solids and bio-solids, with a high fraction of organic compounds. Sludge also contains microorganisms, including pathogens, parasites, and other microbiological pollutants. Hence, direct exposure to sludge is considered detrimental to public health because of the possible contact with vectors infectious to humans. In addition, the presence of other toxic pollutants contained in sludge such as heavy metals (e.g. Zn, Pb, Cu, Cr, Ni, Cd, Hg, and As) and recalcitrant organic compounds (e.g. polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins, pesticides, endocrine disruptors, etc.) makes sludge a potentially harmful substance to the environment. However, sludge can also be considered as a valuable source of organic carbon, nitrogen, phosphorous, as well as some inorganic compounds such as silicates, aluminates, etc., which can be recycled or further utilized for industrial or agricultural purposes [1-5]. Moreover, as a waste biomass, sludge, particularly undigested sludge, is a potential renewable energy source with a stored chemical energy content of 9-29 MJ/kg of total suspended solid [6]. This amount of chemical energy was originally transformed from solar energy through photosynthesis, and can be recovered when the chemical bonds
between adjacent oxygen, carbon, and hydrogen molecules are broken by various biological and thermo-chemical processes [3,6]. Typical chemical compositions and properties of untreated and digested municipal wastewater sludge are shown in Table 2.1.

2.2.2 General sludge processing approaches

Sludge management and treatment is a capital-intensive process that accounts for up to 50% of the total cost of wastewater treatment [7]. Historically, sludge was simply applied to land and harmful components were left to be naturally attenuated. However, with this practice disease and parasitism spread, threatening human health [4,7].

Given the intrinsic characteristics of sludges, the contemporary sludge treatment approaches aim to achieve: 1) a reduction in total weight and volume to facilitate transportation and provide additional treatment; 2) stabilization by destroying pathogenic microorganisms, eliminating unpleasant odors, and decreasing the potential for putrefaction by reducing the volatile solid content; and, more recently, 3) the economically viable recovery of energy and useful constituents [3,4,6-8].
<table>
<thead>
<tr>
<th>Item</th>
<th>Untreated primary sludge</th>
<th>Digested primary sludge</th>
<th>Untreated activated sludge, range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dry solids (TS), %</td>
<td>5-9</td>
<td>6</td>
<td>2-5</td>
</tr>
<tr>
<td>Volatile solids (% of TS)</td>
<td>60-80</td>
<td>65</td>
<td>30-60</td>
</tr>
<tr>
<td>Grease and fats (% of TS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ether soluble</td>
<td>6-30</td>
<td>-</td>
<td>5-20</td>
</tr>
<tr>
<td>Ether extract</td>
<td>7-35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Protein (% of TS)</td>
<td>20-30</td>
<td>25</td>
<td>15-20</td>
</tr>
<tr>
<td>Nitrogen (N, % of TS)</td>
<td>1.5-4</td>
<td>2.5</td>
<td>1.6-3.0</td>
</tr>
<tr>
<td>Phosphorus (P$_2$O$_5$, % of TS)</td>
<td>0.8-2.8</td>
<td>1.6</td>
<td>1.5-4.0</td>
</tr>
<tr>
<td>Potash (K$_2$O, % of TS)</td>
<td>0-1</td>
<td>0.4</td>
<td>0.0-3.0</td>
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<td>Cellulose (% of TS)</td>
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<td>10</td>
<td>8-15</td>
</tr>
<tr>
<td>Iron (not as sulfide)</td>
<td>2.0-4.0</td>
<td>2.5</td>
<td>3.0-8.0</td>
</tr>
<tr>
<td>Silica (SiO$_2$, % of TS)</td>
<td>15-20</td>
<td>-</td>
<td>10-20</td>
</tr>
<tr>
<td>pH</td>
<td>5.0-8.0</td>
<td>6.0</td>
<td>6.5-7.5</td>
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<tr>
<td>Alkalinity (mg/L as CaCO$_3$)</td>
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<td>600</td>
<td>2500-3500</td>
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<tr>
<td>Organic acids (mg/L as HAc)</td>
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<td>100-600</td>
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<tr>
<td>Energy content, kJ/kg TSS</td>
<td>23,000-29,000</td>
<td>25,000</td>
<td>9000-14,000</td>
</tr>
</tbody>
</table>

Table 2.1

Typical chemical compositions and properties of untreated and digested municipal wastewater sludge [6].
A generalized wastewater sludge-processing flow path in a wastewater treatment plant can be simply divided into preliminary operation, thickening, stabilization, conditioning, dewatering, heating, drying and other processing, thermal reduction, and final reuse and disposal. Thickening, conditioning, dewatering, and drying are dedicated to reducing water content, which leads to decreases in sludge volumes since sludge is largely composed of water (> 88-99 wt%) [6]. Stabilization follows thickening to convert sludge into a safe material for final disposal. Commonly used stabilization methods are alkaline stabilization and anaerobic/aerobic digestion. Alkaline stabilization can be achieved through the addition of alkaline materials, such as lime, which destroy pathogenic organisms by elevating pH levels (pH ≈ 12). Anaerobic/aerobic digestions involve the biological conversion of organic compounds in the absence/presence of air or oxygen (O₂) by certain types of microorganisms. In some cases, the stabilized sludge can go to final land disposal directly. However in most cases, further processing, such as dewatering, composting, or thermo-chemical treatment (e.g., incineration) is required [6].

### 2.2.3 Primary sludge-management approaches

There are currently various approaches for sludge management. Among these, the three main approaches are: land application, landfill disposal, and incineration/thermal technologies [3,7].

Land application for agricultural use is currently the favoured alternative for disposing of sludge [3]. Given the characteristics of the sludge generated, it requires plant operators to reliably consider the potential human and animal health risks associated with exposure,
impacts on receiving environments, long-term soil protection, public acceptance, and compliance with all regulatory authorities involved. For small wastewater treatment plants (e.g. < 20,000 Population Equivalent), direct land application may be the most economic solution [8]. However, it is gradually losing its prominence because of arising health concerns from the public with regard to the detrimental effects of heavy metals, as well as more stringent compliance criteria set by regulatory agencies [7]. In contrast, composting as another form of land application, is considered a more environmentally acceptable approach, if odours can be well controlled.

Landfilling is a conventional approach for the disposal of municipal solid waste. However, it becomes a questionable approach when used for the disposal of sludge, as a number of concerns arise, such as the reduced lifetime of the landfill resulting from an overloaded leachate system and issues with compacting the sludge/garbage mixture. Disposal of dewatered sludge in landfills should also be minimized due to the associated increased ammonia (NH₃) production and leaching which requires long-term monitoring of the landfill sites [8]. In addition, landfilling is not practical for countries with limited space availability such as Japan.

Incineration is a thermo-chemical process that converts organic compounds into carbon dioxide (CO₂), water (H₂O), and a certain amount of heat; it greatly minimizes the volume of sludge. Major concerns associated with incineration are emissions of airborne, mono-nitrogen oxides (NOₓ), sulphur dioxide (SO₂) and dioxins, and the intensive energy requirement associated with the drying of the sludge.
2.2.4 Overview of the techniques for energy and nutrient recovery from sludge

Sludge is a potentially valuable source of nutrients and energy, hence, the aim in waste minimization should be to maximize its use as a resource. For instance, nutrients (carbon, phosphorus and nitrogen), particularly phosphorus, can be reused on land as components of compost or as organic fertilizers [3,5,8]. It has been reported that the apatite mines, from which phosphorus is extracted, will be exhausted within 150 years given the current consumption rate [5]. As shown in Table 2.1, the content of phosphorus (P$_2$O$_5$, % of TS) is as high as 0.8-2.8, 1.5-4.0 and 2.8-11.0 in the untreated primary sludge, digested primary sludge and untreated activated sludge, respectively. Therefore, from the perspective of sustainable development, it would be beneficial to recover phosphorus from sludge, which is currently a significant contributor to regional phosphorus fluxes [1,5,8].

As an energy source, sludge can be combusted to release heat, which will generate steam for electricity production or for process heat. In addition, the stored energy can be converted into a series of solid, liquid, and gaseous fuels by various biological and thermo-chemical methods such as anaerobic digestion, liquefaction, pyrolysis, and gasification [2,3,5,7,9]. These types of bio-energy may be potential alternatives to fossil fuels.

As another aspect of sludge reuse, dried sludge can be utilized in the production process of Portland cement, in which the organic and inorganic compounds are employed as the fuel and raw materials, respectively [10].
The purpose of the present work is to review some important biological (e.g., anaerobic digestion and composting) and thermo-chemical (e.g., combustion/incineration, pyrolysis, conventional gasification and supercritical water gasification (SCWG), liquefaction, wet oxidation, wet electrolytic oxidation (WEO), and supercritical water oxidation (SCWO)) treatment processes for sludge management. Since sludge is considered as a valuable energy and nutrient source rather than a waste material in this work, the emphasis will be placed on the recovery and utilization of various forms of bio-fuels and other valuable products from sludge.

2.3 Recent advances in biological treatment processes

2.3.1 Anaerobic digestion

Anaerobic digestion is a process that converts organic waste into useful biogas and high-quality stabilized soil fertilizers for agricultural use [11,12]. It is considered an energy producing process due to the formation of methane (CH₄) gas. As shown in Fig. 2.1, there are three major stages in the anaerobic digestion process. During the first stage, complex organic compounds, e.g. fat, cellulose, and proteins, are hydrolyzed into small soluble compounds by various groups of decomposing microorganisms. This is followed by the second stage, during which the soluble organic compounds are fermented into acetic acid, hydrogen (H₂) and CO₂, which will eventually be converted into CH₄ and CO₂ in the third stage in the presence of methanogenic bacteria [12-14]. During the anaerobic process, electrons in the organic matter are transferred to CH₄, where the carbon is at its most
reduced oxidation state and the organic matter is stabilized. Theoretically, one gram of organic matter can generate 0.35 L of CH₄ under standard condition (i.e., 0°C and 1 atm) [13].

![Fig. 2.1 Stages of the anaerobic digestion process.](image)

Generally, for organic feedstocks from domestic wastewater, municipal wastes, and most industrial wastewaters, hydrolysis and fermentation (Stages 1 and 2) proceed faster than methane formation (Stage 3) due to higher energy yields from the first two reactions. Thus, the third stage is rate-limiting. In contrast, hydrolysis typically dominates the overall reaction rate for lignocellulosic materials [13].

Anaerobic digestion can be employed to treat a large group of organic compounds. Nevertheless, it is more suitable to process heterogeneous, poorly-structured, easily degradable wastes, such as sewage sludge and food wastes, compared to highly structural
materials, such as woody and agricultural residues, because the poorly-structured wastes are more readily hydrolyzed [15].

2.3.1.1 Biogas properties and factors affecting biogas production

From a bio-energy perspective, biogas is the valuable end-product of anaerobic digestion. It is composed primarily of CH$_4$ (55-75%) and CO$_2$ (25-45%) with small amounts of hydrogen sulphide (H$_2$S) (0-1%), NH$_3$ (0-1%), H$_2$ (0-3%), nitrogen (N$_2$) (0-5%), and oxygen O$_2$ (0-2%) [16-18]. Biogas has a heating value of 21.48 MJ/m$^3$ (assuming it is composed of 60% CH$_4$, 38% CO$_2$ and 2% other compounds), which is lower than that of a natural gas (36.14 MJ/m$^3$). However, purification processes can yield a biogas with similar characteristics as natural gas [16,17]. Therefore, biogas can be considered a natural gas substitute for heating and power generation. From an environmental point of view, the use of biogas as an energy source can not only alleviate the energy crisis caused by the depletion of fossil fuels, but can also contribute to reductions in greenhouse gas emissions, as sludge can be regarded as carbon-neutral. Finally, the utilization of biogas is also economically beneficial [11,19].

Several factors have been demonstrated to effectively enhance biogas production, such as increasing the digestion temperature, providing suitable pre-treatments, optimizing mixing intensity, or co-digesting sludge with other sources of organic wastes (e.g., food waste), as will be described in Section 2.3.1.2.
Temperature is an important parameter to control biogas production. Generally, thermophilic processes (50-57°C) exhibit higher gas production potential than mesophilic processes (30-38°C) [20-22]. This is the result of an increase in the activity of methanogenic bacteria and an enhanced conversion from dissolved organic carbon compounds to volatile fatty acids (VFAs) [21]. In addition, there is an optimal temperature range for both the mesophilic and thermophilic processes, during which the highest biogas yields could be achieved [20]. Therefore, to obtain a high gas yield, it is crucial to maintain the reaction temperature in this optimal range. However, it should be noted that higher operational temperatures have the potential to inhibit the growth of microorganisms due to the release of free NH₃. In addition, thermophilic processes decrease the quality of the supernatant, aggravate odour problems, and require higher energy inputs [22].

Various pre-treatments can be applied prior to anaerobic digestion to enhance gas production and improve sludge stabilization. For example, adding alkaline agents, e.g., sodium hydroxide (NaOH) assists in the breaking down of cross-linkages in lignocellulosic materials and thus facilitates their hydrolysis [23,24]. Thermal pre-treatment, which involves the curing of sludge under high temperature (i.e. 150°C) for several minutes (i.e. 30 minutes), is also an effective process because it enhances the solubility and biodegradability of the organic compounds [25]. As a combination of the abovementioned methods, Kim et al. [26] treated sludge by adding NaOH to achieve an initial pH of 12 and then cured the sample at 121°C for 30 minutes. As a result, they observed a much higher chemical oxygen demand (COD) solubility (51.8%) over the control (8.1%). In addition to chemical and thermal treatments, ultrasonic disintegration
at low frequencies has also been proved as an effective pre-treatment method to increase the volatile solids degradation and gas production in the subsequent anaerobic digestion of waste activated sludge. This enhanced production was attributed to the floc de-agglomeration, as well as the release of intracellular material from broken biomass cell walls [27,28]. A detailed description of the principles of anaerobic digestion, effects of different process parameters, as well as the biogas utilization has been discussed elsewhere by Appels et al. [22].

2.3.1.2 Co-digestion

In the last three decades, co-digestion of sludge and other organic wastes has gradually attracted research attention. Conventional sewage sludge digesters in wastewater treatment plants are often oversized by 15-30%; as such, co-digestion of the sludge with organic wastes can not only provide an alternative approach for treating the organic fraction in municipal solid waste, but can also make full use of the available capacity. The addition of other organic compounds to sludge may also balance the C/N ratio and nutrient mixture, consequently increasing the yield of biogas. The produced biogas can be used directly or be sold to enhance the operational economics of wastewater treatment plants [29-32]. Intensive research on sludge/organic waste co-digestion that has been conducted to date including a wide range of organic wastes as co-substrates, such as waste paper [30], rice straw [32], FOG (fat, oil, and grease) [33], animal by-products from meat-processing industry [34], and a number of other organic solid waste streams, particularly food waste [21,31,35-44].
2.3.2 Composting

Composting is a land-based biological process that converts sludge into stable and humus-like materials under aerobic and anaerobic conditions (mostly aerobic). During this process, approximately 20-30% of volatile organic compounds are converted to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), and the pathogenic microorganisms are destroyed by the heat, which can raise the sludge temperature to a range of 57-70°C, generated during the composting process. Most of the composting processes are designed to operate under aerobic conditions because of the higher reaction rates and minimized odour production associated with aerobic composting [7].

In order to achieve effective aeration, bulking agents, such as wood chips, chipped brush, recycled compost and rice hulls, are needed to reduce the bulk weight and moisture content of the sludge and to increase the size of the void spaces inside the sludge mixture [6,45].

Composting generally proceeds in three consecutive stages which are mesophilic, thermophilic and cooling stages. It is accomplished with the collaboration of bacteria, actinomycetes, and fungi and the maximum stabilization is achieved during the thermophilic stage [6,45].

The basic steps of a typical composting process involve pre-processing, high-rate phase, curing, and post-processing phases. Aeration is required in the high-rate phase either by mechanical mixing of the material or by the addition of air; it is a controllable stage. In
contrast, the curing phase is less engineered. Depending on how air is introduced, composting can be classified into agitated and static processes. For an agitated composting process, such as the windrow system, the materials are mixed and turned periodically. For a static composting process, such as aerated static pile, the materials are motionless and air is injected [6,45].

Composting is an economically and environmentally beneficial approach for the stabilization of sludge: it requires little external energy input and produces compost that can be used as a soil amendment [45]. However, the problems associated with the effective control of odour emissions still needs to be addressed.

2.3.2.1 Fate of the toxic organic compounds and heavy metals during composting

Composting has been reported to successfully remove toxic organic compounds, such as PAHs [46], PCBs [47], trinitrotoluene (TNT) [48], etc., in sewage sludge or contaminated soil through various mechanisms. However, these contaminants may not be completely mineralized but adsorbed onto the compost matrix [46] or transformed into various intermediates [48].

The fate of heavy metals during composting processes has been investigated by a number of researchers [49-53]. It is relatively clearly understood that metals cannot be removed from the system, but can only be transformed into less mobile forms, with reduced detrimental effects to the environment. For example, Zheng et al. [49] investigated the changes in the speciation of Cr and Ni in sewage sludge during a 31-day forced aeration
composting process. It was found that both Cr and Ni were stabilized with less mobility after composting. A similar test was conducted on Pb [50] and a reduced bio-availability was also observed during the composting treatment.

2.4 Recent advances in thermo-chemical treatment processes

Thermo-chemical treatment is another major category of sludge treatment. Compared to biological treatment processes, which take several days, weeks, or months to accomplish, thermo-chemical treatment processes require much less reaction times (a few seconds, minutes, or hours) [54]. In addition, thermo-chemical processes can maximize bulk volume reductions and destroy pathogenic microorganisms and toxic organic compounds. Moreover, these processes present a potential for energy recovery either through combustion heat recycling or the production of liquid or gaseous bio-fuels [3,6].

Werther and Ogada [55] classified thermo-chemical processes into three categories: mono-incineration, co-combustion, and new and alternative thermal processes, which mainly include pyrolysis, gasification, wet oxidation, and various combinations of these approaches. In fact, there are three other emerging techniques that should also be included in the last category: liquefaction, SCWG, and SCWO (Fig. 2.2). These three techniques are particularly suitable for treating sludge directly as the energy-intensive processes of dewatering and drying are not required.
2.4.1 Combustion/Incineration

Combustion/incineration is a complete oxidation process that occurs at high temperature, and is aimed at destroying toxic organic contaminants present in the dewatered/dried sludge. It is one of the three basic ultimate routes for sludge disposal, and is currently considered the most widely used thermo-chemical process for the treatment of sludge [2,3,7]. Combustion/incineration is an attractive option because of the reduced sludge volume resulting from shrinkage and ash agglomeration [56], destruction of organic contaminants, minimized odour generation, as well as the potential for energy recovery through the collection and reuse of the hot flue gas heat [2,3,7].
Sludge combustion is distinct from coal combustion because of the particular characteristics of sludge in terms of the moisture (88-99 wt%), ash (max. 50 wt% dry mass basis in sludge), volatiles (max. 90% dry and ash-free mass basis), and fixed carbon (less than 10%) contents [55].

There are three main stages occurring during the sludge combustion process: (1) drying (or dehydration) for the removal of water; (2) devolatilization (or pyrolysis), which involves a series of complex chemical reactions leading to the decomposition of the organic matters into individual gases [55]; and (3) combustion of volatiles and sludge chars [55,56]. Apart from mono-incineration, sludge could also be co-combusted with municipal solid wastes, as has been reported by Werther and Ogada [55].

2.4.1.1 Problems associated with combustion/incineration

Combustion/incineration is not generally well accepted by the public, as it is associated with the release of toxic airborne contaminants such as dioxins, furans, NO\textsubscript{x}, nitrous oxide (N\textsubscript{2}O), SO\textsubscript{2}, as well as hydrogen chloride (HCl), hydrogen fluoride (HF), and hydrocarbons [55]. According to the revised emission standards for existing incinerators promulgated by the US Environmental Protection Agency (USEPA) in 2002 [57], the upper emission limits for dioxin/furan, Hg, HCl/chlorine gas, and hydrocarbons are 0.2 ng TEQ/dscm, 130 μg/dscm, 77 ppmv, and 10 ppmv, respectively. In addition, as specified in the US national ambient air standards [58], the concentration of nitrogen dioxide (NO\textsubscript{2}) and SO\textsubscript{2} should not exceed 0.053 ppm (annual mean) and 0.5 ppm (3-hour
mean, not to be exceeded more than once per year), respectively to protect the welfare of the public. Campbell [7] remarked that current techniques are capable of reducing air emissions to such low levels that stringent air quality standards can be met. However, combustion/incineration is highly capital-intensive and, as such, not likely to be viable options for sludge treatment if these air quality standards are to be met. Hence, air emission is in fact an economic issue rather than a technological limitation [7].

High ash content in sludge is another important concern, as the ash produced may be toxic considering the high amounts of heavy metals present in some sludges [3,7,55]. Nevertheless, the presence of these metals in ash is not critical, as they are generally not readily leachable from disposal sites [2,7].

2.4.2 Pyrolysis

Pyrolysis is a promising technology for treating waste sludge from municipal or industrial sources. It is a thermal decomposition process conducted in the absence of O$_2$ to convert biomass into solid charcoal, liquid (bio-oil or bio-crude) and gases at elevated temperatures. Having a high fuel-to-feed ratio, pyrolysis has become one of the most efficient processes for biomass conversion [59-62]. When applied to sludge, pyrolysis is capable of achieving multiple goals simultaneously, such as the energy recovery through the production of bio-oil and synthetic gas (syngas), sludge volume reduction and the control of heavy metals, pathogens, and organochlorine compounds, as well as phosphorous recycling [63].
2.4.2.1 Factors affecting products distribution

Table 2.2 summarizes the sludge characteristics, experimental parameters, as well as the solid, liquid, and gaseous product yields of selected research on sludge pyrolysis. Generally, product distribution is closely correlated to the sludge characteristics, such as volatile matter (VM) and ash contents. For example, an increase in VM content increases the yields of gas and oil, but decreases the formation of char [65,66]. In contrast, a high ash concentration corresponds to a higher gas (especially H₂) yield but lower oil and solid yields [69].

Moreover, the product yields are also dependent on reaction temperature, where an increase in temperature increases the sludge conversion into gas and liquid (especially gas) but decreases the yield of char. In addition, a higher heating rate favours the formation of gas and liquid products rather than solid products [65,68]. Last but not least, there is an optimal temperature range that corresponds to the highest oil yield; above this temperature range the production of gas will become dominant [60].
<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Proximate analysisa (wt %)</th>
<th>Operational conditions</th>
<th>Average yield (wt%) and gross calorific values of the products</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed chemical and activated sludge (MS)</td>
<td>Moisture: 2.4</td>
<td>500 °C (heating rate: 7°C/min), 60 min</td>
<td>Gas: 20.9 (29.9 MJ/Nm³), aqueous: 26, oil: 13.2 (32.86 MJ/kg), char: 39.9</td>
<td>[64]</td>
</tr>
<tr>
<td>Oil sludge (OS)</td>
<td>Moisture: 26.3</td>
<td></td>
<td>Gas: 14.9 (35.8 MJ/Nm³), aqueous: 14.1, oil: 29.8 (43.86 MJ/kg), char: 41.2</td>
<td></td>
</tr>
<tr>
<td>Primary sludge</td>
<td>Dried sludge VM: 84</td>
<td></td>
<td>Oil: 8-42 (36-38 MJ/kg), char: 33-85</td>
<td></td>
</tr>
<tr>
<td>Thickened waste activated sludge</td>
<td>Dried sludge VM: 69</td>
<td>250-500 °C, 20 min</td>
<td>Oil: 12-33 (37 MJ/kg), char: 43-77</td>
<td>[65]</td>
</tr>
<tr>
<td>Digested sludge (anaerobic digestion)</td>
<td>Dried sludge VM: 59</td>
<td></td>
<td>Oil: 4-26 (38-39 MJ/kg), char: 53-87</td>
<td></td>
</tr>
<tr>
<td>Sludge from aerobic digestion</td>
<td>Moisture: 71</td>
<td>1000 °C, 20 min (82 and 70°C/min)</td>
<td>Gas: 62.9, oil: 5.2, char: 32</td>
<td>[66]</td>
</tr>
<tr>
<td>Sludge from anaerobic digestion</td>
<td>Moisture: 81</td>
<td></td>
<td>Gas: 55.6, oil: 4.6, char: 39.8</td>
<td></td>
</tr>
<tr>
<td>Sewage sludge subjected to aerobic digestion</td>
<td>Moisture: 71</td>
<td>1040 °C (74.3°C/min), 24 min</td>
<td>Oil: ~1 (36.43 MJ/kg)</td>
<td>[67]</td>
</tr>
<tr>
<td>Anaerobic sewage sludge</td>
<td>Moisture: 5</td>
<td>450, 650, and 850 °C (5 and 60°C/min)</td>
<td>Oil: ~40 (22.45-27.98 MJ/kg)</td>
<td>[68]</td>
</tr>
</tbody>
</table>

*a Ash and VM (volatile matter) are on a dry basis.

### 2.4.2.2 Pyrolysis products

The liquid phase, composed of aqueous products and bio-oils, is one of the target products from sludge pyrolysis. The aqueous phase mainly contains alcohols, ethers, aldehydes, and carboxylic acids [64]. While the bio-oil is composed of a variety of aliphatic hydrocarbons, aromatic hydrocarbons, polyaromatic hydrocarbons, oxygen-
containing aliphatic and aromatic compounds, nitrogen-containing aliphatic and aromatic compounds, steroids, halogen-containing compounds, sulphur-containing compounds [69,70], long-carbon-chain organic acids [71] and alcohols [70]. As shown in Table 2.2, the oils produced through pyrolysis exhibit high gross calorific values, implying their potential utilization as alternative fuels [64,65].

Solid chars produced via pyrolysis are also valuable, as they can be either upgraded to activated carbon for pollutant removal (depending on the surface area) [68,72] or incinerated as solid fuels [63,64,68]. Interestingly, a recent study by Bridle and Pritchard [63] demonstrated that the phosphorus in pyrolysis chars is plant available and thus these chars could be utilized as fertilizers in agriculture.

It is also important to mention that most of the metals, with the exception of Hg and Cd, in solid chars can be concentrated; therefore, the natural lixiviation problem is not as severe as that reported for the raw sludge or ashes from incineration [64,68,73]. In fact, to reduce the chance of metal release from pyrolysis char, a pre-treatment with an acid solution (composed of HCl and nitric acid (HNO₃), v/v=4/3) can be used to decrease the heavy metal contents in the sludge [74].

Apart from the liquid and solid products, the gaseous product from pyrolysis is a mixture of carbon monoxide (CO), CO₂, H₂, CH₄, and small volatile organic compounds (C₁-C₆). The percentage of each gas product depends on the particular properties of the sludge. For example, sludge with an elevated moisture content produces more H₂ because of the
occurrence of the water gas reaction (Eq. 2.1) and the water gas shift reaction (Eq. 2.2) [64,66]. In addition, the Boudouard reaction also takes in this system (Eq. 2.3).

\[
\begin{align*}
\text{C} + \text{H}_2\text{O} & \leftrightarrow \text{CO} + \text{H}_2 \quad (2.1) \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \\
2\text{CO} & \leftrightarrow \text{C} + \text{CO}_2
\end{align*}
\]

In addition, a high content of carboxylic groups in the sludge will result in higher yields of CO and CO$_2$ [64].

### 2.4.2.3 Microwave-induced pyrolysis

Microwave-induced pyrolysis is currently being investigated by some researchers, where the heating source is the microwave rather than electric furnaces that are employed in conventional pyrolysis processes [67,72]. Microwave pyrolysis requires less energy input and shorter processing times than conventional heating in order to obtain the same pyrolysis efficiency [72]. However, wet sludge alone cannot adsorb microwaves efficiently to heat itself to a temperature of 200°C or higher. To solve this problem, small amounts of microwave absorber, e.g., pyrolysis char, can be intermixed with sludges, allowing for temperatures as high as 900°C to be reached [72].

In comparison to conventional pyrolysis, microwave-induced pyrolysis has been noted to increase the portions of syngas in the products [75]. In addition, the bio-oils produced via microwave-induced pyrolysis are more environmentally friendly because of the reduced
formation of polycyclic aromatic compounds (PACs) that are initially converted from aliphatic, ester or carboxylic groups [67].

### 2.4.3 Liquefaction

Liquefaction is a low-temperature and high-pressure thermo-chemical process that breaks down biomass into fragments of small molecules in water with or without the aid of solvents and catalysts. These small fragments, which are unstable and reactive, can then re-polymerize into oily compounds of various molecular weights [62,76,77]. Liquefaction is applicable to biomass with high moisture contents and hence can be a suitable alternative approach for energy recovery from sludges [78].

Table 2.3 summarizes the experimental conditions and results obtained from some sewage sludge liquefaction studies conducted in the 1980s and 1990s. One of the most important observations is the close correlation noted between the yield of oil and the sludge characteristics. Suzuki et al. [80] examined the oil yields from various sources of sludge (primary sludge, waste activated sludge, digested sludge, and mixed sludge) and found that digested sludge generally produced the lowest quantities of heavy oils, probably due to the relatively low content of non-degradable volatile matter. Crude fat (an ether-soluble material) content is another factor that attributed to the high oil yield. For instance, primary sludge typically exhibited higher oil yields than the waste activated sludge because of the higher content of crude fat in the primary sludge.
### Table 2.3

Experimental conditions and product yield from selected research on sewage sludge liquefaction.

<table>
<thead>
<tr>
<th>Source of sludge</th>
<th>Moisture content</th>
<th>Reaction temperature/pressure</th>
<th>Catalyst</th>
<th>Reactor and residence time</th>
<th>Heavy oil yielda</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture of primary and waste activated sludge</td>
<td>75%</td>
<td>250-340 °C 3 MPa for N₂ (cold pressure)</td>
<td>0-20 wt% Na₂CO₃</td>
<td>Batch reactor 0-120 min</td>
<td>25.3-51.8%b</td>
<td>[79]</td>
</tr>
<tr>
<td>Digested sludge</td>
<td>55.8%</td>
<td></td>
<td></td>
<td>Batch reactor 0 min (The reactor was cooled down right after the desired temperature was reached.)</td>
<td>~ 20%</td>
<td></td>
</tr>
<tr>
<td>Raw waste activated sludge</td>
<td>81.9%</td>
<td>300 °C 12 MPa</td>
<td>5 wt% Na₂CO₃</td>
<td></td>
<td>32.7%/35.1%c</td>
<td>[80]</td>
</tr>
<tr>
<td>Raw primary sludge</td>
<td>79.9%</td>
<td></td>
<td></td>
<td></td>
<td>44.7%/43.8%c</td>
<td></td>
</tr>
<tr>
<td>Raw mixed sludge</td>
<td>74.1%</td>
<td></td>
<td></td>
<td></td>
<td>42.7%/37.5%c</td>
<td></td>
</tr>
<tr>
<td>Dewatered sludge</td>
<td>80-83.4 %</td>
<td>290-300 °C 8.8-9.8 MPa</td>
<td>none</td>
<td>Flow reactor Mass flow rate: 240 kg/h</td>
<td>~48%d</td>
<td>[78]</td>
</tr>
</tbody>
</table>

---

In addition, higher reaction temperatures and the addition of appropriate catalyst (e.g., Na₂CO₃, max 5 wt% on a dry solid basis) were also found to be effective in improving the oil yield and facilitating the separation of oily materials from the aqueous products [79]. In contrast, residence time did not significantly affect the oil yield [79].

In order to evaluate the properties of heavy oils as a potential fuel or source for the production of chemicals, Dote et al. [81] investigated the composition of the oils using steam distillation followed by an acid-base extraction combined with a gas...
chromatography/mass spectrometry (GC/MS). The liquefaction was conducted using a mixture of primary and waste activated sludges in a continuous reactor at 330°C, 15.5 MPa, with a residence time of 60 minutes. Upon analytical characterization of the oil, 71 compounds were identified, including both hydrophilic and hydrophobic constituents. A large fraction of the constituents (56%) were found to be acid-base neutral and were composed of aliphatic compounds, alicyclic compounds, alcohols, ketones, aromatic compounds, sulphur-containing compounds, nitrogen-containing compounds and oxygen-containing heterocyclic compounds.

Recently, Xu and Lancaster [82] investigated the conversion of secondary pulp/paper sludge powder into liquid oil by direct liquefaction in hot-compressed water (subcritical/supercritical water (SCW)). In this research, the dried secondary pulp/paper sludge powders were mixed with water to achieve solids concentrations in the range of 4.8-16.7%. After being liquefied in a N₂ atmosphere using water as the solvent, the sludges were converted into water-soluble oils (yields: 20-45%, heating value: 10-15 MJ/kg) and heavy oils (yields: 15-25%, heating value: >35 MJ/kg) at temperatures of 250-380°C and residence times ranging between 5 and 20 minutes. When a reducing environment (2 MPa H₂) and a 0.1 M calcium hydroxide (Ca(OH)₂) catalyst were provided, a heavy oil yield as high as 26 wt% could be achieved. In addition, Li et al. [83] liquefied dried sewage sludge powders in ethanol/water/ethanol-water mixtures (1g sludge powder/40 ml solvent) at various temperatures (260-380°C), ethanol/water ratios (0/10, 3/7, 7/3, and 10/0) and solvent filling ratios (10-25 vol%) with and without the addition of catalysts (e.g., Na₂CO₃, NaOH, iron (II) sulphate (FeSO₄), and iron (II) sulphide (FeS)). The heating values of the heavy oils obtained from this treatment were significantly enhanced in
comparison to that of the original sludge powders (~ 40 MJ/kg vs. ~15 MJ/kg). The highest yield of heavy oil reported in this research was approximately 55 wt%, achieved using 100% ethanol at 400°C. These results provide a promising perspective for energy recovery from waste sludge in the future.

2.4.4 Gasification

Gasification is a process that converts carbonaceous biomass into combustible gases (e.g. non-condensable gases such as H₂, CO, CO₂, and light hydrocarbons such as CH₄, acetylene (C₂H₂), ethylene (C₂H₄), ethane (C₂H₆), propane (C₃H₈), and propylene (C₃H₆)) with usable heating values in the presence of a partial O₂ supply (typically 35% of the O₂ demand in combustion). It is a special form of pyrolysis that takes place at a higher temperature to achieve a high gas yield. The product of gasification, syngas, is a gaseous form of bio-energy. Depending on their specific heating values, syngas can be used as a fuel for steam or heat generation, for H₂ production, for the synthesis of some chemical compounds, etc [61,84].

As an alternative treatment process, gasification has attracted great interest for sludge management, and considerable research has been conducted to date on the use of various types of gasifiers for sludge gasification. For example, Midilli et al. [85] employed a downdraft gasifier to treat sewage sludge. A mixture of combustible gases (H₂, CO, CH₄, C₂H₂, and C₂H₆) was produced with average calorific values ranging between 2.55-3.2 MJ/Nm³. In addition, Petersen and Werther [86] studied the performance of dried sewage sludge in a circulating fluidized bed and determined the optimal air ratio (λ=0.3), reaction
temperature and feeding height. Moreover, the reaction kinetic models were also developed for its future scale-up use.

2.4.4.1 On-site utilization of sewage sludge gasification

An ETVS (German abbreviation, Entwässern, Trocknen, Vergasen, Strom erzeugen)-Process has been described by Groβ et al. [87] to convert sewage sludge into valuable syngas on the site of a wastewater treatment plant. Since the gasification utilities are connected to a combined heat and power (CHP) unit, the produced syngas can be utilized directly on site as a source of energy. This process evolves four main sequential steps: dewatering, drying, gasification, and electric power generation. Generally, dewatering and drying together increase the solid content of the original sewage sludge from approximately 2.5 wt% to 90 wt%. The dried sludge particles (1-3 mm) are then gasified at around 870°C in a fluidized bed gasifier with an air flow rate of 500 Nm³/h. The produced syngas, once chilled and cleaned (in a counter current washer to remove the tars, solids, mercury, and moisture) is fed into a CHP unit for the generation of electricity, which provides internal load demand of the wastewater treatment plant. In addition, the heat in the exhaust gas could be utilized in a sludge drying process. As proposed by the authors, this ETVS-Process could be self-sustaining if the sludge solid content is higher than 30 wt%. In addition, the ash produced can be safely disposed of through landfilling.

In addition to energy recovery, Ptasinski et al. [88] proposed an innovative method for methanol production by connecting a sludge gasification process to a subsequent methanol plant using cleaned syngas (mainly composed of H₂ and CO) obtained from
sludge gasification as the raw reactant. Computer modeling was applied to simulate the entire process. It was found that this sludge gasification-methanol production process has higher exergetic efficiency in comparison to that from the traditional thermal sludge treatment.

2.4.4.2 Fate of heavy metals during gasification

Metals are always problematic for sludge disposal because of their detrimental effects on human health. Marrero et al. [89] tested the fate of selective heavy metals (Cd, Sr, Cs, Co, As, Hg, Zn, and Cu) during gasification by tracing the partitioning of radioactive metals. They found that most of the metals, such as Cd, Sr, Cs, Co, Zn and Cu, were retained in the chars produced during gasification; whereas Hg, the most mobile metal, was mainly accumulated in a char filter set after the gasifier. The partitioning of metals was partially associated with the volatility of the individual metal constituent. For instance, Hg is very volatile and therefore more likely to go into a vapour phase and condense together with aerosols in the filters. Similarly, arsenic, which is also volatile to some extent, was partially retained in the char filter. However, it should be noted that although these metals seemed to be held by solid chars, they were in fact in leachable forms as more than 50% of most metals with the exception of As were noted to be leached out of the char product using of a 50% HNO₃ solution [89].
2.4.4.3 Supercritical water gasification

Supercritical water gasification of biomass is a novel technique for biomass conversion. It has been widely investigated for H₂ production. Supercritical water is a special water phase at which the pressure and temperature of water are increased to or above the critical point (22.1 MPa and 374°C). Many physical properties of water, such as density, dielectric constant, and the solubility of organic and inorganic compounds, are changed significantly in the supercritical region [90,91]. In comparison to water under ambient condition, SCW exhibits higher diffusivity, lower viscosity, as well as superior solubility for organic compounds. All these properties enable SCW a distinct medium for biomass gasification [92].

During the gasification process, SCW is not only a solvent but also a reactant. As such, SCWG of biomass promotes high H₂ yields, reduces tar formation, and eliminates the need for a drying process, which is necessary for most thermo-chemical biomass conversion approaches [90,91,93-97]. In comparison to conventional gasification processes, SCWG requires a much lower reaction temperature to achieve similar H₂ yields [98].

Wood and agricultural wastes have been widely studied in SCWG processes. However, there are very few investigations that have focused on the use of sludges as feedstocks. Xu et al. [99] employed ground and homogenized sewage sludge, pumped as a slurry into a supercritical flow reactor at a temperature of 600°C, pressure of 34.5 MPa, using coconut shell activated carbon as the catalyst for H₂ production. They observed that at a
low feedstock concentration (2.8 wt %) and a low weight hourly space velocity (WHSV, the mass flow rate of the feed over the mass of the catalyst) of 0.5 h⁻¹, almost all of the sludge was converted into gaseous product, with a H₂ yield of 0.027 g H₂/g sludge. However, they did not attempt to use a higher solid concentration due to the experimental challenge associated with the pumping system. Xu and Antal [96] overcame pumping issues by mixing the sludge in a corn starch paste and utilizing a cement pump. In using this approach, a higher sludge solids concentration (up to 7.69 wt %) was achieved. This experiment employed a temperature and pressure of 650°C and 28 MPa, respectively, as well as a packed bed of coconut shell activated carbon as the catalyst. At a low solids concentration (2.1 wt % sludge + 5.1 wt % corn starch; flow rate: 2.0 g/min; WHSV: 1.48 h⁻¹), 99% of the feed was converted to a gas product with H₂ mol fraction of 42%. However, when a higher solids content in the feedstock was used (7.69 wt % sludge + 7.69 wt % corn starch), the fractions of CO₂ and H₂ were found to decrease while CH₄ increased; the CO percentage did not change significantly. However, reactor plugging was noted in both of these tests because of the high ash content of the sludge (25.1%, dry basis). Zhang et al. [98] studied the effect of reaction temperature (400-600°C), pressure (24-30 MPa), residence time (3-15 min), and catalyst (with and without NaOH) on the H₂ yield from a sewage sludge sample with a 95% water content, using a continuous flow reactor, in the presence of 30 wt % hydrogen peroxide (H₂O₂) for partial oxidation. It was observed that several factors, such as higher temperature, pressure, residence time, and the presence of a NaOH catalyst contributed to the enhanced H₂ production in this SCWG and partial oxidation process. In addition, Zhang et al. [98] evaluated the energy efficiency for this process. In an ideal scenario assuming no external energy loss and considering the energy input for pumping and heating and the energy recovery from the
hot-compressed water, the estimated energy yield could reach 85%. In addition, the heat recovery from the hot-compressed water was of great importance to ensure a high overall energy utilization efficiency.

Most recently, Zhang et al. [100] published a work on SCWG of secondary pulp/paper-mill sludge (SPP) and three types of sewage sludge (primary, secondary, and digested sewage sludges) in a batch reactor at various temperatures (400-550°C) and reaction times (20-120 minutes). Secondary pulp/paper-mill sludge demonstrated the highest potential for gas production, where 37.7 wt% gas yield (on a dry basis) was achieved at 550°C, with the H₂ yield as high as 14.5 mol/kg SPP. The better performance of SPP in terms of gas production could be attributed to a combination of several factors, such as the high initial pH, as well the higher contents of alkali metals (e.g., Na) and VMs in the feedstock.

### 2.4.5 Wet oxidation

Wet oxidation is the oxidation of organic and inorganic compounds with O₂ in the liquid phase. It is a thermo-chemical process used for treating waste streams from petrochemical, chemical and pharmaceutical industries, as well as sludges from wastewater treatment plants (e.g. municipal sewage sludge, alcohol distillery waste, effluent from pulp and paper mill, cyanide, cyanate, nitrile wastewater, etc.). These streams cannot be efficiently degraded by conventional aerobic and anaerobic biological treatment processes [101-103] and they are too diluted for incineration [102].
During the wet oxidation process, organic carbons are converted into CO$_2$ and other low-molecular-weight compounds under subcritical water conditions at designed temperatures and pressures (typically in the range of 180-315°C and 2-15 MPa, respectively) with a residence time of 30-120 minutes [101,102]. In addition, halogen and sulphur are converted to inorganic halides and sulphate, respectively, after the reaction [101]. Wet oxidation can achieve a significant mass and volume reduction for sludge [104]. Furthermore, it is a “clean” technique because it generates very little emissions of airborne contaminants (NO$_x$, SO$_2$, HCl, etc.) and fly ash, a by-product from sludge incineration [102].

