Catalytic Gasification of Activated Sludge in Near-critical Water

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

This thesis was the report of the research done on the near-critical water gasification (NCWG) as an application for activated sludge treatment. The research started with the use of model compounds and binary mixtures of these compounds as feeds for the NCWG. High gasification yields were obtained using a commercial catalyst (Raney nickel), and it was found that interactions between model compounds in the binary mixtures resulted in lowering the gasification efficiencies. The research then shifted to the use of actual activated sludge samples and the search for novel catalysts for that application. Almost 70% of the sludge was gasified in the presence of the high amounts of Raney nickel. Hydrogen was the main product in the gas phase. However, Raney nickel lost half its activity after only 8 minutes of exposure to supercritical water. For some model compounds, novel catalysts formulated in our laboratories had better activities than the commercial ones. This was not the case for the NCWG of activated sludge.
Acknowledgments

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1 Introduction

1.1 Background

Activated sludge is a mixture of microorganisms (bacteria, fungi…) used to treat wastewater in the biological reactor of the treating plant. The live biomass in activated sludge consumes the organic contaminants in the wastewater to reduce their concentrations to below the allowable discharge limits. In the process, the microorganisms multiply and therefore a part of the activated sludge has to be discarded in order to maintain a constant amount of microorganisms in the reactor. The waste activated sludge (the portion to be discarded) is a water rich sludge (up to 98wt% water) that also has high organic content, heavy metals and pathogenic cultures that could be threatening to human health and to the environment. Therefore, the activated sludge must undergo proper treatment before discharge, a costly step that constitutes 30 to 50% of the total operating cost of the treatment plant [1, 2].

With the growth of the urban population and the demand for better treatment of effluents, there has been a big increase in waste sludge generation. In the United States alone, the production of these biosolids increased from 7.1 million tons in 2000 to 8.2 million tons in 2008 [3]. Conventional sludge treatment methods include landfilling and incineration of the sludge. In landfilling, sludge has to be dried and biologically stabilized to eliminate the pathogenic risks. Incineration also requires a dry feed and results in the emission of harmful gases and particles to the environment. Due to stringent environmental regulations and lack of social acceptance, these methods are becoming a thing of the past. Therefore, treatment processes that transform the waste sludge into useful products, such as fuel, biopolymers and fertilizers are gaining attention in recent years. Gasification is one of such processes that convert the organic matter in the sludge to a fuel gas with a high heating value. But the organic feed has to have low water content, which renders this application for activated sludge treatment expensive and not economically viable.

One way to avoid drying cost is by using treatment methods that require high water content feeds. In particular, conversion and treatment processes that are based on supercritical water (SCW),
water above 374°C and 22.1MPa, show the most potential. SCW has significant differences in physical properties than water at room temperature. The differences make SCW an ideal medium to carry out organic conversion reactions that result in high yields. Initially, SCW oxidation (SCWO) of activated sludge was carried out in lab testing. In SCWO, an oxidizing agent (oxygen or hydrogen peroxide) is added to the sludge. The oxidizing agent converts the organic content of sludge to carbon dioxide and water. Using this technique, the total organic content of the sludge is reduced (and eliminated in some cases), but no value-added product can be generated in the process. On the other hand, SCW gasification (SCWG), thermal treatment in the absence of an oxidizing agent, results in the production of valuable gases such as hydrogen and methane.

SCWG of activated sludge is a promising alternative for sludge treatment and disposal. Previous studies show that activated sludge can be completely gasified in SCW at high temperatures and pressures [4, 5], well above the critical point of water. However, reliable operation of SCWG reactors under these conditions requires special and expensive material of construction (MOC) that can withstand the high temperatures and pressures and the high corrosion rates. The need for special MOC and the high energy demand to maintain the high reaction temperatures significantly increase the operating cost of SCWG process and are detrimental to its commercial viability.

In order to address this problem, research has been focusing on the development of suitable catalysts that could result in high gasification yields at significantly lower temperatures and pressures; i.e. ideally under the critical point of water.

Critical review of literature shows that even though many active metals have been identified for SCWG of biomass [6, 7]; only few remain active after a prolonged exposure to supercritical conditions. Considering various commercially available catalysts, Raney nickel has been shown to be an effective catalyst in supercritical water gasification processes. This is a porous catalyst with a high nickel surface area that is commonly used for hydrogenation reactions. However, its thermal stability under SCW conditions is of concern. Several supported catalysts has been also
reported in the literature for such applications, [7-9]; however, only few supports remained stable in SCW, whereas the rest changed phases, got dissolved or were subject to sintering.

In addition, wastewater sludge is a complex mixture of several compounds. However, most of the previous research is focused on using a single model biomass compound. Limited studies were made on the interaction in complex multi-component systems during SCWG.

The aim of this research is to develop a better understanding of the efficacy of catalytic supercritical water gasification for the conversion of activated sludge biomass. Both municipal sludge and mixtures of model compounds representing typical substances found in activated sludge are examined in this study.

1.2 Objectives

The overall objective of this thesis is to develop new insights and a better understanding of the supercritical water gasification of municipal sludge as an alternative for sludge treatment and disposal. Specific objectives of this research are:

- To examine the interactions among model compounds; representing constituents of municipal activated sludge, in SCWG process and their effects on the product yield and distribution using Raney nickel as catalyst.

  In this study, glucose, glycine, glycerol and humic acid were selected as model compounds and interactions among them in binary mixtures were quantified.

- To systematically examine the performance of Raney nickel for SCWG of municipal sludge.

  In this study, the effects of temperature, residence time and catalyst loading on the product distribution and gasification yield were investigated. Additionally, the deactivation of the catalyst was studied during the process and the roots of the loss of activity were identified.
• To compare performance of a novel catalyst developed in our laboratory with that of commercially available catalysts for the SCWG of municipal sludge.

In this study, the gasification yield and product distribution of a novel catalyst was compared to 3 commercially available catalysts for the SCWG of the models compounds and the activated sludge samples. The effect of active metal concentration on the support was explored. The aim of this part is to compare the performance of the formulated catalyst to that of the commercial ones and to understand how its performance can be improved.