As wet oxidation takes place in the aqueous phase, elevated temperatures and pressures are necessary to increase the solubility of oxygen in water. Water itself plays the role of both heat transfer medium and heat adjustor, by which extra heat can be removed by water evaporation [101]. Wet oxidation cannot achieve a 100% mineralization of organic materials (75-90% COD removal) because of the presence of newly formed, resistant but soluble organic compounds, such as acetic and propionic acids. Therefore, further treatment, e.g. biological treatment process, is required in some cases [102,104].

To improve the oxidation efficiency, catalysts (e.g., precious metal and/or base metal oxide) can be used to decrease the reaction temperature, pressure, and residence time, and to destroy refractory compounds that cannot be decomposed at normal pressure [102]. An extensive review paper on wet oxidation can be found elsewhere [101].
2.4.5.1 Wet electrolytic oxidation

Recently, Serikawa [105] employed an innovative WEO process, combing wet oxidation and electrochemical reaction, to treat sludge resulting from a CH₄ fermentation facility. The treatment process was conducted under subcritical water conditions. In comparison to water under ambient condition, subcritical water exhibits higher ionic product, which translates to an enhanced dissociation of water molecules, and hence facilitating the occurrence of electrochemical reactions. Moreover, subcritical water is capable of dissolving inorganic salts, allowing the use of an electrolytic solution (e.g. sodium chloride (NaCl) solution). It was found that WEO increased the biodegradability of the organic sludge as noted through the formation of VFAs and the increased biochemical oxygen demand (BOD)/COD ratio. In addition, WEO is able to degrade NH₃, which is extremely refractory in conventional wet oxidation reactions, to N₂ and H₂, and to reduce the viscosity of sludge and enhance its dewaterability. Despite that WEO is able to completely mineralize the organic constituents in the sludge, it is more economical to combine the WEO with a biological treatment process (aerobic or anaerobic) as further treatment.

2.4.5.2 Supercritical water oxidation

Supercritical water oxidation is a special wet oxidation process conducted in SCW to completely destroy organic compounds and bacteria in sludge without forming harmful gas contaminants, thereby eliminating stack gas scrubbing requirements [92,101,106-108]. As mentioned in the Section 2.4.4.3, SCW can merge liquid and gas together as one
single phase, where O₂ becomes miscible. In addition, SCW has a low dielectric constant, which means that it is able to dissolve organic compounds initially present in the wastes and facilitate the interaction between the organic constituents and the dissolved O₂\cite{104}. During the SCWO process, almost all of the organic constituents (including some toxic chemicals, such as PCBs) can be destroyed via various chemical reactions: hydrocarbons are mineralized to CO₂ and H₂O; metals are oxidized to metal oxides; the N, P, and S are converted to N₂, PO₄³⁻, and SO₄²⁻; and the organic chlorides are decomposed to CO₂, H₂O, and HCl\cite{106-109}. In addition to the excellent treatment efficiency, heavy metals have been reported to be well stabilized in the ash produced by SCWO (tested by standard TCLP leaching test)\cite{109}. This characteristic is of particular importance when considering the safe disposal of SCWO residues. In fact, SCWO is a technique that has been investigated for more than twenty years and has also been commercialized\cite{92,106,110}.

Plugging is always an issue for SCWO because of the limited solubility of inorganic compounds, which have the potential to be accumulated inside the reactor\cite{101,106}. To solve this problem, high-pressure water can be injected from the bottom of the reactor to cool down the effluent and to dissolve the salts. Moreover, a tubular reactor with suspension flow can also prevent the occurrence of clogging in the reactor\cite{106}. It is worth noting that the cost of some SCWO processes has been reduced considerably primarily due to the reactor design improvements in the last decade\cite{106}. 

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2.5 Conclusions

Selected biological and thermo-chemical sludge treatment processes have been briefly reviewed along with the characteristics of the different product recovery streams. Among the three primary alternatives for sludge treatment, direct land application and landfilling are no longer considered suitable for sludge disposal considering the land limitations, public health concerns, as well as some operational difficulties. Instead, combustion/incineration has attracted more attention because of its cost and treatment efficiency and the potential for combustion heat recycling. However, combustion/incineration is closely associated with airborne emissions and high ash production. Anaerobic digestion is a conventional approach applied to achieve sludge stabilization and the production of biogas, which is mainly composed of CH₄ and could act as a natural gas substituent. As an improvement, the co-digestion of sludge with other organic wastes not only increases biogas yield but also makes full use of the existing anaerobic digester capacities in wastewater treatment plants. Thermo-chemical processes are efficient at destroying complex organic compounds in sludge to reduce their potential detrimental effects on public health and the environment. In addition, they are capable of converting sludge into various forms of bio-fuels and valuable products, such as syngas via gasification and SCWG, bio-oil via pyrolysis and liquefaction, charcoal via pyrolysis, etc. Among these techniques, liquefaction and SCWG are more practical given the extremely high moisture content of sludge, because the energy-and-capital-intensive drying process could be eliminated. As another two approaches for treating sludge without drying, wet oxidation and SCWO are aimed at reducing the BOD levels and destroying some toxic chemicals present in sludge. In comparison to wet oxidation,
SCWO exhibits higher treatment efficiency in terms of its ability to destruct organic materials. Neither of these techniques, however, focuses on bio-energy recovery.

Among all the biological and thermo-chemical processes reviewed herein, liquefaction and SCWG are considered to be the most efficient in terms of their potentials for organic compound destruction and energy recovery within a short period of time. However, since both these processes are operated under harsh conditions (e.g., elevated temperatures and pressures), cost-intensive facilities and high energy inputs are required, which might be a barrier for their future scale-up applications. Instead, the authors would recommend anaerobic co-digestion with organic waste as the most effective and practical approach for current sludge treatment, due to the lower modification requirements for existing facilities, as well as the significantly improved biogas yield in comparison to the digestion of sludge as a single substrate.
2.6 References


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Chapter 3
Overview of Recent Advances in Thermo-Chemical Conversion of Biomass

3.1 Abstract

Energy from biomass, bio-energy, is a potential source to replace fossil fuels in the future, as it is abundant, clean, and carbon dioxide neutral. Biomass can be combusted directly to generate heat and electricity, and by means of thermo-chemical and bio-chemical processes it can be converted into bio-fuels in the forms of solid (e.g., charcoal), liquid (e.g., bio-oils, methanol and ethanol), and gas (e.g., methane and hydrogen), which can be used further for heat and power generation. This paper provides an overview of the principles, reactions, and applications of four fundamental thermo-chemical processes (combustion, pyrolysis, gasification, and liquefaction) for bio-energy production, as well as recent developments in these technologies. Some advanced thermo-chemical processes, including co-firing/co-combustion of biomass with coal or natural gas, fast pyrolysis, plasma gasification and supercritical water gasification, are introduced. The advantages and disadvantages, potential for future applications and challenges of these processes are discussed. The co-firing of biomass and coal is the easiest and most economical approach for the generation of bio-energy on a large-sale. Fast pyrolysis has attracted attention as it is to date the only industrially available technology for the production of bio-oils. Plasma techniques, due to their high destruction and reduction efficiencies for any form of waste, have great application potential for hazardous waste treatment. Supercritical water
gasification is a promising approach for hydrogen generation from biomass feedstocks, especially those with high moisture contents.

3.2 Introduction

Bio-energy is a renewable and clean energy source that is derived from biomass. It has been attracting great attention these days due to the declining fossil fuel reserves and the ever-increasing greenhouse effects produced through fossil fuel utilization. Biomass refers to all organic materials that stem from green plants as a result of photosynthesis. It is a stored source of solar energy in the form of chemical energy, which can be released when the chemical bonds between adjacent oxygen, carbon, and hydrogen molecules are broken by various biological and thermo-chemical processes. Fossil fuels, including primarily coal, oil and natural gas, also originated from “ancient” biomass that has been transformed through microbial anaerobic degradation and metamorphic geological changes over millions of years [1,2]. Considering the rate of formation (millions of years) and consumption, fossil fuels are generally considered to be non-renewable. In contrast, biomass is a renewable energy source. In addition, the lower emission of environmentally detrimental gases, such as sulphur dioxide (SO$_2$) and nitrogen oxides (NO$_x$), during the combustion of biomass also plays a positive role in reducing global acid rain formation [1,3-8].

Biomass includes a wide range of organic materials, which are generally composed of cellulose, hemicellulose, lignin, lipids, proteins, simple sugars and starches. Among these compounds, cellulose, hemicellulose, and lignin are the three main constituents (Table 3.1)
Biomass also contains inorganic constituents and a fraction of water [5]. As for the elementary composition, carbon (51 wt%) and oxygen (42 wt%) together contribute to over 90% of the dry weight of a typical biomass. In addition, there are trace amounts of hydrogen (5 wt%), nitrogen (0.9 wt%) and chlorine (0.01-2 wt%) [11].

**Table 3.1**

Typical levels of cellulose, hemicellulose, and lignin in biomass [9,10].

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent dry weight</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>40-60%</td>
<td>A high-molecular-weight (10⁶ or more) linear chain of glucose linked by β-glycosidic linkage. This chain is stable and resistant to chemical attack.</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>20-40%</td>
<td>Consists of short, highly branched chains of sugars (five-carbon sugars such as D-xylose and L-arabinose, and six-carbon sugars such as D-galactose, D-glucose, and D-mannose) and uronic acid. Lower molecular weight than cellulose. Relatively easy to be hydrolyzed into basic sugars.</td>
</tr>
<tr>
<td>Lignin</td>
<td>10-25%</td>
<td>A biopolymer rich in three-dimensional, highly branched polyphenolic constituents that provide structural integrity to plants. Amorphous with no exact structure. More difficult to be dehydrated than cellulose and hemicellulose.</td>
</tr>
</tbody>
</table>

Wood, energy crops, as well as agricultural and forest residues, which are the main renewable energy sources, are typical examples of biomass. Moreover, food processing wastes, sewage sludge, and the organic components of municipal solid waste (MSW) and pulping by-products (e.g., black liquor) can also be considered biomass [3,4,12].

In comparison to fossil fuels, biomass has lower heating values on a similar weight basis. Specifically, the heating value of biomass is in the range of 15-19 GJ/t, where heating values for agriculture residues and woody materials are 15-17 GJ/t and 18-19 GJ/t, respectively, compared to 20-30 GJ/t for coals. In addition, the bulk density, also known
as energy density, is only 10-40% of that of most fossil fuels [13]. However, in comparison to fossil fuels, biomass has much higher volatile matter content (80% in biomass vs. 20% in fossil fuels) [11], therefore, biomass has a high ignition stability and can be easily processed thermo-chemically into other higher-value fuels, such as methanol (C₂H₅OH) and hydrogen (H₂).

Fig. 3.1 [4] illustrates biomass from industry, agriculture, forestry, and waste sources, as well as their potential final bio-energy applications. It can be seen that various types of waste biomass, such as food residuals, agricultural crops, animal wastes, and municipal solid wastes have the potential to be eventually converted into energy and other bio-products, which can be applied for power generation, transportation, as well as the production of biomaterials.

![Fig. 3.1 Biomass resources converted to bio-energy carriers [4].](image-url)
As a renewable energy source, biomass has been extensively utilized in many regions to date. It currently contributes to 14% of the world’s primary energy demand and is considered as the fourth largest energy source [14]. In Canada, which is rich in fossil fuels, approximately 4.7% of the national primary energy for 2006 was derived from the conversion of renewable biomass and waste. This fraction is projected to increase to 6-9% over the next 20 years [15].

The usage of biomass as a source of energy has been further enhanced in recent years in Europe as well. Fig. 3.2 depicts the net power generating capacity for 1990, 1995, and 2000 in European Union countries. It can be seen that the net power generation from both municipal waste and solid biomass has been steadily increasing from 1990 to 2000.

Fig. 3.2 Development of net power generating capacity from municipal waste and solid biomass in European Union countries [16].
Furthermore, the International Energy Agency (IEA) data indicates that the electricity generation from solid biomass in the European Union had been growing at an average rate of 2.5% per year over the last decade [16].

Bio-energy can be converted from biomass via two main types of processes: thermo-chemical and bio-chemical/biological processes [6]. Generally, thermo-chemical processes have higher efficiencies than bio-chemical/biological processes in terms of the lower reaction time required (a few seconds or minutes for thermo-chemical processes vs. several days, weeks or even longer for bio-chemical/biological processes) [17] and the superior ability to destroy most of the organic compounds. For example, lignin materials are typically considered to be non-fermentable and thus cannot be completely decomposed via biological approaches, whereas they are decomposable via thermo-chemical approaches [5,18,19].

Thermo-chemical conversion processes mainly include direct combustion, pyrolysis, gasification, and liquefaction [17,20]. As shown in Fig. 3.3, the stored energy within biomass could be released directly as heat via combustion/co-firing, or could be transformed into solid (e.g., charcoal), liquid (e.g., bio-oils), or gaseous (e.g., synthetic gas and short for syngas) fuels via pyrolysis, liquefaction, or gasification with various utilization purposes. In this article, the authors will provide an overview of the principles, applications and recent developments of the four abovementioned fundamental thermo-chemical biomass conversion approaches.
Fig. 3.3 Thermo-chemical processes for bio-energy production and the corresponding products [20].

3.3 Combustion

Combustion is the most widely used process for biomass conversion. It contributes to over 97% of bio-energy production in the world. In some less-developed countries, combustion of traditional biomass plays an important role in people’s daily lives as it is the main source of energy available for cooking and heating. Regarded as a proven low cost, but highly reliable technology, combustion is relatively well understood and commercially available [21-23]. There are three main stages that occur during biomass combustion: drying, pyrolysis and reduction, and combustion of volatile gases and solid char [23]. The combustion of volatile gases contributes to more than 70% of the overall heat generation. It takes place above the fuel bed and is generally evident by the presence of yellow flames. Char is combusted in the fuel bed and is noted by the presence of small blue flames [23,24]. The combustion of biomass on a large scale is still considered to be a
complex process with technical challenges associated with the biomass fuel characteristics, types of combustors, and the challenges of co-firing processes.

### 3.3.1 Distinct characteristics of biomass fuels

In comparison to fossil fuels, biomass fuels have relatively low heating values. This can be explained by two of their distinct characteristics: high moisture and high oxygen contents [5,21].

The high moisture content is one of the most significantly disadvantageous features of using biomass as a fuel. Although the combustion reactions are exothermic, the evaporation of water is endothermic. To maintain a self-supporting combustion process, the moisture content (on wet basis) of biomass fuels cannot be higher than 65% [5]. In addition, the heating value of the fuel is negatively correlated with the relative amount of water even when the moisture content is within the maximum acceptable limit [5,21,24].

Fig. 3.4 exhibits the negative linear relationship between the moisture content and the heating value. As the moisture content increases, both the higher heating value (HHV) and lower heating value (LHV) decrease. HHV and LHV are used to describe the heat production of a unit quantity of fuel during its complete combustion. In determining the HHV and LHV values of a fuel, the liquid and vapour phases of water are selected as the reference states, respectively. As HHV incorporates the heat of the condensation of water vapour during the combustion, it is not surprising to observe that the curve of the HHV is always above that of the LHV [24,25].
Fig. 3.4 Relationship between heating value and moisture content of biomass fuel [24].

Another important feature of biomass fuel is its elevated oxygen content. Typically, the oxygen content of biomass is as high as 35 wt%, approximately ten times higher than that of a high-rank coal, which is below 4 wt% [21].

Fouling and corrosion of the combustor are typical issues associated with biomass combustion. These are considered to be detrimental because of the resulting reduction in heat transfer in the combustor. Fouling is commonly associated with the presence of alkali metals and some other elements (such as silicon, sulphur, chlorine, calcium and iron) in the biomass ash. With a series of complex chemical reactions, these elements are deposited in the forms of chlorides, silicates or sulphates on the wall of the combustor or the surface of the heat transfer elements [5,21,26,27]. Generally, herbaceous biomass, such as straws and grass with comparatively higher contents of alkali, sulphur, chlorine,
etc., has a higher potential for the occurrence of ash deposition and corrosion in comparison to woody biomass [21,28].

3.3.2 Biomass combustion systems

Fixed-bed, fluidized-bed, and entrained flow reactors are the three typical combustion systems, with increasing carrier gas velocity within the reactor [28]. A higher gas velocity translates to an intensive mixing of the feedstock, which enhances the combustion efficiency and the heat exchange rate. Hence, the entrained flow systems would be expected to exhibit the best performance among these three types of combustion systems [24].

Fixed-bed systems have been widely used for biomass combustion for a number of years. The simplest fixed-bed system is composed of one combustion room with a grate. Generally, as soon as the new biomass feed is added into the furnace, it is pyrolyzed into volatile gases and chars. Primary and secondary air supplies are provided under and above the grate for the combustion of chars and volatile gases, respectively. The heat generated through the combustion of chars is responsible for providing enough heat for the pyrolysis of newly added biomass. Because of the high content of volatile matter in biomass fuels, a greater secondary air supply is required than the primary air supply; this is one of the major differences from the process of coal combustion. A fixed-bed biomass combustion system is typically operated at around 850-1400°C [23,24]. Typical examples of fixed-bed systems are manual-fed systems, spreader-stoker systems, underscrew systems, through-screw systems, static grates, and inclined grates [24]. Recent
developments have been made to enhance the combustion efficiency. One example is the
cyclonic combustion system, which may be viewed as a modified fixed-bed system,
suitable for the combustion of agricultural residues and particulate wood wastes at a high
efficiency [24].

Compared with fixed-bed systems, fluidized systems have higher combustion efficiency
and they are more suitable for large scale operations [23]. Fluidized-bed systems employ
silica sand, limestone, dolomite, or other non-combustible materials for the bed material.
The typical operating temperature is 700-1000°C, which is lower than that of fixed-bed
systems. The bed materials act as the heat transfer media which are fluidized by the air
flow coming from the bottom. The biomass which is intermixed with the moving medium
has a high combustion efficiency. Depending on the blowing air velocity, fluidized-bed
systems can be further divided into bubbling fluidized-bed (BFB) and circulating
fluidized-bed (CFB) systems [24]. As an example, for a BFB combustor in a pilot plant,
the average bed temperature was maintained at 775 ± 75°C, the mean fluidization velocity
was set at 1.2 m/s, and the injected air was divided into primary air (taking 60% of the
total airflow) and secondary air [29]. Due to the high mixing intensity created by the
upward-flowing air at a high velocity, CFB systems behave more efficiently than BFB
systems. In a CFB combustor, fuel particles and the bed materials are separated from the
fast flowing gas stream in the cyclone and then re-enter into the reactor. Circulating
fluidized-bed systems exhibit several advantages, such as the adaptation to various fuels
with different properties, sizes, shapes, and moisture (up to 60%) and ash contents (up to
50%). In addition, the CFB units can achieve high heat transfer and reaction rates with a
compact construction [24].
An example of an entrained flow reactor is illustrated in Fig. 3.5 [30]. The fuel particles are transported into an externally heated SiC tube pneumatically through an insulated and water-cooled injector. Prior to the injection, the feeding stream, composed of air and fuel particles, has to pass through an agitation chamber for “disaggregation and filtering of pulses in the feeding”. The feeding fuel is ignited by a natural gas/air burner at the reactor entrance.

![Schematic view of an entrained flow reactor](image)

**Fig. 3.5** Schematic view of an entrained flow reactor [30].
3.3.3 Co-firing

Co-firing biomass and coal (directly by burning biomass and coal or indirectly by gasifying biomass first to produce clean fuel gas that is then burnt with coal in a generation boiler) has been proven to be a cost-effective technology to achieve the goal of increasing use of biomass-to-energy processes for power generation, thereby significantly reducing greenhouse gas emissions. Significant improvements have been achieved in some traditional coal-fired power plants. In comparison with other thermo-chemical processes for biomass utilization and bio-energy production (including sole biomass-based combustion), co-firing is most cost-effective because of the few modifications that are required to upgrade the original coal-based power plants [31]. IEA has reported that more than 150 coal-fired power plants (50-700MWe) in the world, to date, have been exposed to the co-firing of coals with woody biomass or waste materials [4]. Various types of biomass, such as woody and herbaceous materials, agricultural residuals, and energy crops can be easily co-fired with different types of coal in percentage fractions as high as 15% (Table 3.2). Biomass co-firing with coal could reduce the occurrence of fouling and corrosion, when compared to using biomass alone, due to the dilution and the consumption of alkali metals via interactions with sulphur or silica in the coal [38]. In addition to coal, biomass can also be co-fired with natural gas [5,37]. This approach is particularly applicable to biomass with high moisture content (>60%) that cannot be burned individually in a combustor [5]. Moreover, co-firing of natural gas with fuel gas derived from low-heating-valued biomass materials (sometime referred to as the indirect co-firing approach) can be another promising option for bio-energy utilization [36,39,40].
Table 3.2
Summary of the feedstocks used in previous co-firing studies.

<table>
<thead>
<tr>
<th>Types of biomass feed</th>
<th>Coal or natural gas</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw, sewage sludge, wood chip and WPOS (woody matter from olive stones)</td>
<td>Federal and Bellambi coals</td>
<td>[32]</td>
</tr>
<tr>
<td>Foot cake (waste from the olive oil industry)</td>
<td>Coal (lignite and anthracite)</td>
<td>[33]</td>
</tr>
<tr>
<td>Paper mill sludge</td>
<td>Coal</td>
<td>[34]</td>
</tr>
<tr>
<td>Sludge and hog fuel</td>
<td>Sub-bituminous coal</td>
<td>[35]</td>
</tr>
<tr>
<td>Gasified sugarcane residues</td>
<td>Natural gas</td>
<td>[36]</td>
</tr>
<tr>
<td>Cellulose biomass and non-hazardous waste (institutional-household waste with plastics and food-related paper components)</td>
<td>Natural gas</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Depending on the manner biomass is mixed with coal, co-firing can generally be classified into three categories. In the first category, biomass is simply blended with coal and then introduced into the boiler. Due to the inferior properties of biomass (e.g., higher moisture contents, low bulk densities, etc.), co-firing processes for this group normally are limited to low co-firing ratios. In the second category, the biomass feedstock has to be processed separately and injected into the boiler through dedicated lines. Although the biomass introduction is separate from that of coal, the feedstocks are combusted simultaneously. A common challenge for categories one and two is the changed fly ash composition caused by the addition of biomass. Fly ashes from co-firing processes containing biomass are currently unaccepted for cement manufacture due to the strict interpretation of ASTM C618 [41]. In the last category, also called indirect co-firing, biomass is gasified before the subsequent co-firing process. This method is particularly suitable for co-combustion with natural gas and for the utilization of low-grade biomass and wastes. More importantly, the indirect co-firing approach is useful for ash
management as it separates ash from biomass and coals, alleviating concerns associated with the utilization of the biomass-based fly ash for cement industries [42].

Although co-firing biomass with coal may not be as efficient as the coal-based combustion process for power generation [32], it is promising due to the following distinct merits over the traditional coal-based processes. From an environmental point of view, co-firing reduces the emissions of toxic gases, such as SO$_x$ and NO$_x$ and the net emission of CO$_2$ [23,32-34,38,43-46]. The reduction in sulphur emissions is not only due to the lower sulphur content in biomass, but also due to the retention of sulphur by alkali/alkaline earth compounds present in the biomass [38,45]. The decreased NO$_x$ emissions obtained in co-firing [34] can be attributed to the high moisture content in biomass, which lowers the combustion temperature and consequently results in lower NO$_x$ emissions. However, Armesto et al. [33] observed an increased amount of N$_2$O when coal was co-fired with foot coke, a waste of high moisture-content from the olive oil industry, in a bubbling fluidized combustor. From an economic point of view, the co-combustion of biomass and coal could stimulate the production of perennial crops, the greatest potential biomass supply [38], support economic development and increase employment in areas where there are rich woody or agricultural biomass resources.

### 3.4 Pyrolysis

Pyrolysis is a thermal decomposition process that takes place in the absence of oxygen to convert biomass into solid charcoal, liquid (bio-oil), and gases at elevated temperatures. Pyrolysis is considered to be an industrially realized process for biomass conversion [3,
Based on thermal gravity analysis (TGA) testing of biomass, there are three stages for a typical pyrolysis process [47]. The first stage, pre-pyrolysis, occurs between 120 and 200°C with a slight observed weight loss, when some internal rearrangements, such as bond breakage, the appearance of free radicals, and the formation of carbonyl groups take place, with a corresponding release of small amounts of water (H₂O), carbon monoxide (CO), and CO₂. The second stage is the main pyrolysis process, during which solid decomposition occurs, accompanied by a significant weight loss from the initially fed biomass. The last stage is the continuous char devolatilization, caused by the further cleavage of C-H and C-O bonds.

Depending on the reaction temperature and residence time, pyrolysis can be divided into fast pyrolysis, intermediate pyrolysis, and slow pyrolysis. Table 3.3 lists the reaction conditions and the product yields of various pyrolysis processes, in comparison with the gasification process. Typically, fast pyrolysis has an extremely short residence time (~ 1 s); the reaction temperature is approximately 100°C higher than that of slow pyrolysis (~500°C vs. ~400°C). Short reaction times combined with an elevated temperature generally results in a higher yield of liquid product. In contrast, slow pyrolysis with comparatively lower reaction temperatures and longer residence times would produce similar amounts of liquid, solid char, and gas products [3]. Combining all the factors mentioned above, it may be generally concluded that in order to maximize the charcoal yield, low temperature and low heating rates are necessary. If liquid is the desired product, a combination of moderate temperature, short gas residence time, and high heating rate is essential [49].
Table 3.3

Typical product yields (dry wood basis) of pyrolysis compared with those of gasification [3].

<table>
<thead>
<tr>
<th>Mode</th>
<th>Conditions</th>
<th>Liquid</th>
<th>Char</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast</td>
<td>Moderate temperature (around 500°C), short hot vapor residence time ~ 1 second</td>
<td>75%</td>
<td>12%</td>
<td>13%</td>
</tr>
<tr>
<td>Slow (carbonization)</td>
<td>Low temperature (around 400°C), very long solids residence time</td>
<td>30%</td>
<td>35%</td>
<td>35%</td>
</tr>
<tr>
<td>Gasification</td>
<td>High temperature, (around 800°C), long solids and vapor residence time</td>
<td>5%</td>
<td>10%</td>
<td>85%</td>
</tr>
</tbody>
</table>

3.4.1 Fast pyrolysis

Fast pyrolysis is a pyrolysis process with high heating rate (as high as hundreds of °C/min) and short residence time. It particularly favours the formation of liquid products, but inhibits the formation of solid chars (Table 3.4) [47,50,56,58]. The liquid products (bio-oils) are composed of an aqueous phase which contains several light organo-oxygen compounds of low molecular weight, and a non-aqueous phase (tar) which includes a variety of insoluble aromatic organic compounds of high molecular weight. Bio-oil, the major product from fast pyrolysis, is a potential liquid fuel that can be easily stored and transported. The physical properties of bio-oil derived from wood pyrolysis are shown in Table 3.5, in comparison with the properties of a typical heavy fuel oil [59]. Compared with petroleum heavy fuel oil, bio-oil has a high content of water (15-30 wt%), a low (<3) and hence corrosive pH, a much higher content of oxygen (35-40 wt%), as well as a lower heating value (HHV of 16-19 MJ/kg). To date, a number of bio-oils have been tested to
be successfully utilized in turbines and boilers. In addition, bio-oils can also be used as a feedstock for chemical production, and be upgraded to high-quality fuels.

**Table 3.4**  
Summary of previous research on biomass fast pyrolysis for bio-oil production.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Reactor</th>
<th>Reaction temperature (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Vapor residence time (s)</th>
<th>Bio-oil yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corncob, wheat straw, oregano stalk</td>
<td>Fluidized bed</td>
<td>500</td>
<td>-</td>
<td>1-2</td>
<td>41</td>
<td>35</td>
</tr>
<tr>
<td>Hybrid poplar Corn stover</td>
<td>Fluidized bed</td>
<td>500</td>
<td>-</td>
<td>~0.4</td>
<td>66</td>
<td>58</td>
</tr>
<tr>
<td>Cotton straw and stalk</td>
<td>Fixed bed</td>
<td>550</td>
<td>550</td>
<td>200a</td>
<td>39.51</td>
<td>[52]</td>
</tr>
<tr>
<td>Sunflower (<em>Helianthus annus</em> L.)-pressed bagasse</td>
<td>Fixed bed</td>
<td>550</td>
<td>5</td>
<td>50a</td>
<td>52.85</td>
<td>[53]</td>
</tr>
<tr>
<td>Linseed (<em>Linum usitatissimum</em> L.)</td>
<td>Fixed bed</td>
<td>550</td>
<td>300</td>
<td>100a</td>
<td>57.7</td>
<td>[54]</td>
</tr>
<tr>
<td>Rape seed (<em>Brassica napus</em> L.)</td>
<td>Fixed bed</td>
<td>550</td>
<td>300</td>
<td>100a</td>
<td>68</td>
<td>[55]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Fixed bed</td>
<td>&gt; 500</td>
<td>&gt; 200</td>
<td>500-1500a</td>
<td>&gt; 40</td>
<td>[56]</td>
</tr>
<tr>
<td>Olive cake</td>
<td>Fixed bed</td>
<td>550</td>
<td>300</td>
<td>100a</td>
<td>39.4</td>
<td>[57]</td>
</tr>
</tbody>
</table>

*a* Sweep gas flow rate (cm³/min)
Table 3.5
Typical properties of wood pyrolysis bio-oil and of heavy fuel oil [59]

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Bio-oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (wt %)</td>
<td>15-30</td>
<td>0.1</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Elemental composition (wt %)

<table>
<thead>
<tr>
<th>Element</th>
<th>Bio-oil</th>
<th>Heavy fuel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>54-58</td>
<td>85</td>
</tr>
<tr>
<td>H</td>
<td>5.5-7.0</td>
<td>11</td>
</tr>
<tr>
<td>O</td>
<td>35-40</td>
<td>1.0</td>
</tr>
<tr>
<td>N</td>
<td>0-0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>ash</td>
<td>0-0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>16-19</td>
<td>40</td>
</tr>
<tr>
<td>Viscosity (at 50 °C, cP)</td>
<td>40-100</td>
<td>180</td>
</tr>
<tr>
<td>Solids (wt %)</td>
<td>0.2-1</td>
<td>1</td>
</tr>
<tr>
<td>Distillation residue (wt %)</td>
<td>Up to 50</td>
<td>1</td>
</tr>
</tbody>
</table>

Several factors need to be considered to maximize liquid yield in a fast pyrolysis process. These may include: a finer particle size (smaller than 1 mm); a carefully controlled temperature, for which it has been reported that optimal temperatures should be in the range of 450°C and 550°C to obtain the highest bio-oil yield [47,50,52,54,55,60]; a higher heating rate (> 200 °C/s); a shorter hot vapour residence time (< 4 s with a typical value of 2 s); and rapid cooling of the vapours [3,47,56,58].

The most commonly used reactors for fast pyrolysis are bubbling fluidized-bed [10], circulating fluidized-bed, ablative, entrained flow [3], rotating cone, and vacuum reactors [10]. The major characteristics of the first four categories of reactors are listed in Table 3.6. As the mobility of the bed increases from ablative to entrained flow, the solid bulk density decreases, the primary method of heat transfer changes from solid-solid to gas-
Table 3.6

Summary of characteristics of some common pyrolysis systems [10,58].

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Ablative</th>
<th>Bubbling fluid bed (BFB)</th>
<th>Circulating fluid bed (CFB)</th>
<th>Entrained flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Heating method</td>
<td>Reactor wall/disc</td>
<td>Heated recycle gas, Hot inert gas, Partial gasification, Fire tubes</td>
<td>In-bed gasification of char to heat sand</td>
<td></td>
</tr>
<tr>
<td>Primary heat transfer method</td>
<td>Solid-solid</td>
<td>Solid-solid, gas-solid</td>
<td>Solid-solid, gas-solid</td>
<td>Gas-solid</td>
</tr>
<tr>
<td>Modes of heat transfer (suggested)</td>
<td>95% conduction, 4% convection, 1% radiation</td>
<td>90% conduction, 9% convection, 1% radiation</td>
<td>80% conduction, 19% convection, 1% radiation</td>
<td>4% conduction, 95% convection, 1% radiation</td>
</tr>
<tr>
<td>Main features</td>
<td>Accepts large size feedstock, Very high mechanical char abrasion from biomass, Compact design, Heat supply problematical, Particulate transport gas not always required</td>
<td>High heat transfer rates, Heat supply to fluidizing gas or to bed directly, Limited char abrasion, Very good solids mixing, Particle size limit &lt; 2mm in smallest dimension, Simple reactor configuration, Residence time of solids and vapors controlled by the fluidizing gas flow rate</td>
<td>High heat transfer rate, High char abrasion from biomass and char erosion leading to high char in product, Char/solid heat carrier separation required, Solid recycle required, Increased complexity of system, Maximum particle size up to 6 mm, Possible liquid cracking by hot solids, Possible catalytic activity from hot char, Greater reactor wear possible</td>
<td>Low heat transfer rates, Particle size limit &lt; 2mm, Limited gas/solid mixing</td>
</tr>
</tbody>
</table>
solid, and the heat transfer modes vary from predominantly conduction to predominantly convection [58]. A comprehensive description of the aforementioned reactors can be found elsewhere [10].

In addition to bio-oil production, fast pyrolysis has also been reported to generate hydrogen gas at higher temperatures (700-1000°C) [59,61-68]. Two types of reactions were found to be mainly responsible for converting methane (CH₄) and other hydrocarbon vapours (C₂-C₅), simple aromatics, etc. into H₂; steam reforming (Eq. 3.1) and water-gas shift (Eq. 3.2) reactions [6,62,69]. Steam reforming reactions convert hydrocarbons into CO and H₂. The CO then reacts with H₂O to form H₂ and CO₂ through water-gas shift reactions [69]:

\[
C_nH_mO_k + (n - k)H_2O = (n + \frac{m}{2} - k)H_2 + CO \tag{3.1}
\]

\[
nCO + nH_2O \rightarrow nH_2 + nCO_2 \tag{3.2}
\]

When combining the two reactions together, the hydrogen production equation can be summarized as Eq. 3.3 [62,65]:

\[
C_nH_mO_k + (2n - k)H_2O = (2n + \frac{m}{2} - k)H_2 + CO_2 \tag{3.3}
\]

The potential hydrogen yield is positively correlated with the high steam-to-carbon (S/C) ratio [62] and the presence of proper catalysts, such as the co-precipitated Ni-Al catalysts and the ceria-zirconia supported Rh or Pt catalysts [66,68], in the systems.
3.4.2 Conventional moderate and slow pyrolysis

A conventional moderate or slow pyrolysis process, with a relatively long vapour residence time and low heating rate, has been used to produce charcoal for thousands of years [10,50]. The product, charcoal, can be utilized in a wide range of areas, from domestic cooking and heating to metallurgical or chemical use as the raw material for the production of chemicals, activated carbon, fireworks, absorbents, soil conditioners, and pharmaceuticals [70]. As reported by Mok et al. [71], a higher yield of charcoal can be obtained from biomass feedstocks with higher lignin contents and lower hemicellulose contents. In contrast to fast pyrolysis, slow pyrolysis does not necessarily require a fine feedstock particle size (smaller than 1 mm). A conventional pyrolysis process in a rotary-kiln reactor or a moving-bed reactor can be used for raw materials that are not available as powders or fine particles [47].

3.5 Gasification

Biomass gasification is a process that converts carbonaceous biomass into combustible gases (e.g. H₂, CO, CO₂, and CH₄) with specific heating values in the presence of a partial oxygen (O₂) supply (typically 35% of the O₂ demand for complete combustion) or suitable oxidants such as steam and CO₂. When air or oxygen is employed, gasification is similar to combustion, but it is considered a partial combustion process. A detailed comparison between biomass gasification and combustion has been provided by Rezaiyan and Cheremisinoff [7] and is summarized in Table 3.7. In general, combustion focuses on
heat generation, whereas the purpose of gasification is to create valuable gaseous products that can be used directly for combustion, or be stored for other applications. In addition, gasification is considered to be more environmentally friendly because of the lower emissions of toxic gases into the atmosphere and the more versatile usage of the solid by-products [7].

Table 3.7
Comparison of gasification and combustion [7].

<table>
<thead>
<tr>
<th>Features</th>
<th>Gasification</th>
<th>Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purpose</td>
<td>Creation of valuable, environmental friendly, usable products from waste or lower value material</td>
<td>Generation of heat or destruction of waste material</td>
</tr>
<tr>
<td>Process Type</td>
<td>Thermal and chemical conversion using no or limited oxygen</td>
<td>Complete combustion using excess oxygen (air)</td>
</tr>
<tr>
<td>Raw Gas Composition (before gas cleanup)</td>
<td>H₂, CO, H₂S, NH₃, and particulates</td>
<td>CO₂, H₂O, SO₂, NOₓ, and particulates</td>
</tr>
<tr>
<td>Gas cleanup</td>
<td>Syngas cleanup at atmospheric to high pressures depending on the gasifier design</td>
<td>Flue gas cleanup at atmospheric pressure</td>
</tr>
<tr>
<td></td>
<td>Treated syngas used for chemical, fuels, or power generation</td>
<td>Treated flue gas is discharged to atmosphere</td>
</tr>
<tr>
<td>Solid by-products/products</td>
<td>Recovers sulphur species in the fuel as sulphur or sulphuric acid</td>
<td>Any sulphur in the fuel is converted to SO₂ that must be removed using flue gas primarily consists of CO₂ and H₂O Bottom and fly ashes</td>
</tr>
<tr>
<td>Ash/char or slag handling</td>
<td>Char or slag</td>
<td>Bottom ash and fly ash are collected, treated, and disposed as hazardous waste in most cases or can be sold as a material for making concrete [71]</td>
</tr>
<tr>
<td>Pressure</td>
<td>Low temperature processes produce a char that can be sold as fuel</td>
<td>Bottom ash and fly ash are collected, treated, and disposed as hazardous waste in most cases or can be sold as a material for making concrete [71]</td>
</tr>
<tr>
<td></td>
<td>High temperature processes produce a slag, a non-leachable, non-hazardous material suitable for use as construction materials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fine particulates are recycled to gasifier. In some cases fine particulates may be processed to recover valuable metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atmospheric to high</td>
<td>Atmospheric</td>
</tr>
</tbody>
</table>
Gasification can be viewed as a special form of pyrolysis, taking place at higher temperatures to achieve higher gas yields. Biomass gasification offers several advantages, such as reduced CO$_2$ emissions, compact equipment requirements with a relatively small footprint, accurate combustion control, and high thermal efficiency [7,48]. The product of gasification, syngas, is a gaseous form of bio-energy. In terms of the specific heating values, synthetic gases can be classified into four groups. The typical ranges of the heating values and the industrial applications of each type of syngas are listed in Table 3.8. It can be seen that synthetic gas applications range from steam or heat generation as a fuel gas, for hydrogen production, as a substitute for natural gas production, as a fuel cell feed, and for the synthesis of some chemical compounds [7].

Table 3.8
Heating values and applications of four types of synthetic gases [7].

<table>
<thead>
<tr>
<th>Type of synthetic gas</th>
<th>Typical heating values (MJ/m$^3$)</th>
<th>Applications in industry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low heating-value gas</td>
<td>3.5-10</td>
<td>Gas turbine fuel, boiler fuel, and fuel for smelting</td>
</tr>
<tr>
<td>Medium heating-value gas</td>
<td>10-20</td>
<td>Gas turbine fuel, hydrogen production, fuel cell feed, chemical and fuel synthesis, and substitute natural gas with methanation process</td>
</tr>
<tr>
<td>High heating-value gas</td>
<td>20-35</td>
<td>Gas turbine fuel, SNG and hydrogen production, fuel cell feed, and chemical and fuel synthesis</td>
</tr>
<tr>
<td>Substitute natural gas (SNG)</td>
<td>&gt;35</td>
<td>Substitute for natural gas, hydrogen and chemical production, fuel cell feed</td>
</tr>
</tbody>
</table>

Gasification technology has been utilized commercially in several regions of the world. For instance, in the 1990s, China built more than 70 biomass gasification systems for household cooking. Each of the system has an average gas delivery of 200-400 m$^3$/h to serve 800-1600 families. While in India, gasification has been selected as a perspective method for electricity generation. A report published in 1999 indicated that the Indian
Ministry of Non-conventional Energy Source had launched a power plant with a 31 MWe total capacity. In addition, two larger projects for more than 200 MWe were either commissioned or under consideration [72].

3.5.1 Stages of a typical gasification process

Pyrolysis (Eq. 3.4) is the first stage of biomass gasification. During this stage, biomass feedstocks are decomposed into tars and volatile hydrocarbon gases containing certain quantities of hydrogen before the commencement of the gasification reactions. Thereafter, a series of reactions take place in the gasifier shown as Eq. 3.2 (presented in Section 3.1.) and Eqs. 3.5-3.13 [7,73,74]:

\[
C_nH_mO_p \rightarrow CO_2 + H_2O + CH_4 + CO + H_2 + (C_2 - C_5) \quad (3.4)
\]

\[
C + O_2 \rightarrow CO_2 \quad (3.5)
\]

\[
C + \frac{1}{2}O_2 \rightarrow CO \quad (3.6)
\]

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (3.7)
\]

\[
C + H_2O \rightarrow CO + H_2 \quad (3.8)
\]

\[
C + 2H_2O \rightarrow CO_2 + 2H_2 \quad (3.9)
\]

\[
C + CO_2 \rightarrow 2CO \quad (3.10)
\]

\[
C + 2H_2 \rightarrow CH_4 \quad (3.11)
\]

\[
CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (3.12)
\]

\[
C + H_2O \rightarrow \frac{1}{2}CH_4 + \frac{1}{2}CO_2 \quad (3.13)
\]
Reactions 3.5 to 3.7 are oxidation reactions that occur in the presence of oxygen. Since Reactions 3.5 and 3.6 are exothermic, enough heat is generated to dry the feedstock, to break up the chemical bonds (pyrolysis of biomass), and to maintain a high temperature for driving the gasification reactions. Among these reactions, Reaction 3.5 has the greatest energy release. In contrast, the heat generation capacity of Reaction 3.6 is only 65% of that of Reaction 3.5. Reactions 3.8 and 3.9 are the main gasification reactions; they are called water-gas reactions. Reaction 3.12 is the methanation reaction, it proceeds slowly at low temperatures and in the absence of any catalysts. In addition, the water-gas shift reaction (Eq. 3.2), as mentioned in Section 3.1., is also of great importance since it plays a significant role for hydrogen generation. Both Reactions 3.2 and 3.12 take place in either direction depending on the specific temperature, pressure, and the reactant concentrations in the system. From these reactions it can be seen that the syngas is a mixture that is mainly composed of CO, H₂, CO₂, CH₄, and H₂O vapour [7,73,75].

3.5.2 Gasifiers

Gasifiers are the reactors in which gasification reactions take place. Based on the types of reactions, a typical air-blown gasifier can be divided into four process zones— the drying zone, where water present in biomass is evaporated; the pyrolysis zone, in which biomass is pyrolyzed into medium-energy calorific volatile gases, liquid, and char; the combustion zone, a region where combustion reactions take place with limited amounts of air or oxygen provided; and the reduction zone, in which CO and H₂ are produced [73]. Similar to combustors, various types of gasifiers have been developed such as fixed-bed gasifiers,
fluidized gasifiers, and entrained flow gasifiers, whose main advantages and disadvantages are listed in Table 3.9.