1.3 Thesis outline

Based on the above objectives, the subsequent chapters of this thesis are organized as following:

• Chapter 2 will first discuss the process generating activated sludge as well as its chemical and biological characteristics. The discussion will then shift to the available methods of disposal of activated sludge and their advantages and drawbacks compared to SCWG. Beyond that point, a more in-depth analysis of SCWG is presented. This analysis includes the characteristics of SCW and why it is a good medium for organic conversion reactions, the first works done in SCWG, thermodynamics analysis and preliminary works done on SCWG of activated sludge. The chapter will then provide a review on the catalysts studied for SCWG applications and the major findings in their activity and stability.

• Chapter 3, 4 and 5 will focus on the three objectives of research discussed above. In each chapter, the research methodology is introduced followed by a presentation of the results obtained along with discussions and conclusions that were drawn from these results.

• Chapter 6 will present key conclusions obtained from this research. The author will also recommend on how the research can be continued and what are the areas that would require more work to be done.
1.4 References

2 Literature Review

2.1 Activated Sludge

2.1.1 Biological Treatment Process

Activated sludge process is the most widely used process for the biological treatment of wastewater. Its sole purpose is the reduction of organic pollutants in wastewater. The process, usually aerobic, is a suspended-growth process where a high microorganism population (biomass) consumes biodegradable organics and other inorganics (such as nitrogen and phosphorous) present in the wastewater. These nutrients are converted by the biomass into new cells and products of metabolism.

Figure 2-1 shows a diagram of the activated sludge process. The incoming wastewater is mixed with activated sludge at the entrance of the biological reactor to form the mixed liquor (ML). The ML consists of microorganisms, biodegradable and non-biodegradable organics and inorganic matter.

![Figure 2-1 Schematic of the activated sludge process](image)
The microorganisms are a mixture of flocculated bacteria, fungi, protozoa and rotifers. After a sufficient time in the biological reactor, the ML is transferred to a clarifier where the suspended solids are separated from the treated water. Part of the settled solids are then returned to the reactor (as return activated sludge RAS) and mixed with the incoming wastewater. This is done to maintain a high concentration of microorganisms in the biological reactor. The remainder settled solids are discarded as waste activated sludge (WAS) and sent to solid treatment facilities.

2.1.2 Activated Sludge Characteristics

Activated sludge is a mixture of microorganisms, organics and inorganic matter. Usually, its water content is over 95wt%. The chemical composition of activated is summarized in Table 2-1. Activated sludge contains 60-80% volatile solids. The volatile content provides an estimate of the organic content in the sludge. The remainder total solids are either fixed carbons or inorganic matter (referred to as ash). Sludge also contains heavy metals such as arsenic, mercury and nickel [3].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dry solids (TS), %</td>
<td>2.0 – 8.0</td>
</tr>
<tr>
<td>Volatile solids, % of TS</td>
<td>60 – 80</td>
</tr>
<tr>
<td>Grease and fats, % of TS</td>
<td>15 – 35</td>
</tr>
<tr>
<td>Proteins, % of TS</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Nitrogen, % of TS</td>
<td>1.5 – 4</td>
</tr>
<tr>
<td>Phosphorous, % of TS</td>
<td>0.28 – 2.8</td>
</tr>
<tr>
<td>Cellulose, % of TS</td>
<td>8.0 – 15.0</td>
</tr>
<tr>
<td><strong>Polymer (mg/g MLSS)</strong></td>
<td>[2]</td>
</tr>
<tr>
<td>Protein</td>
<td>250 – 380</td>
</tr>
<tr>
<td>Humic substances</td>
<td>90 – 250</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>60 - 130</td>
</tr>
</tbody>
</table>

Table 2-1 Typical chemical composition of activated sludge

Being a mixture of many species of viruses, bacteria and protozoa, the microbial community in activated sludge contains lots of biological agents. Many pathogens were detected in activated
These pathogens are linked to severe symptoms, such as Cholera and Meningitis to name a few [4, 5].

2.1.3 Sludge Disposal and Reuse

Activated sludge accounts for the largest volume of solid waste generated by a municipal wastewater treatment plant. The sludge utilization and disposal are very difficult and very costly. The costs can be between 30 to 50% of the total operating cost of the plant [6, 7]. And with the increase in water treatment demand, the amount of sludge to be disposed of is increasing too. In 2000, wastewater treatment in the United States generated 7.1 million tons of biosolids [8]. In 2005, this figure grew to 7.6 million tons and reached 8.2 million tons in 2008.

Due to its high water content and the presence of pathogens, sludge cannot be disposed without pretreatment since this will damage the ecosystem. Sludge must undergo various treatment processes before reuse or disposal. Thickening and dewatering are used to reduce the water content. Dewatering is usually done by means of centrifugation, filtration or thermal drying, which considerably add to the disposal cost. In some cases, sludge must also undergo biological stabilization in order to reduce the pathogens concentration. The current means of sludge disposal are briefly introduced here, along with their advantages and drawbacks.

2.1.3.1 Landfilling

In landfilling, dry sludge is buried in the ground. It is oldest method of sludge disposal. The water content of the sludge must be low; therefore sludge dewatering is required. In areas where large acres of land are available, landfilling provided a relatively cheap mean of disposal. Among its drawbacks are land availability and the presence of heavy metals in the sludge. These metals resulted in soil contamination and toxicity for the microorganisms. Landfilling also decreased the water quality and resulted in the ecosystems degradation. New stringent environmental regulations and social aspects (such as public anxiety) try to limit landfilling as a sludge disposal option.
2.1.3.2 Incineration

Incineration is a thermal treatment where sludge is burned in a stack. This process results in a significant reduction of solids volume. Sludge is converted to gas, light particulates and ash. The ash remains in the stack and is then disposed of by landfilling. Incineration requires reducing the water content in the sludge, though biological stabilization is not needed. The heat of incineration is enough to kill any pathogens. Incineration is very costly. No useful gases can be recovered from the process. Energy recovery is very poor and the process results in the release of toxic particulate to the atmosphere along with contributing to global warming. Many countries have banned the use of this technology as a mean of sludge disposal.

2.1.3.3 Recycle to Land

Sludge contains organic matter that could be used as nutrients and fertilizers. Recycle to land has been used as a mean of disposal of sludge containing low amounts of pathogens and heavy metals. The sludge must undergo water reduction and biological stabilization before it is used as a fertilizer. Aside from its high cost, recycle to land was shown to decrease the soil value and the crop yield compared to conventional fertilizers. It also resulted in degradation of ecosystems and reduction in soil microorganisms.

2.1.3.4 Gasification

Gasification is a thermal process for converting the carbonaceous material in sludge to carbon monoxide and hydrogen. The process takes place at high temperatures (above 700°C) in the presence of a controlled amount of oxygen or steam. The gas produced can have a high heating value and can be used as a utility stream in the treatment plant. Gasification is associated with high costs. Sludge has to have low water content, and therefore drying is a pre-treatment step. Also, high temperatures add considerably to the operating cost.
2.1.3.5 Supercritical Water Oxidation (SCWO)

The total organic content (TOC) of activated sludge can be reduced considerably using supercritical water oxidation. As it will be discussed later, supercritical water properties along with the presence of an oxidizing agent (usually \( \text{O}_2 \) or \( \text{H}_2\text{O}_2 \)) facilitate the oxidation of organic matter in the sludge to carbon dioxide and water. Total removal of TOC was achieved by this method, although no useful product can be recovered. Unlike the other methods described earlier, SCWO does not require any pre-treatment. Excess water in the sludge plays a major role in the destruction of the TOC. This process requires relatively high temperatures and pressures (above 374°C and 22.1MPa) which results in high operating cost and costly material of construction.

2.1.3.6 Supercritical Water Gasification (SCWG)

SCWG is a relatively new technique with great potential for use to convert activated sludge into useful products (such as fuel gas and oil). In supercritical water and in the absence of an oxidizing agent, the carbonaceous matter in sludge is converted to gas (mainly hydrogen, methane, carbon dioxide and carbon monoxide) and tar and char in the liquid phase. Similar to SCWO, SCWG does not require drying of the sludge and no biological stabilization. Any pathogens will be killed due to the harsh reaction conditions. Being the topic of this thesis, a more extensive review of SCWG will be presented now.

2.2 Supercritical Water Gasification (SCWG)

2.2.1 Early Works

In 1978, Antal et al. [9] carried out thermodynamics analysis to predict the thermochemical equilibrium as a function of reaction temperature and high pressure on the reaction products of 1 mole of cellulose and 7 moles of water. A hydrogen rich gas (also containing methane, carbon dioxide and carbon monoxide) with a complete gasification of cellulose was predicted at temperatures higher than 600°C. Experiments done at atmospheric pressures showed that biomass does not react directly with steam [9-11]. Significant amounts of tar and char were produced. At a lower reaction temperature, tar and char are stable intermediates of the steam
reforming reaction in the aqueous phase. Unlike tar, char cannot be converted to gas by further increasing the temperature [12]. In 1985, Modell et al. [13, 14] showed that the liquefaction and gasification of forest product in supercritical water is technically feasible. Maple wood sawdust decomposed to tars and some gases, but no char formation was reported. The hypothesis is that cellulose, the major component of the biomass used, decomposes rapidly in water at temperatures well below the supercritical temperature of water [15, 16]. At temperatures above 190°C, rapid solvolysis of lignin and hemicellulose macromolecules in hot liquid water occurs [14-19]. Beyond that temperature, the biomass undergoes isomerization, dehydration, fragmentation and condensation reactions that converts it to gas and tars [19-28].

2.2.2 Supercritical Water Characteristics

In SCWG, water acts as a solvent, catalyst or catalyst precursor and as a reactant. Supercritical water (SCW) is water above its critical point of 374°C and 22.1MPa. Near or above its critical point, water significantly changes its properties as a function of temperature and pressure. Compared to normal conditions, water above its critical point witnesses a drastic reduction of density which translates in a significant decrease in the static relative dielectric constant. SCW dielectric constant is one fifth of that of acetone at normal conditions. This decrease in dielectric constant renders SCW a non polar solvent; the solubility of salts decreases, while the solubility of organic substances and permanent gases such as nitrogen, hydrogen and oxygen increases. Above its critical point, water can be mixed with these gases and many organics at any ratio [29-32]. SCW also has a low viscosity, close to that of vapors. Water at the supercritical condition consists of one phase; there are no transfer resistances between phases. This lack of resistances combined with the low viscosity result in a high diffusion coefficient and therefore high reaction rates in SCW. At the supercritical conditions, water also exhibits a drop in the ion product, which indicates a switch from ionic reaction mechanism to a free radical mechanism.

During SCWG, water plays several major roles; it suppresses tar and char formation by solvation and dilution. Complex molecules (containing double bonds) are dissolved in SCW at very low concentrations, therefore having less chance to meet and polymerize into char. SCW also
accelerates biomass depolymerization by hydrolysis. Large polymers rapidly hydrolyze into monomers. SCW acts as an acid catalyst and therefore can catalyze the gasification reaction.

The change in water characteristics at supercritical conditions makes it an ideal medium to carry out chemical conversion reactions [33].

As will be discussed in the next section, increasing water content will result in increasing hydrogen yield. On the other hand, having a high content water feed is not economically viable. Water at supercritical conditions is an aggressive medium: SCW results in strong corrosion and many heterogeneous catalysts are unstable at these conditions (as well be discussed later). Also, due to the high heat capacity of water, high water content is an obvious disadvantage and heat recovery is essential for the viability of SCWG.

2.2.3 Thermodynamics Analysis

Following Antal’s first thermodynamic analysis, other studies were carried out to determine the effect of other parameters on the SCWG products. These parameters included temperature, pressure and concentration. In the absence of catalysts, high yield of hydrogen were obtained at temperature above 600°C. At lower temperatures, methane is the favored product in the gas phase [34-37]. Thermodynamic analysis also showed that methane yield also increased with increasing pressure and initial biomass concentration, while hydrogen yield decreased. Carbon monoxide content in the gas was predicted to be low. Lu et al. [35] calculated the chemical equilibrium based on the Gibbs free energy minimization as a function of temperature for a 5wt% dry biomass content. Their findings are summarized in Figure 2-2. The chemical equilibrium yields as a function of dry biomass concentration are plotted in Figure 2-3. Experimental results showed that the measured gas composition is far from the calculated equilibrium data, indicating that the SCWG is kinetically driven.
Figure 2-2 Equilibrium gas yields in the reactor as a function of temperature for biomass gasification at 25MPa with 5wt% dry biomass content (Reprinted from Lu et al. [35]).