### Table 3.9

Advantages and disadvantages of selected types of gasifiers [76].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fixed/moving bed, updraft</strong></td>
<td></td>
</tr>
<tr>
<td>Simple, inexpensive process</td>
<td>Large tar production</td>
</tr>
<tr>
<td>Exit gas temperature about 250°C</td>
<td>Potential channelling</td>
</tr>
<tr>
<td>Operates satisfactorily under pressure</td>
<td>Potential bridging</td>
</tr>
<tr>
<td>High carbon conversion efficiency</td>
<td>Small feed size</td>
</tr>
<tr>
<td>Low dust levels in gas</td>
<td>Potential clinking</td>
</tr>
<tr>
<td>High thermal efficiency</td>
<td></td>
</tr>
<tr>
<td><strong>Fixed/moving bed, downdraft</strong></td>
<td>Minimum feed size</td>
</tr>
<tr>
<td>Simple process</td>
<td>Limited ash content allowable in feed</td>
</tr>
<tr>
<td>Only traces of tar in product gas</td>
<td>Limits to scale up capacity</td>
</tr>
<tr>
<td></td>
<td>Potential for bridging and clinking</td>
</tr>
<tr>
<td><strong>Fluidized bed</strong></td>
<td></td>
</tr>
<tr>
<td>Flexible feed rate and composition</td>
<td>Operating temperature limited by ash clinking</td>
</tr>
<tr>
<td>High ash fuels acceptable</td>
<td>High product gas temperature</td>
</tr>
<tr>
<td>Able to pressurize</td>
<td>High tar and fines content in gas</td>
</tr>
<tr>
<td>High CH₄ in product gas</td>
<td>Possibility of high C content in fly ash</td>
</tr>
<tr>
<td>High volumetric capacity</td>
<td></td>
</tr>
<tr>
<td>Easy temperature control</td>
<td></td>
</tr>
<tr>
<td><strong>Circulating fluidized bed</strong></td>
<td>Corrosion and attrition problems</td>
</tr>
<tr>
<td>Flexible process</td>
<td>Poor operational control using biomass</td>
</tr>
<tr>
<td>Up to 850 °C operating temperature</td>
<td></td>
</tr>
<tr>
<td><strong>Entrained bed</strong></td>
<td></td>
</tr>
<tr>
<td>Very low in tar and CO₂</td>
<td>Low in CH₄</td>
</tr>
<tr>
<td>Flexible to feedstock</td>
<td>Extreme feedstock size reduction required</td>
</tr>
<tr>
<td>Exit gas temperature</td>
<td>Complex operational control</td>
</tr>
<tr>
<td></td>
<td>Carbon loss with ash</td>
</tr>
<tr>
<td></td>
<td>Ash slagging</td>
</tr>
</tbody>
</table>
3.5.2.1 Fixed-bed gasifiers

Fixed-bed gasifiers generally produce low-heating-valued syngas. They are suitable for small or medium-scale thermal applications. Since there is no mixing within the reactor, uniform reaction temperatures are difficult to achieve [7]. Fixed-bed gasifiers include updraft (counter-current), downdraft (co-current), cross-flow, and open-core gasifiers [7,24,73,75].

Updraft (counter-current) gasifiers. The updraft gasifier is the simplest type of gasifier. As shown in Fig. 3.6, the biomass is fed at the top while the air is injected at the bottom. Biomass and air move in a counter-current direction. During its downward movement, biomass is firstly dried when it goes through a “drying zone”. Then in the “distillation zone” (also called pyrolyzation zone), biomass undergoes decomposition and is converted into volatile gases and solid char. The gases and char will be further converted into CO and H₂ as they go past the “reduction zone”. Since some of the char settles down in the bottom of the reactor, heat is generated through its combustion in the “hearth zone” and is transported upward by the up-flowing gas to maintain the pyrolysis and drying processes. In addition, CO₂ and H₂O vapour are also produced from char combustion. Updraft gasifiers can accept biomass with relatively high moisture content (up to 60%). However, the resulting product gas has a high tar content because the tar, newly formed during pyrolysis, does not have the opportunity to pass through the combustion zone. Nowadays, most of the updraft power gasifiers have been decommissioned because of environmental issues, such as the water pollution from tarry residues [7,24,48].
**Downdraft (co-current) gasifiers.** The downdraft gasifier is currently one of the most widely used fixed-bed gasification systems. Different from the updraft gasifier, air in the downdraft gasifier is introduced into the reactor from the middle part. This design leads to the reversed order of the hearth zone and the reduction zone. In this gasifier, the injected air and biomass move co-currently. The drying and distillation zones are heated primarily by the heat radiated from the hearth zone where some char is burned. After passing through the oxidation zone in which air is introduced, the remaining char, CO₂, and H₂O are eventually converted into CO and H₂. In comparison to the updraft gasifier, the produced tar from pyrolysis passes through a hot reaction zone and can be destroyed via thermal cracking, consequently, reducing a significant amount of tar in the product gas [7,24,48].

![Diagram of the updraft (counter-current) gasifier](image-url)
**Cross-flow gasifiers.** In a cross-flow gasifier, biomass is added at the top of the reactor and moves downwards. Air is introduced from one side of the reactor and the gas products are released from the other side of the reactor on the same horizontal level. The combustion zone is located in the area of air injection, and the drying and pyrolysis zones are above the vessel [75].

**Open-core gasifiers.** Open-core gasifiers are generally employed to gasify biomass with low bulk density and high ash content. An example of this kind of biomass is rice husk. Instead of the narrow throat characteristic of other gasifiers, the open-core gasifier has a wide mouth for biomass injection to prevent fuel flow inhibition caused by bridging. In addition, the rotating grates and the water basin at the bottom of the gasifier are specifically designed to remove the ash produced during the gasification process [24].

### 3.5.2.2 Fluidized-bed gasifiers

As described previously for the combustion and pyrolysis processes, fluidized-bed reactors are widely employed as gasifiers. Fluidized-bed gasifiers can also be further classified into bubbling fluidized gasifiers and circulating fluidized gasifiers. In a bubbling fluidized gasifier, air is injected from the bottom of a grate, above which the moving bed is mixed with the biomass feed. The bed temperature is maintained at 700-900°C. Biomass is pyrolyzed and cracked through contact with the hot bed material. In a circulating fluidized gasifier, the hot bed material is circulated between the reactor and a cyclone separator. During this circulation, bed materials and char go back to the reactor, while the ash is separated and removed from the system.
The major advantage of fluidized-bed gasification over fixed-bed gasification is the uniform distribution of temperature within the reactor. In addition, fluidized-bed gasifiers can be sized effectively for middle or large scale facilities [7,48].

### 3.5.2.3 Entrained-flow gasifiers

In an entrained-flow gasifier, as shown in Fig. 3.7, the feed and air move co-currently and the reactions occur in a dense cloud of very fine particles at high pressures, varying between 19.7 and 69.1 atm, and very high temperatures > 1000°C. This type of gasifier has an elevated throughput of syngas. However, due to the high operating temperature and pressure, gas cooling is required before use, which can reduce the overall thermal efficiency of the system if the heat recovered in cooling is not re-used [48].

![Fig. 3.7 Configuration of the entrained flow gasifier [48].](image-url)
3.5.3 Tar elimination

The presence of tars in the syngas is generally considered undesirable as it is not only an indicator of a low gasification efficiency, but also brings in additional operational difficulty for syngas cleanup, which if not operate properly, may foul or plug the pipes and tubes and result in subsequent operational problems [7, 48, 77]. Tar elimination approaches can be classified into two categories: primary methodologies, for which treatments takes place inside the gasifier, and secondary methodologies, for which the hot gas clean up is conducted outside the gasifier. Primary methodologies are considered to be more economically practical and have attracted much more attention [74]. They include the addition of catalysts, the control of some experimental parameters, and the innovative design of gasifiers.

Catalysts play an important role in increasing the reaction rate at low-temperature conditions inside the gasifier. They also facilitate the tar conversion into valuable combustible gases via steam reforming, dry reforming, thermal cracking, hydroreforming and hydrocracking, or water-gas reactions [77]. Catalysts can be utilized either as bed materials or as additives to the feedstocks [78]. El-Rub et al. [77] divided gasification catalysts into synthetic catalysts and minerals (Fig. 3.8). Synthetic catalysts are produced by chemical methods at a relatively high cost, examples are char, alkali metal-based catalysts (e.g. Li, Na, K, Rb, Cs, and Fr), transition metal-based catalysts (e.g., Ni, Pt, Ru, and Rh), etc. Compared to synthetic catalysts, minerals are formed naturally and are thus
more cost effective. The typical examples of minerals are calcined rocks, olivine, clay minerals, and iron oxides [77].

**Fig. 3.8** Classification and types of catalysts used for tar elimination [77].

Gasifier configuration is another key factor that affects tar formation, especially when it is combined with catalysts. Cao et al. [74] introduced an innovative fluidized-bed gasifier in which a freeboard region with partial circulating fuel gas is located above the fluidized hot sand bed. The feedstock and primary air stream are injected into the gasifier from the top and the bottom, respectively. This particular design produces a tar-free fuel gas with improved heating value. In addition, Brandt and Larsen [79] observed the reduced tar content in the gas products by using a two-stage gasifier that is composed of a pyrolysis unit and a gasification unit with a charcoal bed. Nunes et al. [80] also noted a reduction in
tar formation when the product gas was passed through a second-stage bed packed with char in a two-stage fixed-bed reactor with downdraft gasifiers.

### 3.5.4 Plasma gasification

Plasma gasification is a gasification process that decomposes biomass into basic components, such as H₂, CO, and CO₂ in an oxygen-starved environment at an extremely high temperature. Plasma is regarded as the 4th state of matter, it is an ionized gas produced by electric discharges. A Plasma torch is a tubular device that has two electrodes to produce an arc. It is an independent heat source that is not affected by the feed characteristics nor the air/oxygen/steam supply. When electricity is fed, an arc is created, and the electricity is converted into heat through the resistance of the plasma. A plasma torch can heat the biomass feedstock to a temperature of 3000°C or higher (up to 15000°C). Under such extremely elevated temperature, the injected biomass stream can be gasified within a few milliseconds without any intermediate reactions. In addition to the conversion of complex organic compounds into simple molecules (H₂, CO, and CO₂), other products including molten metals, vitrified inorganic compounds [7,81,82] are also formed. The plasma technique has high destruction and reduction efficiencies. Any form of wastes, e.g., liquid or solid, fine particles or bulk items, dry or wet, can be processed efficiently. In addition, it is a clean technique with little environmental impact. Plasma technique has great application potential for treating a wide range of hazardous wastes. During the plasma gasification process, the toxicity of the waste can be significantly reduced, and some of the mineral compounds are converted into vitrified slag that can be utilized in road construction or landscape design [7,83,84].
The configuration of a shaft-type plasma gasifier reactor is shown in Fig. 3.9 [84], and the same type of reactor was used by Hlína et al. [85] for the treatment of waste streams. The plasma generator, in this case, was mounted on one of the side flanges, and the plasma flow was distributed through a series of side holes that were uniformly arranged over the shaft circumference. Waste was filled from the top and distributed on a fire grate at the bottom of the gasifier. Gas escaping from the bottom of the reactor was cooled by spraying water from a nozzle, burned with air in an afterburner and then cleaned prior to being released into the atmosphere; while slag was collected in a bath [84].

![Fig. 3.9 Configuration of a shaft-type plasma gasifier reactor. 1) plasma generator, 2) bin with waste, 3) cover, 4) charging batch, 5) fire grate, 6) bath with water for quenching the slag, 7) fire grate rotation drive, 8) gas duct, 9) temperature sensors, 10) gas sampling](image)

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Although the main application of plasma gasification is currently to treat non-biomass solid wastes [82-84,86,87], plasma gasification has been considered as a potential thermo-chemical approach for syngas production owing to its high H₂ and CO yields and extremely low tar generation [85,88].

### 3.5.5 Supercritical water gasification

Water exists in three states under normal conditions: solid, liquid, and gas. When the pressure and temperature are increased to or above their critical points (22.1 MPa and 374°C), water goes into supercritical state, where the gas and liquid phases are miscible [89,90]. Supercritical water (SCW) has found many applications in recent years due to its unique properties, as shown in Fig. 3.10. For instance, when the pressure is fixed at 25.3 MPa, water density decreases as temperature increases; the most significant drop occurs at the critical temperature [90]. As the density becomes lower, water molecules separate further from each other, hydrogen bonds are broken, and water loses its distinct properties as a liquid due to the loss of order between different water molecules [90,91]. Consequently, the dielectric constant decreases correspondingly. Fig. 3.10b illustrates the significant decrease in the dielectric constant with increased temperature; the constant at the critical point is only 1/10 of that under room temperature. The dielectric constant is a measure of the polarity of the liquid, it is also a reflection of the solubility of polar molecules in a fluid. Thus, the lower dielectric constant of SCW translates into an enhanced solubility of organic compounds (Fig. 3.10c), but reduced solubility of inorganic compounds (Fig. 3.10d) [90,91]. Supercritical water has the unique ability to
dissolve materials that are normally insoluble in either ambient liquid water or steam and has complete miscibility with the liquid/vapour products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions. The advantages of a single supercritical phase reaction medium are apparent in that the inter-phase mass transport processes that could hinder reaction rates are eliminated.

![Graphs showing properties of water at 25.3 MPa](image)

**Fig. 3.10** Properties of water at 25.3 MPa [90, 91].

Supercritical water has been utilized as an ideal gasification medium for biomass primarily because of its strong solubility for organic compounds, as well as its high
reactivity. As water moves into the supercritical region and if the pressure is maintained at a relatively low value (while still above its critical pressure, i.e., 22.1 MPa), free-radical mechanisms would replace ionic mechanisms in the system and thus the formation of tar can be minimized [92,93]. Moreover, it has been reported by Feng et al. [94] that water is a strong oxidant at temperatures greater than 600°C. Because of this, oxygen atoms present in water can be transferred to carbon atoms in biomass to form CO₂ and CO, while the hydrogen atoms in both the water and biomass are liberated to form H₂. As such, a portion of the hydrogen gas produced can originate from water rather than the biomass [91]. Compared to conventional gasification processes, supercritical water gasification presents a higher gasification efficiency and hydrogen yield [95], with a lower tar formation [96]. In addition, as wet biomass can be gasified directly, the expensive and energy-intensive drying process can be eliminated [97,98]. Moreover, due to the high pressure of the reaction, the reactor can be compact, and the hydrogen gas product can be pressured, which is convenient for storage and transportation [98].

A few supercritical water gasification studies have been conducted to date, covering a wide range of biomass. Some model compounds have been investigated, such as cellulose [99-102], starch [99], glucose [99,103-105], and lignin [100,102,104]. In addition, a few waste biomass feedstocks, e.g., cassava waste [99], corn silage [106], fruit shells [97], sawdust [101,102], rice straw [102], corn and clover grass [107], and sewage sludge [96] have been investigated.

Similar to the conventional gasification process, the addition of a small quantity of catalyst to a biomass supercritical water gasification process can enhance gasification
efficiency and hydrogen yield, especially at low reaction temperatures. Examples of these catalysts include Ru/TiO$_2$ [100], Ru/C, Pd/C, CeO$_2$ particles, nano-CeO$_2$, nano-(CeZr)$_x$O$_2$ [101], carbon (spruce wood charcoal, macadamia shell charcoal, coal activated carbon, and coconut shell activated carbon) [108], and potassium hydroxide [109].

### 3.6 Direct liquefaction

Direct liquefaction is a low-temperature and high-pressure thermo-chemical process during which biomass is broken down into fragments of small molecules in water or another suitable solvent. These light fragments, which are unstable and reactive, can then re-polymerize into oily compounds with various ranges of molecular weights [12,49,110]. Direct liquefaction has some similarity with pyrolysis in terms of the target products (liquid products). However, they are different in terms of operational conditions. Specifically, direct liquefaction requires lower reaction temperatures but higher pressures than pyrolysis (5-20 MPa for liquefaction vs. 0.1-0.5 MPa for pyrolysis). In addition, drying of the feedstock is not a necessary step for direct liquefaction, but it is crucial for pyrolysis. Moreover, catalysts are always essential for liquefaction, whereas they are not as critical for pyrolysis. Compared with pyrolysis, liquefaction technology is more challenging as it requires more complex and expensive reactors and fuel feeding systems [49].

Lignocellulosic biomass materials are the most widely used types of biomass for bio-oil production through liquefaction, as summarized in Table 3.10. Lignocellulosic materials are rich in hydroxyl groups, thus they can be converted into intermediates by liquefaction
for the production of biopolymers, such as epoxy resins, polyurethane foams, adhesives for plywood, etc. [111,114].

Table 3.10

Summary of some work done by previous researchers on direct liquefaction of biomass.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woody materials:</td>
<td>na</td>
<td>no catalyst or K$_2$CO$_3$</td>
<td>[110]</td>
</tr>
<tr>
<td>Cunninghamia lanceolata;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fraxinus mandshurica;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pinus massoniana Lamb.;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Populus tomentosa Carr.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crop residues</td>
<td>ethylene carbonate</td>
<td>sulphuric acid</td>
<td>[111]</td>
</tr>
<tr>
<td>Corn stover</td>
<td>ethylene glycol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice straw</td>
<td>polyethylene glycol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wheat straw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine wood(Pinus desiflora)</td>
<td>ethanol and small</td>
<td>sulphuric acid</td>
<td>[112]</td>
</tr>
<tr>
<td>Poplar wood(Populus alba × glandulosa)</td>
<td>amount of phenol</td>
<td>sulphonic acids</td>
<td></td>
</tr>
<tr>
<td>Sawdusts of white birch</td>
<td>ethylene glycol</td>
<td></td>
<td>[113]</td>
</tr>
<tr>
<td>(Betura Platypylla Sukatchev var. japonica Hara)</td>
<td>ethylene carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japanese cedar</td>
<td>propylene carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Cryptomeria japonica D. Don)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Japanese cypress</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Chamaecyparis obtusa Endl)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood meal of birch (Betula papyrifera Marsh)</td>
<td>phenol</td>
<td>alkalies or salt</td>
<td>[114]</td>
</tr>
<tr>
<td>Wood meal of aspen (Populus tremuloides Michx)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermomechanical pulp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kraft pulp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cotton</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jute fibre</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kenaf plant meal</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the beginning of the liquefaction process, biomass undergoes depolymerization and is decomposed into monomer units. These monomer units, however, may be re-polymerized or condensed into solid chars, which are undesirable. A solvent is generally added to slow down the higher order solid-state reactions, thus reducing the detrimental condensation
reactions [115]. Generally, the biomass liquefaction yield is positively correlated with the dielectric constant of the solvent [111]. For example, Liang et al. [111] observed a much higher liquefaction yield and reaction rate from corn stover using ethylene carbonate as the solvent rather than ethylene glycol for which the dielectric constants for ethylene carbonate and ethylene glycol are 90.5 and 38.4, respectively, at 40°C. Phenol, with a dielectric constant of 15 at 40°C, is also a very effective solvent for lignin liquefaction as it prevents condensation reactions. In addition, phenol can dissolve cellulose in the presence of some catalysts, e.g., zinc chloride [115]. However, phenol recovery from the liquefied material can be challenging. Hence, to solve this problem, a mixture composed of a small amount of phenol and some lower alcohols, which can be easily recovered, can be employed [11,112]. Furthermore, as summarized by Yamada and Ono [113], several organic solvents can convert a large fraction of woody materials into soluble products. Examples of these solvents include dioxane, MDSO, DMF, acetone, and methyl alcohol.

The use of catalysts is a critical factor in biomass liquefaction as it can reduce the required reaction temperature, enhance reaction kinetics, and improve the yield of desired products [114]. Alkalis and acids are the two typical groups of catalysts employed in biomass liquefaction (Table 3.10). Specifically, alkaline catalysts are able to enhance the yield of heavy oils and decrease the formation of residues [110], while acid catalysts (e.g. sulphonic acids and sulphuric acid), although they are capable of decreasing the temperature and time required for the liquefaction of lignocellulosic biomass by enhancing the hydrolysis of cellulosic components, also have the potential to condense lignin materials, consequently increasing the amount of insoluble residue (char) [112].
3.7 Concluding remarks

Bio-energy is an abundant, clean, and renewable energy source derived from biomass. It can be released via direct combustion or co-firing/co-combustion with coal or natural gas to generate heat and electricity, or can be converted into bio-fuels (e.g., syngas, bio-oils, and charcoal) through other thermo-chemical processes, such as pyrolysis, gasification, and direct liquefaction. The co-firing of biomass and coal is the easiest and most economical approach for the generation of bio-energy on a large-sale because of the few modifications that are required to upgrade the original coal-based power plants. Fast pyrolysis has attracted a great deal of attention as it is, to date, the only industrially realized technology for the production of bio-oils. Plasma gasification is mainly applied for hazardous waste treatment because of the high destruction and reduction efficiencies. However, it also has great potential for producing syngas owing to its high yields of H₂ and CO, but extremely low yield of tar. Supercritical water gasification is a promising approach for hydrogen generation from biomass feedstocks, particularly those with high moisture contents, such as sewage sludge. Since water can be considered an effective and “green” solvent, direct liquefaction is also able to process wet biomass feedstocks directly. In contrast to supercritical water gasification, direct liquefaction focuses more on the production of valuable liquid products at comparatively lower temperatures.
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Chapter 4
Energy Recovery from Secondary Pulp/Paper-Mill Sludge and Sewage Sludge with Supercritical Water Treatment

4.1 Abstract

Secondary pulp/paper-mill sludge (SPP) and sewage sludges (primary, secondary, and digested sewage sludges) were treated in supercritical water at temperatures ranging between 400-550°C over 20 to 120 min for energy recovery. Low temperature and short reaction time favoured the formation of heavy oil (HO) products, which were mainly composed of a variety of phenol and phenolic compounds, as well as some nitrogen-containing compounds, long-chain alkenes and alcohols, etc., with high gross calorific values (> 36 MJ/kg). By contrast, the formation of synthetic gases, a mixture of hydrogen, carbon monoxide, carbon dioxide, methane, and other light hydrocarbons, were not significantly affected by reaction time but greatly enhanced with increasing temperature. The highest gas yield was obtained at 550°C, where 37.7 wt% of the SPP (on dry basis) was converted into gases, with hydrogen yields as high as 14.5 mol H₂/kg SPP (on a dry basis). In comparison to sewage sludges, SPP exhibited a greater capability for the production of HO and gases owing to its higher contents of volatiles and alkali metals, indicating a prospective utilization potential for SPP as a source of bio-energy.
4.2 Introduction

Secondary pulp/paper-mill sludge (SPP) is the residue produced in the biological treatment process of wastewaters from the pulp/paper industry. It is a liquid suspension that contains approximately 2 wt% solids, and is composed of cells, biodegradable and recalcitrant organic compounds (e.g., carbohydrates and lignin), as well as ashes. SPP can also be considered a waste biomass that can potentially be recovered into a series of solid (e.g., charcoal), liquid (e.g., bio-oils), and gaseous (e.g., biogas and synthetic gas) bio-fuels using various biological and thermo-chemical processes [1,2].

Supercritical water (SCW) is a special water phase where the pressure and temperature of water are increased to or above their respective critical points (22.1 MPa and 374°C). As a superior reaction medium, SCW is featured as having a high diffusivity, a low viscosity, and a high solvating ability for organic compounds [3]. In addition, water is also an active reactant in steam reforming and water-gas shift reactions (shown below in Eqs. 4.1 and 4.2) in the supercritical region. Therefore, SCW is able to transform biomass feedstock into hydrogen (H$_2$)-rich gaseous products with reduced tar and coke formation, and this process is commonly regarded as supercritical water gasification (SCWG) [4-8].

\[
\begin{align*}
\text{CH}_x\text{O}_y + (1 - y)\text{H}_2\text{O} & \leftrightarrow \text{CO} + (1 - y + \frac{x}{2})\text{H}_2 \quad (4.1) \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (4.2)
\end{align*}
\]
For most conventional thermo-chemical treatment processes, such as combustion, pyrolysis, and gasification, a pre-dried feedstock is typically required [9]. Considering the extremely high water content (>90% on wet mass basis) of sludges, the pre-drying operation would hence be energy and capital intensive. However, sludge can be treated directly with SCW, eliminating the need for drying.

In comparison to anaerobic digestion (biomethanation), a conventional biological method for the methane (CH$_4$)-rich biogas product generation from sludge, SCWG can be considered to be more advantageous in terms of providing a higher treatment efficiency. SCWG requires much less reaction time (several seconds, minutes, to hours for SCWG vs. several days to weeks for anaerobic digestion) to accomplish [10] and is able to destroy lignin compounds, which are typically recalcitrant in anaerobic digestion. In addition, SCWG may be a more capital effective process in comparison to biomethanation, as noted by Matsumura [11]. As such, the use of SCWG for the treatment of sludge for energy recovery was the focus of this research.

A number of studies have recently been conducted on SCWG covering a wide range of biomass feedstocks, such as model compounds (e.g., glucose, cellulose, lignin, and starch), fruit shells, sawdust, rice straw, municipal solid waste, etc. However, there are very few investigations that have focused on the use of sludges as feedstocks. Xu et al. [12] employed ground and homogenized sewage sludge, pumped as a slurry into a supercritical flow-type reactor at a temperature of 600°C and pressure of 34.5 MPa, using coconut shell activated carbon as the catalyst. They observed that with a low feedstock concentration (2.8 wt %) and a low weight hourly space velocity (WHSV) of 0.5 h$^{-1}$,
almost all of the sludge was converted into gaseous product, with a H\textsubscript{2} yield of 13.5 mol H\textsubscript{2}/kg sludge (dry basis). However, they did not attempt to use a higher solids concentration due to the experimental challenge associated with the pumping system. Xu and Antal [13] overcame pumping issues by mixing the sludge in a cornstarch paste and utilizing a cement pump. By doing this, a higher sludge solids concentration (up to 7.69 wt %) could be employed as a feedstock. In this experiment, the temperature and pressure were 650°C and 28 MPa, respectively, and a packed bed of coconut shell activated carbon was also used as the catalyst. At a low solid concentration (2.1 wt % sludge + 5.1 wt % corn starch; flow rate: 2.0 g/min; WHSV: 1.48 h\textsuperscript{-1}), 99% of the feed was converted to a gas product with a mole fraction of H\textsubscript{2} of 42%. When a higher solids concentration of the feedstock was used (7.69 wt % sludge + 7.69 wt % corn starch), the fractions of carbon dioxide (CO\textsubscript{2}) and H\textsubscript{2} were found to decrease, while CH\textsubscript{4} increased, and carbon monoxide (CO) did not change significantly. However, reactor plugging occurred in both of these tests because of the high ash content of the sludge (25.1%, on a dry basis). Zhang et al. [14] studied the effect of reaction temperature (400-600°C), pressure (24-30 MPa), residence time (3-15 min), and catalyst (with and without sodium hydroxide) on the H\textsubscript{2} yield from a sewage sludge sample with a 95% water content, using a continuous flow reactor, in the presence of 30 wt% hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) for partial oxidation. It was observed that higher temperature and pressure, longer residence time, and the presence of a sodium hydroxide (NaOH) catalyst, all contributed to the enhanced H\textsubscript{2} production in this SCWG and partial oxidation process. In addition, the authors evaluated the energy efficiency for this process. In an ideal scenario assuming no external energy loss considering the energy input for pumping and heating, and taking into consideration the energy recovery from hot-pressured water, the estimated energy yield could reach 85%.
As the overall reaction is endothermic, it was recommended that heat recovery from the hot-pressured water would be of significant importance for a better energy yield.

Despite these limited studies on the SCWG of sewage sludge, there is very little documented information on the SCWG behaviour of sludge from industrial sources (e.g., from the pulp/paper industry), although Xu and Lancaster [15] reported on conversion of secondary pulp/paper sludge to bio-oils by direct liquefaction in hot compressed or sub-and near-critical water at 280-380°C. As such, the primary objective of this study was to investigate the potential of recovering energy from secondary pulp/paper sludge by SCWG. More specifically, the effects of reaction temperature, reaction time and sludge dry matter content (or water content) on product yields in the SCWG of SPP for H₂ production were investigated using a batch reactor. In addition, the various forms of products recovered from this SCWG process were characterized with respects to chemical compositions. For comparison, three types of municipal sewage sludges: primary sewage sludge (PS), secondary sewage sludge (SS) and digested sewage sludge (DS) were also examined under similar experimental conditions to those of SPP, to investigate the relationships between sludge composition and product yields.
4.3 Material and methods

4.3.1 Materials

The sludge feedstocks used in this work were the SPP, supplied by the AbitibiBowater Thunder Bay Corporation, and PS, SS, and DS supplied by the Thunder Bay Municipal Wastewater Treatment Plant. DS is the biosolids product resulting from the anaerobic digestion of the PS and SS, which is commonly disposed to landfill after further dewatering. The compositions, in terms of the water content, proximate and ultimate analyses, as well the mineral elemental compositions of each type of sludge are given in Tables 4.1 and 4.2. The solvents used in this work for product separation were distilled water and A.C.S. reagent-grade ethyl acetate and acetone from Canadawide Scientific and used as received.

Table 4.1
Properties of PS, SS, DS, and SPP.

<table>
<thead>
<tr>
<th>Type of sludge</th>
<th>water content (wt%)a</th>
<th>pH</th>
<th>Proximate analysis (wt%)(d.b.)</th>
<th>Ultimate analysis (wt%)(d.b.)</th>
<th>HHVd (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>VM</td>
<td>FC</td>
<td>Ash</td>
</tr>
<tr>
<td>PS</td>
<td>97.2</td>
<td>5</td>
<td>67.8</td>
<td>10.7</td>
<td>21.5</td>
</tr>
<tr>
<td>SS</td>
<td>95.5</td>
<td>8</td>
<td>60.1</td>
<td>12.2</td>
<td>27.7</td>
</tr>
<tr>
<td>DS</td>
<td>97.2</td>
<td>8</td>
<td>48.9</td>
<td>9.30</td>
<td>41.8</td>
</tr>
<tr>
<td>SPP</td>
<td>98.0</td>
<td>9</td>
<td>60.6</td>
<td>15.0</td>
<td>24.4</td>
</tr>
</tbody>
</table>

a Water content = 100% - dry matter content;
b On a dry basis;
c By difference (O%=100%-ash%-C%-H%-N%) assuming negligible sulphur content;
d Higher heating value (HHV) calculated by the Dulong Formula, i.e., HHV(MJ/kg) = 0.3383C + 1.422(H-O/8)
Table 4.2
Mineral elemental compositions of PS, SS, DS, and SPP.

<table>
<thead>
<tr>
<th>Type of sludge</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>0.24</td>
<td>0.34</td>
<td>0.56</td>
<td>1.91</td>
<td>0.03</td>
<td>3.32</td>
<td>0.03</td>
<td>1.57</td>
<td>0.09</td>
<td>1.26</td>
<td>0.25</td>
</tr>
<tr>
<td>SS</td>
<td>0.36</td>
<td>0.72</td>
<td>0.56</td>
<td>2.97</td>
<td>0.14</td>
<td>7.33</td>
<td>0.05</td>
<td>5.81</td>
<td>0.19</td>
<td>4.61</td>
<td>0.57</td>
</tr>
<tr>
<td>DS</td>
<td>0.47</td>
<td>0.76</td>
<td>0.92</td>
<td>4.11</td>
<td>0.14</td>
<td>6.37</td>
<td>0.08</td>
<td>4.80</td>
<td>0.13</td>
<td>4.28</td>
<td>0.79</td>
</tr>
<tr>
<td>SPP</td>
<td>7.04</td>
<td>0.53</td>
<td>0.81</td>
<td>1.42</td>
<td>0.03</td>
<td>0.48</td>
<td>0.06</td>
<td>1.65</td>
<td>0.08</td>
<td>0.87</td>
<td>2.33</td>
</tr>
</tbody>
</table>

a Determined by ICP-OES;  
b On a dry basis.

The water content was determined by measuring the weight loss of each sludge sample before and after it was dried at 105°C in an oven for at least 12 hours. The volatile matter (VM) and fixed carbon (FC) contents were tested by using a thermogravimetric analyzer (TGA)-i1000 (Instrument Specialist Inc.): heating the pre-dried sample in a nitrogen atmosphere at 10°C/min up to 900°C. The ash content was obtained by recording the weight of the remaining portion of the pre-dried sludge sample after it had been burned in a muffle furnace at 575°C for 8 hours. The elemental (e.g., C, H, and N) composition was determined with a CEC (SCP) 240-XA elemental analyzer, and the composition of oxygen (O) was estimated by difference, assuming negligible amounts of sulphur. In addition, the ash samples were analyzed for their mineral composition using a Varian Vista-PRO CCD Simultaneous ICP-OES (inductively coupled plasma-optical emission spectroscopy) with a Cetac ASX-510 Autosampler. Specifically, each ash sample was digested in aqua regia (3:1 HCl/HNO₃) using microwave CEM Mars 5 open vessels for 3 to 4 hours, diluted with distilled deionized water and then injected into ICP using an inert spray chamber with a cross-flow nebulizer. The major operational conditions of the ICP-OES were: power: 1.10 kW; plasma flow: 15.0 L/min; auxiliary flow: 1.50 L/min;
nebulizer flow: 0.75 L/min; replicate time: 15,000s; stabilization time: 20s; and replicates: 3.

4.3.2 Sludge supercritical water gasification

The SCWG tests were performed in a 75 mL Parr High-Pressure reactor, constructed of Hastelloy alloy, with maximum working pressure of 41.37 MPa at 600°C. In each experimental run, approximately 20 g of raw/concentrated/diluted sludge was loaded into the reactor. The residual air in the reactor was completely removed with at least 3 cycles of vacuuming and nitrogen purging. The reactor was pressurized to 2 MPa using high-purity N₂ to prevent the boiling of water during heating, then heated at about 10°C/min to a specified temperature and maintained for a pre-determined period of time (i.e. 20, 40, 60, and 120 min), which represented the reaction times investigated in this research. During each experimental run, the pressure inside the reactor was recorded. Since the reaction pressure was a function of the reaction temperature inside the sealed batch reactor, it could not be adjusted manually. The reaction pressures for the tests throughout the study were all noted to be above 22.1 MPa (the critical pressure for water) at all reaction temperatures. After the desired reaction time elapsed, the reactor was cooled down rapidly to room temperature using a wetted cloth towel.
4.3.3 Separation and analyses of the reaction products

Gas products were collected in a gas cylinder and analyzed with an Agilent 3000 Micro-Gas Chromatograph (GC) equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors (TCDs). The remaining solid/liquid products were recovered thoroughly from the reactor by washing with ethyl acetate solvent and filtered under reduced pressure through a pre-weighed No. 5 filter paper. The solids retained on the filter paper were oven dried at 105°C for at least 12 hours and weighed to obtain the weight of the solid residue (SR), while the filtrate which was composed of an aqueous phase and an ethyl acetate soluble phase was separated in a separatory funnel. As the aqueous filtrate was composed of water-soluble products (WSPs) and the dissolved ethyl acetate, the total organic carbon (TOC) analysis results for the WSPs were not usable. As such, the TOC results for the WSPs were not reported in this paper. The ethyl acetate soluble phase was further transferred into a pre-weighed evaporation flask and evaporated at 56°C at a reduced pressure of 10 KPa to remove the solvent. The remaining brown liquid was weighed and referred to as heavy oil (HO).

The yields of total gas, HO and SR were defined as percentages (%) of the mass of each product in relation to the mass of dried matter in the sludge fed into the reactor prior to the reaction, and the yield of WSPs and pyrolytic water were lumped and calculated by difference. Two to three duplicate runs were conducted for each experimental condition and the average yields were calculated and reported. The error between replicate runs was maintained to within 5% of the yields for most of the gas and solid products while 10% of the yields for most liquid products. Higher reproducibility for the liquid yields was
challenging due to the difficulty in liquid product separation and their low formation amounts in the SCWG process under investigation.

The elemental compositions (C, H, and N) of selected HOs and SRs were determined using a CEC (SCP) 240-XA elemental analyzer, and the composition of oxygen (O) in HOs was estimated by difference assuming negligible contents of sulphur and ash in the samples. In addition, the HO product samples from SCWG of PS, SS, DS, and SPP were dissolved in acetone and analyzed with a Shimadzu gas chromatograph/mass spectrometer (GC/MS)-QP2010S equipped with a SHRXI-5MS capillary column (30m × 0.25mm × 0.25 μm). Approximately 1 μL of HO-acetone solution was injected into the instrument in a split mode with a split ratio of 20.0. The column temperature was initially 40°C, held for 2 min, and raised to 190°C at a heating rate of 12°C/min. The column was then heated at a heating rate of 8°C/min to 290°C, followed by another isothermal hold for 30 min at this temperature. The ion source and interface temperature were set at 200°C and 275°C, respectively. Data was acquired in a scan mode with a solvent cut time of 2.5 min, and the m/z ranged between 40 and 500. The obtained chromatographic peaks were identified using the WILEY8 library.
4.4 Results and discussions

4.4.1 Effects of temperature

The product yields obtained at various reaction temperatures (400-550°C) are presented in Fig. 4.1. The corresponding pressures inside the reactor were 23.79 MPa (400°C), 30.34 MPa (450°C), 37.00 MPa (500°C), and 45.51 MPa (550°C), respectively, indicating that water in all cases was in supercritical state. The gaseous products were mainly composed of H₂, CO, CO₂, CH₄, and small quantities of light C₂ and C₃ compounds, such as ethylene (C₂H₄), ethane (C₂H₆), acetylene (C₂H₂), propane (C₃H₈), and propylene (C₃H₆).

As expected, higher temperature facilitated the formation of gases, which is in good agreement with Demirbas [5] and Zhang et al. [14]. In addition, an increase in the yield of SR and a decrease in the yield of HO were also observed as temperature was increased. Specifically, at the low temperature of 400°C, the yield of gaseous products was 16.4 wt%, while the yields of HO and SR were as high as 28.8 wt% and 29.1 wt%, respectively. As the temperature increased from 400°C to 500°C, the yield of gas products was improved considerably to 30 wt% (almost double that observed at 400°C) at the expenses of HO (17 wt% yield) and SR (26 wt% yield). As the temperature was increased further, from 500 to 550°C, the gas yield was further increased at the expense of HO, suggesting cracking of the heavy oil product into gases. From a thermodynamic perspective, a high temperature favours gas formation, since the overall biomass SCWG process is endothermic [4].
Fig. 4.1 Effects of temperature on product distribution in different phases (a), and yields of main gaseous products (H2, CO2, CO and CH4) (b) from SCWG of raw SPP for 60 min. (Lines are added to guide the eye.)

As the temperature was increased from 500 to 550°C, however, a surprisingly large increase in the yield of SR, from 26 wt% at 500°C to 39 wt% at 550°C, was observed. Similar results, where the formation of SR (or char) increased with temperature, were
observed in previous work by Xu and Lancaster [15], when liquefying SPP in hot-compressed water (280-380°C). The increase in char formation at higher temperatures could be attributed to the condensation of the lighter fragments (intermediates) derived from cellulose and lignin compounds in the system [6,7]. For example, phenolic compounds and formaldehydes, both of which are hydrolysis products from lignin, may polymerize into high molecular-weight condensed products or solid chars via condensation/cross-linking reactions. These phenol and phenolic compounds may not only be decomposed from lignin compounds, but can also be converted from glucose/fructose, the products of cellulose hydrolysis [16]. Hence, it is likely that the increase in gases and solids resulted from the cracking or the condensation of the phenolic compounds in the HO. Additionally, it has been widely accepted that as temperature increases, the dehydration of low-molecular-weight carbohydrates and some soluble organic acids, present in the WSPs as a product of lignocellulosic or cellulose feedstock hydrolysis, would occur at a high temperature to form oily intermediates which would further be condensed into char [6]. As shown in Fig. 4.1a, the net increase in SR yield (~14 wt%) was almost balanced by a corresponding decrease in WSPs+H₂O yield as temperature increased from 500°C to 550°C, implying the possibility of WSPs dehydration to form oily intermediates, followed by the condensation of these intermediates into char at 500-550°C.

The production of H₂ and other combustible gases were of primary interest in this study. The yields of each main gaseous compound (e.g., H₂, CO, CO₂, and CH₄) in mole per kg of sludge (on a dry basis) are presented in Fig 4.1b. As was expected, the yield of all
individual gas components (except CO) increased continuously with temperature. In particular for H₂ and CH₄ formation, significant increases were observed between 500 and 550°C. Overall, increasing the temperature from 400°C to 550°C led to an almost 10-fold increase in the yields of H₂ and CH₄, the H₂ yield reaching as high as 14.5 mol/kg dried sludge at 550°C, which was comparable to the results reported by Xu et al. [12] who obtained a H₂ yield of 13.5 mol H₂/kg sewage sludge (dry basis) at 600°C, 34.5 MPa and WHSV of 0.5 h⁻¹ with a supercritical flow-type reactor using coconut shell activated carbon as the catalyst.

4.4.2 Effects of reaction time

The product yields and the formation of the main gaseous products (H₂, CO₂, CO and CH₄) from the SCWG of raw SPP (dry matter content: 2 wt%) at 500°C over various reaction times (20-120 min) are shown in Fig. 4.2. Compared with temperature, reaction time had a lower influence on SR yields and total gas yields (Fig. 4.2a), as well as the yield of individual gaseous species such as H₂, CO, CO₂ and CH₄ (Fig. 4.2b). These results were generally consistent with previous work by Xu and Lancaster [15] treating a similar SPP feedstock in hot-compressed water. The results (Fig. 4.2a) indicated that reaction time significantly affected the distribution of the liquid products between HO and WSPs, where the lumped WSPs+H₂O yield increased at the expense of the HO yield as reaction time increased from 20 to 120 min at 500°C. Williams and Onwudili [17] investigated the effect of reaction time on product distribution using glucose as the model compound for biomass, and similar results were obtained where a significant decrease in HO yield corresponded to a higher WSPs yield at a longer reaction time. The above result
implies the conversion of HO to WSPs with longer residence time, which is probably via hydration reactions. However, the mechanism governing the conversion of HO into WSPs is not yet clear. Future work is thus needed.