Although the reactions occurring during SCWG are numerous and differ from one compound to another, few key reactions are believed to always take place. These include the steam reforming reaction, water gas shift reaction and methanation reactions. The steam reforming reaction of cellulose is shown by Equation 2-1. The water gas shift reaction along with the possible methanation reactions are shown by Equation 2-2, Equation 2-3 and Equation 2-4, respectively.

\[
C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2 \quad \text{Equation 2-1}
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad \text{Equation 2-2}
\]

\[
CO + 3H_2 \rightarrow CH_4 + H_2O \quad \text{Equation 2-3}
\]

\[
CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \text{Equation 2-4}
\]
2.2.4 SCWG of Model Compounds

Even though early experiments involved the use of real biomass, its complexity makes it hard to understand the chemistry involved during the gasification. Model compounds have since then been used to simulate complex biomass molecules. These molecules and the model compounds usually share similar functional groups. This notion started when Minowa et al. showed that the gasification of cellulose and glucose (the monomer of cellulose) was the same. In a series of SCWG experiments [28, 38-41], Minowa et al. studied the product distribution in the gas and aqueous phases for the SCWG of cellulose and glucose at 200°C to 350°C. Gas, oil and char distribution of the SCWG of glucose was similar to that of cellulose gasification at the different temperatures. This confirmed that the hydrolysis was the first step. The suggested reaction path is as follows:
Several amino acids were tested as model compounds for proteins [42-44]. Kang et al. studied the decomposition of silk fibroin protein in subcritical water into amino acids [45]. At lower temperatures, the decomposition of the protein yielded complex amino acids. However, as the decomposition temperature increased (up to 300°C), the production of low molecular weight amino acids (such as glycine and alanine) was favored. Glycine and alanine were used as model compounds for proteins [43, 46]. During proteins gasification, hydrolysis to form ammonia competes with decarboxylation and therefore decreases the gasification efficiency. Glycine as a model compound also showed to be resistant to gasification. However there are some limitations of using glycine or alanine as a model compounds for proteins; proteins contain some elements not contained in these low molecular weight amino acid (such as sulfur). Glycerol, a by-product of biodiesel production was also used as a model compound for fats [46]. It was completely gasified and yielded a hydrogen rich gas. Fats consist of fatty acid portions linked together by a glycerol portions. One limitation of using glycerol to represent fats is that the elemental composition of the fatty acid portion could be different from that of glycerol. Therefore the gasification of the two portions could be quite dissimilar.

2.2.5 SCWG of Mixtures

Most of the work done on SCWG involved using a single compound as a reaction feedstock. But real biomass is usually a mixture. Natural cellulosic biomass is typically a mixture of cellulose, lignin and hemicellulose. Live biomass is a mixture of carbohydrates, proteins and fattiness. In some instances, live biomass (such as activated sludge) can contain humic substances.

Yoshida and Matsumura [47] studied the interaction between cellulose, lignin and xylan (as a model compound for hemicelluloses) in binary mixtures. For binary mixtures containing lignin,
they witnessed large deviations from the calculated yields (i.e. yields calculated using the rule of mixture). Hydrogen and methane yields were also significantly lower than the calculated ones. For the mixture of cellulose and xylan, the yields were identical to the calculated ones. It was concluded that hydrogen is suppressed in the presence of lignin. Even though the chemistry is not quite clear, one hypothesis is that the degradation intermediates of cellulose and xylan react with lignin to form stable molecules that are harder to gasify.

Kruse et al [48] studied the effect of proteins in the mixture. They mixed alanine with glucose and used it as a feedstock for SCWG. Feedstock containing alanine exhibited unexpected low gas yields compared to the ones not containing the protein model compound.

### 2.2.6 SCWG of Activated Sludge

Few studies have been carried out using activated sludge as feedstock for SCWG. Xu et al. [49] used Coconut Shell activated carbon catalyst to gasify sewage sludge in a continuous reactor at 600°C and 34MPa and got total gas yield of 77%. Xu et al. [50] also gasified a mixture of sewage sludge and corn starch in SCW at 650°C and 28MPa using the same catalyst. Near complete gasification of the organic in the feed was achieved and a hydrogen-rich (42%) gas was obtained. Zhang et al. [51] tested the effect of several types of sludge on the catalyst free gasification product at 400 to 550°C. At 500°C and for the secondary sludge used, they obtained a gas yield of 18% containing high amounts of CO₂. Yamamura et al. [52] studied the SCW gasification of sewage sludge in the presence of RuO₂ as catalyst at 375°C to 500°C. At 450°C, 47.1MPa and 120 minutes reaction time, a total gas yield of 11% based on carbon was achieved (23.1% based on hydrogen). The gas product was a hydrogen rich gas but also contained a high fraction of methane. Schmieder et al. [53] used K₂CO₃ as a homogeneous catalyst for the SCW gasification of sludge at 450°C and 330bar. The use of the catalyst increased the gas yield from 55.2% to 85.3%, while it did not change the gas composition significantly where a hydrogen-rich (48%) gas was obtained in both cases.
2.2.7 Advantages of SCWG

SCWG could play a major role in the production of energy from renewable sources and for the treatment of solid wastes. SCWG can be an economical option for treating wet biomass since no drying is required. Drying can be a costly pre-treatment step, especially for biomass with high water content. These include agriculture wastes, wastes from the food and beverage industries, by-product of bioenergy production processes and wastewater treatment. Running at high pressures, the gas produced is already pressurized and does not require further compression for storage. High pressures also provide easier separation of carbon dioxide from hydrogen and methane since carbon dioxide is much more soluble in water at these conditions. SCWG also produces low amount of carbon monoxide, a toxic gas with low heating value. Carbon monoxide is converted to carbon dioxide via the water gas shift reaction, producing hydrogen as a by-product. In addition, an important by-product of this process is high quality steam that can be used as a source of heat and energy.

2.2.8 Challenges in SCWG

Many challenges still need to be overcome in order for SCWG be viable. A key challenge is material of construction limitations. The reactor material must be able to withstand the high temperatures and pressures that are needed to carry out SCWG. The special alloys that do are extremely expensive and could render the process uneconomical. Also corrosion issues due to the harsh nature of SCW arise. One major challenge also reported is the plugging of continuous reactor, often by salts that precipitate under supercritical conditions.

In order to solve these challenges that stem from high operating temperatures and pressures, the use of a suitable catalyst to lower the operating pressure and temperature was proposed. But the “hunt” for the suitable catalyst is also a challenge. Most of the catalysts used today for SCWG are unstable, have short lifetime or exhibit poisoning at supercritical conditions. In this next section, an overview of the catalysts used for SCWG is presented with a focus on heterogeneous catalysts and the advances made to make them more stable.
2.3 Catalysts in SCWG

2.3.1 Homogeneous Catalysts

Salts were shown to have catalytic effects on SCWG, and hence they were used by some researchers as homogeneous catalysts. These salts included potassium and sodium hydroxide and potassium and sodium carbonate to name a few. It was Minowa et al. [28, 38] that first showed that the presence of these salts has an effect on the SCWG. They noticed that the addition of sodium carbonate resulted in the cellulose degradation at lower temperatures. Kruse et al. [33, 54-56] examined the influence of salts on the SCWG of biomass. They found that in the presence of these inorganics, the CO yield dropped while the hydrogen and carbon dioxide yields increased. The total gas yield also increased. The addition of the alkali salts also suppressed char formation. The same was observed by Matsumura et al. [57] who also added that the addition of these salts resulted in more tar in the aqueous phase. Alkali salts were found to catalyze the water gas shift reaction [58-60] and suppress char formation from tar.

Homogeneous catalysts are soluble in water at room temperature but insoluble in SCW. During continuous gasification process, most of the reactor plugging is attributed to salts precipitation. And at normal conditions, the recovery of these salts is hard. Heterogeneous (metal) catalysts have better activity than the homogeneous ones and are more easily recovered. The next section gives an extensive review of the development of heterogeneous catalysts for SCWG.

2.3.2 Heterogeneous Catalysts

2.3.2.1 Active metals

Modell et al. [15] were the first to describe SCWG. In batch tests, a range of nickel based catalyst showed little catalytic effect. The nickel metal used was in the oxide form. Elliott et al. [61-64] showed that the use of an active catalyst can facilitate the SCWG even below the critical point of water. Using several feedstocks, they tested the catalytic effects of several nickel based catalysts at a temperature range of 350°C to 450°C. Significant improvements were observed in the presence of the nickel catalyst; higher gas and methane yields were obtained. However,
nickel is only active in its reduced form [63]. The following reaction pathway was proposed by Minowa in the presence of a nickel catalyst [40]:

$$\text{Cellulose} \xrightarrow{\text{Decomposition}} \text{Water Soluble Products} \xrightarrow{\text{Gasification/Ni}} \text{Gases (H}_2\text{+CO}_2) \xrightarrow{\text{Gasification/Ni}} \text{Gases (CH}_4\text{+CO}_2)$$

Elliott et al. also studied the catalytic effect of several transition metals. Among these metals, copper and cobalt exhibited some level of catalytic activity, but resulted in low methane yields. On the other hand, tungsten, molybdenum, zinc, chromium, rhenium, tin and lead had no useful activities during SCWG. Modell et al. [14, 65] showed that platinum was not active for this application. This was confirmed by Elliott [64], who also showed that palladium and silver were also not active in SCWG. Ruthenium and Rhodium showed useful levels of activity and iridium show some catalytic effect.

### 2.3.2.2 Raney Catalysts

Raney catalysts are metal spongy catalysts with large specific surface areas. Starting from a metal-aluminum alloy, aluminum is leached by sodium hydroxide to obtain high amounts of the target metal. After leaching, the metal catalyst contains only few percents of aluminum. Several commercial Raney catalysts are available. They include nickel, cobalt, copper and iron.

Azadi et al. [66] compared the activity of several Raney catalysts for the SCWG of glucose in near-critical water. Raney nickel exhibited the highest activity followed by Raney copper and then Raney cobalt. Vogel et al. [67] used Raney nickel for the SCWG of wood. Near complete gasification was achieved at a temperature range of 370°C to 420°C.

### 2.3.2.3 Supported Catalysts

Another type of heterogeneous catalysts is the supported catalysts. They consist of an active metal and in some cases promoters dispersed on a catalyst support with high surface area. This enhances the dispersion and stability of the active metal and promoter. As discussed previously, the active metals for SCWG included nickel, ruthenium and rhodium. Supports that were tested...
for SCWG include alumina, titania, silica and carbon. Typical surface areas of these materials range from 1 to 2000m$^2$/g and the average pore diameter range from 0.4-2000nm.

### 2.3.2.3.1 Alumina

Aluminas are the second most abundant minerals in the earth crust, only after silicates. Aluminas (aluminum oxide) have been considered for the SCWG application due to their excellent thermal stability. Several phases of aluminas are available, differing in surface area, pore size and acidity. These properties can vary significantly based on the preparation, purity and dehydration of the support. Alumina treated at low temperature has a high surface area and is more acidic than the one treated at a higher temperature. As temperature increases, the alumina undergoes a phase change by losing surface to hydroxyl groups which also result in a decrease in acidity. Typical physical properties of various aluminas can be found in Table 2-2.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Calcination Temperature (°C)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gamma</td>
<td>450</td>
<td>335</td>
<td>6.4</td>
</tr>
<tr>
<td>Delta</td>
<td>950</td>
<td>120</td>
<td>16.6</td>
</tr>
<tr>
<td>Theta</td>
<td>1050</td>
<td>50</td>
<td>28</td>
</tr>
<tr>
<td>Alpha</td>
<td>1200</td>
<td>1-5</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2 Physical properties of various aluminas

### 2.3.2.3.2 Silica

Silicas are also used as a support for various applications. Their surface area ranges from 300 to 400m$^2$/g. Compared to aluminas, silicas are less acidic and less thermally stable. They tend to form volatile hydroxides in high temperature steam, which is why their application in SCW processes is limited. Silicas have found increasing applications for sulfur-containing feed due to their resistance to sulfur poisoning. Silica gel, a drying agent with higher surface area (400-800m$^2$/g), can also be used as a support for highly dispersed metal catalysts.
2.3.2.3.3 Titania

Titania was also used by several researchers as a catalyst support for SCWG. Titania is produced by the precipitation of titanate solution or by the decomposition of organo-titanates. Its surface area varies between 25 to 100m$^2$/g, depending on the ratio between its anatase and rutile crystal structure. The higher the treating temperature, the more anatase is converted to rutile leading to a decrease in the surface area.