Fig. 4.2 Effects of reaction time on product distribution in different phases (a), and yields of main gaseous products (H₂, CO₂, CO and CH₄) (b) from SCWG of raw SPP at 500°C. (Lines are added to guide the eye.)
4.4.3 Effects of dry matter content (water content) in the sludge feedstock

In this study, the raw SPP with an original solid concentration of 2.0 wt% was thickened by vaporization of water to produce condensed feedstock with dry matter contents of 6.0 wt% and 8.8 wt%, respectively, to investigate the effects of dry matter content on product yields. The results are illustrated in Fig. 4.3. It can be noted from Fig. 4.3a that the change in feedstock dry matter content did not result in a significant change in the SR yield. However, the dry matter content of the feedstock did influence the yields of gaseous and liquid products. Generally, an increase in the dry matter content of the feedstock from 2 wt% to 8.8 wt% was accompanied by decreased yields of HO and total gas (Fig. 4.3a), but an increased WSPs yield. An increase in the dry matter content of the feedstock also led to significant reductions in the formation of H2 and CO2, while the effect of feedstock dry matter content on the formation of CO and CH4 gases was minimal (Fig. 4.3b). Similar results were reported in other work by Kruse et al. [8] and Onwudili and Williams [18], where a lower water density (or higher dry matter content) decreased H2 production. Kruse [19] has summarized the following two equations (Eqs. 4.3 and 4.4) for H2 and CH4 formation from glucose, respectively:

\[ C_6H_{12}O_6 + 6H_2O \leftrightarrow 6CO_2 + 12H_2 \]  
\[ C_6H_{12}O_6 \leftrightarrow 3CO_2 + 3CH_4 \]
It can be seen that 6 mol of water is required to convert 1 mol of \( \text{C}_6\text{H}_{12}\text{O}_6 \) into \( \text{H}_2 \)-rich gas, whereas no water is needed for \( \text{CH}_4 \) formation. Therefore, \( \text{H}_2 \) formation was suppressed as the water content decreased.
4.4.4 Effects of different sources of sludge

Four types of raw sludge as received, i.e., PS, SS, and DS from a municipal source, and the SPP from an industrial source, were investigated for their potential for \( \text{H}_2 \) production via SCWG. The products yields at 500\(^\circ\)C for 60 min are displayed in Fig. 4.4. Clearly, SPP appeared to be the best candidate among these four feedstocks since it exhibited the highest yields of valuable products such as \( \text{H}_2 \), \( \text{CH}_4 \), and oil. Conversely, DS showed the least potential due to its low yields of gas and oil, but a high yield of SR.

To eliminate any possible influence caused by the different levels of water content (dry matter content), the three municipal sewage sludges: PS, SS, and DS, were diluted with distilled water to obtain a similar dry matter content (~2 wt%) as that of SPP to evaluate their potentials for gas production in SCW. SCWG of these sludge feedstocks was also performed at 500\(^\circ\)C for 60 min, and the yields of gas, HO, and solid SR products, as well as the yields of the major gaseous components are illustrated in Fig. 4.5.
Fig. 4.4 Effects of various types of sludges (raw) on product distribution in different phases (a) and yields of main gaseous products (H₂, CO₂, CO and CH₄) (b) from the SCW treatment at 500°C for 60 min.
Fig. 4.5 Effects of various types of sludges (whose dry matter contents were adjusted to approximately 2 wt%) on product distribution in different phases (a) and yields of main gaseous products (H₂, CO₂, CO and CH₄) (b) from SCWG at 500°C for 60 min. (PS’’: a modified primary sewage sludge with an initial pH of 9.)

Obviously, product distribution and gas formation are strongly dependent on the type of sludge (or the properties of the feedstock). Similar to that observed from Fig. 4.4, SCWG of SPP produced the highest yields of total gas, HO as well as the yields of H₂, CH₄ and
With respect to the production of H₂ and CH₄ and HO, the four types of sludges tested in this work showed the following priority sequence: SPP > PS > SS > DS. The difference in the performance of these feedstocks may be associated with their distinct compositional characteristics, such as the contents of volatile matter and ash as well as the ash compositions (alkali metal content). Specifically, the low yields of total gas and individual gas species of H₂, CH₄ and CO₂ from DS was likely due to its low content of volatile matter (Table 4.1). Moreover, an alkaline environment was proven to decrease the degradation temperature of cellulose, a major component in biomass material, and to reduce the yields of tars/chars by suppressing the formation of tar-precursor compounds such as furfurals and 5-hydroxymethylfurfural (5-HMF) [20,21]. In addition, the presence of alkali is also effective for improving biomass gasification and H₂ formation due to its catalytic effects on the water-gas shift reaction (Eq. 4.2) through the mechanism involving the formation of metal formate and CO [8,14,20]. Furthermore, Onwudili and William [20] proposed that the removal of CO₂ as sodium carbonate or bicarbonate in a NaOH surrounding also contributed to shift the water-gas reaction towards the formation of hydrogen gas. As shown in Table 4.2, the SPP feedstock contained high concentrations of alkali metals, e.g., 7.04 wt% Na in relation to <0.5% Na for the other feedstocks (PS, SS, and DS). In addition, it also exhibited the highest pH among these sludges (Table 4.1). These two factors might account for the greater yields of total gas and H₂ from SPP. To validate this explanation, several drops of concentrated NaOH solution were added to PS to increase its pH from 5 to 9 (labeled as PS” in Fig. 4.5). As predicted, greatly enhanced yields of gaseous species (H₂ and CH₄ and CO₂), with the exception of CO were observed (Fig. 4.5a). As shown in Fig. 4.5b, it can be seen that the H₂ yield from PS” was almost 6 times that of PS, accompanied by a great increase in CO₂ yield and a drastic decrease in
CO yield, suggesting a catalytic effect of NaOH on the water-gas shift reactions. Although different from what was obtained by Onwudili and Williams [20] where a significant amount of CO₂ was converted into carbonates or bicarbonates in the aqueous phase, the carbonates or bicarbonates-combined CO₂ would not be significant in the study due to the acidity of the aqueous phase (pH~6). Moreover, the dissolved CO₂ in the aqueous phase was less significant either (accounting for only 3-4% of the amount of CO₂ in the gaseous phase, based on Henry’s Law calculation). Accordingly, the CO₂ formed in this study was believed mainly present in the gaseous phase.

In addition, as shown in Table 4.2, although SPP had a higher Na content than SS, SS contained higher levels of Ca, Fe, Al, and P. Ca and Fe have been noted by other researchers to be effective in enhancing hydrogen yield from coal or biomass material via SCWG [22,23], therefore they might have promoted hydrogen production from SS to some extent as well. However as shown in Fig. 4.5, despite that SPP and SS exhibited similar VM contents (Table 4.1), the hydrogen yield from SS was much lower than that from SPP. One possible reason was the pH: the pH of SS was lower than that in SPP (8 in SS vs. 9 in SPP). It is also possible that the catalytic effects of Ca and Fe were not as obvious as that of Na, or that the presence of P or other compounds exerted negative influence and thus decreasing hydrogen yield. Future work is needed to clarify the contribution of each compound in this complex reaction system.
4.4.5 Characterization of the liquid/solid products

Carbon balance has been commonly employed to evaluate the material balance for various biomass conversion processes. It is, however, very difficult to test the level of TOC in the aqueous phase due to the presence of the dissolved ethyl acetate. In addition, for most tests the mass of solid feed was very small (i.e. approximately 0.4 g), hence, the quantities of recovered products were not large enough for CHN elemental analysis. Consequently, carbon balance analysis was not performed in the present study. However, the fractions of recovered carbons from the gaseous products (e.g., CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈, C₃H₆, etc.) in all the tests have been calculated and were found to fall into the range of 12.6-33.6 wt%. In addition, the CHN elemental analysis has been performed on the HO and SR products from the condensed SPP (with the dry matter content of 8.8 wt%) and the original SS (with the dry matter content of 4.5 wt%). For both tests, approximately 30 wt% of the total carbon from the feedstock went into the HOs (32.1 wt% for the condensed SPP and 30.0 for the original SS), while only less than 8 wt% of the carbon retained in SRs (7.33 wt% for the condensed SPP and 4.29 for the original SS), indicating high biomass conversion efficiencies.

As the by-products of the SCWG process, the elemental and chemical compositions of the HOs are of particular interest in this work. The elemental (C, H, and N) analysis results for the HOs from SCWG of the condensed SPP and the original SS are presented in Table 4.3. From this table it can be seen that both HOs exhibited very high carbon contents (i.e. ~80%) and very low oxygen content (i.e. ~9%) compared with the respective feedstock (Table 4.1). This translates to much higher gross calorific values of the oils (> 36 MJ/kg),
more than twice those for the original dried sludge powders. The increased energy density from sludge to HO would provide a greater ease of utilization, storage and transportation of the liquid fuels. In addition, the calculated empirical formula shows that the organic compounds within the HO have a high degree of unsaturation, indicating the presence of aromatics of benzene, phenol, or their derivatives.

**Table 4.3**

Elemental compositions of the heavy oils obtained from SCWG of original SS and condensed SPP at 500°C for 60 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental compositions (wt%)(d.b.ª)</th>
<th>HHVª (MJ/kg)</th>
<th>Empirical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO from SS</td>
<td>77.3 8.8 3.5 10.4</td>
<td>36.8</td>
<td>CH$<em>{1.37}$O$</em>{0.101}$N$_{0.0392}$</td>
</tr>
<tr>
<td>HO from SPP</td>
<td>80.7 8.6 3.3 7.4</td>
<td>38.2</td>
<td>CH$<em>{1.27}$O$</em>{0.0691}$N$_{0.0347}$</td>
</tr>
</tbody>
</table>

*ª On a dry basis;  
*ªª By difference (O% = 100% - C% - H% - N%) assuming negligible sulphur and ash contents;  
*ª Higher heating value (HHV) calculated by the Dulong Formula, i.e., HHV(MJ/kg) = 0.3383C + 1.422(H-O/8)

Table 4.4 presents the GC/MS analysis results of the HO products obtained from SCWG of the four types of raw sludge at 500°C for one hour. The chemical compounds were identified using the WILEY8 library based on the GC/MS chromatographs. The relative area% for each compound identified (defined by percentage of the compound’s chromatographic area out of the total area) is shown in the table. To better understand the contents, a typical chromatogram of the HO product is also displayed (Fig. 4.6). It can be seen that the compositional differences were relatively small among the HOs originating from various sources. Phenol and phenolic compounds (e.g., phenol, 2-methyl-, phenol, 2,6-dimethyl-, etc.) were the major components of all these four types of HOs. In addition, there were also a variety of alkanes (e.g., heptanes and hexane, 2,3,5-trimethyl-),
cycloalkane and cycloalkene derivatives (e.g., cyclohexane, 1,2-dimethyl-, trans- and 2-cyclopenten-1-one, 2-methyl-), furan derivatives (e.g., furan, 2,5-dimethyl- and 2(3H) furanone, dihydro-), long-chain alcohols (e.g., 1-tetradecanol and 1-octadecanol) and alkenes (e.g., 1-heptadecene and 1-pentadecene), pyridine derivatives (e.g., pyridine, 3-methyl- and 2-pyridinamine), and 1H-indole and derivatives (e.g., 1H-indole, 3-methyl- and 1H-indole, 2,3-dimethyl-). Considering the complexity in sludge compositions, it is very difficult to identify the reaction pathways of these compounds. Some of the compounds may have originated from the waste. Some may be converted from sugars and other compounds through hydrolysis, dehydration, hydrogenation, carbon-carbon scission, cyclization, Diels-Alder cycloaddition, ring expansion, contraction (ring rearrangement), etc. [16,17]. For example, the phenolic compounds primarily originated from degradation of lignin, although they might also form from cellulose via hydrolysis to sugars followed by dehydration and ring closure reactions [16]. The long-chain alkenes and alcohols were probably converted from fatty acids in biomass cells or they were initially present in the sewage. As a basic unit of cellulose polymers, glucose can be converted into a variety of compounds. As proposed by Williams and Onwudili [17], the furan, 2,5-dimethyl-, and 2-cyclopenten-1-one, 2-methyl- as detected in this study, were probably converted from glucose involving the formation of 5-HMF. In another proposed reaction pathway, glucose could firstly hydrolyze into erythrose, which would further convert into 2(3H) furanone, dihydro-, another compound detected in the HO. In the present research, each of the four types of sludge has certain amount of nitrogen-containing organic compounds, such as proteins, amino acids, urea, etc. These compounds might react with sugars to form pyridines via the Maillard reaction [24,25].
Table 4.4
GC/MS qualitative analysis results for the heavy oils obtained from SCWG of four types of raw sludges (PS, SS, DS, and SPP) at 500°C for 60 min.

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Compound name</th>
<th>PS</th>
<th>SS</th>
<th>DS</th>
<th>SPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.058</td>
<td>Heptane</td>
<td>1.79</td>
<td>2.30</td>
<td>1.50</td>
<td>3.09</td>
</tr>
<tr>
<td>3.194</td>
<td>Furan, 2,5-dimethyl-</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>0.72</td>
</tr>
<tr>
<td>4.051</td>
<td>Benzene, methyl-</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>4.216</td>
<td>Cyclohexane, 1,2-dimethyl-, trans-</td>
<td>nd</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>0.76</td>
</tr>
<tr>
<td>4.240</td>
<td>Butyric acid</td>
<td>1.36</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>4.792</td>
<td>Hexane, 2,3,5-trimethyl-</td>
<td>&lt;0.52</td>
<td>0.56</td>
<td>0.32</td>
<td>0.86</td>
</tr>
<tr>
<td>4.842</td>
<td>4-Hydroxypentan-2-one</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>nd</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>4.906</td>
<td>Heptane, 2,4 (or 2,5 or 2,6)-dimethyl-</td>
<td>0.54</td>
<td>1.86</td>
<td>1.41</td>
<td>3.27</td>
</tr>
<tr>
<td>5.542</td>
<td>Pyridine, 3-methyl-</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>5.791</td>
<td>Pentanoic acid</td>
<td>0.94</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>6.260</td>
<td>2-Cyclopenten-1-one, 2-methyl-</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>6.332</td>
<td>2(3H) Furaneone, dihydro-</td>
<td>1.13</td>
<td>0.68</td>
<td>0.42</td>
<td>nd</td>
</tr>
<tr>
<td>6.567</td>
<td>Benzene, (1-methylethyl)-</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>7.267</td>
<td>Hexanoic acid</td>
<td>0.52</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>7.374</td>
<td>Phenol</td>
<td>8.86</td>
<td>9.65</td>
<td>14.28</td>
<td>11.87</td>
</tr>
<tr>
<td>8.271</td>
<td>2-Cyclopenten-1-one, 2,3-dimethyl-</td>
<td>0.75</td>
<td>&lt;0.56</td>
<td>0.37</td>
<td>1.34</td>
</tr>
<tr>
<td>8.451</td>
<td>Phenol, 2-methyl-</td>
<td>10.61</td>
<td>6.71</td>
<td>13.27</td>
<td>3.15</td>
</tr>
<tr>
<td>8.724</td>
<td>Phenol, 4-methyl-</td>
<td>14.09</td>
<td>17.96</td>
<td>18.49</td>
<td>9.21</td>
</tr>
<tr>
<td>8.994</td>
<td>Phenol, 2-methoxy-</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>9.018</td>
<td>3(or 4)-Pyridinol</td>
<td>2.65</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>9.142</td>
<td>2(or 3)-Pyridinamine</td>
<td>nd</td>
<td>0.74</td>
<td>&lt;0.32</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>9.216</td>
<td>Phenol, 2,6-dimethyl-</td>
<td>2.71</td>
<td>1.23</td>
<td>2.7</td>
<td>&lt;0.67</td>
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<tr>
<td>9.595</td>
<td>Phenol, 2-ethyl-</td>
<td>0.84</td>
<td>0.61</td>
<td>0.69</td>
<td>0.67</td>
</tr>
<tr>
<td>9.734</td>
<td>Phenol, 2,4-dimethyl-</td>
<td>11.03</td>
<td>6.55</td>
<td>10.87</td>
<td>2.5</td>
</tr>
<tr>
<td>9.960</td>
<td>Phenol, 4-ethyl-</td>
<td>3.61</td>
<td>5.36</td>
<td>4.04</td>
<td>5.54</td>
</tr>
<tr>
<td>10.334</td>
<td>1,2-Benzenediol</td>
<td>2.37</td>
<td>1.46</td>
<td>1.8</td>
<td>nd</td>
</tr>
<tr>
<td>10.497</td>
<td>Phenol, 2,3,5-trimethyl-</td>
<td>2</td>
<td>1.47</td>
<td>2.23</td>
<td>nd</td>
</tr>
<tr>
<td>10.75</td>
<td>Phenol, 2-ethyl-6-methyl-</td>
<td>0.87</td>
<td>1.08</td>
<td>1.02</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>10.998</td>
<td>Isoquinoline</td>
<td>0.63</td>
<td>0.71</td>
<td>0.47</td>
<td>0.69</td>
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<tr>
<td>11.516</td>
<td>1-Decene</td>
<td>0.79</td>
<td>0.84</td>
<td>0.57</td>
<td>1.65</td>
</tr>
<tr>
<td>11.634</td>
<td>1H-Indole</td>
<td>1.47</td>
<td>2.92</td>
<td>1.86</td>
<td>4.21</td>
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<tr>
<td>11.899</td>
<td>Phenol, 4-allyl-</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>1.08</td>
</tr>
<tr>
<td>11.918</td>
<td>Naphthalene, 2-methyl-</td>
<td>0.78</td>
<td>0.79</td>
<td>0.48</td>
<td>&lt;0.67</td>
</tr>
<tr>
<td>12.145</td>
<td>1H-Inden-5-ol, 2,3-dihydro-</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>1.03</td>
</tr>
<tr>
<td>12.259</td>
<td>1-Tetradecene</td>
<td>nd</td>
<td>0.83</td>
<td>0.42</td>
<td>0.77</td>
</tr>
<tr>
<td>12.719</td>
<td>1H-Indole, 3-methyl-</td>
<td>1.22</td>
<td>2.17</td>
<td>1.4</td>
<td>2.65</td>
</tr>
<tr>
<td>13.554</td>
<td>1-Heptadecene</td>
<td>0.96</td>
<td>1.62</td>
<td>&lt;0.32</td>
<td>2.4</td>
</tr>
<tr>
<td>13.743</td>
<td>1-Pentadecene</td>
<td>nd</td>
<td>1.43</td>
<td>0.66</td>
<td>nd</td>
</tr>
<tr>
<td>13.864</td>
<td>1H-Indole, 2,3 (or 2,5)-dimethyl-</td>
<td>0.96</td>
<td>0.92</td>
<td>&lt;0.32</td>
<td>0.96</td>
</tr>
<tr>
<td>15.785</td>
<td>1-Tetradecanol</td>
<td>&lt;0.52</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>1.21</td>
</tr>
<tr>
<td>17.742</td>
<td>1-Octadecanol</td>
<td>nd</td>
<td>0.80</td>
<td>&lt;0.32</td>
<td>1.32</td>
</tr>
<tr>
<td>18.555</td>
<td>Anthracene, 1-methyl-</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>1.22</td>
</tr>
<tr>
<td>18.559</td>
<td>Hexadecanoic acid</td>
<td>0.55</td>
<td>&lt;0.56</td>
<td>&lt;0.32</td>
<td>nd</td>
</tr>
<tr>
<td>21.599</td>
<td>Phenanthrene, 1-methyl-7-(1-methylethyl)-</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>2.44</td>
</tr>
</tbody>
</table>

*a nd = not detected*
Fig. 4.6 GC/MS chromatogram of the heavy oil product obtained from SCWG of PS at 500°C for 60 min. The labeled major components are A: heptane; B: 2-pentanone, 4-hydroxy-4-methyl- (from acetone); C: phenol; D: phenol, 2-methyl-; E: phenol, 4-methyl-; F: 3(or 4)-pyridinol; G: phenol, 2, 6-dimethyl-; H: phenol, 2,4-dimethyl-; I: phenol, 4-ethyl-; J: 1,2-benzenediol; K: phenol, 2,3,5-trimethyl-; L: 1H-indole; M: 1H-indole, 3-methyl-.

4.5 Conclusions

A comprehensive study on the SCWG of four types of sludge feedstocks, supplied from pulp/paper-mill and municipal wastewater treatment plants was conducted. Process parameters including reaction temperature, reaction time, dry matter content, and type/properties of the sludge were investigated to explore SCWG as a potential technology for the cost-effective disposal of high-water-content sludge and for energy recovery. The major conclusions of this work may be summarized as follows:
1) A higher temperature favoured gasification reactions, while decreasing the yield of HO products. The yield of H\textsubscript{2} was increased significantly from 1.5 to 14.5 mol/kg sludge (on a dry basis) by increasing the reaction temperature from 400 to 550\degree C.

2) Reaction time was observed to be less effective for varying the yields of gas and solid residual products, while a longer reaction time could inhibit HO formation.

3) A high water content (or a low dry matter content) of the sludge was demonstrated to be favourable for high yields of total gas and H\textsubscript{2}.

4) Secondary pulp/paper-mill sludge (SPP) exhibited a greater potential for recovering energy, particularly for H\textsubscript{2} production, than the sludges from municipal wastewater treatment plant. The better performance of SPP in SCWG for H\textsubscript{2} production could most likely be attributed to its higher contents of volatile matters and alkali salts, as well as the high pH value of the feedstock.

5) Based on the GC/MS analysis, phenol and phenolic compounds were the major components of the HO products. In addition, there were also various types of alkanes, cycloalkane and cycloalkene derivatives, furan derivatives, pyridine and 1H-indole derivatives, as well as long-chain alkenes and alcohols. In comparison to the raw sludge powders, the heating values of the HOs (> 36 MJ/kg for HOs vs. ~15MJ/kg for the raw sludge powders) were significantly improved.
4.6 References


Chapter 5
Bio-Crude Production from Secondary Pulp/Paper-Mill Sludge and Waste Newspaper via Co-Liquefaction in Hot-Compressed Water

5.1 Abstract

Co-liquefaction of secondary pulp/paper-mill sludge (solids concentration: 1.6 wt%) and waste newspaper with a total solids concentration of 11.3 wt% was investigated with and without the addition of catalysts in a 75 ml Parr High-Pressure reactor at temperatures of 250-380°C for 20 min. The yield of heavy oil (HO) without catalyst was between 16.7 and 28.0 wt% within this temperature range, and peaked at 350°C. The addition of HCO$_2$H, FeS, or KOH at 5 wt% of the total solids (on a dry basis) was found to enhance the HO yield at 300°C, particularly HCO$_2$H, which increased the yield of HO from 24.9 to 34.4 wt%. More interestingly, synergistic effects between secondary pulp/paper-mill sludge and waste newspaper were observed in the co-liquefaction operations. For example, the HO yield attained was 26.9 wt% at 300°C in the co-liquefaction of the mixture of 33 wt% sludge-67 wt% waste newspaper, and was noted to be 9 wt% and 6 wt% higher than the yields obtained from liquefaction of sludge and waste newspaper alone, respectively. The HOs from liquefaction or co-liquefaction at 300°C for 20 min exhibited significantly higher energy contents (HHV≥30 MJ/kg), almost doubled those (~16 MJ/kg) of the original feedstocks.
Secondary pulp/paper-mill sludge (SPP) is the residue produced in the biological treatment process of wastewaters from the pulp/paper industry. It is a liquid suspension that contains approximately 2 wt% solids, and is composed of biodegradable and recalcitrant organic compounds, as well as heavy metals. SPP can also be considered a waste biomass with stored chemical energy that can potentially be recovered through various biological and thermo-chemical processes [1,2].

High-pressure direct liquefaction is a thermo-chemical process that converts biomass feedstocks into valuable liquid organic products (phenols, carboxylic acids, aldehydes, ester, carbohydrates, etc.) at temperatures ranging between 150 and 420°C in the presence of appropriate solvents [3]. Water (hot-compressed or sub/supercritical waters) is an effective and “green” solvent for the direct liquefaction of biomass and, given the high water content of sludge, it can act directly in the liquefaction process. Hence, the energy-and-capital-intensive dewatering/drying step, which is typically required for most conventional thermo-chemical treatment processes (e.g., incineration, pyrolysis, gasification, etc.), can be eliminated [4]. In addition, direct liquefaction offers advantages over anaerobic digestion with respect to higher reaction rates and the ability to decompose lignin compounds [5].

The liquefaction of SPP powder in hot-compressed water was investigated by Xu and Lancaster [6], where approximately 60 wt% of the sludge organic matter was converted
into water-soluble oils (20-45 wt%) and heavy oils (HOs) (15-25 wt%) when treated at temperatures ranging between 250 and 380°C for 15-20 min. The HO products obtained had gross calorific values higher than 35 MJ/kg. In addition, the liquefaction of dewatered sewage sludge has been examined by other researchers [7-9] at temperatures ranging between 250 and 340°C, with reported oil yields reaching as high as 50 wt%. In all of the abovementioned studies, the sludge was thickened either by vaporization of the water or mechanical dewatering processes to achieve a high solids content (> 10 wt%). However, to reduce the cost associated with dewatering, the raw sludge can also be pre-mixed and co-liquefied with other waste biomass feedstocks, such as agricultural/forestry waste streams and municipal solid waste (MSW). In this work, waste newspaper was used as a typical MSW, as it is readily available, homogeneous, relatively consistent in composition, and has high volatile and lignin contents [10]. Moreover, the use of waste newspaper for the production of used newspaper pulp has become less promising in recent years due to the shrinking paper demand worldwide, especially in North America. The alternative use of waste newspaper as a source of bio-energy and bio-fuels is thus of particular interest with respects to both waste disposal and energy recovery from MSWs.

Catalysts have been reported to significantly affect biomass liquefaction processes by improving the yield of valuable liquid products, but suppressing the formation of chars [6,11-16]. The most widely employed catalysts are alkaline solutions (e.g., potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium carbonate (K₂CO₃), sodium carbonate (Na₂CO₃), rubidium carbonate (Rb₂CO₃), sodium formate (HCO₂Na), potassium formate (HCO₂K), etc. [6,11-15]). In addition, some iron-based catalysts (e.g.,
iron (II) sulphide (FeS), iron (II) sulphate (FeSO₄) [16], and iron ore powder [17]), formic acid (HCO₂H) [13], cobalt catalyst (e.g., cobalt oxide (Co₃O₄)) [13], and nickel catalyst (e.g., Engelhard, NI-3288, ca. 50 wt% nickel on silica-alumina; this catalyst was crushed and treated in a reducing atmosphere at 350°C for 4 hour prior to use) [14] have also been reportedly utilized in biomass liquefaction processes.

The objective of this research was to investigate the effects of reaction temperature and the addition of selected catalysts (KOH, HCO₂H, and FeS) on product yields in the co-liquefaction of SPP/newspaper mixtures in a batch process. In addition, various SPP-to-newspaper mixing ratios were tested under similar experimental conditions to explore the synergistic effects between these two types of feedstocks.

5.3 Materials and methods

5.3.1 Materials

The sludge feedstocks used in this work was SPP, supplied by the AbitibiBowater Thunder Bay Corporation, with an initial dry solids (total suspended solids, TSS) concentration of approximately 1.6 wt% and a higher heating value (HHV) of 16.9 MJ per kg of TSS on a dry mass basis. In most cases, the SPP was used directly as received (raw SPP) in this work. However, for some particular tests, the SPP was dewatered either to a slurry with a dry solid concentration of 11.3 wt% (dewatered SPP) or to dried powders (dried SPP powder). Used newspaper collected locally was employed as the
waste newspaper in the tests. The collected waste newspaper was soaked in water for 24 hours, and then crushed into pulps with a domestic-use blender. The pulps were filtered and then dried at 105°C for 12 hours, ground with a Wiley Mill into particles < 20 mesh, and stored for future use. Results of the proximate/ultimate analyses, mineral elemental compositions, and lignin contents of the SPP and newspaper are given in Table 5.1. As shown in the table, compared with the waste newspaper, the SPP exhibited higher fixed carbon, FC (15.97 wt% vs. 9.90 wt% for the waste newspaper), lower volatile matter, VM (58.74 wt% vs. 89.66 wt% for the waste newspaper), and slightly lower lignin (16.85 wt% vs. 21.06 wt% for the waste newspaper) contents on a dry mass basis. The SPP, however, had a much higher ash content, 25.3 wt% d.b. (mainly Al, Ca, Fe, K, Mg, Na, S and Si) than the waste newspaper (0.4 wt% ash). The solvents used for product separation were distilled water and A.C.S. reagent-grade acetone purchased from the Canadawide Scientific and used as received. The catalysts were A.C.S. reagent-grade KOH, FeS and HCO$_2$H, received from Sigma-Aldrich.
Table 5.1
Proximate/ultimate analyses, mineral elemental compositions, and lignin contents of SPP and newspaper.

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis (wt%)(d.b.)</th>
<th>Ultimate analysis (wt%)(d.a.f.)</th>
<th>Lignin content (wt%)(d.b.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM&lt;sup&gt;b&lt;/sup&gt; FC&lt;sup&gt;b&lt;/sup&gt; Ash&lt;sup&gt;c&lt;/sup&gt;</td>
<td>C H N O&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>SPP</td>
<td>58.7 16.0 25.3</td>
<td>41.3 5.1 4.5 23.9</td>
<td>16.9</td>
</tr>
<tr>
<td>Newspaper</td>
<td>89.7 9.9 0.4</td>
<td>48.6 5.7 0 45.3</td>
<td>21.1</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Mineral elemental composition&lt;sup&gt;h&lt;/sup&gt; (wt%)(d.b.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al     Ba    Ca    Fe    K     Mg    Mn    Na    P    S    Si    Zn</td>
</tr>
<tr>
<td>SPP</td>
<td>1.36   0.02  1.04  0.39  0.37  0.63  0.03  4.9  0.67  1.35  0.24  0.05</td>
</tr>
<tr>
<td>Newspaper</td>
<td>0.02   &lt;0.01 0.11  0.02  &lt;0.01 0.02 &lt;0.01 0.04 &lt;0.01 0.03 0.01 &lt;0.01</td>
</tr>
</tbody>
</table>

<sup>a</sup> On a dry basis;
<sup>b</sup> VM= volatile matter, FC= fixed carbon; determined by using a thermogravimetric analyzer (TGA)-i1000 (Instrument Specialist Inc.)
<sup>c</sup> Ashed at 575°C for 8 hours in air;
<sup>d</sup> Determined with a CEC (SCP) 240-XA elemental analyzer
<sup>e</sup> On a dry-and-ash-free basis;
<sup>f</sup> By difference (O%=100%-ash%-C%-H%-N%) assuming negligible sulphur content;
<sup>g</sup> Determined in accordance with the ASTM E-1721-01 Standard;
<sup>h</sup> Determined with an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) with a Varian Vista Pro ICAP Radial spectrometer.

5.3.2 Co-liquefaction experiments

The liquefaction tests were operated in a 75 ml Parr High-Pressure reactor, constructed of Hastelloy alloy, with a maximum working pressure of 41 MPa at 600°C. A schematic diagram of the reaction system is illustrated in Fig. 5.1. For the temperature and catalyst series of tests, approximately 22 g of the raw SPP/waste newspaper mixture (total solids concentration: 11.3 wt%), composed of 20 g of raw SPP (1.6 wt% TSS) and 2.2 g of the dried waste newspaper powder, was pre-loaded into the reactor for each experimental run. Catalysts were added as outlined in the experimental plan. For the tests examining the effects of different SPP-to-newspaper ratios, the feedstocks employed were dewatered
SPP (11.3 wt% TSS) or various pre-mixed dried SPP powder/waste newspaper/water mixtures (11.3 wt% TSS). A summary of all the sample compositions as well as the experimental conditions is provided in Table 5.2. Before each experimental run, the residual air in the reactor was completely displaced with nitrogen (N\textsubscript{2}) by at least 3 cycles of vacuuming and N\textsubscript{2} purging. The reactor was then pressurized to 2 MPa (cold pressure) using high-purity N\textsubscript{2} (or hydrogen (H\textsubscript{2}) for some tests) to prevent the boiling of water during heating. The reactor was externally heated with an electric furnace at 10\degree C/min to a specified experimental temperature (e.g., 250, 300, 350, and 380\degree C) and maintained for 20 min. After the desired reaction time elapsed, the reactor was cooled down to room temperature rapidly by using a wet cloth to stop the reaction.

![Fig. 5.1 Schematic diagram of the liquefaction apparatus.](image)
Table 5.2
Sample compositions\(^{a}\) and experimental conditions\(^{b}\).

<table>
<thead>
<tr>
<th>Test #</th>
<th>Types of feedstock (SPP-to-newspaper ratio)</th>
<th>Temp. (°C)</th>
<th>Types and conc. of catalysts(^{c})</th>
<th>Reaction atmosphere</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-250</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>250</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>T-300</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>T-350</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>350</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>T-380</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>380</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>T-300-H(_2)</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>None</td>
<td>2 MPa H(_2)</td>
<td></td>
</tr>
<tr>
<td>C-HCO(_2)H</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>HCO(_2)H (5 wt %)</td>
<td>2 MPa N(_2)</td>
<td></td>
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<tr>
<td>C-FeS</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>FeS (5 wt %)</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>C-KOH-2%</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>KOH (2 wt %)</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>C-KOH-4.5%</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>KOH (4.5 wt %)</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>C-KOH-5%</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>KOH (5 wt %)</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>C-KOH-10%</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>300</td>
<td>KOH (10 wt %)</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>C-Ash</td>
<td>Waste newspaper water mixture</td>
<td>300</td>
<td>SPP ash(^{d})</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>R-1:0</td>
<td>Dewatered SPP</td>
<td>300</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>R-2:1</td>
<td>Dried SPP/newspaper (2:1) water mixture</td>
<td>300</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>R-1:1</td>
<td>Dried SPP/waste newspaper (1:1) water mixture</td>
<td>300</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>R-1:2</td>
<td>Dried SPP/newspaper (1:2) water mixture</td>
<td>300</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
<tr>
<td>R-0:1</td>
<td>Waste newspaper water mixture</td>
<td>300</td>
<td>None</td>
<td>2 MPa N(_2)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) The total solid concentration was fixed at 11.3 wt% for all types of samples and tests;

\(^{b}\) The reaction time was 20 min for all the experimental runs;

\(^{c}\) Based on the mass of the solids in the feedstock;

\(^{d}\) The ash content of this mixture was 25.42 wt%, similar to that of the dried SPP powder (25.29 wt%).

5.3.3 Separation, recovery, and analyses of the reaction products

The gas products were collected in a gas cylinder of known volume and analyzed with an Agilent 3000 Micro-Gas Chromatograph (GC) equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors (TCDs). The remaining solid/liquid products were washed with approximately 50 ml distilled water, collected in a 250 ml beaker and then filtered under reduced pressure through a pre-weighed Whatman
No. 5 filter paper. The filtrate, designated as filtrate 1, was an aqueous phase containing water-soluble products (WSPs). This aqueous phase was sampled for total organic carbon (TOC) analysis with a Shimadzu TOC-V CPN total organic carbon analyzer after being collected and diluted to 100 ml with distilled water in a 100 ml volumetric flask. The reactor was then thoroughly rinsed with acetone. The resulting solution, as well as the retained filter paper and water-insoluble solid residue (SR), containing a mixture of chars, unconverted feedstock, ash, and in some cases, catalyst were collected in the previously used beaker. The beaker containing the product mixture was then shaken in a reciprocating shaker at 16 RPM in a 25°C water bath for 30 min, and filtered under reduced pressure through a second pre-weighed Whatman No. 5 filter paper. The filtrate, designated as filtrate 2 (the acetone-soluble phase), was transferred into a 250 ml pre-weighed evaporation flask and evaporated at 40°C under reduced pressure to completely remove the acetone. The remaining brown viscous liquid was weighed and referred to as HO. The solids retained on the filter paper, as well as the two filter papers were oven dried at 105°C for at least 12 hours and weighed to obtain the weight of SR.

The yields of total gas, HO and SR were defined as percentages (%) of the mass of each product in relation to the mass of dried matter in the feedstock loaded into the reactor prior to the reaction. The aqueous organic products and pyrolytic water were lumped together as WSPs and their yield was calculated by difference between 100% and the total yields of gas, HO and SR products. Two to three duplicate runs were conducted for most experimental conditions and the average yields were calculated and reported. The maximum errors between replicate runs were maintained within 5% of the yields for the
gas and SR products, and 10% of the yields for the HO products. The higher error observed in the HO yield was attributed to the existence of low concentrations of water that remained in the water-insoluble residue after the first stage of filtration.

The elemental composition (C, H, and N) of selected HO and SR samples was determined with a CEC (SCP) 240-XA elemental analyzer, and the composition of O in the HOs was estimated by difference \((O\%=100\%-C\%-H\%-N\%)\) assuming negligible contents of S and ash in the liquid oil samples. In addition, these HO samples were dissolved in acetone and analyzed with a Shimadzu gas chromatograph/mass spectrometer (GC/MS)-QP2010S equipped with a SHRXI-5MS capillary column (30m × 0.25mm × 0.25 μm). The initial column temperature was set at 65°C and then increased to 200°C at a heating rate of 10°C/min. After being held at 200°C for 2 min, the temperature was further raised to 280°C at 8°C/min. The temperatures at the ion source and the interface were 200 and 280°C, respectively. The data was acquired in a scan mode with the m/z ranging between 40 and 600. The first 30 peaks with the largest integration areas in the obtained chromatograph were identified using the WILEY8 library.

5.4 Results and discussion

5.4.1 Effects of temperature

For the experiments using the typical feed mixture of raw SPP/waste newspaper without catalyst, the product yields obtained at reaction temperatures ranging from 250°C (hot-
compressed water) to 380°C (near/supercritical water) are shown in Fig. 5.2. As expected, at low temperature, poor biomass conversion efficiency (defined as the weight percentage of organic matter converted into gas/liquid products in relation to the initial weight of the feedstock loaded into the reactor; i.e. the difference between 100% and the yield of SR in this work) was observed. For example, only 50 wt% of the feedstock was converted into valuable products in the form of HO, WSPs, or gases at 250°C. As temperature increased from 250 to 380°C, the yield of gases, mainly composed of carbon dioxide (CO₂), H₂, carbon monoxide (CO), methane (CH₄), and small quantities of light C₂ and C₃ compounds, tripled from 6.3 to 18.4 wt%, which was in good agreement with Zhang et al. [18] and Xu and Lancaster [6]. These gases are primarily formed as a result of the decarboxylation of the organic fraction of the feedstock (Eq. 5.1) and cracking/fragmentation reactions of the intermediate/liquid products (Eq. 5.2), or from the steam reforming/gasification reactions of the intermediate/liquid/char products (Eq. 5.3) [6,11].

Decarboxylation: \[ R - \text{COOH} \leftrightarrow R - \text{H} + \text{CO}_2 \] (5.1)

Fragmentation or cracking: \[ R - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \leftrightarrow R - \text{H} + \text{C}_3\text{H}_6 \]

or \[ R - \text{CH}_3 + \text{C}_2\text{H}_4 \] (5.2)

Char gasification: \[ \text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2 \] (5.3)

Overall reaction: \[ \text{CH}_x\text{O}_y + (2 - y)\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + (2 - y + \frac{X}{2})\text{H}_2 \] (5.4)
From a thermodynamic perspective, a high temperature favours gas formation, since the overall reaction between biomass and water (Eq. 5.4) is endothermic [19]. In fact, the yields of CO$_2$ and H$_2$ were significantly improved from 1.4 and 0 mol/kg feedstock, respectively, at 250°C, to 3.8 and 0.3 mol/kg feedstock, respectively, at 380°C.

The liquid products, which are the targeted products in biomass liquefaction, were composed of WSPs and HO. WSPs mainly consisted of simple organic acids (e.g., formic acid, acetic acid, and glycolic acid), alcohols, furfural, aldehydes, sugars, pyrolytic water,
etc., which are primarily formed from the conversion of cellulose and hemicellulose via de-polymerization and hydrolysis reactions [3,6]. In contrast, the HO, primarily composed of phenols, phenolic compounds, as well as long-chain carboxylic acids, esters, etc., results from the pyrolysis/hydrolysis/degradation of lignin or from the dehydration of intermediate products derived from holocelluloses [3,6]. As shown in Fig. 5.2, as the temperature increased from 250 to 350°C, the yields of both HO and WSPs were enhanced, accompanied by a corresponding reduction in the SR yield, mainly because of the easier defragmentation of the polymers (e.g., cellulose, hemicellulose, and lignin) present in the feedstocks to liquid products. The highest yields of HO (26.2 wt%) and total liquid products (67.1 wt%) were achieved at 350°C, after which these yields started to decrease with increasing temperature. This decrease coincided with increasing yields of gaseous products and SR, which was primarily composed of chars. As previously discussed, the enhanced gaseous product formation can be explained by the cracking/fragmentation of the HO and WSPs. The increased SR formation, however, could be attributed to the condensation/re-polymerization reactions of HO products or liquid intermediates that were initially formed in the process [20].

5.4.2 Effects of catalysts

Fig. 5.3 shows the effects of the addition (at 5 wt% of TSS in the feed) of various catalysts (KOH, HCO₂H, and FeS) on the distribution of product yields in the co-liquefaction of the raw SPP/waste newspaper mixture at 300°C for 20 min. With respects to the ability to improve the HO yield, the three catalysts tested in this work showed the
following priority sequence: $\text{HCO}_2\text{H} > \text{KOH} > \text{FeS}$. However, in terms of the overall biomass conversion efficiency, the sequence changed to: $\text{KOH} > \text{FeS} > \text{HCO}_2\text{H}$. As an iron-based catalyst, FeS did exhibit some positive effects, increasing the HO yield from 24.9 (without catalyst) to 27.7 wt% (with 5 wt% FeS). This result is consistent with the results observed by Xu and Etcheverry [16]. Moreover, the improvement of HO yield in the presence of FeS further increased at higher temperatures (>350°C) [16].

![Bar chart showing the product yields for different catalysts](image_url)

**Fig. 5.3** Effects of the addition of various catalysts (at 5 wt% of the TSS in the feed) on the product yields in the co-liquefaction of the raw SPP/waste newspaper mixture at 300°C for 20 min.

As one of the most effective catalysts for improving the HO yield, the performance of $\text{HCO}_2\text{H}$ is presented in Fig. 5.3. The presence of $\text{HCO}_2\text{H}$ (5 wt% of TSS in the feed) significantly enhanced the formation of HO, noting an increased yield of HO from 24.9 (without catalyst) to 34.4 wt% (with 5% $\text{HCO}_2\text{H}$). In addition, the yield of SR was
reduced from 22.2 (without catalyst) to 19.9 wt% (with 5% HCO₂H). An improved HO yield using HCO₂H has also been previously observed by Watanabe et al. [13]. Formic acid has been used as a highly effective hydrogenating agent, as the hydrogen formed in-situ could be in the form of hydrogen atom or radical (H⁺). Free radicals (H⁺) are highly reactive for the hydro-cracking of long-chain polymers (cellulose, hemicellulose, and lignin) into lower-molecular-weight fragments, and can be an effective capping/stabilization agent, preventing the re-polymerization/condensation of small biomass-derived fragments/intermediates into undesirable chars [15,21,22]. As such, the presence of HCO₂H could promote HO formation and reduce char yields due to the presence of the free radicals (H⁺) formed in-situ, as observed in Fig. 5.3. Recombination of the in-situ hydrogen atom/radical would form H₂ gas, as evidenced by high concentrations of H₂ in the gas products from the experiment with HCO₂H catalyst. The presence of reducing gases (e.g. H₂ or CO), especially H₂, is believed to improve the yield of oil but suppress the formation of char [6,21,22]. To investigate the effect of H₂ gas on the co-liquefaction process, the reactor was charged with either 2 MPa H₂ or 2 MPa N₂ before the reaction was initiated. No significant improvement on HO yield was observed with 2 MPa H₂, which, however, was different from observations reported in the literature [6] where, with the use of a mechanically agitated micro-reactor, the liquefaction of SPP under H₂ atmosphere was noted to produce much higher HO yields than those under N₂ atmosphere. The negligible effect of the H₂ atmosphere in this study could be primarily attributed to limitations associated with the reactor configuration, which was not equipped with an agitation/mixing device (such as a stir or a mechanical shaker). This could have consequently translated to a poor H₂ mass transfer in the reactor system. This might also
explain the higher HCO$_2$H activity in HO formation, as shown in Fig. 5.3, since the hydrogen formed *in-situ* would likely have a much higher contact efficiency with the biomass-degraded fragments/intermediates than externally supplied hydrogen.