2.3.2.3.4 Carbon

Natural occurring carbon can be treated to change its properties and make it a suitable catalyst support. The treatment conditions and the source of carbon play a major role in the carbon support final physical and chemical properties. Treated at moderate temperatures in an active atmosphere, the resulting carbon support is referred to as activated carbon and has a high surface area. On the other hand, carbon treated in an inert atmosphere at higher temperatures yields a low surface area graphite. The surface area of carbon support can vary from 1000-1500m$^2$/g, and therefore can be used to produced highly dispersed catalysts.

2.3.2.3.5 Promoters

Promoters are chemical substances added in small quantities to the active metal and support in order to improve the performance of the catalyst or to adjust the product distribution. Although by itself the promoter has no significant catalytic activity, it interacts with the active metal of the catalyst to alter its structure on the support. Several promoters were used in SCWG. These include cesium, potassium and sodium [62, 64].

2.3.2.4 Activity and Stability for SCWG

Minowa et al. [40, 68] made several supported nickel catalyst for the SCWG of glucose and cellulose. These supports included silicas and aluminas. Even though no lifetime assessment was made, this study showed that the catalyst activity varied depending on the support type. This
variation was not only attributed to the kind of support but also to the catalyst particle size which indicates that only the metal particle on the external surface could contribute in the catalysis [68].

Elliott et al. [63] studied the stability of several supported catalysts in SCW. The supports included a range of alumina and silica based materials. They found that the silicas, alumina (other than α-alumina), various ceramic supports, and other silica-alumina supports are unstable in SCW. At these conditions, the supports were subject to dissolution, phase transition and hydrolysis. Other supports were useful but had limited lifetimes (less than 100 hours) due to support break down, active metal oxidation and crystallite sintering. Osada et al. [70] studied the stability of three ruthenium-based catalysts (on titania-anatase, carbon and γ-alumina) at 400°C. They found that the most stable out of the three was the titania (anatase) supported catalyst. The carbon supported ruthenium showed slight metal crystal growth which translated in a loss of activity. On the other hand, the alumina supported catalyst was destroyed in the process. Alumina changed phases from γ-alumina to α-alumina and ruthenium was dissolved in water. Miura et al. [71] formulated a carbon supported nickel catalyst by ion exchanging the nickel onto a resin and then carbonizing the resin. High nickel content was obtained (about 47%), dispersed on a high surface area of 170m²/g. The catalyst had good activity and was stable for over 50 hours of continuous testing. At the end of the testing, some sintering of nickel was observed. Pedersen et al. [72] formulated a nickel catalyst on alumina-magnesia spinel, but continuous tests of over 100 hours showed a dramatic loss in methanation activity.

Vogel et al. [67] compared the catalytic activity of α-alumina supported nickel to that of Raney nickel in small batch test at 370°C to 420°C. Raney nickel was found to be more active than α-alumina supported nickel but it was not clear if the nickel loadings were the same. In another study, Vogel [73] found that Raney nickel tends to deactivate rapidly over time (about 50 hours of continuous experiments) however exact mechanism behind the deactivation of this catalyst was not proposed.

Elliott et al. [62] tested the effect of promoters on SCWG of a number of feedstock. They found that cesium-promoted nickel catalyst was more active than potassium- and sodium-promoted nickel catalysts. They also examined other promoting metals in search of a stable formulation.
They found that the use of 1wt% copper, silver or tin were the most useful. Ruthenium not only increased stability, but also increased the gasification efficiency. In lab tests at 350°C, these catalysts exhibited high activities and lifetimes of over 6 months. Vogel et al. [76] improved Raney nickel stability by adding promoters, though the deactivation still occurred relatively fast (100 hours). They also studied the catalytic activity of several doped skeletal nickel catalysts [77]. High yields were reported without doping and with the use of ruthenium and copper as promoters. Molybdenum promoted catalysts exhibited lower activities than the non-promoted ones.

### 2.4 Concluding Remarks

The literature reviewed in this section show that SCWG is a promising technology for the conversion of wastewater sludge to value added gaseous fuels. The key challenges associated with this technology stem from harsh operating conditions, i.e. high temperatures and pressures, required for SCWG. To address these challenges, it is possible to reduce the reaction temperature and pressure while maintaining acceptable gasification yield by using suitable active metal catalysts. However, a systematic study that addresses the validity of this approach for the supercritical water gasification of sludge is missing from the literature. This study if focused on addressing this gap.

### 2.5 References


3 Catalytic Gasification of Model Compounds and their Mixtures in Supercritical Water

3.1 Introduction

Amid concerns over global warming and our dependence on fossil fuels, energy from renewable sources, such as biomass, has become a hot research topic. Of the many suggested methods for converting biomass into energy, supercritical water gasification (SCWG) has shown to have a great potential for the production of useful products.

Supercritical water (SCW), water above 374°C and 22.1MPa, is an excellent medium for organic chemical conversions. At those conditions, SCW acts as a non-polar solvent; organics not soluble in water at room temperature are readily soluble in SCW. SCW also has a low viscosity and a high diffusion coefficient. This leads to high reaction rates under supercritical conditions.

Early works in SCWG of biomass used cellulosic materials as a feedstock. Modell et al. [1-2] studied the gasification of forest biomass in SCW and proved it to be a technically feasible technology. Thermodynamics analysis of cellulose gasification by Antal [3] suggested that above 600°C, a complete gasification was achieved and a hydrogen rich gas could be obtained. The gaseous product also contained CO₂, methane and small amounts of CO.

Since real biomass is often a complex mixture of various components, model compounds are frequently used to better understand the reaction mechanisms of biomass. Minowa et al. [4-9] showed that gasification of glucose and cellulose in SCW are essentially the same, and therefore, glucose was used as a model compound for cellulose. Other model compounds used for cellulosic biomass include phenol for lignin, and xylan for hemicellulose.

Apart from cellulosic biomass, live biomass is also widely used as a gasification feedstock. The catalytic-free gasification of proteins and the gasification in presence of salts resulted in low gas yields as was shown by Kruze et al. [10]. Experiments with glycine as a model compound for
proteins showed it to be resistant to gasification [11-12]. Glycerol was also used as a model compound for fats [13-14].

Yoshida and Matsumura [15] studied the interaction between cellulose, lignin and xylan (representing hemicellulose) in mixtures. They showed that in the presence of lignin, yields deviated from the calculated ones, and that hydrogen production was suppressed. For mixtures not containing lignin, the yields found experimentally were similar to the calculated ones.

Elliott et al. [16] studied the gasification of 10% p-cresol in water at 350°C using several metal catalysts on different supports. They found that nickel and ruthenium showed good activities for SCW gasification. Considering various nickel-based catalysts, Raney nickel had the best activity with 93% carbon conversion and a methane-rich gaseous product. In our group, the activity of several industrial catalysts on the SCW gasification of glucose in near-critical water have been studies and reported [17-19]. These studies showed that Raney nickel had the highest activity among the examined catalysts.

In this study, we examine the near-critical gasification of four model compounds representing substances commonly found in live biomass (such as activated sludge). These compounds are glucose (for carbohydrates), glycine (for proteins), glycerol (for fattiness) and humic acid (for humic substances). Raney nickel was used as the catalyst. Interactions between these model compounds in a mixture were also studied.

### 3.2 Experimental

The experimental setup used in this work consisted of a batch reactor made of 316SS with 50ml volume. Four model compounds were gasified in this study: Glucose (Aldrich), Glycine (Mallinckrodt U.S.P), Glycerol (ACP Montreal) and Humic acid (Aldrich). Raney nickel was obtained from Sigma Aldrich (Canada) as slurry with 50wt% solid content. For each run, 9.7g nano-pure water was added to 0.3g of model compounds to obtain a total weight of 10g at a 3wt% of dissolved organic matter. The desired amount of catalyst was then added and the mixture was loaded to the reactor. The reactor consisted of a 50ml T-shaped Stainless Steel union with a high temperature and pressure valve linked to a pressure gauge and a collection valve (Figure 3-1).
The reactor was immersed in a molten salt bath maintained at the 380°C and kept for 15 minutes. The molten salt bath consists of a mixture of potassium nitrate, sodium nitrate and sodium nitrite and has an extremely high heating rate (~500°C/min). The salt bath temperature was measured using a K-type thermocouple (Omega) and controlled by a PID controller (Hanyoung NX4). At the end of the experiment, the reactor was quenched to room temperature by immersing it in a cold water bath. The final pressure inside the reactor was measured using a digital pressure gauge (Cecomp Electronics) and was used to calculate the total gas yield. The produced gas was collected in a gas bag and analyzed using a Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector. Based on the total gas yield and gas composition, the specific yield of each compound was obtained.

![Figure 3-1 Schematic of the experimental setup used in this work; TI: Temperature Indicator, TC: Temperature controller, PG: Pressure gauge, 1: K Thermocouple, 2: Heater, 3: Molten salt bath, 4: Stainless Steel reactor, 5: High temperature and pressure valve, 6: collection valve.](image)

### 3.2.1 Binary Mixtures

In this paper, six binary mixtures of the four model compounds were gasified. All the mixtures contained two model compounds, each at an initial concentration of 50wt% of the dry weight (without water). Table 3-1 summarizes the weight% of each model compound used in binary mixtures B1 through B6.
<table>
<thead>
<tr>
<th>Binary Mixture</th>
<th>Glycine (wt%)</th>
<th>Glycerol (wt%)</th>
<th>Glucose (wt%)</th>
<th>Humic Acid (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>1.5</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td>1.5</td>
<td>0</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>B3</td>
<td>1.5</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>B4</td>
<td>0</td>
<td>1.5</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>B5</td>
<td>0</td>
<td>1.5</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>B6</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3-1 Composition of binary mixtures B1 to B6 used in this study

3.2.2 Calculated yields

In order to determine if the rule of mixture applies for mixtures of model compounds, experimental yields were compared to calculated yields. For binary mixtures, the calculated yield was defined as the arithmetic average yields obtained for the gasification of a solution of the individual model compounds with a concentration equal to the total concentration of organic matter in the original binary system (3wt% in this case). A similar procedure was used to determine the calculated yields of gaseous products, Carbon Gasification Ratio (CGR) and Hydrogen Gasification Ratio (HGR) values.

3.3 Results and discussions

In this section, experimental results regarding the SCW gasification of individual model compounds and binary mixtures of those compounds are examined. These results are reported in terms of gas yield (i.e. amount of gas produced (in mmol) per amount of organic matter (in g) initially loaded to the reactor), carbon gasification ratio or CGR (i.e. the ratio of the amount of carbon in the gas phase to the amount of carbon in the feed) and hydrogen gasification ratio or HGR (i.e. the ratio of the amount of hydrogen in the gas phase to the amount of hydrogen in the feed).
3.3.1 Model Compounds Gasification

3.3.1.1 Total yield, CGR, and HGR

Figure 3-2 shows the effect of catalyst loading on the total gas yield for the SCW gasification of model compounds at 380°C for a residence time of 15 minutes. As can be seen from Figure 3-2, in general, the total gas yield increased with increasing catalyst loading. For glucose, the total yield increased dramatically by increasing the catalyst loading to 0.028g, where its value increased from 9mmol/g in absence of catalyst to 42mmol/g. Further increase in catalyst loading resulted in little increase in the yield reaching a maximum of 45mmol/g at a loading of 0.22g. Therefore, above 0.028 g catalyst the reaction is not limited by the catalyst amount and instead there is excess active site available for the gasification reaction. A similar behavior was observed for glycine; however, the maximum yield in this case was 31mmol/g that was achieved for the catalyst loading of 0.056g. In the case of glycerol, the highest yield was obtained at the lowest catalyst loading (79mmol/g at 0.014g catalyst), 10 times higher than the yield obtained in the absence of catalyst (7.7mmol/g) and 2.5 times larger than the total yield for glycine. However, further increase in catalyst loading resulted in lowering the total gas yield where it dropped to 55mmol/g at 0.11g catalyst and remained constant with increasing catalyst amounts. Finally, for humic acid, the total gas yield increased linearly with catalyst loading from 5.5mmol/g at a loading of 0.028g to 18mmol/g at a loading of 0.22g. This increasing trend indicates that even at highest catalyst loading, there is excess amount of humic acid and the reaction was limited by the catalyst amount.