Adding KOH (5 wt%) significantly improved the yields of HO (31.2 vs. 24.9 wt%) and gas (14.4 vs. 11.9 wt%), and reduced SR formation (15.6 vs. 22.2 wt%) (Fig. 5.3) compared to results obtained from the control experiment without catalyst. The catalytic effect of KOH for HO formation was in good agreement with Ogi et al. [12], who observed a dramatic increase in HO yield (from 22.2 to 51.0 wt%) from the direct liquefaction of wood when 3.2 wt% KOH was added. The high activity of KOH might be related to its strong alkalinity, facilitating the hydrolysis of polymers through the rupture the glycosidic bonds in cellulose and hemicellulose and the ester bonds in lignin [3]. In addition, the hydroxyl ion may react with CO, which was formed through the decomposition of cellulose or hemicellulose, to regenerate the formate ion via Eq. (5.5) [12]. The formate ion could then react with the carbonyl group in the ketone, which might be transformed from the vicinal hydroxyl groups, to form the corresponding alcohol [12].

$$\text{OH}^- + \text{CO} \leftrightarrow \text{HCOO}^- \quad (5.5)$$

In this study, varying quantities of KOH (0-10 wt% of the TSS in the feed) were added to the co-liquefaction reaction system to examine the relationships between the product yields and the concentration of KOH (Fig. 5.4). An increasing KOH load corresponded to a decrease in SR yield (from 22.2 wt% without KOH to 13.4 wt% with 10 wt% KOH),
indicating an enhanced biomass conversion efficiency, generally accompanied with an increased gas yield. For the HO yield, however, a maximum benefit was reached with a KOH addition of 2 wt%, and then the yield decreased slightly with further KOH addition. Hence, it appeared that the optimal amount of KOH addition was approximately 2 wt% of the TSS in the feed.

Fig. 5.4 Effects of the addition of various amount of KOH (0-10 wt% of the TSS in the feed) on the product yields in the co-liquefaction of the raw SPP/waste newspaper mixture at 300°C for 20 min. Standard deviations of the yields of HO, SR, and gas appear as error bars, however, for most tests, the errors were too small to be seen. (Lines are added to guide the eye.)
5.4.3 Effects of sludge-to-newspaper ratio

In order to investigate the synergistic effects between SPP and waste newspaper, feedstock mixtures with the same total solids content (11.3 wt%) but varying SPP-to-newspaper ratios (1:0, 2:1, 1:1, 1:2, 1:6.7, and 0:1 wt/wt) were prepared and liquefied at 300°C for 20 min without catalyst. As shown in Fig. 5.5, the HO yields for SPP or waste newspaper alone were 18.0 wt% and 21.0 wt%, respectively. The higher potential of waste newspaper to yield HO could be related to its higher volatile organic matter (90.0 wt% in waste newspaper vs. 58.7 wt% in SPP) and lignin (21.1 wt% in waste newspaper vs. 16.9 wt% in SPP) contents. On the other hand, the gas yield for SPP (12.1 wt%) was higher in comparison to that of newspaper (9.7 wt%). This could possibly be due to the catalytic effects of the high initial pH value (e.g., 8-9) and the presence of alkali metals, particularly Na, naturally present in the SPP ash (Table 5.1). However, of particular interest was the HO yield obtained from the co-liquefaction of the SPP/waste newspaper mixture. As can be seen from Fig. 5.5, under the same experimental conditions, the HO yield was higher than that recovered from either the waste newspaper or SPP alone. The best performance was noted for an SPP-to-newspaper ratio of 1:2 (i.e., with 33 wt% SPP and 67 wt% waste newspaper), at which the yields of both HO (26.9 wt%) and gaseous products (12.8 wt%) reached their highest values, coinciding with a minimum formation of SR (21.7 wt%). These results strongly suggest synergistic effects between SPP and the waste newspaper in the co-liquefaction process. The synergistic effects were more likely related to the inherent presence of alkali and alkaline earth metals (Na, K, Ca, Ba, Mg, etc.) in SPP, which could have catalyzed the conversion of organic matter in the waste.
newspaper to HO products. In order to verify this assumption, 2.42 g of newspaper/SPP ash mixture, composed of 1.81 g dried newspaper and 0.61 g SPP ash (obtained by heating the dried SPP powder at 550°C for 8 hours) was liquefied at 300°C for 20 min. This mixture exhibited similar ash content (25.4 wt%) to that of the dried SPP powder (25.3 wt%), with a total metal content of approximately 8.8 wt% of TSS as calculated with data provided in Table 5.1. As expected, the HO yield was greatly enhanced from 24.9 wt% (without catalyst) to 39.6 wt% (with 25.4 wt% SPP ash) under similar experimental conditions. The gas yield was also improved to a lesser extent (14.5 wt% with vs. 11.9 wt% without SPP ash). In addition, the high content of N in the SPP powder (> 4 wt% N) (Table 5.1) might also play a role in assisting biomass conversion as demonstrated by Inoue et al. [23]. N-containing compounds in the SPP might be reduced to ammonia acting as a base catalyst for the degradation of lignin to form HO products.

5.4.4 Characterization of the products

Table 5.3 demonstrates the carbon balances conducted on selected tests, as well as the carbon distributions among various phases of the products. As can be seen, all total carbon mass balances were between approximately 90 and 110% of the carbon could be accounted for, indicating reasonably accurate carbon recoveries. The relatively high carbon recovery (110.5 wt%) in the products with the addition of 5 wt% HCO\textsubscript{2}H (Test# C-HCO\textsubscript{2}H) was attributed to the possible incorporation of carbon from HCO\textsubscript{2}H. In comparison to the waste newspaper sample, a much lower proportion of carbon remained in the SR of the SPP sample (Test# C-1:0), translating to higher carbon conversion
efficiency. Moreover, it can also be noted that for the experiments involving catalyst addition (Test\# C-HCO$_2$H, C-KOH-5%, and C-FeS), a higher portion of carbon was transferred to HO, instead of SR, than without catalyst addition (Test\# T-300).

**Fig. 5.5** Effects of SPP-to-waste newspaper ratio on the product yields in the co-liquefaction of SPP/waste newspaper mixture at 300°C for 20 min without catalyst. Standard deviations of the yields of HO, SR, and gas appear as error bars, however, for most tests, the errors were too small to be seen. (Lines are added to guide the eye.)
Table 5.3
Carbon recovery in the products of different phases for some selected co-liquefaction tests at 300°C for 20 min under 2 MPa N₂ (cold pressure).

<table>
<thead>
<tr>
<th>Test #</th>
<th>Test conditions</th>
<th>Carbon recovery in the products (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gas</td>
<td>HO</td>
</tr>
<tr>
<td>R-0:1</td>
<td>Waste newspaper water mixture</td>
<td>10.6</td>
<td>30.0</td>
</tr>
<tr>
<td>R-1:0</td>
<td>Dewatered SPP</td>
<td>16.1</td>
<td>30.1</td>
</tr>
<tr>
<td>R-1:2</td>
<td>Dried SPP/newspaper (1:2) water mixture</td>
<td>15.0</td>
<td>39.1</td>
</tr>
<tr>
<td>T-300</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>13.1</td>
<td>39.3</td>
</tr>
<tr>
<td>C-HCO₂H</td>
<td>Raw SPP/newspaper mixture (1:6.7) with HCO₂H (5 wt %)</td>
<td>16.2</td>
<td>47.2</td>
</tr>
<tr>
<td>C-KOH-5%</td>
<td>Raw SPP/newspaper mixture (1:6.7) with KOH (5 wt%)</td>
<td>16.1</td>
<td>46.4</td>
</tr>
<tr>
<td>C-FeS</td>
<td>Raw SPP/newspaper mixture (1:6.7) with FeS (5 wt%)</td>
<td>13.2</td>
<td>41.4</td>
</tr>
</tbody>
</table>

*The total solid concentration was fixed at 11.3 wt% for all types of samples and tests.

The results of the CHN elemental analysis for the HO products from selected samples are shown in Table 5.4. The higher heating values (HHVs), calculated using the Dulong Formula, are also presented in Table 5.4. Compared with the raw feedstocks (waste newspaper and SPP), the recovered HO’s have significantly higher carbon, and lower oxygen contents, similar to the results reported by Qu et al. [24], who liquefied woody biomass in water at temperatures ranging between 280 and 360°C. As can be noted from the table, the heating values obtained for the target products, HO products, were almost double those of the original waste newspaper or SPP feedstocks (~30 MJ/kg vs. ~16.5 MJ/kg), indicating that direct liquefaction is an effective thermo-chemical process for upgrading low-heating-value biomass feedstocks. The results of this study were in good agreement with results reported by Yang et al. [11] and Qian et al. [25]. In addition, it can be noted from Table 5.4 that adding HCO₂H, KOH, or FeS did not affect the HO
characterization in terms of the CHN composition, although these catalysts effectively contributed to enhancing the HO product yields (Fig. 5.3). Also, as can be seen from Table 5.4, despite the fact that the two individual raw feedstocks exhibited similar heating values (approximately 16.5 MJ/kg), the HO obtained from the dewatered SPP (Test# R-1:0) had a noticeably higher HHV value (36.8 MJ/kg) than that from the waste newspaper (Test# R-0:1, HHV: 29.9 MJ/kg) under the same liquefaction conditions.

**Table 5.4**

CHN elemental analysis of the feedstocks and the HO products obtained via liquefaction/co-liquefaction at 300°C for 20 min.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Test conditionsa</th>
<th>Elemental composition (wt%)(d.b.)b</th>
<th>HHVd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Waste newspaper feedstock</td>
<td>48.6</td>
<td>5.7</td>
<td>0</td>
</tr>
<tr>
<td>Dried SPP powder feedstock</td>
<td>41.3</td>
<td>5.1</td>
<td>4.5</td>
</tr>
<tr>
<td>R-0:1</td>
<td>Waste newspaper water mixture</td>
<td>71.1</td>
<td>6.9</td>
</tr>
<tr>
<td>R-1:0</td>
<td>Dewatered SPP</td>
<td>75.4</td>
<td>9.4</td>
</tr>
<tr>
<td>R-1:2</td>
<td>Dried SPP/newspaper (1:2) water mixture</td>
<td>72.1</td>
<td>7.3</td>
</tr>
<tr>
<td>T-300</td>
<td>Raw SPP/newspaper mixture (1:6.7)</td>
<td>70.5</td>
<td>6.8</td>
</tr>
<tr>
<td>C-HCO2H</td>
<td>Raw SPP/newspaper mixture (1:6.7) with HCO2H (5 wt %)</td>
<td>69.9</td>
<td>6.9</td>
</tr>
<tr>
<td>C-KOH-5%</td>
<td>Raw SPP/newspaper mixture (1:6.7) with KOH (5 wt%)</td>
<td>70.2</td>
<td>6.9</td>
</tr>
<tr>
<td>C-FeS</td>
<td>Raw SPP/newspaper mixture (1:6.7) with FeS (5 wt%)</td>
<td>71.4</td>
<td>6.7</td>
</tr>
</tbody>
</table>

a The total solid concentration was fixed at 11.3 wt% for all types of samples and tests.

b On a dry basis

c By difference. For the feedstocks, O%=100%-ash%-C%-H%-N%, assuming negligible sulphur content; for the HOs, O%=100%-C%-H%-N%) assuming negligible sulphur and ash contents;

d Higher heating value (HHV) calculated by the Dulong Formula, i.e., HHV(MJ/kg) = 0.3383C + 1.422(H-O/8);

The GC/MS spectrum demonstrates that the HOs obtained from the waste newspaper liquefaction was composed of a variety of phenol and phenolic compounds (Fig. 5.6),
such as 2-methoxyphenol, 1-hydroxy-2-methoxy-4-methylbenzene, 4-ethylguaiacol, 4-
propylguaiacol, 4-hydroxy-3-methoxybenzaldehyde, 2-methoxy-4-(2-propenyl)phenol, 1-
(4-hydroxy-3-methoxyphenyl)ethanone, (4-hydroxy-3-methoxyphenyl)-2-propanone, 4-
hydroxy-3-methoxy-benzeneacetic acid, etc. All of these compounds have a 2-
methoxyphenol group in their structures but have different substituents at the position that
is opposite to the hydroxyl group on the aromatic ring, implying that they are likely
degraded compounds from lignin. Lignin is a “polymeric natural product arising from an
enzyme initiated dehydrogenative polymerization of three primary precursors: trans-
coniferyl, trans-sinapyl, and trans-\textit{p}-coumaryl” [26], among which the trans-coniferyl
precursor also has the 2-methoxyphenol group in its structure. Considering the high lignin
content of the waste newspaper (~21 wt%), it is thus reasonable to deduce that the
abovementioned phenolic compounds were from lignin rich in coniferyl units. Aside from
these phenolic compounds, there were also some compounds (e.g. 2-butoxyethanol, 2-
methyl-1-one-2-cyclopenten, 2,5-hexanedione, and 5-methyl-2-furancarboxaldehyde) that
were likely initially derived from cellulosic components via a series of reactions such as
hydrolysis, dehydration, etc [27].
Fig. 5.6 GC/MS spectrum of the HO from waste newspaper via liquefaction at 300°C for 20 min. A: 2-butoxyethanol, B: 2,5-hexanedione, C: 5-methyl-2-furancarboxaldehyde, D: phenol; E: 2-methoxyphenol, F: 1-hydroxy-2-methoxy-4-methylbenzene, G: 4-ethylguaiacol, H: 4-propylguaiacol, I: 4-hydroxy-3-methoxybenzaldehyde, J: 2-methyl-5-hydroxybenzofuran, K: 2-methoxy-4-(2-propenyl)phenol, L: 1-(4-hydroxy-3-methoxyphenyl)ethane, M: (4-hydroxy-3-methoxyphenyl)-2-propanone, N: 4-hydroxy-3-methoxy-benzeneacetic acid.
In comparison to the HOs derived from the waste newspaper (as shown in Fig. 5.6), the GC/MS spectrum of the HO product obtained from dried SPP powder (Fig. 5.7) exhibited two more distinct features: the existence of N-containing compounds, such as 1H-indole and 3-methyl-1H-indole, and long-chain alkenes and alcohols. As shown in Table 5.1, the SPP powder had a high nitrogen content (4.5 wt% in SPP vs. 0 wt% in newspaper), which was more than likely initially present in microbial cells and was then transferred to the HO products via the liquefaction reaction. As for the long carbon chains, one possible source is the fatty acids present in cells. To substantiate this assumption, the dried SPP powder was digested with concentrated hydrochloric acid, extracted with diethylether and petroleum ether, and analyzed by GC/MS using a similar method to that employed for HO product analysis. Not surprisingly, various long-chain acids (e.g., 9-octadecenoic acid), ethers (e.g., tetradecanoic acid, ethyl ester, octadecanoic acid, ethyl ester, and hexadecanoic acid, ethyl ester), aldehydes (e.g., tetradecanal and octadecanal), and alkenes (e.g., nonane, decane, 4-ethyloctane, hexadecane, and pentadecene) were observed (spectra not shown). The GC/MS spectra of the HO products from the raw SPP/waste newspaper mixture with and without catalysts were similar to that from newspaper alone, consistent with the results of CHN elemental analyses as noted in Table 5.3, and hence will not be further discussed.

5.5 Conclusions

In an attempt to investigate cost-effective disposal and energy recovery from high-water-content sludges and other solid waste streams, mixtures of secondary pulp/paper-mill sludge and waste newspaper were co-liquefied at temperatures of 250-380°C with and
without the addition of various catalysts. Some major conclusions drawn from this work may be summarized as follows:

1) The HO yield from the raw SPP/waste newspaper mixture increased with temperature in the range of 250-350°C, peaking at a maximum yield of 28.0 wt% at 350°C. Further increases in temperature decreased the HO yield, due to the conversion of HO products into gaseous products or solid chars via cracking/fragmentation or re-polymerization reactions.

2) The addition of HCO₂H, FeS, or KOH was found to enhance HO yield to varying extents at 300°C. HCO₂H was demonstrated to be the most effective catalyst among the catalysts tested, increasing the yield of HO from 24.9 to 34.4 wt%. The high activity of the HCO₂H for HO formation was attributed to the in-situ formation of highly reactive hydrogen atoms or free radicals.

3) KOH was an active catalyst for enhancing biomass conversion. The yield of SR continuously decreased as KOH addition was increased from 0 to 10 wt% (22.2 wt% without KOH vs. 13.4 wt% with 10 wt% KOH). However, the addition of approximately 2 wt% KOH of the TSS in the feed produced the highest HO yield.

4) Some synergistic/catalytic effects between SPP and waste newspaper were observed at various mixing ratios of the SPP and the waste newspaper feedstocks. The HO yield was highest at an SPP-to-waste newspaper ratio of 1:2 (33 wt% dried SPP
powder plus 67 wt% waste newspaper), which was approximately 9 wt% and 6 wt% higher than that obtained from either the SPP or the waste newspaper feedstocks alone. The synergistic effects were believed to be related to the inherent presence of alkali and alkaline earth metals (Na, K, Ca, Ba, Mg, etc.) in SPP, which could catalyze the conversion of volatile organic matter in the waste newspaper to HO products. Considering the cost associated with the use of catalysts (e.g., preparation, addition, recovery and regeneration), co-liquefaction of SPP with other waste biomass materials could present an economical alternative.

5) The HO obtained from the waste newspaper via liquefaction was mainly composed of a variety of phenolic compounds, derived from lignin, with a heating value of approximately 30 MJ/kg, which was almost doubled that of the original waste newspaper (~16 MJ/kg). In contrast, the SPP-derived HO exhibited a higher heating value (~37 MJ/kg), which was mainly attributed to the existence of long-chain alkenes, alcohols, etc. that were originally present in and converted from microbial cell materials.

6) Despite the fact that adding catalysts enhanced the HO yields, there were no significant differences noted in the HO product characteristics in terms of the CHN elemental compositions and the types of compounds detected by GC/MS.
5.6 Recommendations for future work

This study was conducted in a bench-scale batch reactor and has yet to be applied on an industrial scale. Before its future application in wastewater sludge treatment for energy recovery on a pilot scale, more preliminary laboratory-scale experiments are recommended. For example, as an expansion of this work, it would be beneficial to investigate other types of high-water-content organic wastes (e.g. kitchen waste) as the feedstocks, and to examine other catalysts with low cost (commercial, natural, etc.) in the co-liquefaction process. In addition, other experimental variables, such as solid contents of the feedstocks and reaction time could also be investigated to optimize the experimental conditions and to provide more valuable information on its scale up. Moreover, as by-products of this co-liquefaction process, the resulting SR could be used as an agricultural fertilizer or a solid fuel, and the WSPs could be gasified into valuable H₂-rich synthetic gas via supercritical water gasification in order to maximize the bio-energy production and to produce a clean effluent that can be discharged directly into the surface water. It would be very helpful to assess the economics and industrial application of the co-liquefaction process reported in this work. Although an overall economic analysis of the co-liquefaction process has not been studied to date, the co-liquefaction approach is believed to be advantageous, with respect to recovering bio-renewable energy and fuels from waste materials (wastewater sludge and solid municipal wastes), when compared to the conventional methods such as incineration, pyrolysis and gasification that involve energy-intensive drying. The co-liquefaction process could lead to a much higher energy efficiency due to its milder operational temperatures (<400°C) and the
elimination of the need for feedstock drying as water itself would act as a reaction medium in the reactor system. Moreover, the process under investigation could convert waste streams, which would require subsequent disposal, into valuable energy products (bio-oils and bio-chars), achieving dual goals of both waste disposal and bio-energy production.
5.7 References


Chapter 6

Screening of Supported Transition Metal Catalysts for Hydrogen Production from Glucose via Catalytic Supercritical Water Gasification

6.1 Abstract

In total 17 heterogeneous catalysts, with combinations of 4 transition metals (Ni, Ru, Cu and Co) and various promoters (e.g., Na, K, Mg, or Ru) supported on different materials ($\gamma$-Al$_2$O$_3$, ZrO$_2$, and activated carbon (AC)), were investigated with respect to their catalytic activity and stability for H$_2$ production from glucose via supercritical water gasification (SCWG). The experiments were carried out at 600°C and 24 MPa in a bench-scale continuous-flow tubular reactor. Ni (in metallic form) and Ru (in both metallic and oxidized forms) supported on $\gamma$-Al$_2$O$_3$ exhibited very high activity and H$_2$ selectivity among all of the catalysts investigated for a time-on-stream of 5-10 h. With Ni20/$\gamma$-Al$_2$O$_3$ (i.e., $\gamma$-Al$_2$O$_3$ with 20 wt% Ni), a H$_2$ yield of 38.4 mol/kg glucose was achieved, approximately 20 times higher than that obtained during the blank test without catalyst (1.8 mol/kg glucose). In contrast, Cu and Co catalysts were much less effective for the glucose SCWG reactions. As for the effects of catalyst support materials on activity, the following order of sequence was observed: $\gamma$-Al$_2$O$_3$ > ZrO$_2$ > AC. In addition, Mg and Ru were found to be effective promoters for the Ni/$\gamma$-Al$_2$O$_3$ catalyst, suppressing coke and tar formation.
6.2 Introduction

Supercritical water gasification (SCWG), a cost-effective technology to produce hydrogen (H\textsubscript{2})-rich synthesis gas (syngas) employing supercritical water (T\geq 374^\circ\text{C}, P\geq 22.1 MPa), has attracted considerable interest in the last two decades as it can convert aqueous organic waste or other wet biomass directly into syngas with reduced tar and coke formation [1,2]. In addition, SCWG provides a promising alternative for generating H\textsubscript{2}, which is an environmentally friendly and clean fuel and can be utilized in fuel cells. In a SCWG process, water is not only a reaction medium but also a reactant as it participates in the steam reforming (Eq. 6.1) and water-gas shift (Eq. 6.2) reactions, therefore eliminating or minimizing the energy and cost-intensive drying process. It has been reported that up to 50% of the H\textsubscript{2} formed via biomass SCWG could be originally from water [3].

\begin{align*}
\text{CH}_x\text{O}_y + (1 - y)\text{H}_2\text{O} & \leftrightarrow \text{CO} + (1 - y + \frac{x}{2})\text{H}_2 \quad (6.1) \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (6.2)
\end{align*}

Normally homogeneous or heterogeneous catalysts (e.g., alkali metals, activated carbon (AC), supported transition metals such as Ni, Pt, etc.) are employed to enhance the carbon gasification efficiency and H\textsubscript{2} yield by promoting C-C bond cleavage and the water-gas shift reaction (Eq. 6.2) [2]. In comparison to homogenous catalysts, such as alkali metal catalysts, heterogeneous catalysts have been shown to be more advantageous with respect to their high selectivity and recyclability [2]. The most widely used heterogeneous
catalysts for SCWG are Ni and Ru based catalysts due to their high activity and selectivity for H₂ generation [4-7]. Ni can promote a series of reactions such as tar cracking, water-gas shift, methanation and hydrogenation reactions. Ru actively promotes C-C bond rupture and maintains stability over a long period of time compared to other metal catalysts [8]. Compared to Ru, which is an expensive noble metal, Ni is more cost effective and hence more advantageous. However, Ni was found to be less stable and its activity could substantially decrease during the SCWG process due to catalyst deactivation [2]. On the other hand, Cu has been applied widely in steam reforming processes owing to its high efficiency in catalyzing the water-gas shift reaction [9,10]. Co proved to be highly effective in catalyzing the hydrodeoxygenation (HDO) reactions [11,12]. Nevertheless, the effects of these metals (Cu and Co) on the SCWG of glucose for hydrogen production have not been explored.

Apart from catalyst activity (the ability to enhance C-C bond cleavage and improve H₂ selectivity), catalyst stability (the ability to maintain activity for a long time-on-stream during operation) is another critical parameter in the evaluation of catalysts. Catalyst deactivation and reactor plugging have been long-standing challenges for the SCWG technology, and in most investigations using continuous flow reactor systems, the maximum operating time has normally been on the order of a few hours before the reactor is plugged due to coke/tar deposition. Various alkali or alkaline-earth metals (e.g., Na, K, Ca, Mg, etc.) have been employed as promoters in Ni/Al₂O₃ catalysts for dry (CO₂) reforming of methane to reduce coke formation [13-15]. These promoters have played a positive role in enhancing metal dispersion and retarding Ni sintering [13]. These promoters, however, have yet to be utilized in the SCWG process.
As such, the main objectives of the present research were: 1) to screen twelve catalysts with combinations of transition metals (Ni, Ru, Cu and Co) on various support materials (gamma-alumina (γ-Al₂O₃), zirconium (IV) oxide (ZrO₂), and AC), for their activity and stability for H₂ production from biomass via SCWG; and 2) to investigate catalyst resistance to coking for six γ-Al₂O₃-supported Ni catalysts containing various promoters (e.g., Na, K, Mg, or Ru). In this study, glucose was used as a biomass model compound as it is the representative “building block” of cellulose, one of the major constituents of biomass materials [16,17].

6.3 Materials and methods

6.3.1 Catalyst preparation

The catalysts were prepared by wet impregnation method (or co-impregnation for those containing more than one metal) [18-21] using water-soluble metal salts including nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), copper (II) nitrate hydrate (Cu(NO₃)₂·2.5H₂O), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·7H₂O), potassium nitrate (KNO₃), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O) and ruthenium (III) nitrosyl nitrate solution in dilute nitric acid (HN₄O₁₀Ru), all supplied by Sigma-Aldrich. Various support materials including γ-Al₂O₃ (Inframat Advanced Materials), ZrO₂ (Sigma-Aldrich) and AC were used in the impregnation. The AC used in this research was a biomass-derived AC prepared from pine wood sawdust (containing 0.2 wt% (d.b.) ash, and an ultimate analysis (on a dry-and-ash-free basis) of 53.3 wt% C,
Detailed AC preparation method was given elsewhere by Xu et al. [21]. Briefly, pine wood sawdust (sieved to particles of 850-2000 μm size) was activated using H₃PO₄ at 200°C for 15 min, and then carbonized at 450°C for 45 min, followed by thoroughly washing with hot-distilled water to remove the H₃PO₄. All the catalysts were first oven-dried at 105°C for 12 h and then calcined for 6.5 h at 550°C in air (except for the AC-supported catalyst which was calcined in N₂), followed by crushing and sieving to obtain granules with nominal diameters ranging between 300-850 μm. The compositions and physical properties of the 17 catalysts are presented in Table 6.1.

6.3.2 Catalyst characterization

The BET surface area, total pore volume and the average pore diameter of selected representative catalysts were determined by N₂ isothermal (at -196°C) adsorption with a Quantachrome Nova 2200e Surface Area & Pore Size Analyzer (Table 6.1). It can be seen that the surface areas of the supported catalysts were primarily dominated by the support materials, where AC exhibited the highest surface area (>1000 m²/g), followed by γ-Al₂O₃ (~ 40 m²/g) and ZrO₂ (< 20 m²/g). As expected, a higher metal loading decreased the surface area and pore volume of the catalyst due to the masking of the support material by deposition of the metal particles. The isotherms of the Ni10/γ-Al₂O₃, Ni20/ZrO₂ and Ni10/AC catalysts are shown in Fig. 6.1. According to the IUPAC classification of the five types of adsorption isotherms [22], the adsorption isotherms of the γ-Al₂O₃ and ZrO₂-supported catalysts may be grouped into Type III isotherms, while
the isotherm of AC-supported catalyst is similar to the Type I isotherm.

Table 6.1
Catalyst compositions and physical characteristics.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal type and content (wt%)</th>
<th>Support</th>
<th>BET surface area (m²/g)b</th>
<th>Total pore volume (cm³/g)b</th>
<th>Average pore diameter (nm)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni20/γ-Al₂O₃</td>
<td>20%Ni γ-Al₂O₃</td>
<td></td>
<td>36.1</td>
<td>0.08</td>
<td>8.8</td>
</tr>
<tr>
<td>Ni20/ZrO₂</td>
<td>20%Ni ZrO₂</td>
<td></td>
<td>14.5</td>
<td>0.02</td>
<td>7.1</td>
</tr>
<tr>
<td>Ni10/AC</td>
<td>10%Ni AC</td>
<td></td>
<td>1.12×10⁶</td>
<td>0.68</td>
<td>2.4</td>
</tr>
<tr>
<td>Ru10/γ-Al₂O₃</td>
<td>10%Ru γ-Al₂O₃</td>
<td></td>
<td>42.1</td>
<td>0.12</td>
<td>11.0</td>
</tr>
<tr>
<td>Co10/γ-Al₂O₃</td>
<td>10%Co γ-Al₂O₃</td>
<td></td>
<td>34.3</td>
<td>0.07</td>
<td>8.4</td>
</tr>
<tr>
<td>Cu20/γ-Al₂O₃</td>
<td>20%Cu γ-Al₂O₃</td>
<td></td>
<td>33.2</td>
<td>0.10</td>
<td>11.8</td>
</tr>
<tr>
<td>Ru5Ni5/γ-Al₂O₃</td>
<td>5%Ni+5%Ru γ-Al₂O₃</td>
<td></td>
<td>38.3</td>
<td>0.12</td>
<td>12.2</td>
</tr>
<tr>
<td>Ni15Co5/γ-Al₂O₃</td>
<td>15%Ni+5%Co γ-Al₂O₃</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Ni5Co5/γ-Al₂O₃</td>
<td>5%Ni+5%Co γ-Al₂O₃</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Ru10Cu10/γ-Al₂O₃</td>
<td>10%Ru+10%Cu γ-Al₂O₃</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Ni10Cu10/γ-Al₂O₃</td>
<td>10%Ru+10%Cu γ-Al₂O₃</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Ni10/γ-Al₂O₃</td>
<td>10%Ni γ-Al₂O₃</td>
<td></td>
<td>41.9</td>
<td>0.13</td>
<td>12.3</td>
</tr>
<tr>
<td>K₀.₅Ni10/γ-Al₂O₃</td>
<td>10%Ni+3.33%K γ-Al₂O₃</td>
<td></td>
<td>25.6</td>
<td>0.07</td>
<td>5.8</td>
</tr>
<tr>
<td>Cu₀.₁Ni10/γ-Al₂O₃</td>
<td>10%Ni+0.68%Ca γ-Al₂O₃</td>
<td></td>
<td>35.6</td>
<td>0.10</td>
<td>5.4</td>
</tr>
<tr>
<td>K₀.₅Cu₀.₁Ni10/γ-Al₂O₃</td>
<td>10%Ni+3.33%K+0.68%Ca γ-Al₂O₃</td>
<td></td>
<td>23.0</td>
<td>0.06</td>
<td>5.6</td>
</tr>
<tr>
<td>Mg₀.₁Ni10/γ-Al₂O₃</td>
<td>10%Ni+0.41%Mg γ-Al₂O₃</td>
<td></td>
<td>38.1</td>
<td>0.13</td>
<td>6.6</td>
</tr>
<tr>
<td>Ru₀.₁Ni10/γ-Al₂O₃</td>
<td>10%Ni+1.72%Ru γ-Al₂O₃</td>
<td></td>
<td>34.2</td>
<td>0.09</td>
<td>10.7</td>
</tr>
</tbody>
</table>

a The number (5, 10, 15 or 20) after the metals of Ni, Ru, Cu or Co represents the weight percentages of these metals with respect to the mass of the support material. The subscript (0.1 or 0.5) on the metals as promoters (e.g., K, Ca, Mg or Ru) indicates the specific molar ratios of that metal to the base metal of nickel. For example, K₀.₅Ni10/γ-Al₂O₃ has 10 wt% Ni and a molar ratio of K to Ni at 0.5:1.
b na = not analyzed.
Fig. 6.1 N\textsubscript{2} adsorption-desorption isotherms (at -196°C) of the (a) Ni\textsubscript{10}/\textgamma-Al\textsubscript{2}O\textsubscript{3}, (b) Ni\textsubscript{20}/ZrO\textsubscript{2} and (c) Ni\textsubscript{10}/AC catalysts.

The crystal structures of selected catalysts were examined by powder X-ray diffraction (XRD) with a PANalytical X’Pert Pro diffractometer with Cu K\textalpha as the radiation source. Step-scans were taken over the range of 2\texttheta from 6 to 76°. In addition, the morphologies of carbons deposited on spent Ni\textsubscript{10}/\textgamma-Al\textsubscript{2}O\textsubscript{3} and Ru\textsubscript{0.1}Ni\textsubscript{10}/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalysts were analyzed using a JEOL 2100F transmission electron microscopy (TEM) equipped with an energy-dispersive X-ray spectroscopy (EDS, INCA system from Oxford Instrument).
6.3.3 Supercritical water gasification experiment

The SCWG experiments were conducted in a bench-scale continuous-flow tubular reactor (Inconel 625 tubing, 9.55 mm OD, 6.34 mm ID, 472 mm length) heated with an electric furnace (as illustrated in Fig. 6.2). A 50 g/L glucose solution, composed of anhydrous D-glucose (J.T.Baker) and distilled water, was used as the biomass feedstock. For each experiment, 1 g of the crushed catalyst was pre-loaded into the catalyst bed, in which the catalyst particles were supported on a porous Inconel metal disc (pore size: 100 μm) and some quartz wool. The catalyst in the reactor was then reduced in-situ under flowing H2 (30 mL/min) at 500°C for 1 h before use. The feedstock was pumped into the reactor system using an HPLC pump (Eldex) at a flow rate of 1 or 2 mL/min. This translates to a WHSV of 3.0 or 6.0 h⁻¹, where WHSV is weight hourly space velocity, which is the mass of reactant (glucose) in the aqueous feed solution per mass of catalyst per hour. All of the experiments were performed at fixed temperature and pressure (600°C and 24 MPa), which was controlled by a back-pressure regulator. For most of the experiments, approximately 8 h of time-on-stream was applied, with the exception of tests during which reactor plugging occurred due to the formation of coke and tar in the presence of certain lower activity catalysts.
6.3.4 Product recovery and analysis

The gas products were collected continuously in a cylinder of known volume during the experiment and subsequently analyzed with an Agilent 3000 Micro-Gas Chromatograph (GC) equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors (TCDs). In addition, the steady-state aqueous effluent was collected in sample vials and analyzed for TOC content with a Shimadzu TOC-V CPN TOC Analyzer.

After the SCWG experiment, A.C.S. reagent-grade ethyl acetate was pumped through the reactor to wash out water-insoluble organic compounds once the system was depressurized and cooled down to the ambient temperature. The ethyl acetate-soluble
phase was then separated from water by using a separatory funnel, transferred into a pre-
weighed evaporation flask, and evaporated at 60°C under a reduced pressure of 10 kPa to
remove the solvent. The remaining brown viscous liquid was weighed and is further
referred to as tar. The elemental compositions (C, H, and O) of selected tars were
determined with a CEC (SCP) 240-XA elemental analyzer and the composition of O was
calculated by difference (O% = 100% - C% - H%). In addition, the solid residue (SR),
composed of the used catalyst, coke and small amount of quartz wool, was collected and
oven dried at 105°C for 12 h to obtain the mass of SR. The mass of coke was determined
using a thermogravimetric analyzer (TGA)-i 1000 (Instrument Specialist Inc.) by heating
the SR under an air atmosphere (air flow rate: 40 mL/min) at 10°C/min up to 900°C. The
weight loss between 120 and 900°C was attributed to the combustion of coke.

The definitions of the product yields used in this study are described in Eqs. (6.3-6.6) as
below:

\[
H_2\text{yield (mol/kg feed)} = \frac{\text{moles of } H_2 \text{ produced}}{\text{mass of glucose consumed}} \quad (6.3)
\]

Carbon gasification efficiency (%) = \[\frac{\text{Moles of carbon in the gas product}}{\text{Moles of carbon in the feed}} \times 100 \approx 1 - \frac{\text{TOC of the aqueous effluent}}{\text{TOC of the glucose solution}} \times 100 \quad (6.4)\]

Tar yield (%) = \[\frac{\text{mass of tar recovered}}{\text{total mass of glucose consumed}} \times 100 \quad (6.5)\]

Coke yield (%) = \[\frac{\text{mass of coke recovered}}{\text{total mass of glucose consumed}} \times 100 \quad (6.6)\]
Duplicate experiments were conducted on the blank test (without catalyst) as well as selected catalysts such as Ni20/γ-Al2O3 and Ni20/ZrO2, and reproducible results were obtained, as shown in Figs. 6.3 and 6.7 and Tables 6.2 and 6.3 in the following section. However, since the time intervals for gas collections between these duplicate runs were not identical, the average results (e.g., H2 yield and carbon gasification efficiency) as a function of time-on-stream could not be calculated.

6.4 Results and discussion

6.4.1 Effect transition metals

The H2 yields from the blank (without catalyst) and five catalytic SCWG experiments conducted at 600°C and 24 MPa with a WHSV of 3 h⁻¹ are shown in Fig. 6.3. As expected, the least amount of H2 was produced in the blank test, for which the H2 yield was only 1.8 mol/kg glucose. Correspondingly, the carbon gasification efficiency of the blank test was also noted to be the lowest (ca. 75.2%), as shown in Table 6.2. In addition, the gas product from the blank test contained the highest percentage of CO (55.1 vol%, Table 6.2), implying a low efficiency of the water-gas shift reaction in the absence of a catalyst.
In comparison to the blank test, adding Ni or Ru catalysts led to a more than 20-fold increase in $\text{H}_2$ yield, attaining as high as ~38 mol of $\text{H}_2$/kg glucose (Fig. 6.3), representing 57% of the theoretical yield (66.7 mol/kg glucose) as calculated based on Eq. (6.7):

$$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} \leftrightarrow 6\text{CO}_2 + 12\text{H}_2 \quad (6.7)$$

Correspondingly, nearly complete conversion of glucose was observed, with a carbon gasification efficiency of >99%, accompanied by a minimum tar and coke formation. In addition, it should be noted that there was no significant difference between the performances of Ni10/γ-Al$_2$O$_3$ and Ni20/γ-Al$_2$O$_3$ catalysts. On the one hand, increasing the metal loading could increase the active sites of the catalyst. On the other hand, however, a high metal loading could also lead to reduced dispersion of the metal (with a
Table 6.2
Product yields and compositions of gas products from the SCWG of 50 g/L glucose solution with and without the addition of γ-Al2O3-supported transition metal catalysts (reaction temperature: 600°C, pressure: 24 MPa, WHSV = 3 h⁻¹).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon gasification efficiency (%)</th>
<th>Yield of coke (%)ᵃ</th>
<th>Yield of tar (%)ᵇ</th>
<th>Gas composition (vol%)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>Blank</td>
<td>75.2</td>
<td>2.1</td>
<td>4.4</td>
<td>8.7±0.5</td>
</tr>
<tr>
<td>Ni20/γ-Al₂O₃</td>
<td>99.9</td>
<td>2.5</td>
<td>0.3</td>
<td>58.2±3.4</td>
</tr>
<tr>
<td>Ni10/γ-Al₂O₃</td>
<td>99.7</td>
<td>1.3</td>
<td>0.8</td>
<td>55.2</td>
</tr>
<tr>
<td>Ru10/γ-Al₂O₃</td>
<td>99.9</td>
<td>1.6</td>
<td>0.5</td>
<td>55.7</td>
</tr>
<tr>
<td>Ni5Ru5/γ-Al₂O₃</td>
<td>99.9</td>
<td>na</td>
<td>na</td>
<td>55.2</td>
</tr>
<tr>
<td>Co10/γ-Al₂O₃</td>
<td>81.0</td>
<td>3.6</td>
<td>7.0</td>
<td>15.3</td>
</tr>
<tr>
<td>Ni15Co5/γ-Al₂O₃</td>
<td>99.8</td>
<td>na</td>
<td>na</td>
<td>53.1</td>
</tr>
<tr>
<td>Ni5Co5/γ-Al₂O₃</td>
<td>88.0</td>
<td>1.0</td>
<td>3.0</td>
<td>51.8</td>
</tr>
<tr>
<td>Cu20/γ-Al₂O₃</td>
<td>81.7</td>
<td>na</td>
<td>na</td>
<td>31.3</td>
</tr>
<tr>
<td>Ru10Cu10/γ-Al₂O₃</td>
<td>88.8</td>
<td>na</td>
<td>na</td>
<td>45.2</td>
</tr>
<tr>
<td>Ni10Cu10/γ-Al₂O₃</td>
<td>80.9</td>
<td>na</td>
<td>na</td>
<td>41.3</td>
</tr>
</tbody>
</table>

ᵃ na = not analyzed.
ᵇ Averaged compositions at the steady state. Other light hydrocarbons, e.g., C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, etc., are not listed due to their negligible amounts. In addition, duplicate tests were conducted for the experiments without and with the Ni20/γ-Al₂O₃ catalyst. The averages and standard deviations from these parallel experiments were calculated and expressed as average ± standard deviation in this table.

larger crystalline size) in the catalyst, and decreased surface area and porosity of the catalyst, which would hence reduce the catalytic activity. As evidenced from the textural results presented in Table 6.1, the BET surface area and total pore volume of Ni20/γ-Al₂O₃ were 36.1 m²/g and 0.08 cm³/g, respectively, compared to 41.9 m²/g and 0.13 cm³/g for Ni10/γ-Al₂O₃. Thus, too high a metal loading for the supported catalyst does not necessarily translate into higher catalytic activity.
The XRD patterns of the fresh and spent Ni10/γ-Al2O3 and Ru10/γ-Al2O3 catalysts are shown in Fig. 6.4. It can be seen that both the Ni and Ru in the calcined fresh catalysts were present in oxidized form (NiO and RuO2). In the spent catalysts, after 8 h on stream (these two catalysts were reduced by H2 before use), the Ni and Ru species detected were primarily in their metallic forms, implying that the metallic forms of these metal catalysts might be the active sites for the glucose SCWG.

Fig. 6.4 XRD analysis of the Ni10/γ-Al2O3 and Ru10/γ-Al2O3 catalysts: (a) and (c) before the reaction (fresh catalysts), (b) and (d) after the reaction (1 h reduction under 30 mL/min H2 flow at 500°C and ~ 8 h on-stream at 600°C and 24 MPa with the WHSV = 3 h⁻¹) (● NiO, ○ Ni, ■ RuO2, □ Ru, ? represents unidentified peaks, which might be assigned to Ru(II) or Ru(III) compounds.).

To confirm this assumption, 1 g of Ni20/γ-Al2O3 or Ru10/γ-Al2O3 was used directly under similar experimental condition without H2 reduction and the resulting H2 yields are displayed in Fig. 6.5. After 5 h on stream, the H2 yield with non-reduced Ni20/γ-Al2O3
Fig. 6.5 H₂ yield from the catalytic SCWG of 50 g/L glucose solution with the H₂-reduced or non-reduced Ni20/γ-Al₂O₃ or Ru10/γ-Al₂O₃ catalysts (reaction temperature: 600°C, pressure: 24 MPa, WHSV = 3 h⁻¹). The error bar represents the standard deviation of the H₂ yields obtained from the two parallel experiments with the reduced Ni20/γ-Al₂O₃ catalyst.

was only 5.7 mol/kg glucose, approximately 1/7 of that with the reduced catalyst, with a corresponding carbon gasification efficiency as low as 56.2%. Although the H₂ yield increased to 10.3 mol/kg glucose after 7 h on stream, the reactor was plugged due to the formation of coke and tar. Similar results were also reported by Yan et al. [6] for the SCWG of polyethylene glycol (PEG), where the NiO/ZrO₂ catalyst was found to be much less active than the Ni/ZrO₂ catalyst. In addition, Inaba et al. [7] proposed that metallic Ni could catalyze the steam reforming (Eq. 6.1) and methanation (Eqs. 6.8 and 6.9) reactions. As such, we may conclude that the metallic form of Ni is the active site for the SCWG reaction.

\[
\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (6.8)
\]
In contrast, there was no significant difference between the performances of the reduced and non-reduced (oxidized) Ru10/γ-Al2O3 catalysts, both producing approximately 35 mol H₂ per kg of glucose. These results were in agreement with Park and Tomiyasu [23] who conducted SCWG experiments using aromatic compounds (e.g., polystyrene) with RuO₂ as the catalyst at 450°C and 44 MPa for 2 h, and achieved nearly complete gasification of organic compounds, with CH₄ as the major component in the gas products (54 vol%) due to the lower reaction temperature. The activity of RuO₂ may be due to the redox mechanism between the Ru⁴⁺/Ru²⁺ couple, as proposed by Park and Tomiyasu [23].

According to the “redox mechanism”, the RuO₂ first oxidizes the organic compound to CO and H₂O, and in the meantime, the Ru (IV) is reduced to Ru (II), which can then be oxidized to Ru (IV) again by H₂O. From the high activity observed in the present study for the reduced Ru catalyst (Table 6.2 and Figs. 6.3 and 6.5), metallic Ru could also be active in catalyzing the SCWG reactions. In fact, metallic Ru has been investigated previously in a number of studies for the gasification of organic feedstocks such as glycerol [5] and lignin [24]. As such, a modified redox mechanism between the Ru⁴⁺/(Ru²⁺ and Ru) is proposed in this study, as illustrated in Fig. 6.6. However, to elucidate this reaction mechanism, more investigation is required in the future.
Fig. 6.6 Possible mechanism for the catalytic activity of RuO$_2$ in SCWG of biomass.

Although the carbon gasification efficiency and H$_2$ yield with either Ni or Ru catalysts supported on $\gamma$-Al$_2$O$_3$ remained relatively constant during 8 h of operation in this study, coke formation was evident in both spent catalysts (Table 6.2), as confirmed by TGA and XRD analyses. For example, as can be seen from Fig. 6.4 the broad X-ray diffraction peaks at $2\theta \approx 22^\circ$ in all the spent catalysts were attributed to amorphous carbon. Coke deposition is generally believed to be a cause of catalyst deactivation and reactor plugging. In order to examine the long-term stability of these catalysts, experiments for longer reaction times or at a higher WHSV should be conducted in future studies.

In comparison to the Ni and Ru catalysts, Cu and Co catalysts were much less effective in catalyzing the SCWG reactions (Table 6.2). Azadi et al. [25] investigated the catalytic effects of Raney-Ni and Raney-Cu, for the gasification of 6 wt% (or 60 g/L) glucose solution at a temperature 370°C for 15 min in a batch microreactor. Raney-Cu exhibited moderate activity for glucose degradation with a H$_2$ yield of 4.8 mol/kg glucose, lower than that with Raney-Ni (6 mol/kg glucose). Similarly, in this research the H$_2$ yield with Cu$_2$O/$\gamma$-Al$_2$O$_3$ was very low (~7 mol/kg glucose), only 1/5 of that noted with Ni$_2$O/$\gamma$-Al$_2$O$_3$ (~38 mol/kg glucose). Compared with the blank test, the presence of Cu$_2$O/$\gamma$-Al$_2$O$_3$
did not improve the carbon gasification efficiency significantly (81.7% vs. 75.2% with and without the catalyst), but enhanced the H₂ yield on the consumption of CO in the gas product (Table 6.2 and Fig. 6.3), suggesting enhanced water-gas shift reaction. Accordingly, it may be concluded that Cu does not show activity for the cleavage of C-C bonds in SCW, but it is effective for catalyzing the water-gas shift reaction [9]. Similar to the results found for the Cu catalyst, Co10/γ-Al₂O₃ did not appear to have a positive effect on the SCWG of glucose, only slightly increasing the carbon gasification efficiency from 75.2% to 81.0% (Table 6.2), although synergistic effects between Co and Ni were reported by Yan et al. [6] for the SCWG of PEG at 390°C and 24 MPa.

The results in Table 6.2 also indicate that the activities of binary metallic catalysts (combination of two metals at an equal or comparable amount, e.g., Ni5Ru5, Ni15Co5, Ni5Co5, Ru10Cu10 and Ni10Cu10) were predictable from their component activities as the results showed additive effects between the component metals. For instance, the Ni5Ru5 and Ni15Co5, led to a high carbon gasification efficiency (close to 100%) due to the high activity of either Ni or Ru, while the Ni5Co5, Ru10Cu10 and Ni10Cu10 produced reduced carbon gasification efficiency (<90%) due to the much lower activities of Co and Cu.

6.4.2 Effect of different support materials

Ni catalysts supported on three different support materials (γ-Al₂O₃, ZrO₂ and AC) were compared for their effects on H₂ generation from glucose via SCWG at 600°C and 24 MPa. Their effects on H₂ yields, char/tar yields and composition of the gas products from
the SCWG are shown in Fig. 6.7 and Table 6.3. As shown in Fig. 6.7, these three supported Ni catalysts exhibited the following order of catalytic activities for producing H₂: γ-Al₂O₃ > ZrO₂ > AC.

![Graph showing H₂ yield vs. time-on-stream for different catalysts](image)

**Fig. 6.7** Effects of Ni catalysts supported on different materials on H₂ yields from the SCWG of 50 g/L glucose (reaction temperature: 600°C, pressure: 24 MPa, WHSV = 3 h⁻¹). Lines are added to guide the eye.

γ-Al₂O₃, due to its acidity, high surface area and high-temperature stability, has been extensively utilized as a catalyst support for a wide variety of processes including the application of SCWG [4,26]. In this study, the H₂ yield with the Ni20/γ-Al₂O₃ catalyst (38.4 mol/kg glucose) was almost doubled in comparison to that with the Ni20/ZrO₂ catalyst (21.3 mol/kg glucose), as shown in Fig. 6.7. However, although not observed in this study, γ-Al₂O₃ had been reported to gradually lose activity over a period of time due to its structural transformation from gamma- to alpha-phase [4] or hydrolysis to γ-AlOOH, accompanied by a reduced surface area and physical strength [27].
Table 6.3
Product yields and the composition of the gas products from the SCWG of 50 g/L glucose solution with and without the addition of various supported Ni catalysts (Reaction temperature: 600°C, pressure: 24 MPa, WHSV = 3 h⁻¹).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon gasification efficiency (%)</th>
<th>Yield of coke (%)</th>
<th>Yield of tar (%)</th>
<th>Gas composition (vol%)b</th>
<th>H₂</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>75.2</td>
<td>2.1</td>
<td>4.4</td>
<td>8.7±0.5</td>
<td>11.5±1.0</td>
<td>55.1±0.2</td>
<td>18.3±1.2</td>
<td></td>
</tr>
<tr>
<td>Ni₂₀/γ-Al₂O₃</td>
<td>99.9</td>
<td>2.5</td>
<td>0.4</td>
<td>58.2±3.4</td>
<td>10.6±0.04</td>
<td>0.6±0.03</td>
<td>30.5±3.3</td>
<td></td>
</tr>
<tr>
<td>Ni₁₀/γ-Al₂O₃</td>
<td>99.7</td>
<td>1.3</td>
<td>0.8</td>
<td>55.2</td>
<td>9.4</td>
<td>0.6</td>
<td>34.9</td>
<td></td>
</tr>
<tr>
<td>Ni₂₀/ZrO₂</td>
<td>81.9</td>
<td>2.4</td>
<td>4.4</td>
<td>52.6±0.5</td>
<td>6.3±0.2</td>
<td>3.3±0.2</td>
<td>35.9±0.5</td>
<td></td>
</tr>
<tr>
<td>Ni₁₀/AC</td>
<td>78.2</td>
<td>naa</td>
<td>4.1</td>
<td>24.9</td>
<td>12.3</td>
<td>29.2</td>
<td>27.3</td>
<td></td>
</tr>
</tbody>
</table>

*a naa = not analyzed.

b Averaged compositions at the steady state. Other light hydrocarbons, e.g., C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, etc., are not listed due to their negligible amounts. In addition, duplicate tests were conducted for the experiments without and with the Ni₂₀/γ-Al₂O₃ and Ni₂₀/ZrO₂ catalysts. The averages and standard deviations from these parallel experiments were calculated and expressed as average ± standard deviation in this table.

ZrO₂ is a basic catalyst support and was demonstrated to be more stable than γ-Al₂O₃ in SCWG [6]. However, the Ni catalyst supported on ZrO₂ only exhibited intermediate activity for H₂ production (Fig. 6.7) in this study, being more effective than that supported on AC, but less active than that supported on γ-Al₂O₃. Interestingly, as shown in Table 6.3, the syngas CH₄ fraction with the Ni₂₀/ZrO₂ catalyst was lower (6.3%) than those with either the γ-Al₂O₃ (9.4%) or AC (12.3%) supported catalysts, suggesting that ZrO₂ could effectively inhibit the methanation reactions (Eqs. 8 and 9). Basic catalyst supports normally have a higher selectivity for H₂ than alkanes in biomass gasification [9]. The AC-supported Ni catalyst exhibited much less activity than the γ-Al₂O₃ and ZrO₂-supported catalysts despite its high BET surface area (1.12×10³ m²/g) in relation to < 50 m²/g for Ni₁₀/γ-Al₂O₃ or Ni₂₀/ZrO₂. The carbon gasification efficiency for the Ni₁₀/AC (78.2%) was almost the same as the blank control test (75.2%) (Table 6.3). In contrast,
Xu et al. [28] observed very high activities of coconut shell-derived AC as the catalyst for SCWG of 216 g/L glucose solution at 600°C, 25.5 MPa and a WHSV of 16.1 h⁻¹, achieving approximately 99% carbon gasification efficiency. Comparison of the results obtained in this study with those from Xu et al. [28] is provided in Table 6.4, with respect to reaction conditions, gas compositions, carbon gasification efficiencies and H₂ yields. From Table 6.4, it can be observed that both studies produced similar gas compositions irrespective of the source of the AC catalysts. Nevertheless, the hydrogen yield and carbon gasification efficiency in the present study when using Ni catalyst supported on the pine wood derived AC (78.2%) were lower than those achieved in the work of Xu et al. [28] using the coconut derived AC catalyst. The higher activity of the coconut derived

**Table 6.4**
Comparison of gas compositions, carbon gasification efficiencies, and H₂ yields from SCWG of glucose between the present study and the previous study by Xu et al. [28].

<table>
<thead>
<tr>
<th>Product</th>
<th>Blank experiments</th>
<th>Catalytic experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This research</td>
<td>Xu’s et al.</td>
</tr>
<tr>
<td>Experimental condition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>24</td>
<td>34.5</td>
</tr>
<tr>
<td>Glucose concentration (g/L)</td>
<td>50</td>
<td>216</td>
</tr>
<tr>
<td>WHSV (h⁻¹)</td>
<td>na²</td>
<td>na²</td>
</tr>
<tr>
<td>Gas composition (vol%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>8.7</td>
<td>11.5</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.5</td>
<td>17.3</td>
</tr>
<tr>
<td>CO</td>
<td>55.1</td>
<td>65.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>18.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Carbon gasification efficiency (%)</td>
<td>75.2</td>
<td>80</td>
</tr>
<tr>
<td>H₂ yield (mol/kg glucose)</td>
<td>1.8</td>
<td>3.1</td>
</tr>
</tbody>
</table>

¹ With Ni catalyst supported on the pine wood derived AC;
² With coconut shell derived AC.
³ na = not applicable;
AC catalyst as reported by Xu et al. [28] may be attributed to the inherent minerals (Ca and Fe, etc.) contained in the ash of its precursor (i.e., coconut shell). As is commonly known, coconut shell normally contains a high ash content of 2-3 wt%, compared to as low as 0.2 wt% for the pine wood sawdust (d.b.). The inherent minerals (Ca and Fe, etc.) are normally present in highly dispersed states in charcoal [29], which would make them exceptionally active as catalysts for some reactions such as ammonia decomposition [30].

In this study, the AC-supported Ni catalyst exhibited much less activity than the $\gamma$-Al$_2$O$_3$-supported catalyst which was in good agreement with a previous study by Lee and Ihm [30] examining the SCWG of glucose (54-160 g/L) using a Ni/AC catalyst with 16 wt% Ni loading. Moreover, another drawback of using AC-based catalysts in SCWG of biomass is its stability at high temperatures under which itself may be gasified by SCW. As such, AC may not be an ideal catalyst support for biomass SCWG.

6.4.3 Performance of modified Ni10/$\gamma$-Al$_2$O$_3$ catalysts with various promoters

In this study the Ni10/$\gamma$-Al$_2$O$_3$ catalyst was further modified with various promoters (e.g., K, Ca, Mg and Ru) in order to investigate the effect of the promoter on reducing coke and tar formation at a relatively higher WHSV (6 h$^{-1}$), which was double the WHSV used for the investigation of the catalytic effects of different transition metals and support materials (i.e., WHSV of 3 h$^{-1}$) as discussed in the previous sections. This higher WHSV was achieved by increasing the feedstock flow rate from 1 mL/min to 2 mL/min while keeping the other reaction conditions the same (e.g., with 50 g/L glucose solution, at
600°C and 24 MPa, and for a time-on-stream of ~8 hours). The performance of these modified Ni10/γ-Al2O3 catalysts with K, Ca, Mg and Ru promoters is summarized in Table 6.5. The table presents yields of tar and coke and compositions of the syngas obtained from the experiments over various modified Ni10/γ-Al2O3 catalysts. However, as a result of the increased WHSV or the feeding flow rate, more coke was built up inside the reactor, and in most of the experiments partial plugging of the reactor started to occur only a few hours after pumping of the feed into the reactor was initiated, as shown in Table 6.5. The plugging of the reactor resulted in a loss of feedstock through the pressure relief valve, such that accurate H2 yields and carbon gasification efficiencies could not be computed. In comparison to the unmodified Ni10/γ-Al2O3 catalyst, the Mg and Ru modified catalysts (Mg0.1Ni10/γ-Al2O3 and Ru0.1Ni10/γ-Al2O3) produced lower yields of both tar and coke without significantly affecting the composition of the gas products. In contrast, the addition of K or Ca promoters to Ni10/γ-Al2O3 did not exhibit positive effects in terms of reducing tar and coke formation. Particularly the K0.5Ni10/γ-Al2O3 doubled the tar yield from 3.1% to 6.8%. Although it was reported that a K-Ca-promoted Ni/α-Al2O3 catalyst (8 wt% Ni on α-Al2O3 with a K-to-Ni molar ratio of 0.5:1 and a Ca-to-Ni molar ratio of 0.1:1) exhibited higher activity and better coke-resistance in a CH4 dry reforming process [13], the K0.5Ca0.1Ni10/γ-Al2O3 however, did not show any beneficial effects on reducing the coke and tar formation, and the reactor containing this catalyst was partially plugged within 2 hours after the SCWG reaction was started.
Table 6.5
Yields of tar and coke and compositions of the syngas obtained from glucose SCWG at 600°C, 24 MPa and a WHSV of 6 h⁻¹ with various modified Ni10/γ-Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield of tar (%)</th>
<th>Yield of coke (%)</th>
<th>Gas composition (mol%)</th>
<th>Time at partial plugging of the reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂</td>
<td>CH₄</td>
</tr>
<tr>
<td>Ni₁₀/γ-Al₂O₃</td>
<td>3.1</td>
<td>1.6</td>
<td>51.2</td>
<td>10.8</td>
</tr>
<tr>
<td>K₀.₅Ni₁₀/γ-Al₂O₃</td>
<td>6.8</td>
<td>1.8</td>
<td>57.7</td>
<td>4.7</td>
</tr>
<tr>
<td>Ca₀.₁Ni₁₀/γ-Al₂O₃</td>
<td>3.6</td>
<td>1.8</td>
<td>49.1</td>
<td>11.7</td>
</tr>
<tr>
<td>K₀.₅Ca₀.₁Ni₁₀/γ-Al₂O₃</td>
<td>1.6</td>
<td>1.9</td>
<td>51.0</td>
<td>11.7</td>
</tr>
<tr>
<td>Mg₀.₁Ni₁₀/γ-Al₂O₃</td>
<td>1.5</td>
<td>1.5</td>
<td>51.4</td>
<td>11.9</td>
</tr>
<tr>
<td>Ru₀.₁Ni₁₀/γ-Al₂O₃</td>
<td>1.1</td>
<td>1.3</td>
<td>48.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

a Averaged values after the gas compositions were getting stable. Other light hydrocarbons, e.g., C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, etc., are not listed due to their negligible amounts.

To quantify the amount of coke deposition on the catalyst during the reaction, the spent Ni₁₀/γ-Al₂O₃, Mg₀.₁Ni₁₀/γ-Al₂O₃ and Ru₀.₁Ni₁₀/γ-Al₂O₃ catalysts after approximately 8 h on stream were characterized using TGA. The TG (thermogravimetry) profiles are shown in Fig. 6.8a. The initial weight loss (below 300°C) was mainly attributed to the removal of water and easily oxidable amorphous carbonaceous species, while the larger weight loss at higher temperatures (above 500°C) may be attributed to the oxidation of coke [31]. From the TG results, the spent catalysts contained approximately 30-40 wt% of coke. Fig. 6.8b illustrates the DTG (derivative thermogravimetry) profiles of the spent catalysts, which were obtained by plotting the weight loss rates, the derivatives of the weight loss percentages of the spent catalysts versus time, as a function of temperature ranging between room temperature and 900°C. The main DTG peak for the spent Ni₁₀/γ-Al₂O₃ catalyst was observed at 680°C, similar to that of Mg₀.₁Ni₁₀/γ-Al₂O₃. In contrast, the peak appeared at a lower temperature (approximately 580°C) for the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst. According to Wang and Lu [14], the carbon species that are oxidable at
lower temperature more likely exist in filamentous and amorphous form; whereas the species that are oxidized at higher temperature are in a graphite-like crystalline form. The formation and deposition of the crystalline form of carbon on the catalyst would mask the active sites and hence resulting in catalyst deactivation. Therefore, the addition of Ru as a promoter could enhance the catalyst stability possibly by reducing the coke/tar formation and forming carbon in a filamentous and amorphous form rather than a graphite-like crystalline form during the SCWG reactions.

In order to confirm the change in carbon morphology with the addition of Ru, TEM analysis was performed on spent Ni10/γ-Al2O3 and Ru0.1Ni10/γ-Al2O3 catalysts and the high resolution images are shown in Fig. 6.9. It can be seen that the carbons deposited on both Ni10/γ-Al2O3 and Ru0.1Ni10/γ-Al2O3 look similar and both of them are amorphous, which is however different from what was observed by DTG analysis. One possible explanation is that the carbon formed on the unmodified catalyst was a Turbostratic (T-) carbon, a partly graphitized carbon which could not be distinguished from amorphous carbon using TEM [32]. However, further investigation is needed as to confirm the existence of this T-carbon in the spent Ni10/γ-Al2O3 catalyst.
Fig. 6.8 TG (a) and DTG (b) profiles of spent Ni10/γ-Al2O3, Mg0.1Ni10/γ-Al2O3 and Ru0.1Ni10/γ-Al2O3 catalysts under air atmosphere.
Fig. 6.9 High resolution TEM images of carbons (indicated by yellow arrows) deposited on spent Ni10/γ-Al2O3 (a) and Ru0.1Ni10/γ-Al2O3 (b) catalysts. The bar scales represent 10 nm (a) and 5 nm (b), respectively.
Although the DTG peak for the spent Mg$_{0.1}$Ni10/γ-Al$_2$O$_3$ catalyst did not shift to a lower temperature, its coke content was slightly lower in comparison to that of the Ni10/γ-Al$_2$O$_3$ as shown in Table 6.5, suggesting an enhanced coke-resistance with the addition of MgO. As proposed by Koo et al [31] who studied coke formation with a MgO-promoted Ni/Al$_2$O$_3$ catalyst for methane dry reforming using CO$_2$, there are two reasons that may account for the enhanced coke-resistance of the Ni/Al$_2$O$_3$ catalyst with the addition of MgO promoter, i.e., 1) MgO improved the basic strength of the support material that could absorb more CO$_2$, providing more surface oxygen to suppress coke formation, and 2) MgO increased the dispersion of Ni crystallites in the support material.

### 6.4.4 Tar characterization

The formation of tar during the SCWG process is undesirable as it not only reduces the total carbon gasification efficiency but also partially contributes to reactor plugging. In this study, the tarry products in the reactor system were recovered with ethyl acetate flushing at the end of the experiments. The CHO compositions of these tars were analyzed and are shown in Table 6.6. The tars can be presented as an organic mixture with a general empirical formula of C$_{6.0-6.9}$H$_{5.6-6.9}$O$_{0.7-1.4}$ with a higher heating value (HHV) of 29-34 MJ/kg. The empirical formula of C$_{6.0-6.3}$H$_{5.6-6.9}$O$_{0.7-1.4}$ for the tars also implies that they have a high degree of unsaturation (H/C molar ratio of ~ 1.0), suggesting the presence of aromatic compounds in the tars. Although the results are not included in this paper, some tars obtained were analyzed with GC/MS, and the presence of aromatic compounds (2-methyl-benzofuran, 1-methyl-1H-indene, 2-methyl-naphthalene, etc.) in the tars was
Table 6.6
CHO element analysis of the tar products.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CHO analysis of the tar</th>
<th>Empirical formula</th>
<th>HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (%)</td>
<td>H (%)</td>
<td>O (%)</td>
</tr>
<tr>
<td>Blank</td>
<td>78.4</td>
<td>6.6</td>
<td>15.0</td>
</tr>
<tr>
<td>Ni₁₀/γ-Al₂O₃</td>
<td>80.5</td>
<td>5.9</td>
<td>13.6</td>
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<tr>
<td>Ni₅Co₅/γ-Al₂O₃</td>
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<td>6.3</td>
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<tr>
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<td>6.9</td>
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<tr>
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<td>5.8</td>
<td>22.5</td>
</tr>
<tr>
<td>Ni₂₀/ZrO₂</td>
<td>80.8</td>
<td>5.6</td>
<td>13.6</td>
</tr>
<tr>
<td>Ni₁₀/AC</td>
<td>77.3</td>
<td>6.3</td>
<td>16.4</td>
</tr>
</tbody>
</table>

*a* By difference (O%=100%-C%-%H%).

*b* Higher heating value (HHV) calculated by the Dulong Formula, i.e., HHV(MJ/kg) = 0.3383C + 1.422(H-O/8).

noted. The formation of aromatic compounds from glucose in the SCWG process may have resulted from a variety of reactions such as dehydration, cyclization, etc. A detailed reaction pathway from glucose to methoxybenzene and phenol was proposed by Williams and Onwudili [16] and hence will not be described in this work.

6.5 Conclusions

To screen supported catalysts for hydrogen production from glucose via catalytic supercritical water gasification, in total 17 heterogeneous catalysts, with combinations of 4 transition metals (Ni, Ru, Cu and Co) and various promoters (e.g., Na, K, Mg, or Ru) supported on different support materials (γ-Al₂O₃, ZrO₂, and activated carbon), were investigated with respect to their catalytic activity and stability for H₂ production at
600°C and 24 MPa in a bench-scale continuous-flow tubular reactor. The major conclusions drawn from this study can be summarized as follows:

1) Ni and Ru supported on γ-Al₂O₃ exhibited very high activity and H₂ selectivity among all of the catalysts investigated for a time-on-stream of 5-10 h. With Ni20/γ-Al₂O₃ (i.e., γ-Al₂O₃ with 20 wt% Ni), a H₂ yield of 38.4 mol/kg glucose was achieved, ~20 times higher than that obtained from the blank test without catalyst (1.8 mol/kg glucose).

2) The metallic form of Ni is the active site for the SCWG reaction, while both metallic Ru and RuO₂ were comparably active for catalyzing the SCWG reactions.

3) The activities of γ-Al₂O₃-supported binary metallic catalysts (combination of two metals at an equal or comparable amount, e.g., 5%Ni-5%Ru, 15%Ni-5%Co, 5%Ni-5%Co, 10%Ru-10%Cu and 10%Ni-10%Cu) are predictable from their component activities as the results showed additive effects between the component metals.

4) The supported Ni catalysts exhibited the following order of catalytic activities for producing H₂ from SCWG of glucose: γ-Al₂O₃>ZrO₂> AC.

5) The modified Ni10/γ-Al₂O₃ catalysts with promoters of the Mg and Ru could suppress the tar and coke formation. By contrast, the addition of K or Ca promoters
to Ni10/\gamma-Al_2O_3 did not exhibit positive effects in terms of reducing tar and coke formation.
6.6 References


[19] Parizotto NV, Rocha KO, Damyanova S, Passos FB, Zanchet D, Marques CMP, Bueno JMC. Alumina-supported Ni catalysts modified with silver for the stem


Chapter 7
Activity and Long-Term Stability of a Novel Ru Modified Ni Catalyst for Hydrogen Generation by Supercritical Water Gasification of Glucose

7.1 Abstract

The activities and long-term stabilities of \(\gamma\)-Al\(_2\)O\(_3\) supported Ni catalysts (Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\), Ru\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) and Mg\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\)) for hydrogen generation through the supercritical water gasification (SCWG) of glucose were investigated at 700\(^\circ\)C, 24 MPa and a weight hourly space velocity (WHSV) of 6 h\(^{-1}\) in a bench-scale continuous downflow tubular reactor. The Ru\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) catalyst (10 wt% Ni, the Ru-to-Ni molar ratio of 0.1) exhibited the best activity and long-term stability among the three catalysts examined. With the Ru\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) catalyst, negligible catalyst deactivation was observed over a period of 33 h on stream. The H\(_2\) yield was maintained as high as \(~50\) mol/kg glucose throughout the entire stability test. In contrast, the activities of both Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) and Mg\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) catalysts (10 wt% Ni, with a Mg-to-Ni molar ratio of 0.1) decreased after approximately 7 h on stream, accompanied by a marked decrease in the H\(_2\) yield from \(~50\) mol/kg glucose initially to \(~25\) mol/kg glucose after 7 h. The TPR (temperature-programmed reduction) and H\(_2\) chemisorption analysis on the fresh catalysts demonstrated that the addition of a small amount of Ru as a modifier could improve the Ni dispersion, decrease the Ni crystalline size and increase the reducibility of NiO in the catalyst, which hence could account for the enhanced activity and long-term stability of the Ru\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) catalyst. In addition, XRF (X-ray fluorescence) analysis
of the fresh and spent catalysts (Ni10/γ-Al2O3, Ru0.1Ni10/γ-Al2O3 and Mg0.1Ni10/γ-Al2O3) indicated that the Ni-to-Al2O3 ratios were almost unchanged for all the catalysts before and after the SCWG tests, suggesting that all the γ-Al2O3-supported Ni catalysts exhibited excellent resistance to supercritical water.

### 7.2 Introduction

Supercritical water gasification (SCWG) is an innovative hydrothermal process that can directly convert wet biomass material or aqueous organic waste into a valuable H2-rich syngas employing supercritical water (SCW, T≥374°C and P≥22.1 MPa) [1]. The main reactions taking place in SCWG include steam reforming (Eq. 7.1), water-gas shift (Eq. 7.2) and methanation (Eq. 7.3) reactions.

\[
\begin{align*}
\text{CH}_x\text{O}_y + (1 - y)\text{H}_2\text{O} & \leftrightarrow \text{CO} + (1 - y + \frac{x}{2})\text{H}_2 & (7.1) \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 & (7.2) \\
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} & (7.3)
\end{align*}
\]

In most biomass SCWG processes, catalysts are added to improve the yield and selectivity of H2 gas or lower the reaction temperature [2]. To date, three types of catalysts have generally been utilized for biomass SCWG, i.e., alkalis [3,4], activated carbon (AC) [5-7] and supported transition metal catalysts [2,8,9]. Alkali catalysts have been found to be effective in promoting the water-gas shift reaction (Eq. 7.2) via the
formation of an intermediate product of alkali formate, as shown by the following reactions (Eqs. 7.4-7.6), where R represents alkali metals [3].

\[
\begin{align*}
R_2CO_3 + H_2O & \leftrightarrow RHCO_3 + ROH \quad (7.4) \\
ROH + CO & \leftrightarrow ROOCH \quad (7.5) \\
ROOCH + H_2O & \leftrightarrow RHCO_3 + H_2 \quad (7.6)
\end{align*}
\]

Examples of commonly used alkali catalysts are KOH, NaOH, Ca(OH)\textsubscript{2}, KHCO\textsubscript{3}, K\textsubscript{2}CO\textsubscript{3}, etc. Despite their effectiveness in catalyzing SCWG reactions, alkalis as homogeneous catalysts are difficult to recycle and reuse, which could increase the operational cost of the overall process. In addition, alkalis may cause corrosion to metallic reactors under supercritical water conditions [10]. Moreover, the resulting effluent might require further treatment before its final disposal due to the high alkalinity of the effluent.

In comparison to homogeneous catalysts, heterogeneous catalysts are more advantageous in terms of their higher activity and selectivity for H\textsubscript{2} generation and ease of recyclability. In addition, heterogeneous catalysts produce a cleaner effluent that does not require further treatment before its final disposal, thus being more environmentally friendly [2]. Activated carbon (AC) and many AC-derived catalysts have found applications in catalyzing SCWG of organic compounds. For example, Xu and co-workers [6] were able to gasify a 216 g/L glucose solution completely at 600\textdegree C and 25.5 MPa with the aid of a coconut shell-derived AC catalyst. In addition, Lee and Ihm [5] obtained a 4-fold increase in H\textsubscript{2} yield when gasifying a 108 g/L glucose solution at 650\textdegree C and 28 MPa in the presence of an AC-supported Ni catalyst (16 wt\% Ni).
However, among all the catalysts studied for SCWG, the most extensively investigated catalysts are metal oxide (e.g., $\gamma$-Al$_2$O$_3$, ZrO$_2$, MgO, TiO$_2$, SiO$_2$, CeO$_2$, etc.) supported transition metals (e.g., Ni, Fe and noble metals such as Rh, Ru, Pt and Pd) catalysts due to their high activities in promoting the water-gas shift reaction and breaking down the C-C and C-O bonds [9,11,12]. Detailed summaries regarding the behaviours of various supported transition metal catalysts can be found elsewhere [2,10].

Ni and Ru are effective transition metals for catalyzing H$_2$ production reactions via biomass SCWG [2,12,13]. In our previous catalyst screening tests involving the SCWG of glucose solutions at 600ºC and 24 MPa, Ni/$\gamma$-Al$_2$O$_3$ and Ru/$\gamma$-Al$_2$O$_3$ produced the highest H$_2$ yield among all the catalysts tested (Co, Ni, Ru, Cu catalysts supported on $\gamma$-Al$_2$O$_3$, ZrO$_2$, or AC) [12]. Compared to Ni, Ru showed a higher activity and was reported to be more stable because less agglomeration was noted over a long period of time [13]. However, Ni is still more practical owing to its relatively lower cost [2]. As such, a novel highly active Ni-based catalyst modified by a small amount of Ru (the Ru-to-Ni molar ratio of 0.1) (Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$) was developed in our previous research [12]. In addition, Mg was also found to be an effective catalyst promoter that contributed to the reduction in coke formation in the SCWG of glucose [12].

It is well accepted that, the long-term stability for a catalyst is as critically important as the activity and selectivity for the catalyst [8]. In our previous research, although Ru and Mg were found to decrease coke formation, the long-term stabilities of the Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ and Mg$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ catalysts were not investigated. As such, the primary
objective of this work was to examine the long-term performances of these two catalysts for hydrogen generation by SCWG of glucose over a long period of time-on-stream (> 24 h). In addition, the fresh and spent catalysts were also characterized using various analytical methods such as N₂ adsorption-desorption isotherms, X-ray diffraction (XRD), thermogravimetric analyzer (TGA), X-ray fluorescence (XRF), inductively coupled plasma-optical emission spectrometer (ICP-OES), temperature-programmed reduction (TPR) and H₂ pulse chemisorption. For comparison, the non-modified catalyst (Ni10/γ-Al₂O₃) was also investigated under similar experimental conditions.

7.3 Materials and methods

7.3.1 Catalyst preparation

The catalysts were prepared by wetness impregnation (or co-impregnation) of γ-Al₂O₃ powders (Inframat Advanced Materials) with aqueous solutions of Ni(NO₃)₂·6H₂O (Sigma-Aldrich), HN₄O₁₀Ru (Sigma-Aldrich), and/or Mg(NO₃)₂·6H₂O (Sigma-Aldrich) [12]. The compositions of the catalysts are shown in Table 7.1. The impregnated catalysts were firstly oven-dried at 120°C for at least 12 h and then calcined in air at 550°C for 6.5 h. The calcined catalysts were crushed and sieved; particles with sizes between 300-850 μm were selected for this study.
Table 7.1
Catalyst compositions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Weight percentage of Ni (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Type and weight percentage of the promoter (wt%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Molar ratio of the promoter to Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni10/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ru&lt;sub&gt;0.1&lt;/sub&gt;Ni10/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
<td>Ru, 1.72</td>
<td>0.1</td>
</tr>
<tr>
<td>Mg&lt;sub&gt;0.1&lt;/sub&gt;Ni10/γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>γ-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10</td>
<td>Mg, 0.41</td>
<td>0.1</td>
</tr>
</tbody>
</table>

<sup>a</sup> The weight percentage with respect to the mass of γ-Al<sub>2</sub>O<sub>3</sub>;

<sup>b</sup> The subscript “0.1” of Ru or Mg indicates the specific molar ratio of the promoter metal to nickel.

7.3.2 SCWG experiments and the catalyst stability tests

The catalyst stability tests were conducted at 700°C and 24 MPa in a bench-scale continuous down-flow tubular reactor system (Fig. 7.1). The reactor is made of Inconel 625 tubing with 9.55 mm OD × 6.34 mm ID × 472 mm length. For each test, 1 g of the calcined catalyst was placed on the catalyst bed and was reduced <i>in-situ</i> under flowing H<sub>2</sub> (30 ml/min) at 500°C for 1 h before the SCWG reaction. As the only feedstock employed in the stability test, 50 g/L glucose (J.T.Baker) solution was continuously introduced into the reactor system with a HPLC pump (Eldex) at a fixed flow rate of 2 mL/min, corresponding to a WHSV (weight hourly space velocity) of 6 h<sup>-1</sup>. A back-pressure regulator was employed to maintain the reactor at constant pressure of 24 MPa. The reaction effluent including liquid and gas products was cooled down and separated with a liquid-gas separator at atmospheric pressure.
The stability tests lasted for approximately 33 h for the Mg$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ and Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ catalysts, respectively. Each of the tests was completed in four days, during which it continued running for ~ 8 h every day. At the end of Day 1, 2 and 3, the heater was turned off and reactor was cooled down to room temperature by cold water that was continuously pumped into the system. The cooling process normally took approximately 1 h. The back-pressure regulator remained unadjusted during the first three days; therefore the system pressure would be restored to 24 MPa as soon as the reactor was heated to 700°C. Different from that of the Mg$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ or Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ catalyst, the stability test of the Ni$_{10}$/γ-Al$_2$O$_3$ catalyst lasted for only 25 h (or 3 days) due to reactor plugging that occurred on Day 3.
7.3.3 Recovery and analysis of the reaction products

The gaseous product was collected continuously with a known-volume gas cylinder during the experiment and the gas composition was analyzed with an Agilent 3000 Micro-Gas Chromatograph (GC) equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors (TCDs). The tars inside the reactor were washed using A.C.S. reagent-grade ethyl acetate. The ethyl acetate phase was then separated from water by using a separatory funnel, transferred into a pre-weighed evaporation flask, and evaporated at 60°C at a reduced pressure of 10 kPa to remove the solvent. The remaining brown viscous liquid was weighed to obtain the mass of tars. The solid residues (SR), which was composed of spent catalyst and coke, were collected after the experiment and the collected SR was quantified after oven drying at 105°C for 12 h. The amount of coke was determined with a TGA-i 1000 (Instrument Specialist Inc.) by heating the SR in an air atmosphere (air flow rate: 40 ml/min) from room temperature to 900°C at 20°C/min. The weight loss between 120 and 900°C was attributed to the combustion of coke.

7.3.4 Catalyst characterization

The BET surface area, total pore volume, and the average pore diameter of the fresh (calcined without reduction) and spent (collected at the end of the stability test) Ni10/γ-Al₂O₃, Mg₀.₁Ni10/γ-Al₂O₃ and Ru₀.₁Ni10/γ-Al₂O₃ catalysts were measured by N₂ adsorption-desorption isotherms on a Quantachrome Nova 2200e Surface Area & Pore Size Analyzer. XRD analysis was used to identify the crystalline structure and
composition of the catalysts. In this research, the XRD patterns were recorded using a PANalytical X’Pert Pro diffractometer with Cu Kα as the radiation source. The step-scans were taken over the 2θ range of 6–76°. The TPR profiles of the fresh catalysts of Ni10/γ-Al₂O₃ and Ru₀.₁Ni10/γ-Al₂O₃ were obtained with a Micromeritics Autochem 2920 equipped with a TCD detector. The catalysts were firstly pre-treated under a 5% O₂/He mixture flow at 50 mL/min and heated from ambient temperature to 550°C at 10°C/min. The pre-treated catalysts were then exposed to a flowing gas composed of H₂ and Ar (v/v=1:9) at 50 mL/min and were heated from room temperature to 950°C at a heating rate of 10°C/min. The H₂ pulse chemisorptions were also conducted with the same equipment to determine the dispersion and active size of the metallic Ni. The elemental compositions of the catalysts were analyzed using an ICP-OES with a Varian Vista Pro ICAP Radial spectrometer. In addition, the weight percentages of NiO and γ-Al₂O₃ in the fresh and spent catalysts were determined with a Panalytical Axios Advanced wavelength dispersive XRF.

7.4 Results and discussion

7.4.1 Catalyst stability experiments

Fig. 7.2 shows the H₂ yields as a function of time-on-stream from the SCWG of 50g/L glucose solution at 700°C, 24 MPa and a WHSV of 6 h⁻¹ in the presence of Ni10/γ-Al₂O₃, Ru₀.₁Ni10/γ-Al₂O₃ or Mg₀.₁Ni10/γ-Al₂O₃. The H₂ yield in this research is defined as the moles of H₂ produced in relation to the mass (kg) of glucose consumed. It can be seen
that each of the three catalysts exhibited comparably high activities on Day 1 in terms of H₂ formation, each producing ~50 mol/kg glucose. These represented H₂ yields were approximately 4-fold higher than those obtained from the non-catalytic experiment (10.7 mol/kg glucose, data not shown in the figure). However, the activities of the Mg₀.₁Ni₁₀/γ-Al₂O₃ and Ni₁₀/γ-Al₂O₃ decreased significantly after Day 1, with corresponding H₂ yields decreased by half, from ~50 to ~25 mol/kg glucose. In contrast, the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst remained highly active from Day 2 to Day 4; the H₂ yield remained at ~50 mol/kg glucose throughout the entire stability test, which lasted for a total of 33 h. Therefore, the addition of a small amount of Ru as a modifier was noted to enhance the long-term stability of the Ni₁₀/γ-Al₂O₃ catalyst in SCWG of glucose.

![Graph showing H₂ yields from the catalyst stability tests](image_url)

**Fig. 7.2** H₂ yields from the catalyst stability tests of the Ni₁₀/γ-Al₂O₃, Ru₀.₁Ni₁₀/γ-Al₂O₃ and Mg₀.₁Ni₁₀/γ-Al₂O₃ catalysts (50 g/L glucose, 700°C and WHSV = 6 h⁻¹). Lines are added to guide the eye.
The compositions of the syngases from the three stability tests are shown in Table 7.2. The syngas was mainly composed of H₂, CH₄, CO and CO₂, with negligible quantities of C₂ and C₃ compounds, such as ethylene (C₂H₄), ethane (C₂H₆), acetylene (C₂H₂), propane (C₃H₈), and propylene (C₃H₆).

**Table 7.2**

Average compositions (vol%) of the syngas produced from the stability tests with the Ni₁₀/γ-Al₂O₃, Ru₀.₁Ni₁₀/γ-Al₂O₃ and Mg₀.₁Ni₁₀/γ-Al₂O₃ catalysts (50 g/L glucose, 700°C and WHSV = 6 h⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>Ni₁₀/γ-Al₂O₃</th>
<th>Ru₀.₁Ni₁₀/γ-Al₂O₃</th>
<th>Mg₀.₁Ni₁₀/γ-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>H₂</td>
<td>62.8</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>3.1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>1.2</td>
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</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>32.9</td>
<td>34.3</td>
</tr>
<tr>
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<td></td>
<td>CO</td>
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<td>6.6</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>32.8</td>
<td>32.3</td>
</tr>
</tbody>
</table>

For each of the tests, at Day 1 H₂ was the major component of the syngas, contributing ≥ 60% of the total gas volume. The syngas volume percentages of CH₄ and CO were only 3.1-5.0 vol% and 1.1-1.4 vol%, respectively. From Day 2 to Day 4, the gas compositions remained relatively stable for the test with the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst, indicating the
enhanced long-term stability of this catalyst. However, the percentage of CH\textsubscript{4} increased significantly with either Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} or Mg\textsubscript{0.1}Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} from Day 2 onward (from < 5 vol\% on Day 1 to ≥ 8 vol\% on Days 2-4), accompanied by increased concentrations of CO (from < 1.5 vol\% on Day 1 to > 6 vol\% on Days 2-4) and significantly decreased H\textsubscript{2} contents (from > 61 vol\% on Day 1 to < 51 vol\% on Days 2-4). The increases in CH\textsubscript{4} and CO concentrations in the syngas after Day 1 imply a suppression of the steam reforming and water-gas shift reactions (Eqs. 7.1 and 7.2), likely due to the deactivation of the Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} and Mg\textsubscript{0.1}Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts after Day 1. These results were in good agreement with the observations found in Fig. 7.2.

Table 7.3 shows the overall yields of tar and coke formed throughout the stability tests for the Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3}, Ru\textsubscript{0.1}Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} and Mg\textsubscript{0.1}Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. The tar (or coke) yield was calculated by dividing the mass of tar (coke) by the total mass of glucose (g) consumed. The tar and coke yields obtained from other tests conducted under exactly the same experimental conditions but for a shorter reaction time are also presented in this table for comparison. Tar is a by-product generated during glucose SCWG. As analyzed by GC/MS in previous research, tar is mainly composed of a variety of organic compounds that are highly unsaturated (H/C molar ratio of ~ 1.0) such as aromatic compounds [12]. The formation of tar is undesirable as it is an indicator of low carbon gasification efficiency. More importantly, the build-up of tar may cause reactor plugging. Fortunately, due to the high reaction temperature (700°C) and with the aid of the catalysts, the formation of tar was negligible in each of the three experiments, particularly with Ru\textsubscript{0.1}Ni\textsubscript{10}/γ-Al\textsubscript{2}O\textsubscript{3}, where only 0.04 wt\% of the glucose was converted to tar. It is
interesting to note that the tar yields obtained with a shorter reaction time were generally higher than those attained from the long-term stability tests, which would indicate that more tars were formed at the beginning of the experiments before the catalyst’s activity and the experimental conditions had achieved the stable state.

Table 7.3
Yields of tar and coke formed during the SCWG of 50 g/L glucose with Ni10/γ-Al2O3, Ru0.1Ni10/γ-Al2O3 or Mg0.1Ni10/γ-Al2O3 catalyst (700°C and WHSV = 6 h⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>Ni10/γ-Al2O3</th>
<th>Ru0.1Ni10/γ-Al2O3</th>
<th>Mg0.1Ni10/γ-Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stability test</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment duration (h)</td>
<td>24.9</td>
<td>33.1</td>
<td>32.6</td>
</tr>
<tr>
<td>Total glucose consumed (g)</td>
<td>137.6</td>
<td>189.1</td>
<td>168.5</td>
</tr>
<tr>
<td>Total tar recovered (g)</td>
<td>0.3063</td>
<td>0.0832</td>
<td>0.1449</td>
</tr>
<tr>
<td>Yield of tar (%)</td>
<td>0.22</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>Total coke recovered (g)</td>
<td>0.7088</td>
<td>1.1767</td>
<td>0.9399</td>
</tr>
<tr>
<td>Yield of coke (%)</td>
<td>0.52</td>
<td>0.62</td>
<td>0.56</td>
</tr>
<tr>
<td><strong>Comparison tests</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment duration (h)</td>
<td>8.0</td>
<td>8.5</td>
<td>8.2</td>
</tr>
<tr>
<td>Total tar recovery (g)</td>
<td>0.1578</td>
<td>0.0397</td>
<td>0.083</td>
</tr>
<tr>
<td>Yield of tar (%)</td>
<td>0.34</td>
<td>0.08</td>
<td>0.17</td>
</tr>
<tr>
<td>Total coke recovery (g)</td>
<td>0.71</td>
<td>0.27</td>
<td>0.60</td>
</tr>
<tr>
<td>Yield of coke (%)</td>
<td>1.52</td>
<td>0.54</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Coke has been commonly regarded as one of the major factors that contribute to catalyst deactivation and reactor plugging. In our previous research [12], Ru or Mg was shown to be effective in reducing coke formation in the SCWG of 50 g/L glucose solution at 600°C, 24 MPa and a WHSV of 6 h⁻¹. For example, the coke yield decreased from 1.64% (with Ni10/γ-Al2O3) to 1.46% (with Mg0.1Ni10/γ-Al2O3), and 1.34% (with Ru0.1Ni10/γ-Al2O3),
respectively, after approximately 8 h of the SCWG reaction. In addition, the carbon species changed from a graphite-like crystalline form (with Ni10/γ-Al2O3) to a filamentous and amorphous form (with Ru0.1Ni10/γ-Al2O3), as evidenced through the derivative thermogravimetric (DTG) analysis of the spent Ni10/γ-Al2O3 and Ru0.1Ni10/γ-Al2O3 catalysts. As shown in Table 7.3, in this research, similar results were noted for the experiments performed for a shorter reaction time, where the addition of Ru successfully suppressed the formation of coke, reducing the coke yield from 1.52% (with Ni10/γ-Al2O3) to 0.54% (with Ru0.1Ni10/γ-Al2O3). However as shown in Table 7.3, the presence of Ru did not decrease the coke yield compared to the non-modified Ni10/γ-Al2O3 catalyst during the long-term stability tests (0.62% with Ru0.1Ni10/γ-Al2O3 vs. 0.52% with Ni10/γ-Al2O3). Considering the persistent and high activity of the Ru0.1Ni10/γ-Al2O3 catalyst for H2 generation, it may thus be speculated that coke formation was not the only cause of catalyst deactivation.

7.4.2 Catalyst characterization

7.4.2.1 BET analysis

The BET surface area, total pore volume and average pore size of the catalysts before and after the stability tests are shown in Table 7.4. As an example, the N2 adsorption-desorption isotherms of the fresh and spent Ru0.1Ni10/γ-Al2O3 are illustrated in Fig. 7.3. The BET surface area of the non-modified fresh Ni10/γ-Al2O3 catalyst was 41.9 m²/g, and decreased to 34.2 and 38.1 m²/g, respectively, with the addition of Ru or Mg, which was
expected due to the impregnation of the metal ions. Generally, the BET surface areas of each of the catalysts decreased after the SCWG reaction, accompanied by a reduction in total pore volume and average pore size, due to the blockage of the pores by coke deposition and the growth of metal crystals [5,14]. For example, the BET surface area of the Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3} decreased from 41.9 to 30.0 m\textsuperscript{2}/g after the SCWG test, and the corresponding total pore volume and average pore size was reduced by more than 50%, from 0.13 cm\textsuperscript{3}/g and 12.3 nm (fresh catalyst) to 0.05 cm\textsuperscript{3}/g and 6.0 nm (spent catalyst).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Total pore volume (cm\textsuperscript{3}/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>41.9</td>
<td>0.13</td>
<td>12.3</td>
</tr>
<tr>
<td>Spent</td>
<td>30.0</td>
<td>0.05</td>
<td>6.0</td>
</tr>
<tr>
<td>Ru\textsubscript{0.1}Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>34.2</td>
<td>0.09</td>
<td>10.7</td>
</tr>
<tr>
<td>Spent</td>
<td>22.8</td>
<td>0.03</td>
<td>6.0</td>
</tr>
<tr>
<td>Mg\textsubscript{0.1}Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>38.1</td>
<td>0.13</td>
<td>6.6</td>
</tr>
<tr>
<td>Spent</td>
<td>44.4</td>
<td>0.07</td>
<td>6.0</td>
</tr>
</tbody>
</table>

However, it is interesting to note that the BET surface of the Mg\textsubscript{0.1}Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3} actually increased slightly from 38.1 to 44.4 m\textsuperscript{2}/g after the stability test in SCW. On the one hand, the increase in the BET surface of the Mg\textsubscript{0.1}Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst in the SCWG process might be due to the dissolution of the Mg by the SCW. On the other hand, Mg as an alkaline earth metal might activate the deposited coke in the catalyst during the SCWG process [15], and hence result in an increase in the BET surface area for the spent catalyst.
Fig. 7.3 N₂ adsorption-desorption isotherms (at -196°C) for the fresh and the spent catalysts of Ru₀.₁Ni₁₀/γ-Al₂O₃.

7.4.2.2 XRD analysis

The XRD patterns of the fresh, reduced and spent Ni₁₀/γ-Al₂O₃, Ru₀.₁Ni₁₀/γ-Al₂O₃ and Mg₀.₁Ni₁₀/γ-Al₂O₃ catalysts are shown in Fig. 7.4. The peaks of γ-Al₂O₃ and NiAl₂O₄ practically overlap [16]. The loaded Ni was present as either NiO or NiAl₂O₄ in the fresh (calcined) catalysts. After reduction with a 30 mL/min H₂ flow at 500°C for 1 h, the NiO was reduced to metallic Ni. However, since the reduction of NiAl₂O₄ requires higher temperatures (>500°C) [17], the NiAl₂O₄ was unchanged after the H₂ reduction. Metallic Ni is the active species for catalyzing biomass SCWG reactions [11,12]. As shown in Fig. 7.4, the signal of the metallic Ni was visible in all the reduced catalysts, and it was also clearly noticeable in the spent catalysts after 1 day on stream. However, the signals of the metallic Ni disappeared in the spent catalyst of Ni₁₀/γ-Al₂O₃ or Mg₀.₁Ni₁₀/γ-Al₂O₃ after
the long-term stability test. In contrast, the metallic Ni could still be detected in the spent Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ catalyst that was collected at the end of the long-term stability test. The above XRD results imply that the metallic Ni is the active species for catalyzing the glucose SCWG reactions.
Fig 7.4 XRD patterns of the fresh, reduced and spent (a) Ni10/γ-Al2O3, (b) Ru0.1Ni10/γ-Al2O3 and (c) Mg0.1Ni10/γ-Al2O3 before and after the long-term stability tests.
It was reported that $\gamma$-alumina could become unstable in the presence of hot-compressed water under hydrothermal conditions as it could transform into $\alpha$-$\text{Al}_2\text{O}_3$ [8] or metastable forms such as böhmite [18,19]. However, no such Al-containing species were detectable in the spent catalysts in this research. In fact, the signals of $\gamma$-$\text{Al}_2\text{O}_3$ were evident on the XRD spectra of all the fresh and spent catalysts, as shown in Fig. 7.4.

As also shown in Fig. 7.4, there were broad signals appearing between 20 and 30$^\circ$C on the XRD spectra of the spent catalysts. These signals were attributable to the presence of coke, and the signals intensified for a longer time-on-stream, implying the continuous accumulation of coke during the SCWG experiments.

### 7.4.2.3 TPR analysis and $\text{H}_2$ chemisorption

In order to further investigate the effect of the addition of Ru on the properties of the Ni10/$\gamma$-$\text{Al}_2\text{O}_3$ catalyst, TPR and $\text{H}_2$ chemisorptions analyses were conducted on fresh Ni10/$\gamma$-$\text{Al}_2\text{O}_3$ and Ru$_{0.1}$Ni10/$\gamma$-$\text{Al}_2\text{O}_3$ catalysts, and the results are presented in Fig. 7.5 and Table 7.5, respectively. As shown in Fig. 7.5, the TPR profile of the Ni10/$\gamma$-$\text{Al}_2\text{O}_3$ catalyst peaked at 425$^\circ$C, which was ascribed to the reduction of NiO [17]. With the addition of Ru, a similar pattern was noted. However, the peak shifted toward a low temperature (410$^\circ$C), indicating that Ru, as a promoter, increased the reducibility of NiO via modifications of the interaction between Ni and $\gamma$-$\text{Al}_2\text{O}_3$. As with most of the $\text{Al}_2\text{O}_3$ supported Ni catalysts reported in literatures [16,17,20,21], a large TPR peak occurring in the temperature range of 500-1000$^\circ$C was normally present ascribing to the reduction of
NiAl₂O₄. However, no such peaks were observed from neither the Ni₁₀/γ-Al₂O₃ nor the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalysts in this research, although NiAl₂O₄ was detected by XRD as shown in Fig 7.4. This might be due to the enhanced stability of the NiAl₂O₄, even at the maximum temperature (i.e., 900°C) of the TPR tests.

![TPR profiles of the fresh Ni10/γ-Al₂O₃ and Ru0.1Ni10/γ-Al₂O₃ catalysts.](image)

**Fig. 7.5** TPR profiles of the fresh Ni10/γ-Al₂O₃ and Ru₀.₁Ni₁₀/γ-Al₂O₃ catalysts. (The catalysts were heated at a heating rate of 10°C/min under a 50 mL/min flowing gas composed of H₂ and Ar (v/v=1:9)).

Table 7.5 summarizes the results obtained from the H₂ pulse chemisorption analyses of the fresh catalysts of Ni₁₀/γ-Al₂O₃ and Ru₀.₁Ni₁₀/γ-Al₂O₃. The Ni dispersion was 0.69% for the Ni₁₀/γ-Al₂O₃ catalyst with a metallic surface area and cubic crystallite size of 4.63 m²/g metal and 121 nm, respectively. With the small addition of Ru, the dispersion of Ni particles almost doubled (from 0.69 to 1.27%), accompanied by a significant increase in...
the metallic surface area (from 4.63 to 8.49 m²/g metal) and decrease in the size of the Ni crystals (from 121 to 66 nm). An enhanced Ni dispersion translates to a reduction in the risk of the sintering of Ni particles and consequently an enhanced long-term stability of the catalyst [17,21]. In this research, the addition of Ru led to an improved interaction between Ni and γ-Al₂O₃ and therefore the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst exhibited higher durability than the non-modified Ni₁₀/γ-Al₂O₃ catalyst for the SCWG of glucose.

Table 7.5
Summary of the H₂ pulse chemisorption results of the fresh Ni₁₀/γ-Al₂O₃ and Ru₀.₁Ni₁₀/γ-Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Ni₁₀/γ-Al₂O₃</th>
<th>Ru₀.₁Ni₁₀/γ-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal dispersion (%)</td>
<td>0.70</td>
<td>1.27</td>
</tr>
<tr>
<td>Metallic surface area (m²/g sample)</td>
<td>0.46</td>
<td>0.85</td>
</tr>
<tr>
<td>Metallic surface area (m²/g metal)</td>
<td>4.63</td>
<td>8.49</td>
</tr>
<tr>
<td>Active particle diameter (hemisphere, nm)</td>
<td>145</td>
<td>79</td>
</tr>
<tr>
<td>Cubic crystallite size (nm)</td>
<td>121</td>
<td>66</td>
</tr>
</tbody>
</table>

7.4.2.4 ICP-OES and XRF analyses

The elemental compositions of the fresh and spent catalysts of Ni₁₀/γ-Al₂O₃, Ru₀.₁Ni₁₀/γ-Al₂O₃ and Mg₀.₁Ni₁₀/γ-Al₂O₃ were analyzed with ICP-OES and the results are shown in Table 7.6. The purpose of this analysis was to monitor the compositional change, particularly Ni and Al₂O₃, of the catalyst before and after the stability tests under SCW conditions. Not surprisingly, Al and Ni were the two major elements in all of the fresh and spent catalysts, with negligible concentrations of other constituents, such as Ca, Cu, Fe, K, Na, etc. However, the concentrations of Al and Ni obtained, as shown in Table 7.6,
were much lower in comparison to their theoretical values. For example, the wt% of Al in the fresh Ni10/\(\gamma\)-Al\(_2\)O\(_3\) catalyst was calculated to be 1.07 wt% (or 10748.2 mg/kg), which was far below its theoretical value (46.96 wt%, assuming that the fresh Ni10/\(\gamma\)-Al\(_2\)O\(_3\) was exclusively composed of NiO and \(\gamma\)-Al\(_2\)O\(_3\) and the Ni-to-\(\gamma\)-Al\(_2\)O\(_3\) mass ratio was 0.1). The low Al concentration as analyzed with ICP-OES was most likely due to the incomplete dissolution of \(\gamma\)-Al\(_2\)O\(_3\) in the sample preparation for the ICP analysis using aqua regia (3:1 HCl/HNO\(_3\)) digestion. In contrast, the Ni concentrations of the fresh catalysts (~7 wt%) detected by ICP were close to its theoretical value (~8.9 wt%). As for the ICP analysis of the spent catalysts, the results were not accurate, e.g., the Al and Ni contents in the spent catalysts were only 0.077~0.166% and 0.052~0.085%, respectively. The authors believe that these errors were due to the presence of coke in the submitted samples for the ICP analysis and the reduced acid-digestibility of the spent catalysts.

Table 7.6
ICP-OES results of the fresh and spent Ni10/\(\gamma\)-Al\(_2\)O\(_3\), Ru\(_{0.1}\)Ni10/\(\gamma\)-Al\(_2\)O\(_3\) and Mg\(_{0.1}\)Ni10/\(\gamma\)-Al\(_2\)O\(_3\) catalysts.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni10/(\gamma)-Al(_2)O(_3)</th>
<th>Ru(_{0.1})Ni10/(\gamma)-Al(_2)O(_3)</th>
<th>Mg(_{0.1})Ni10/(\gamma)-Al(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Spent</td>
<td>Fresh</td>
</tr>
<tr>
<td>Al</td>
<td>10748.2</td>
<td>765.42</td>
<td>10248.2</td>
</tr>
<tr>
<td>Ca</td>
<td>20.6</td>
<td>26.7</td>
<td>19.4</td>
</tr>
<tr>
<td>Cu</td>
<td>9.56</td>
<td>25.34</td>
<td>14.04</td>
</tr>
<tr>
<td>Fe</td>
<td>27.16</td>
<td>24.52</td>
<td>73</td>
</tr>
<tr>
<td>K</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>27.2</td>
</tr>
<tr>
<td>Mg</td>
<td>2.9</td>
<td>12</td>
<td>2.5</td>
</tr>
<tr>
<td>Na</td>
<td>4.2</td>
<td>15</td>
<td>8.9</td>
</tr>
<tr>
<td>Ni</td>
<td>66199.4</td>
<td>622.08</td>
<td>72319.4</td>
</tr>
<tr>
<td>Si</td>
<td>32.5</td>
<td>5.7</td>
<td>42.3</td>
</tr>
</tbody>
</table>
As such, XRF analysis, which does not require pre-dissolution of the sample, was performed on the abovementioned six catalyst samples. The XRF and TGA results (for the relative amount of coke in the samples) of the fresh and spent Ni10/γ-Al2O3, Ru0.1Ni10/γ-Al2O3 and Mg0.1Ni10/γ-Al2O3 catalysts are given in Table 7.7. From Table 7.7, it can be seen that the wt% of γ-Al2O3 and Ni in the fresh catalysts were ~85% and ~9%, respectively. In addition, the mass of Ni was calculated to be ~10 wt% of that of the γ-Al2O3, which was in agreement with the theoretical value (10 wt%). In contrast, the spent catalysts collected after the stability tests exhibited lower percentages of γ-Al2O3 (< 52 wt%) and Ni (< 5.2 wt%), likely due to the dilution of the deposited coke. However, the Ni-to-Al2O3 ratios in all the spent catalysts after the long-term stability tests were almost unchanged (i.e., ~10%), which suggests that all the γ-Al2O3-supported Ni catalysts had excellent resistance to SCW. In addition, the calculated total mass percentages of γ-Al2O3, Ni and coke were close to 100% for each of the three spent catalysts, implying that there was almost no weight loss of the supported Ni catalysts during the SCWG process.
Table 7.7
XRF and TGA results of the fresh and spent Ni10/$\gamma$-Al2O3, Ru0.1Ni10/$\gamma$-Al2O3 and Mg0.1Ni10/$\gamma$-Al2O3 catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Ni10/$\gamma$-Al2O3</th>
<th>Ru0.1Ni10/$\gamma$-Al2O3</th>
<th>Mg0.1Ni10/$\gamma$-Al2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Spent</td>
<td>Fresh</td>
</tr>
<tr>
<td>$\gamma$-Al2O3 (wt%)</td>
<td>86.06</td>
<td>52.36</td>
<td>84.96</td>
</tr>
<tr>
<td>Ni (wt%)</td>
<td>8.57</td>
<td>5.19</td>
<td>8.82</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>0</td>
<td>38.29</td>
<td>0</td>
</tr>
<tr>
<td>Total (wt%)</td>
<td>94.63</td>
<td>95.84</td>
<td>93.78</td>
</tr>
<tr>
<td>Ni/$\gamma$-Al2O3 (%)</td>
<td>9.95</td>
<td>9.92</td>
<td>10.39</td>
</tr>
</tbody>
</table>

7.5 Conclusions

The long-term stability of the Ni10/$\gamma$-Al2O3, Ru0.1Ni10/$\gamma$-Al2O3 and Mg0.1Ni10/$\gamma$-Al2O3 catalysts for H2 generation from biomass feedstock via SCWG was investigated using a 50 g/L glucose solution as the biomass model compound at 700°C, 24 MPa and a WHSV of 6 h$^{-1}$ for at least 25 h on stream. Ru0.1Ni10/$\gamma$-Al2O3 was found to be the most stable catalyst, and exhibited persistently high activity for H2 production (H2 yield: $\sim$50 mol/kg glucose) during the entire catalyst stability test ($\sim$ 33 h on stream). The metallic Ni as the active species for catalyzing glucose SCWG was detectable by XRD analysis in the spent catalyst of Ru0.1Ni10/$\gamma$-Al2O3 after the test for 33 h on stream, which likely explains the high activity of the Ru0.1Ni10/$\gamma$-Al2O3 catalyst. In contrast, the high activity of the Ni10/$\gamma$-Al2O3 and Mg0.1Ni10/$\gamma$-Al2O3 catalysts only lasted for $\sim$7 h (Day 1), after which the activity decreased significantly with a large decrease in the H2 yield from $\sim$50 mol/kg glucose (on Day 1) to $\sim$25 mol/kg glucose (from Day 2 and on), suggesting deactivation of these catalysts. The enhanced activity of Ni10/$\gamma$-Al2O3 with the aid of Ru was probably...
attributed to the increased dispersion of metallic Ni crystallites (from 0.7% without Ru to 1.3% with Ru addition) and decreased size of Ni crystallite (from 121 nm without Ru to 66 nm with Ru addition), as evidenced from the H$_2$ chemisorption results. In addition, the TPR profiles of the non-modified and Ru-modified Ni$_{10}/\gamma$-Al$_2$O$_3$ catalysts demonstrated that the addition of a small amount of Ru could enhance the reducibility of NiO in the Ni$_{10}/\gamma$-Al$_2$O$_3$ catalyst, thus making Ni$_{10}/\gamma$-Al$_2$O$_3$ more active and durable. The XRF analytical results indicated that all of the $\gamma$-Al$_2$O$_3$-supported Ni catalysts had excellent resistance to supercritical water, and there was no significant weight loss for each of the three Ni$_{10}/\gamma$-Al$_2$O$_3$ catalysts during the glucose SCWG process.
7.6 References


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[21] Koo KY, Roh H-S, Seo YT, Seo DJ, Yoon WL, Park SB. Coke study on Mg-O
promoted Ni/Al₂O₃ catalyst in combined H₂O and CO₂ reforming of methane for gas
Chapter 8
Supercritical Water Gasification of an Aqueous By-Product from Biomass Hydrothermal Liquefaction with Novel Ru Modified Ni Catalysts

8.1 Abstract

Supercritical water gasification (SCWG) of glucose solution (50-200 g/L), a simulated aqueous organic waste (SAW, composed of 84% glucose, 15% acetic acid and 1% guaiacol) and an aqueous organic waste (RAW) stream generated from a sludge hydrothermal liquefaction process was performed in a bench-scale continuous down-flow tubular reactor over novel Ru modified Ni catalysts supported on γ-Al₂O₃ or activated carbon over a temperature range of 600 and 750°C and 24 MPa with weight hourly space velocities (WHSV) ranging from 3 to 24 h⁻¹ for H₂ production. A high carbon gasification efficiency (>90%) was obtained for all experiments conducted using glucose as the feedstock. The H₂ yield increased with increasing reaction temperature, but decreased with increasing feedstock concentration. A very high H₂ yield 53.9 mol/kg was achieved with glucose at 750°C with a WHSV of 6 h⁻¹. Approximately 90-96% of the carbon in the RAW was destroyed via SCWG at 700°C with or without catalyst. The addition of Ru₀.₁Ni₁₀/γ-Al₂O₃ did not significantly affect the H₂ yield and gas composition in comparison to the blank test. The main issue in using the γ-Al₂O₃ based catalyst was associated with the deterioration of the catalyst support materials, likely due to ammonia derived from nitrogen-containing compounds in the RAW, resulting in a shorter catalyst lifetime. In contrast, the use of a Ru₀.₁Ni₁₀/AC catalyst increased the H₂ yield from 43.1
to 71.2 mol per kg carbon in the RAW.

8.2 Introduction

Due to the depletion of fossil fuels and the concerns over climate change associated with fossil fuel uses, hydrogen (H₂) as an environmental friendly, clean, efficient and versatile fuel has attracted growing attention from scientists and engineers recently [1]. H₂ is an energy carrier but not an energy source; it therefore, has to be generated from other primary energy sources, such as fossil fuels, solar energy, biomass, etc. Biomass is a renewable energy source that can be converted into H₂ via two main types of technologies: biological processes (e.g., fermentative H₂ production, biological water-gas shift reaction, etc.) and thermo-chemical processes (e.g., pyrolysis, steam gasification, steam reforming, supercritical water gasification (SCWG), etc.) [1]. As an innovative thermo-chemical approach, SCWG has been widely investigated in the last two decades for the production of H₂-rich synthetic gas (syngas) from a variety of waste biomass feedstocks (e.g., fruit shells, sewage sludge, black liquor, municipal solid waste, etc.) [2-5].

Supercritical water (SCW) is a special phase of water achieved when the pressure and temperature of water are increased to or above their respective critical points (374°C and 22.1 MPa). SCW is an ideal reaction medium as it has higher diffusivity, lower viscosity and better solubility than liquid water for organic compounds [6]. As such, SCW has been widely employed in biomass gasification where the major reactions are steam reforming (Eq. 8.1), water-gas shift (Eq. 8.2) and methanation (Eq. 8.3) reactions [7].
As shown in Eqs. 8.1 and 8.2, water participates in SCWG both as a solvent and a reactant. Therefore, the feedstock pre-drying process, which is inevitable for most of other thermo-chemical processes, such as combustion, air gasification, pyrolysis, etc, can be eliminated or reduced. In addition, the gas and liquid phases become miscible in SCW, hence providing a single-phase reaction medium with reduced tar and char formation [7,8].

Sludge is a semi-solid liquid suspension produced during wastewater treatment. It is a waste biomass that is composed of cells, biodegradable (e.g., carbohydrates) and recalcitrant (e.g., lignin) organic compounds and ashes [9]. Due to the high water content (> 90 wt%), sludge is not considered a suitable feedstock for conventional thermo-chemical processes, but can be considered a suitable feedstock for SCWG treatment. Xu et al. [10] successfully gasified 2.8 wt% sewage sludge in a flow reactor at 600°C and 34.5 MPa with coconut shell activated carbon (AC) as the catalyst. The resulting H₂ yield was 13.5 mol H₂/kg sludge (on a dry basis). In addition, they also observed a decrease in the H₂ and CO₂ fractions of the gaseous products with an increase in feedstock solid concentration (650°C and 28 MPa) [3]. Zhang et al. [11] performed SCWG on a 95 wt% sludge sample with a continuous flow reactor for a range of temperatures (400-600°C) and pressures (24-30 MPa) in the presence of 10 wt% NaOH and 30% H₂O₂ and obtained
gaseous products containing 40 vol% H₂. Recently, our group conducted a series of experiments in a 75 ml batch reactor using secondary pulp/paper-mill sludge (SPP) as the feedstock [9]. The highest H₂ yield was 14.5 mol H₂/kg SPP (on a dry basis), which was achieved at 550°C, 45.51 MPa and 60 min. Moreover, SPP was found to be a better feedstock than sewage sludges because of its higher alkali and volatile matter contents.

However, the pumping of sludge slurry into continuous flow SCWG reactor system configurations at high pressure can be challenging, particularly for sludges with high solids contents. The highest solids concentration that has been successfully utilized for a continuous flow reactor for sludge SCWG to date was 15.38 wt% (7.69 wt% dried digested sludge with 7.69 wt% corn starch), as reported by Xu and Antal [3]. To overcome this obstacle, an innovative two-step treatment process, as shown in Fig. 8.1, was proposed in this work. In the first step, SPP was co-liquefied with waste newspaper in a batch reactor at 300°C for 20 min to produce bio-crude and bio-char [12]. This liquefaction process converted 39.1 wt% of the total organic carbon (TOC) in the SPP to heavy oils (HOs) at a SPP-to-newspaper mixing ratio of 1:2 (w/w). The heating value of the resulting HOs was found to be as high as 31.45 MJ/kg. The co-liquefaction process and the results are presented and discussed elsewhere [12].
Fig. 8.1 A proposed two-step process, combing liquefaction and SCWG, for the treatment of SPP.

As one of the by-products resulting from liquefaction, the aqueous phase still exhibits a high TOC content (16.3 wt%) and hence needs further treatment prior to its final discharge or disposal to surface water receiving environments. This aqueous by-product is primarily composed of water-soluble compounds that can be easily pumped to a continuous flow reactor system. Therefore, in the second step of the proposed process, the aqueous by-product is further treated via SCWG to convert the remaining TOCs into a H$_2$-rich syngas.

The objective of this research was to investigate the H$_2$-producing potential of the aqueous by-product from the hydrothermal liquefaction of sludge or other organic waste materials via catalytic SCWG over novel Ru modified Ni catalysts selected based on our previous catalyst screening tests [13]. In addition, a glucose solution and a simulated aqueous waste (SAW, composed of 84% glucose, 15% acetic acid and 1% guaiacol) were investigated as model feedstocks to explore the effects of various experimental parameters (e.g., temperature, feedstock flow rate, feedstock concentration, etc) on product yields.
8.3 Materials and methods

8.3.1 Feedstocks

Three types of feedstocks were used in this study: a glucose solution, real aqueous waste (RAW) from biomass hydrothermal liquefaction, and a simulated aqueous waste (SAW, composed of 84% glucose, 15% acetic acid and 1% guaiacol). The glucose solution (50, 100, or 200 g/L) was made by dissolving the required amount of anhydrous D-glucose (J.T.Baker) in distilled water. The RAW was obtained by hydrothermal co-liquefaction of a mixture of waste newspaper and SPP at 300°C (w/w=2/1) for 20 min, as reported in Zhang et al. [12]. The TOC of the RAW (8-10 g/L) was determined using a Shimadzu TOC-V CPN total organic carbon analyzer. In addition, the composition of the RAW was analyzed using high-performance liquid chromatography (HPLC, Waters) equipped with either an Aminex HPX-87H or a C18 column. Both acetic and formic acids were identified and quantified with the Aminex HPX-87H column and a refractive index (RI) detector by HPLC, where a 0.005 M \( \text{H}_2\text{SO}_4 \) solution was used as the mobile phase at a flow rate of 0.6 mL/min (column temperature = 65°C). In addition, guaiacol was quantified by HPLC using a C18 column with a UV detector (270 nm), and a water-methanol co-solvent (v/v=3/7) as the mobile phase at a flow rate of 0.5 mL/min (column temperature = 40°C). The HPLC analysis revealed that the RAW contained significant quantities of other components such as carbohydrates, aldehydes, furfurals and their derivatives. Due to the complexity of the RAW composition, these constituents were not quantifiable using the aforementioned methods. A simulated solution (SAW) was
employed to represent a simplified RAW composition. Based on the results obtained by TOC and HPLC analyses, the SAW was composed of A.C.S. reagent-grade anhydrous D-glucose, acetic acid and guaiacol at a mass ratio of 84:15:1 (glucose was used as the model compound to represent unidentified intermediate products).

8.3.2 Catalyst preparation

The two catalysts investigated in this research were Ru$_{0.1}$Ni$_{10}/\gamma$-Al$_2$O$_3$ and Ru$_{0.1}$Ni$_{10}$/AC, both of which contained 10% Ni in relation to the mass of the support (\(\gamma\)-Al$_2$O$_3$ or AC), with a Ru-to-Ni molar ratio of 0.1:1. The catalysts were prepared using the wetness impregnation method [14] that employs water-soluble metal salts (e.g., nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$.6H$_2$O) and ruthenium (III) nitrosyl nitrate solution in dilute nitric acid (HN$_4$O$_{10}$Ru), supplied by Sigma-Aldrich) and \(\gamma\)-Al$_2$O$_3$ (Inframat Advanced Materials) and a self-prepared AC as the catalyst support materials. The AC was derived from pine wood sawdust (850-2000 \(\mu\)m) according to the procedure described by Xu et al. [15]. The \(\gamma\)-Al$_2$O$_3$-supported catalyst was calcined in air at 550°C for 6.5 h and was then crushed and sieved to get particles of nominal diameters ranging between 300 and 850 \(\mu\)m, while the AC-supported catalyst was calcined in N$_2$ at 550°C for 6.5 h. The BET surface areas of Ru$_{0.1}$Ni$_{10}/\gamma$-Al$_2$O$_3$ and Ru$_{0.1}$Ni$_{10}$/AC were 34.2 m$^2$/g and 1.33×10$^3$ m$^2$/g, respectively, as derived by analysis using a Quantachrome Nova 2200e Surface Area & Pore Size Analyzer.
8.3.3 Experimental setup and conditions

The schematic of the bench-scale down-flow tubular reactor is shown in Fig. 8.2. For each experimental run, 1 g catalyst was placed on the catalyst bed supported with a porous metal disc (pore size: 100 μm) and quartz wool. The catalysts were reduced in-situ under a 30 mL/min H₂ flow at 500°C for 1 h before use. The reactor is composed of Inconel 625 tubing with 9.55 mm OD × 6.34 mm ID × 472 mm length and is heated with an electric furnace.

![Fig. 8.2 Schematic of the supercritical water gasification reactor system.](image)

The conditions of each of the experiments are summarized in Table 8.1. It should be noted that the operating pressure for all tests was maintained constant at 24 MPa and controlled with a back-pressure regulator (Fig. 8.2).
Table 8.1
Summary of the experimental conditions.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Feedstock</th>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Feedstock concentration (g/L)</th>
<th>Feedstock flow rate (mL/min)</th>
<th>WHSV\textsuperscript{a} (h\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Glucose</td>
<td>None</td>
<td>700</td>
<td>50</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>G-T-600</td>
<td>Glucose</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>600</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>G-T-650</td>
<td>Glucose</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>650</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>G-T-700</td>
<td>Glucose</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>G-T-750</td>
<td>Glucose</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>750</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>G-C-100</td>
<td>Glucose</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>100</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>G-C-200</td>
<td>Glucose</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>200</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>S-T-600</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>600</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>S-T-650</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>650</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>S-T-700</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>S-T-750</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>750</td>
<td>50</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>S-C-100</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>100</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>S-F-1</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>50</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>S-F-4</td>
<td>SAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>50</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>R-blank</td>
<td>RAW</td>
<td>None</td>
<td>700</td>
<td>7.75\textsuperscript{b}</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>R-Al\textsubscript{2}O\textsubscript{3}</td>
<td>RAW</td>
<td>Ru\textsubscript{0.1}Ni10/γ-Al\textsubscript{2}O\textsubscript{3}</td>
<td>700</td>
<td>9.82\textsuperscript{b}</td>
<td>2</td>
<td>−2.5</td>
</tr>
<tr>
<td>R-AC</td>
<td>RAW</td>
<td>Ru\textsubscript{0.1}Ni10/AC</td>
<td>700</td>
<td>8.22\textsuperscript{b}</td>
<td>2</td>
<td>−2.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} WHSV (weight hourly space velocity) = \frac{\text{feedstock concentration} \times \text{feedstock volumetric flow rate}}{\text{mass of catalyst}}.

\textsuperscript{b} These values are total organic carbon (TOC) contents but not feedstock concentrations.

8.3.4 Separation and analyses of reaction products

Liquid and gas products were separated through a liquid-gas separator (Fig. 8.2). The gases were collected in a gas cylinder of known-volume and analyzed for composition using an Agilent 3000 Micro-Gas Chromatograph (GC) equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors (TCDs). The aqueous
effluent was sampled for TOC analysis. After the desired reaction time elapsed (~8 h for
the glucose-series experiments and ~5 h for the aqueous waste-series experiments), the
system was de-pressurized and cooled using distilled water. A.C.S. reagent-grade ethyl
acetate was then pumped into the system to recover the water-insoluble products. The
ethyl acetate-soluble phase was separated from water with a separatory funnel, and
evaporated at reduced pressure at 60°C to remove the solvent. The remaining brown
viscous liquid was weighed and referred to as tar. In addition, the solids retained on the
catalyst bed, a mixture of the spent catalyst, char/coke and deposited ashes, was collected,
oven dried and weighed to obtain the mass of solid residue (SR). A portion of the SR was
then characterized with a thermogravimetric analyzer (TGA)-i1000 (Instrument Specialist
Inc.) in 40 mL/min air heated at 20°C/min up to 900°C. The weight loss between 120 and
900°C was attributed to the burning of char/coke. In addition, the elemental compositions
of the fresh Ru0.1Ni10/γ-Al2O3 catalyst, SRs from the R-series tests, and initial feedstocks
and aqueous effluents were analyzed using inductively coupled plasma-optical emission
spectroscopy (ICP-OES) with a Varian Vista Pro ICAP Radial spectrometer.

8.3.5 Terms and definitions

The product yields used in this research are defined in Eqs. (8.4-8.7) below:

\[
H_2 \text{ yield (mol/kg feed)} = \frac{\text{moles of } H_2 \text{ produced}}{\text{mass of feedstock consumed}}
\]  

\[
\text{Carbon gasification efficiency (\%)} = \frac{\text{Moles of carbon in the gas product}}{\text{Moles of carbon in the feedstock}} \times 100
\]
\begin{equation}
\approx 1 - \frac{\text{TOC of the aqueous effluent}}{\text{TOC of the feedstock solution}} \times 100 \quad (8.5)
\end{equation}

\text{Tar yield (\%)} = \frac{\text{mass of tar recovered}}{\text{total mass of feedstock consumed}} \times 100 \quad (8.6)

\text{Char yield (\%)} = \frac{\text{mass of coke recovered}}{\text{total mass of feedstock consumed}} \times 100 \quad (8.7)

\section*{8.4 Results and discussion}

\subsection*{8.4.1 Catalytic SCWG of glucose solution}

Glucose, the main hydrolysis product from cellulose, has been extensively investigated as a biomass model compound and feedstock for renewable hydrogen generation via SCWG [10,16]. Table 8.2 summarizes the product yields from the SCWG of glucose solutions (50, 100 and 200 g/L) with and without Ru$_{0.1}$Ni10/\(\gamma\)-Al$_2$O$_3$ (WHSV = 6, 12 and 24 h$^{-1}$) at temperatures ranging between 600 and 750\(^\circ\)C. It should be noted that all the data listed in Table 8.2 were averaged based on values obtained at steady state, during which the H$_2$ yield and gas compositions were considered to be constant with time-on-stream, as supported by Figs. 8.3 and 8.4.
Table 8.2
Product yields from the SCWG of glucose (Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ catalyst, 600-750°C, 24 MPa and WHSV = 6-24 h$^{-1}$)$^a$.

<table>
<thead>
<tr>
<th>Test #</th>
<th>WHSV (h$^{-1}$)</th>
<th>H$_2$ yield (mol/kg glucose)</th>
<th>Main gas composition (vol%)</th>
<th>Tar yield (%)</th>
<th>Char yield (%)</th>
<th>Carbon gasification efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>$na^b$</td>
<td>9.8</td>
<td>30.9 11.8 28.1 23.9</td>
<td>1.8</td>
<td>1.4</td>
<td>93.6</td>
</tr>
<tr>
<td>G-T-600</td>
<td>6</td>
<td>25.5</td>
<td>48.0 12.5 0.5 38.6</td>
<td>1.1</td>
<td>1.3</td>
<td>99.2</td>
</tr>
<tr>
<td>G-T-650</td>
<td>6</td>
<td>40.8</td>
<td>56.8 6.7 0.8 35.7</td>
<td>0.12</td>
<td>1.5</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td><strong>G-T-700</strong></td>
<td><strong>6</strong></td>
<td><strong>53.8</strong></td>
<td><strong>61.9 2.9 1.2 34.0</strong></td>
<td><strong>0.08</strong></td>
<td><strong>0.5</strong></td>
<td><strong>99.9</strong></td>
</tr>
<tr>
<td>G-T-750</td>
<td>6</td>
<td>53.9</td>
<td>63.3 1.8 1.6 33.3</td>
<td>0.09</td>
<td>0.9</td>
<td>99.6</td>
</tr>
<tr>
<td>G-C-100</td>
<td>12</td>
<td>38.0</td>
<td>57.4 7.3 1.9 33.4</td>
<td>0.03</td>
<td>2.1</td>
<td>99.6</td>
</tr>
<tr>
<td>G-C-200</td>
<td>24</td>
<td>23.7</td>
<td>42.1 17.8 2.3 37.9</td>
<td>0.12</td>
<td>4.2</td>
<td>$na^c$</td>
</tr>
</tbody>
</table>

$^a$ Averaged from data obtained after the steady state was reached.
$^b$ $na$ = not applicable.
$^c$ $nd$ = not determined.

Fig. 8.3 Gas composition and H$_2$ yield as a function of time-on-stream of the blank test (50 g/L glucose solution, 700°C and 24 MPa). Lines are added to guide the eye.
The H<sub>2</sub> yield and syngas composition as a function of time-on-stream for the blank and G-T-700 experiments are shown in Figs. 8.3 and 8.4, respectively. In the absence of catalyst (Fig. 8.3), the syngas from the SCWG of glucose contained approximately 30 vol% H<sub>2</sub>, with a corresponding H<sub>2</sub> yield of ~10 mol/kg glucose. Even though more than 90% of the TOC was gasified (Table 8.2), the converted carbon was primarily present in the form of CO (28.1 vol%), implying incompleteness of the water-gas shift reaction (Eq. 8.2). In addition, the CH<sub>4</sub> content was relatively high (11.8 vol%). The addition of the Ru<sub>0.1</sub>Ni<sub>10</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 8.4) produced a greater than 5-fold increase in H<sub>2</sub> yield, from 9.8 to 53.8 mol/kg glucose. In addition, the CO content of the syngas decreased significantly, from 28.1 vol% (without catalyst) to 1.2 vol% (with Ru<sub>0.1</sub>Ni<sub>10</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst) indicating that the Ru<sub>0.1</sub>Ni<sub>10</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was effective in catalyzing the
water-gas shift reaction. Moreover, Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ exhibited superior selectivity for H$_2$ over CH$_4$ or catalyzed steam-methane reforming (Eq. 8.8), as noted by the significant reduction in CH$_4$ formation from 11.8 vol% (blank test) to 2.9 vol% (G-T-700) in the syngas.

\[
\text{CH}_4 + \text{H}_2\text{O (g)} \leftrightarrow 3\text{H}_2 + \text{CO} \quad \Delta H_{298}^0 = 206.2 \text{ kJ/mol} \quad (8.8)
\]

The SCWG process in the presence of supported transition metal catalysts is a complex process that can be simply expressed by Eqs. 8.9-8.11[17].

\[\text{A + S} \leftrightarrow \text{AS} \quad (8.9)\]
\[\text{AS + B} \leftrightarrow \text{ABS} \quad (8.10)\]
\[\text{ABS} \rightarrow \text{Intermediate} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (8.11)\]

where A, B and S represent oxygenated hydrocarbons (e.g., glucose, methanol, glycerol, etc), water and catalysts, respectively. Generally, the oxygenated hydrocarbon is first adsorbed onto the active site of the metallic catalyst surface via the hydroxyl groups (Eq. 8.9). Next, a dehydrogenation reaction and the cleavage of C-C and C-O bonds take place to produce syngas and a variety of intermediate products such as alcohols and organic acids. These intermediate products are then further converted into CO$_2$ and H$_2$ in SCW. Transition metals (Ni and Ru in this research) with proven high activities for C-C bond scission thus play a critical role in promoting this process [17].
In addition to enhancing H₂ yield and modifying syngas composition, the Ru₀.₁Ni₁₀/γ-Al₂O₃ was also shown to be effective in suppressing the formation of tar and char, as shown in Table 8.2. In the experiments with the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst, the yields of tar and char decreased substantially from 1.8% and 1.4% (blank test) to 0.08% and 0.54%, respectively (Table 8.2). As proposed by Kruse et al. [18] and Williams and Onwudili [19], glucose could be converted into tars (or of heavy oil products, such as furfurals, phenol and phenolic compounds, etc.) via various reaction pathways such as dehydration, cyclization, Diels-Alder cycloaddition, ring expansion, ring rearrangement, etc. These compounds may react further with each other to form chars/coke through polymerization reactions. However, when an appropriate catalyst (e.g., Ru₀.₁Ni₁₀/γ-Al₂O₃ in this research) was present, the C-C bond cleavage was more favourable than the dehydration/condensation reactions, and therefore more gases were generated at the expense of tar and char.

8.4.1.1 Effect of reaction temperature

Reaction temperature has been widely demonstrated to be the most important parameter that influences the product yields and gasification efficiency of SCWG [2,7,20]. As shown in Table 8.2, almost complete carbon gasification efficiency was achieved at a temperature above 600°C with the aid of the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst. More importantly, as the temperature increased from 600 to 700°C, the H₂ yield doubled from 25.5 to 53.8 mol/kg glucose, and the yields of tar and char decreased significantly from 1.1% at 600°C to 0.08% at 700°C for tar and from 1.3% at 600°C to 0.5% at 700°C for char. The higher temperature was also coupled with an increase in the percentage of H₂,
accompanied by a decrease of CH$_4$ and CO contents in the syngas. The formation of H$_2$ and CH$_4$ can be expressed by Eqs. 8.12 and 8.13 below, if assuming complete glucose conversion to either H$_2$ or CH$_4$ [8].

\[
C_{6}H_{12}O_{6} + 6H_{2}O (g) \leftrightarrow 6CO + 12H_{2} \quad \Delta H_{298}^{0} = 360.9 \text{ kJ/mol} \quad (8.12)
\]

\[
C_{6}H_{12}O_{6} \leftrightarrow 3CO_{2} + 3CH_{4} \quad \Delta H_{298}^{0} = -134.1 \text{ kJ/mol} \quad (8.13)
\]

Eq. 8.12 is endothermic whereas Eq. 8.13 is exothermic; therefore higher temperatures favour the formation of H$_2$ rather than CH$_4$. Moreover, the formed methane can be converted into H$_2$ via the steam-methane reforming reaction (Eq. 8.8), an endothermic reaction, more favourable at higher temperatures. As the temperature increased further from 700 to 750°C, the CH$_4$ content in the syngas decreased to only 1.8 vol%, and the syngas mainly consisted of H$_2$ and CO$_2$. However, the H$_2$ yield remained relatively constant at >700°C (~54 mol/kg glucose, representing 80% of the maximum theoretical value of 66.7 mol/kg glucose as calculated from Eq. 8.12). This result would suggest that further increasing temperature may not be effective in obtaining a higher H$_2$ yield.

**8.4.1.2 Effect of feedstock concentration and WHSV**

Increasing feedstock concentration and WHSV had a negative effect on H$_2$ yield and gasification efficiency. As the feedstock concentration increased from 50 g/L (WHSV=6 h$^{-1}$) to 200 g/L (WHSV=24 h$^{-1}$), the H$_2$ yield at 700°C decreased from 53.8 to 23.7 mol/kg glucose, and the corresponding yield of char increased by almost 8 times, from 0.54 to
4.2%, which increased the risk of reactor plugging. As for syngas composition, it was observed that the percentage of H₂ decreased, with the increased formation of CH₄. A similar behaviour was also noted by Byrd et al. [17] where 5-40 wt% glycerol was gasified at 800°C in the presence of Ru/Al₂O₃ catalyst. This suggests that the decrease in water-carbon ratio and the residence time of the feedstock in the catalytic bed could suppress H₂ formation via Eq. 8.12 and/or the steam-methane reforming reaction (Eq. 8.8). Decreasing the steam-to-carbon ratio could also promote the methanation reaction (Eq. 8.3) [17]. Moreover, as explained by Kruse [8], more water is needed for the production of H₂ than CH₄ (compare Eqs. 8.12 and 8.13). Thus, a high water content feedstock would be required to achieve a high H₂ yield.

8.4.2 Catalytic SCWG of the aqueous waste from biomass liquefaction

8.4.2.1 SCWG of simulated aqueous waste (SAW)

The product yields of the SCWG of SAW over the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst at 600-750°C are shown in Table 8.3. Similar to the results obtained with 100% glucose, H₂ yields increased significantly with increasing temperature but decreased with increasing feedstock concentration (or WHSV). However, the H₂ yields from the gasification of SAW were comparatively lower than the yields obtained from the pure glucose solution at temperatures ranging between 600 and 700°C, which might be attributed to the presence of guaiacol.
Table 8.3
Product yields from the SCWG of the SAW (Ru$_{0.1}$Ni$_{10}$/γ-Al$_2$O$_3$ catalyst, 600-750°C, 24 MPa and WHSV = 3-12 h$^{-1}$)$^a$.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Temperature (°C)</th>
<th>WHSV (h$^{-1}$)</th>
<th>$\text{H}_2$ yield (mol/kg feed)</th>
<th>Main gas composition (vol%)</th>
<th>Tar yield (%)</th>
<th>Char yield (%)</th>
<th>Carbon gasification efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-T-600</td>
<td>600</td>
<td>6</td>
<td>21.9</td>
<td>$\text{H}_2$</td>
<td>39.5</td>
<td>21.4</td>
<td>0.3</td>
</tr>
<tr>
<td>S-T-650</td>
<td>650</td>
<td>6</td>
<td>28.9</td>
<td>$\text{CH}_4$</td>
<td>49.7</td>
<td>13.2</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>S-T-700$^b$</strong></td>
<td><strong>700</strong></td>
<td><strong>6</strong></td>
<td><strong>50.2 ± 0.8</strong></td>
<td>$\text{H}_2$</td>
<td><strong>62.8 ± 0.4</strong></td>
<td><strong>3.7 ± 0.4</strong></td>
<td><strong>1.1 ± 0.0</strong></td>
</tr>
<tr>
<td>S-T-750</td>
<td>750</td>
<td>6</td>
<td>54.3</td>
<td>$\text{H}_2$</td>
<td>53.8</td>
<td>9.9</td>
<td>1.8</td>
</tr>
<tr>
<td>S-C-100</td>
<td>700</td>
<td>12</td>
<td>39.4</td>
<td>$\text{H}_2$</td>
<td>57.3</td>
<td>7.5</td>
<td>0.8</td>
</tr>
<tr>
<td>S-F-1$^b$</td>
<td>700</td>
<td>3</td>
<td>54.8 ± 0.1</td>
<td>$\text{H}_2$</td>
<td>65.4 ± 0.2</td>
<td>1.6 ± 0.4</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td>S-F-4</td>
<td>700</td>
<td>12</td>
<td>40.1</td>
<td>$\text{H}_2$</td>
<td>44.7</td>
<td>15.8</td>
<td>0.7</td>
</tr>
</tbody>
</table>

$^a$ Averaged from data obtained after steady state was considered to have been reached.

$^b$ Duplicate tests were conducted for the S-T-700 and S-F-1 experiments and the averages and standard deviations were calculated. The results were expressed as average ± standard deviation.

Table 8.4
Product yields from the SCWG of the RAW (700°C, 24 MPa, WHSV ~ 2.5 h$^{-1}$).

<table>
<thead>
<tr>
<th>Test #</th>
<th>Catalyst</th>
<th>$\text{H}_2$ yield (mol/kg carbon)</th>
<th>Main gas composition (vol%)</th>
<th>Carbon gasification efficiency (%)</th>
<th>pH of the RAW (aqueous feedstock for the SCWG)</th>
<th>pH of the aqueous effluent resulted from the SCWG</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-blank</td>
<td>None</td>
<td>43.1</td>
<td>$\text{H}_2$</td>
<td>44.7</td>
<td>15.8</td>
<td>0.7</td>
</tr>
<tr>
<td>R-Al$_2$O$_3$</td>
<td>Ru$<em>{0.1}$Ni$</em>{10}$/γ-Al$_2$O$_3$</td>
<td>41.0</td>
<td>$\text{H}_2$</td>
<td>48.5</td>
<td>14.6</td>
<td>1.6</td>
</tr>
<tr>
<td>R-AC</td>
<td>Ru$<em>{0.1}$Ni$</em>{10}$/AC</td>
<td>71.2</td>
<td>$\text{H}_2$</td>
<td>54.9</td>
<td>12.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>
As noted in the experimental section, guaiacol was used in the SAW as a model compound representative of phenolic compounds present in the aqueous by-product from biomass liquefaction. It has been previously reported that the presence of a small amount of phenol could decrease the conversion efficiency of glucose and reduce the formation of gaseous products [21]. As proposed in the literature [21], the reduction gas formation is probably attributable to the larger conjugated electron systems of phenol, which would consume the free radicals formed during glucose decomposition, and hence reduce gas formation [21].

Large concentrations of organic acids (e.g., formic acid, acetic acid and glycolic acids) are present in the aqueous by-products resulting from biomass liquefaction [12]. In this study, acetic acid was used to represent the organic acids present in the RAW, as formic acid and acetic acid together contributed to 15 wt% of the TOC in the RAW. Acetic acid is not commonly used as a model compound for SCWG, but it has been widely investigated in catalytic steam reforming processes for H₂ production [22-24]. It was reported by Hu and Lu [22] that at a temperature of 450 °C or higher (under atmospheric pressure) and in the presence of Ni/γ-Al₂O₃ (20 wt% Ni loading), 90% of the acetic acid could be converted to H₂ and CO₂ via steam reforming (Eq. 8.14).

\[
\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \leftrightarrow 4\text{H}_2 + 2\text{CO}_2 \quad (8.14)
\]

It is thus proposed that under SCW conditions, acetic acid would react with the SCW to generate H₂-rich syngas. In addition, it should be noted that the theoretical H₂ yields from
both glucose and acetic acid are the same (see Eqs. 8.12 and 8.14), which is 66.7 mol H₂/kg feedstock. Therefore, a replacement of 15 wt% glucose with acetic acid in the SAW should not significantly affect the overall theoretical H₂ yield from SAW.

In addition to the effects of temperature and feedstock concentration, the effect of feedstock flow rate (WHSV) was also experimentally investigated. As shown in Table 8.3, as the flow rate was raised from 1 to 4 mL/min and the corresponding WHSV increased from 3 to 12 h⁻¹, the H₂ yield decreased from 50.2 mol/kg feed (test S-T-700) to 40.1 mol/kg feed (test S-F-4). The lower H₂ yield associated with the increased flow rate or a higher WHSV would indicate that the decrease in feedstock residence time suppressed hydrogen formation. The effect of increasing feedstock flow rate is similar to that of increasing the feedstock concentration in terms of decreasing H₂ yield, as discussed previously. In addition, this behaviour might also be due to limitations in heat transfer efficiency at higher flow rates, reducing the temperature of the feedstock and the catalyst bed. The formation of CH₄ was found to be very low (1.6 vol%) for the S-F-1 experiment which was characterized by a low feedstock concentration, low feeding rate and a high reaction temperature. Consequently, with the appropriate catalyst, a high reaction temperature and a low WHSV would generally be beneficial operational conditions to maximize the H₂ selectivity in biomass SCWG.

8.4.2.2 SCWG of real aqueous waste (RAW)

The product yields from the SCWG experiments at 700°C using RAW as the feedstock over different catalysts (Ru₀.₁Ni₁₀/γ-Al₂O₃ and Ru₀.₁Ni₁₀/AC) are presented in Table 8.4.
It should be noted that the H₂ yield is expressed in units of mol/kg carbon (or TOC) rather than mol/kg feedstock to allow for a comparison between different feedstocks with complex mixtures. As a result of the presence of the catalyst of Ru₀.₁Ni₁₀/γ-Al₂O₃, the R-Al₂O₃ test was expected to perform better than the blank test without catalyst addition. However, the H₂ yield from the R-Al₂O₃ test (41.0 mol/kg carbon) was found to be similar to the yield obtained in the R-blank test (43.1 mol/kg carbon). It is thus of interest to discuss about the possible reasons for this unexpected result. Table 8.5 shows ICP-OES analysis results for the concentrations of selected inorganic elements in the aqueous solutions before and after the R-Al₂O₃ test. As can be clearly seen, the Al concentration in the effluent of the R-Al₂O₃ test (11.8 mg/kg) was much higher than the Al concentration in the RAW (1.1 mg/kg), which would suggest the dissolution of Al from the catalyst support. Hence, it is likely that the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst deteriorated during the SCWG experiment, resulting in a low or negligible catalytic effect on the SCWG of RAW.

Table 8.4 also shows the pH values of the aqueous solutions before and after the SCWG experiments with and without catalysts. Due to the presence of organic acids (e.g., acetic acid, formic acid, etc.), the RAW appeared to be weakly acidic (pH≈5.5). However, after the SCWG experiments, the solution was found to be weakly alkaline (pH≈7.5). The increase in solution pH after the reaction could probably be attributed to the formation of ammonia, formed from the degradation of protein/amino acids originally present in the sludge (N takes 4.45 wt% of the dried SPP [12]). Yanagida et al. [25] gasified poultry manure under SCW with an AC catalyst and noted that the element N was almost
exclusively present in the aqueous phase in the form of NH$_4^+$ after SCWG. Therefore, the solution pH went up because of the formation of NH$_4^+$ which then released OH$^-$ ions that would react with the $\gamma$-Al$_2$O$_3$ support in the reaction medium at a high temperature and consequently resulted in the destruction of $\gamma$-Al$_2$O$_3$ in the solution. In addition to the formation of ammonia, amino acids were also reported to be free radical scavengers that would inhibit free radical chain reactions, consequently reducing the formation of gaseous products due to the formation of nitrogen-containing cyclic organic compounds [18].

### Table 8.5
ICP-OES analysis results of the RAW, effluents of the R-Al$_2$O$_3$ test, fresh R-Al$_2$O$_3$ catalyst and the SRs from the R-Al$_2$O$_3$ R-AC and R-blank experiments (mg/kg).

<table>
<thead>
<tr>
<th>Element</th>
<th>RAW</th>
<th>Effluent of the R-Al$_2$O$_3$ test</th>
<th>R-Al$_2$O$_3$</th>
<th>SR from the R-AC test</th>
<th>SR from the R-blank test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fresh catalyst</td>
<td>SR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.1</td>
<td>11.8</td>
<td>10248</td>
<td>19271</td>
<td>2426</td>
</tr>
<tr>
<td>Ca</td>
<td>469</td>
<td>8.3</td>
<td>19</td>
<td>68408</td>
<td>81440</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;DL$^a$</td>
<td>&lt;DL$^a$</td>
<td>14</td>
<td>499</td>
<td>419</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;DL$^a$</td>
<td>0.13</td>
<td>73</td>
<td>4112</td>
<td>5292</td>
</tr>
<tr>
<td>K</td>
<td>118.8</td>
<td>96.6</td>
<td>27</td>
<td>1285</td>
<td>435</td>
</tr>
<tr>
<td>Mg</td>
<td>22.1</td>
<td>1.1</td>
<td>2.5</td>
<td>3456</td>
<td>4185</td>
</tr>
<tr>
<td>Na</td>
<td>1390.6</td>
<td>812.1</td>
<td>8.9</td>
<td>19651</td>
<td>8151</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;DL$^a$</td>
<td>&lt;DL$^a$</td>
<td>72319</td>
<td>165756</td>
<td>174339</td>
</tr>
<tr>
<td>S</td>
<td>158.2</td>
<td>15.8</td>
<td>&lt;DL$^a$</td>
<td>6456</td>
<td>24940</td>
</tr>
<tr>
<td>Si</td>
<td>50.6</td>
<td>61.2</td>
<td>42</td>
<td>9566</td>
<td>1246</td>
</tr>
</tbody>
</table>

$^a$ Below detection limit. The detection limits of Cu, Fe, Ni and S are 0.05, 0.10, 2.50 and 5.00 mg/kg, respectively

However, even without the assistance of catalysts, high gasification efficiencies (> 90%) and low CO yields (< 2 vol% in the syngas) were achieved in both the R-blank and R-Al$_2$O$_3$ experiments. SPP has a high ash content (25.2 wt%), which was mainly composed
of Na, Al and Ca [12]. As can be seen from the elemental composition of the RAW in Table 8.5, some of these elements still remained in the aqueous phase after liquefaction. It has been reported that biomass ashes, particularly alkali salts, can act as active catalysts in biomass SCWG due to their effectiveness in promoting the water-gas shift reaction (Eq. 8.2) [9,26]. Therefore, the high carbon gasification efficiencies of the R-Al₂O₃ and R-blank tests were likely the result of the high content of alkali elements in the RAW, in particular Na, Ca and K whose concentrations were as high as 1390.6 mg/L, 469mg/L and 118.8 mg/L, respectively.

Although the alkali elements in the feedstock can be beneficial in catalyzing of SCWG reactions, high concentrations of these elements are considered to be detrimental as they could promote severe corrosion in metal reactor systems. For example, after the completion of experiments with the RAW, the porous metal discs that supported the catalytic bed in the down-flow tubular reactor were damaged (broken into pieces) likely by the alkali elements present in the feedstock (RAW) and the ammonia formed during the gasification process. As a result, Ni and Fe concentrations were very high in the resulting solid residues (SRs) (Table 8.5). In addition to corrosion, fouling and plugging of the reactor was also a major issue for high-ash-containing biomass feedstocks. SCW has a low density and low dielectric constant, and as such, behaves as a non-polar solvent and hence exhibits poor solubility for inorganic compounds [6,27,28]. Therefore, the ashes in the RAW can be easily precipitated on the catalyst or the reactor wall. This is evidenced by the high Ca, Cu, K, Mg, Na and Si contents in the SRs recovered from the tests with RAW (Table 8.5). To circumvent these potential operational problems, inorganic constituents in the feedstock (RAW) need to be either removed prior to the
SCWG reaction or be cleaned up after the operation. As reviewed by Marrone et al. [28], various novel reactors have been designed for biomass supercritical water oxidation (SCWO) to prevent ash deposition, such as reverse flow tank reactors with a brine pool, transpiring wall reactors, reversible flow tubular reactors and centrifuge reactors. However, there has been little research on catalyst design to enhance the catalyst’s resistance to corrosion and ash deposition. Future work in this regard is needed for the development of SCWG technologies to treat/gasify organic wastes containing high ash and nitrogen contents for energy recovery.

Because of the deterioration of the \( \gamma \)-Al\(_2\)O\(_3\) support, an AC-supported catalyst was also investigated in order to examine the suitability of AC as a catalyst support under SCW (The metal contents for the Ru\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) and Ru\(_{0.1}\)Ni\(_{10}/\)AC catalysts were identical). In comparison to the R-blank and R-Al\(_2\)O\(_3\) experiments, the H\(_2\) yield was much higher for the R-AC tests using Ru\(_{0.1}\)Ni\(_{10}/\)AC, where approximately 71 mol/kg carbon was achieved (Table 8.4). The use of ACs or AC-supported Ni catalysts has been previously reported for biomass SCWG and was found to be effective in promoting the water-gas shift reaction with a high stability [3,10,16]. Although our previous research demonstrated that the AC-supported Ni catalyst was inferior to \( \gamma \)-Al\(_2\)O\(_3\)-supported Ni catalyst in the SCWG of glucose solutions for H\(_2\) production [13], the Ru\(_{0.1}\)Ni\(_{10}/\)AC catalyst exhibited higher resistance to alkaline/ammonia corrosion than the Ru\(_{0.1}\)Ni\(_{10}/\gamma\)-Al\(_2\)O\(_3\) catalyst in this research for the SCWG of sludge or sludge-derived aqueous by-products.

The three SR samples obtained from the R-Blank, R-Al\(_2\)O\(_3\) and R-AC tests were characterized by TGA, where the SRs were heated under an air atmosphere (40 mL/min)
Fig. 8.5 TGA profiles of a fresh Ni10/AC catalyst (10 wt% Ni supported on AC) and SRs from R-Blank, R-Al2O3 (with Ru0.1Ni10/γ-Al2O3) and R-AC (with Ru0.1Ni10/AC) experiments (heating atmosphere: 40 mL/min O2, heating rate: 20°C/min).

from room temperature to 900°C at 20°C/min and then held at 900°C until the carbon was completely oxidized. The TGA profiles for these SRs are presented in Fig. 8.5. As a comparison, the TGA profile of a fresh Ni10/AC catalyst (10 wt% Ni supported on AC) was also included in this figure. According to Koo et al. [29], the removal of water and easily-oxidizable amorphous carbonaceous species occurs in the low temperature range and is responsible for the initial weight loss below 300°C. In contrast, the oxidation of coke/char takes place at a temperature of 500°C or higher. As can be seen from Fig. 8.5, the SRs from the R-Blank and R-Al2O3 tests exhibited similar TGA patterns, where the largest weight loss of approximately 5-8 wt% appeared at a temperature range of 700 to 850°C, likely due to the combustion of coke. Surprisingly, a weight gain starting from 850°C was observed for both of the SRs from the R-Blank and R-Al2O3 tests. As mentioned previously, the porous Inconel metal discs were corroded during the SCWG
tests with the RAW feedstock and particles of broken discs were intermixed with the SRs from the experiments. It is thus possible that the Ni in the SR was oxidized to NiO during the TGA analysis and, consequently, led to the observed increase in the mass of SR. Compared to the SRs from the R-Blank and R-Al₂O₃ tests, no weight gain was observed for the SR from the R-AC test; instead, the SR weight continued decreasing and finally stabilized at ~61%. The significant SR weight loss from the R-AC experiment was probably resulted from the combustion of the AC support. However, it should be noticed that the TGA profiles of the AC in the SR of R-AC and the fresh Ni10/AC catalyst look differently (Fig. 8.5), where the fresh AC catalyst was completely burnt out at ~ 600°C while the AC in the SR exhibited much higher thermal stability. It is known that fresh AC is mainly amorphous, however after the SCW treatment at high temperatures (e.g., 700°C), the carbon might change from amorphous carbon to “partly graphitized” carbon (Turbostratic carbon) [30] and therefore the spent AC catalyst would require a higher temperature to be burnt out in comparison to fresh AC. However, further investigation is required to confirm the existence of the “partly graphitized” carbon in the SR of the R-AC experiment.

In addition to ammonia formation and ash deposition, another potential threat to the long-term stability of the Ni-based catalyst in the SCWG process may be the presence of sulphur in the feedstock. Sulphur is an inherent element of SPP, as it contributes to 2.32 wt% of the dried SPP. During gasification, sulphur would be released in the forms of various gaseous sulphur compounds, such as hydrogen sulphide (H₂S), carbonyl sulphide, and sulphur dioxide. These sulphur compounds are known to be notorious catalyst poisons since they can easily react with transition metals hence preventing the adsorption
of other reactant molecules on the active sites of the metal [31,32]. As proposed by Ashrafi et al. [32] who investigated the effect of sulphur on the deactivation of Ni-based catalyst for application in the catalytic steam reforming of biogas, sulphur can bind to the surface of Ni via chemisorption shown by Eq. 8.15:

\[ \text{H}_2\text{S} + \text{Ni}_{\text{surface}} \leftrightarrow \text{Ni}_{\text{surface}} - \text{S} + \text{H}_2 \]  

(8.15)

This Ni_{surface}-S is relatively stable and is the main cause of the catalyst deactivation. In this research, the sulphur-induced deactivation of the Ru_{0.1}Ni_{10}/\gamma-Al_2O_3 catalyst may not have been as severe as the deterioration of the catalyst support caused by ammonia and alkali ashes, however, 0.71 wt% organic sulphur was detected in the SR and the spent catalyst of Ru_{0.1}Ni_{10}/\gamma-Al_2O_3 (data not shown), implying the occurrence of chemisorption between sulphur and catalyst during the SCWG process. In future work, promoters such as WO_3 [33], Re [34], etc., could be added to enhance the sulphur-resistance and therefore the long-term stability of the catalyst for the SCWG of sulphur-containing feedstock.

### 8.4.3 Energy recovery from the two-step process for sludge treatment

As shown in Fig. 8.1, an innovative two-step sludge treatment process was proposed in this work. In the first step, SPP was co-liquefied with waste newspaper in a batch reactor at 300°C for 20 min to produce bio-crude and bio-char [12]. This liquefaction process converted 39.1 wt% of the total organic carbon (TOC) that was originally present in the original SPP, into heavy oils (HOs) with a heating value of ~30 MJ/kg. As one of the by-products resulting from liquefaction, the aqueous phase still exhibited a high TOC content
(16.3 wt%) and hence required further treatment prior to its final discharge or disposal in surface water receiving environment. In the second step of the proposed process, the aqueous by-product is further treated via SCWG to convert the remaining TOCs into H2-rich syngas. In this section, the energy recovery efficiency from the proposed two-step treatment process will be discussed. It should be noted that as a preliminary evaluation of energetic efficiency, the external energy supplied to the process (mechanical and electrical energy, mainly used by the high pressure pump and the reactor heater) were not considered in the calculation for simplification. In the first step, SPP was co-liquefied with waste newspaper at 300°C with a mixing ratio of 1:2 (w/w) for HO production. If only considering the energy present in the products of HO, SR and gases of H2, CH4 and CO, the energy recovery efficiency for Step 1 (co-liquefaction process) was calculated as follows (Eq. 8.16):

\[
\text{Energy recovery efficiency } (\%) = \frac{\text{Total energy content of recovered products (HO, SR, H}_2\text{, CH}_4\text{, and CO)}}{\text{Total energy content of feedstocks (SPP and waste newspaper)}} \quad (8.16)
\]

The energy content of each component (feedstock or product) can be obtained by multiplying the mass of this component with its respective higher heating value (HHV). As shown in Table 8.6, the efficiency of energy recovery from Step 1 was 77.1%. The recovered energy was mainly in the form of HO products [12].
Table 8.6
Energy recovery from the co-liquefaction of SPP and waste newspaper.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Mass (kg)</th>
<th>HHV (MJ/kg)</th>
<th>Energy content (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPP</td>
<td>0.33</td>
<td>16.9</td>
<td>5.6</td>
</tr>
<tr>
<td>Waste newspaper</td>
<td>0.67</td>
<td>16.4</td>
<td>11.0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>16.6</td>
</tr>
</tbody>
</table>

Products from stage 1: co-liquefaction

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass (kg)</th>
<th>HHV (MJ/kg)</th>
<th>Energy content (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td>0.27</td>
<td>31.5</td>
<td>8.5</td>
</tr>
<tr>
<td>SR</td>
<td>0.22</td>
<td>19.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Gas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>5.7×10⁻⁵</td>
<td>141.9</td>
<td>8.1×10⁻³</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.5×10⁻⁴</td>
<td>55.5</td>
<td>8.3×10⁻³</td>
</tr>
<tr>
<td>CO</td>
<td>6.1×10⁻³</td>
<td>10.9</td>
<td>6.6×10⁻²</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>12.8</td>
</tr>
</tbody>
</table>

Energy recovered from Step 1: 77.1%

Products from stage 2: SCWG of SAW <c>

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass (kg)</th>
<th>HHV (MJ/kg)</th>
<th>Energy content (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.1×10⁻²</td>
<td>141.9</td>
<td>1.6</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.9×10⁻²</td>
<td>55.5</td>
<td>1.1</td>
</tr>
<tr>
<td>CO</td>
<td>1.1×10⁻³</td>
<td>10.9</td>
<td>1.2×10⁻²</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>2.7</td>
</tr>
</tbody>
</table>

Energy recovered from Step 2: 16.3%

Total energy recovered from the whole process: 93.4%

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<a> Assuming the total mass of SPP and waste newspaper was 1 kg; the mass of each product was calculated by multiplying 1 kg with the yield of the specific product.  

b> The HHV was calculated by the Dulong Formula, i.e., HHV(MJ/kg) = 0.3383C + 1.422(H-O/8); the CHO value of each component was determined previously with a CEC (SCP) 240-XA elemental analyzer.  

c> The calculation was based on the results of the R-AC experiment (Table 8.4).

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In Step 2, the H₂-rich syngas was the target product. Since >90% carbon was converted into gas products (Table 8.4), the amounts of HO and SR were negligible. Therefore for the calculation of the energy recovery efficiency of the second stage, only the gas products (e.g., H₂, CH₄ and CO) were considered. As determined in our previous work.
[12], the aqueous by-product takes 16.3 wt% of the carbon initially present in the feedstock. With the gas yields shown in Table 8.4 (in the unit of mol/kg carbon), the mass of H₂, CH₄ and CO can be easily determined (Table 8.6). The energy recovery efficiency of the second stage was calculated to be 16.3% for the entire treatment process, making the total energy recovery efficiency as high as 93.4%.

8.5 Conclusions

1) Using a glucose solution as a model compound, almost 100% TOC destruction efficiency could be achieved using SCWG at 600-750°C in the presence of Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst, with H₂ yields ranging from 25.5 to 53.9 mol/kg feed. A higher temperature resulted in an increase in H₂ yield, accompanied by a decrease in CH₄ formation. The H₂ yield decreased with increasing the feedstock concentration or WHSV.

2) The H₂ yields from a simulated aqueous organic waste, SAW (composed of 84% glucose, 15% acetic acid and 1% guaiacol) were comparatively lower than those obtained with the glucose solution at 600 - 700°C.

3) Approximately 90-96% of the carbon in the real aqueous waste (RAW) from biomass hydrothermal liquefaction was destroyed via SCWG at 700°C with or without catalyst. The addition of Ru₀.₁Ni₁₀/γ-Al₂O₃ did not significantly affect the H₂ yield and gas composition in comparison to the blank test. The main issue in using the γ-Al₂O₃-based catalyst was associated with the deterioration of the catalyst support materials,
likely due to ammonia derived from the nitrogen-containing compounds in the RAW, and the catalyst deactivation by the deposition of alkali ash from the feedstock.

4) In comparison to the Ru\textsubscript{0.1}Ni\textsubscript{10}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst, the use of Ru\textsubscript{0.1}Ni\textsubscript{10}/AC catalyst in the SCWG of RAW produced a significantly higher H\textsubscript{2} yield at 71.2 mol/kg carbon.

5) SCWG of the real aqueous by-product from biomass hydrothermal liquefaction with Ni-based catalysts was challenging as the high contents of alkali elements, nitrogen and sulphur in the feedstock could deteriorate and deactivate the catalyst and might potentially cause plugging/fouling of the reactor.

6) The energy recovery efficiency of the proposed two-step process combining liquefaction and SCWG for SPP treatment was calculated to be as high as 93.4%, indicating that this innovative process is a promising technique for sludge treatment and energy recovery.
8.6 References


Chapter 9
Conclusions and Recommendations for Future Work

9.1 Engineering contributions

The primary objective of this research was to convert waste sludges (paper sludge or sewage sludges) into a clean effluent and valuable bio-fuels via catalytic SCWG, aiming to achieve the dual goals of sludge treatment and energy recovery simultaneously. To meet this objective and as one of the most significant contributions of this research, a two-step hydrothermal treatment process, combining co-liquefaction and SCWG, was proposed to provide an alternative sludge treatment approach for wastewater treatment facilities (Chapters 5-8). This process not only successfully destroyed the toxic microorganism and recalcitrant organic compounds, turning sludge into a safe effluent for discharge to surface waters, but also produced HOs, a liquid bio-fuel, and H2-rich syngas, that could be utilized on-site to provide internal energy demand for wastewater treatment facilities. In addition, this process employed waste newspaper, a typical municipal solid waste (MSW), as a co-substrate for sludge liquefaction, and therefore proposed a new concept for MSW treatment and utilization. Moreover, the addition of waste newspaper increased the total solids content of the feedstock for the first-step liquefaction treatment, which would enhance the bio-fuel output and consequently make the overall process more economical. Furthermore, synergistic effects between sludge and waste newspaper were observed during the co-liquefaction process: the mixture of 33 wt% sludge and 67% waste newspaper generated a greater amount of HOs than that from either 100 wt% sludge or 100 wt% waste newspapers alone. This observation implies a possibly reduced
usage of catalysts, which could decrease operational costs for wastewater treatment facilities. Last but not least, the proposed two-step sludge treatment process could overcome the pumping difficulties associated with sludge SCWG when employing a flow type reactor, as the sludge slurry could be successfully transformed into water-soluble products before its treatment under SCW.

As the second contribution of this research, an innovative heterogeneous Ru0.1Ni10/γ-Al2O3 catalyst (10 wt% Ni, Ru-to-Ni molar ratio=0.1) was developed (Chapters 6 and 7) for biomass SCWG. Apart from the high activity and selectivity for H₂ generation, Ru0.1Ni10/γ-Al2O3 is more economical and stable compared to traditional supported Ni and Ru catalysts. As discussed in Chapter 7, the Ru0.1Ni10/γ-Al2O3 consistently exhibited high activity during a 33 h stability test (50 g/L glucose solution, 700°C and 24 MPa). The H₂ yield was maintained at ~50 mol/kg glucose throughout the entire experiment with no catalyst deactivation observed.

In addition, a bench-scale continuous down-flow tubular reactor system, with controllable temperature, pressure and feedstock flow rate, was built in this research (Chapters 6-8), which will shed some light on future scaling up of the process for industrial applications.

9.2 Summary of findings

The capacity of a biomass material for H₂ production was closely correlated to its intrinsic compositional characteristics. Generally, higher contents of volatile matters and ashes (e.g., alkali metals) led to a greater yield of H₂ gas (Chapters 4 and 5). As such, SPP
was a better candidate than sewage sludges for H\textsubscript{2} generation without the addition of catalysts.

Increasing reaction temperature promoted the formation of gas products, in particular H\textsubscript{2}, during biomass SCWG. For example, when the original SPP was gasified in a batch reactor (Chapter 4), as the temperature increased from 400 to 550°C, the gas yield was doubled from 16.4 to 37.7%, accompanied by an approximately 10-fold increase in H\textsubscript{2} yield, from 1.5 to 14.5 mol/kg dried SPP. Similar results were observed in Chapter 8 when a 50 g/L glucose solution was gasified with a continuous flow reactor, where the H\textsubscript{2} yield was significantly improved with temperature, from 25.5 mol/kg glucose at 600°C to 53.9 mol/kg glucose at 750°C.

In contrast to reaction temperature, the yield of H\textsubscript{2} gas was observed to be negatively correlated with feedstock concentration (Chapters 4 and 8), likely due to the reduced amount of water per unit of feedstock that inhibited the occurrence of the steam reforming and water-gas shift reactions.

As a widely used type of catalysts, alkalis (e.g., KOH, NaOH, etc) were proved to be effective in enhancing biomass conversion during hydrothermal treatment processes (liquefaction and SCWG) because of their abilities in facilitating the hydrolysis of cellulosic and lignin compounds and promoting the occurrence of the water-gas shift reaction (Chapters 4 and 5). Generally, increasing the alkali load would decrease the yield of SR, accompanied by an improved yield of gas. However during the liquefaction process, there was an optimal level for alkali addition which produced the highest HO
yield. For example, the maximum HO yield was reached with a KOH addition of 2 wt% for the co-liquefaction of sludge-waste newspaper mixture at 300°C (Chapter 5). Further addition of alkali would result in a decrease in HO yield since the HOs could be decomposed into lighter components such as gases.

Woody biomass and animal waste generated different types of HO products via liquefaction. As demonstrated from the GC/MS analysis results in Chapter 5, the HOs obtained from woody biomass (e.g., waste newspaper) were composed of a variety of phenol and phenolic compounds, such as 2-methoxyphenol, 1-hydroxy-2-methoxy-4-methylbenzene and 4-hydroxy-3-methoxybenzaldehyde, which were probably derived from lignin decomposition. In addition, there were also some other compounds that were initially degraded from cellulosic compounds via a series of reactions such as hydrolysis, dehydration, etc., examples were 2-butoxyethanol, 2-methyl-1-one-2-cyclopenten and 2,5-hexanediol. Different from HOs derived from waste newspaper, HOs converted from sludge contained a number of long-chain alkenes and alcohols and N-containing compounds, which were decomposed from fatty acids and proteins, respectively. Sludge-derived HO exhibited a higher heat value than the waste newspaper-derived HO (36.8 vs. 29.9 MJ/kg), which was attributed to the lower oxygen content in the sludge-derived HO (11.9% for the sludge-derived HO vs. 22.1% for the newspaper-derived HO).

Ni and Ru were more effective than Co and Cu in catalyzing gasification reactions in SCW (Chapter 6). The metallic form of Ni was found to be the active site for catalyzing SCWG reactions whereas no catalytic effect was observed for the oxidized form of Ni.
(NiO). In contrast, both metallic Ru and RuO₂ were comparably active for catalyzing SCWG reactions.

As for the catalytic activities of different support materials for H₂ production via SCWG, the order of sequence was observed to be γ-Al₂O₃ > ZrO₂ > AC when employing a glucose solution as the feedstock (Chapter 6). However, the γ-Al₂O₃ support was not stable when exposed to an alkaline environment (Chapter 8). For instance, the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst was deteriorated when it was utilized for the gasification of the aqueous by-product resulting from sludge-waste newspaper co-liquefaction (RAW). In contrast, AC was more resistant to alkali attack.

As a promoter to modify the Ni₁₀/γ-Al₂O₃ catalyst, the addition of Ru increased the long-term stability of Ni₁₀/γ-Al₂O₃. For example, the unmodified Ni₁₀/γ-Al₂O₃ catalyst lost its activity only after approximately 7 h on stream whereas no catalyst deactivation was observed for the Ru₀.₁Ni₁₀/γ-Al₂O₃ catalyst even after 33 h on stream. A small amount of Ru was able to enhance Ni dispersion, decrease the Ni crystalline size and improve the H₂-reducibility of NiO in the Ni₁₀/γ-Al₂O₃ catalyst.

9.3 Recommendations for future work

As mentioned in Chapters 4 and 5, the batch reactor utilized for sludge SCWG and liquefaction/co-liquefaction was not equipped with an agitation/mixing device (such as a stir or mechanical shaker), therefore the feedstock might have encountered diffusion limitations and produced inaccurate results. As such, it is recommended to use a reactor
with an agitation system in the future in order to reduce mass transfer limitations within the feedstock.

In this research, all the gas products produced from either SCWG or liquefaction were collected and analyzed for compositions after the reactor system had been cooled down to room temperature, however, side reactions between various gas products might take place during the cooling process and therefore the analyzed gas compositions/concentrations may not reflect the actual situations inside the reactor during the SCWG/liquefaction processes. As such, thermodynamic analyses with some professional programs could be employed to predict the equilibrium concentration of each gas component under a specific experimental condition and to compare the calculated results with those analyzed by GC.

Ni (metallic form) and Ru (both metallic and oxidized forms) have been shown to be active transition metals to catalyze biomass SCWG reactions. However, the underlying catalytic mechanisms are largely unknown and thus needs further investigation. Moreover, since XRD has limitations for catalyst characterization, for example, XRD can only measure bulk particles but is not able to detect particles smaller than 5 nm, other analytical methods should be utilized together with XRD in the future for catalyst characterization. In addition, in order to better understand the interactions between Ru and Ni and to optimize Ru addition, various Ru-to-Ni molar ratios could be investigated for Ru modified Ni catalysts. Moreover, further investigation is needed to study the mechanisms on how Ru enhanced the stability of the $\gamma$-Al$_2$O$_3$-supported Ni catalyst. The influence of catalyst particle sizes on product yields via biomass SCWG is also worth
trying in the future. Last but not least, the examination of the recyclability and reusability of the developed heterogeneous catalysts are also recommended for future work.

As discussed in Chapter 8, the high ash content and the presence of nitrogen containing compounds (as ammonia-precursors) in the sludge-derived aqueous by-product not only destroyed the $\gamma$-Al$_2$O$_3$-supported catalyst but also led to severe plugging/fouling of the reactor. Therefore, more studies are required to investigate ash removal from the aqueous by-product resulting from sludge liquefaction.

In this research, a significant number of experiments were conducted with a number of valuable results obtained, however, no kinetic models were developed due to the lack of time dependency data at each specific reaction temperature for experiments performed with both the batch and continuous flow reactors. As such, more time dependency data should be collected in the future, particularly for experiments with the addition of catalysts. In addition, other parameters such as the size of the catalyst and the occurrence of adsorption and desorption on the catalyst surface should also be considered to develop comprehensive kinetic models for various catalytic SCWG processes.

In this first attempt, waste newspaper was selected as the only co-substrate that was co-liquefied with waste newspaper, with the initial purpose of increasing the total solid content of the feedstock. Due to the time limitation, no other types of municipal solid wastes (MSWs) were investigated that could potentially be more suitable than waste newspaper for the application of sludge co-liquefaction. Therefore, other types of waste
materials, particularly organic wastes such as kitchen waste could be studied as co-
substrates for sludge co-liquefaction in the future.

SCWG and liquefaction are conducted at elevated temperatures and pressures, which
require high energy input. Although the calculated overall energy recovery efficiency for
the proposed two-step sludge treatment process was as high as 93.4% (Chapter 8), the
energy consumptions from the feedstock transportation, pre-treatments, pumping, heating,
product recovery, etc., were not taken into consideration. As such, future work is needed
to obtain more comprehensive and accurate evaluation on the energetic efficiency of the
proposed sludge hydrothermal treatment process.

In order to improve the energy utilization efficiency of the SCWG/liquefaction process, it
is also of great importance to make full use of the heat recovered from the heat exchanger.

Last but not least, more investigations should be performed on the fate and utilization of
the solid by-products produced from sludge co-liquefaction/SCWG, in particular heavy
metals, in order to completely convert sludge into a safe and useful material with minimal
negative effects to our environment.