As can be seen from Figure 3-3 and Figure 3-4, both CGR and HGR originally increased rapidly with catalyst loading and approached a near plateau region at about 0.06 g (or less) catalyst loading for all model compounds except for humic acid. The only exception to this trend was HGR for glycerol where HGR reached a maximum of 160% at 0.0141 g catalyst and sharply dropped afterwards before reaching a plateau level of 125%. An HGR of above 100% is possible since water participates in the reaction and therefore some hydrogen from the water molecules will end up in the gas phase.
Figure 3-2 Total gas yield versus catalyst loading for the SCW gasification of model compounds at 380°C for 15 minutes (loading of model compound: 0.3g, water loading: 9.7g). glucose (triangles), glycine (squares), glycerol (diamonds), and humic acid (crosses).

Figure 3-3 CGR versus catalyst loading for the SCW gasification of model compounds at 380°C for 15 minutes (loading of model compound: 0.3g, water loading: 9.7g). glucose (triangles), glycine (squares), glycerol (diamonds), and humic acid (crosses).
Figure 3-4 HGR versus catalyst loading for the SCW gasification of model compounds at 380°C for 15 minutes (loading of model compound: 0.3g, water loading: 9.7g). glucose (triangles), glycine (squares), glycerol (diamonds), and humic acid (crosses).

3.3.1.2 Product composition

The yields of individual gasification products are plotted in Figure 3-5. In general, the trends for methane and hydrogen yields with increase in the catalyst loading are similar to those for CGR and HGR, respectively. Furthermore, although not shown in this figure, it is also worth noting that the gas produced also contained less than 1% CO and decreased with increasing catalyst loading.

For glucose, hydrogen yield increased from 3.6mmolH₂/g in the absence of catalyst to 20mmolH₂/g at a catalyst loading of 0.028g. Beyond 0.028g catalyst loading, hydrogen yield decreased almost linearly to 13mmolH₂/g at a loading of 0.22g. At the same time, methane yield increased monotonically as a function of catalyst loading and approached a plateau. Methane yield was negligible in the catalyst-free gasification but increased to 14mmolCH₄/g at a loading of 0.22g, surpassing the yield obtained for hydrogen at that condition. Carbon dioxide yield followed a similar trend to methane where its value increased from 5mmolCO₂/g to 18mmolCO₂/g at 0.056 g catalyst and remained almost constant afterwards.
Figure 3-5 Gas yields of hydrogen (squares), methane (triangles) and carbon dioxide (crosses) versus catalyst loading for the SCW gasification of model compounds at 380°C for 15 minutes (glycerol loading: 0.3g, water loading: 9.7g). (i) glucose, (ii) glycine, (iii) glycerol, and (iv) humic acid.
Figure 3-4 (continued)
The increase in methane production can be attributed to the increase in the methanation reaction rate catalyzed by the nickel catalyst. Since during methanation, 3 to 4 hydrogen molecules react with a carbon source (depending on the carbon source) to produce one molecule of methane, the decrease in hydrogen yield corresponds to a stoichiometric increase in methane.

Gasification products for glycine and glycerol followed a similar trend to glucose, although the hydrogen and methane yields for glycine were less than those for glucose. In addition, hydrogen yield for glycerol showed a sharp maximum of 55mmolH₂/g (increasing from 6mmolH₂/g in the absence of catalyst) at the lowest catalyst loading of 0.014g, after which hydrogen yield was reduced to 27mmolH₂/g at a catalyst loading of 0.11g. The adverse effect of catalyst addition on hydrogen yields was also observed by Xu et al [13]. At an initial glycerol concentration of 1wt% at 500°C and in the presence of sodium carbonate catalyst, hydrogen yield decrease from 51mmol/g at the lowest catalyst loading tested to 18mmol/g at 0.5wt% catalyst. Almost complete gasification was obtained at these conditions independently of the amount of catalyst added. The catalyst amount only changed the final gas product distribution.

Finally, in the case of humic acid, hydrogen and methane yields followed a linear increase with catalyst loading. Hydrogen increased from 1mmolH₂/g at 0.028g catalyst to 9.2mmolH₂/g at a catalyst loading of 0.22g.

Comparison of hydrogen, methane and carbon dioxide yields for various model compounds are given in Table 3-2 and Table 3-4 for two different catalysts loading.

### 3.3.2 Comparison between model compounds

Table 3-2 summarizes the results obtained for the gasification of glycine, glycerol, glucose and humic acid at high Raney nickel loading (0.22g). Humic acid was the hardest to gasify resulting in the lowest yields (total and for each individual gas component) and therefore the lowest CGR and HGR. High amounts of catalyst resulted in large drop in hydrogen yield obtained during glycerol gasification (less than 50% of the value obtained at the smallest catalyst loading). Hydrogen yield also dropped for the glucose gasification. On the other hand, methane yield increased significantly due to higher rates of methanation reaction catalyzed by the nickel
catalyst. The most methane formation was during glycerol gasification. For glucose gasification, methane formation was almost five times larger than the one obtained at the lowest catalyst loading. Glucose was almost completely gasified at higher catalyst loadings. Glycine and humic acid proved to be more difficult to gasify. Earlier works [20-22] also prove that glycine is harder to gasify and results in a loss of yield if added to other model compounds (such as glucose). These results suggest that compared to proteins and humic substances, carbohydrates (represented by glucose) and fatty compounds (represented by glycerol) are far more readily gasified with Raney nickel under supercritical conditions.

<table>
<thead>
<tr>
<th></th>
<th>H₂ Yield (mmol/g)</th>
<th>CH₄ Yield (mmol/g)</th>
<th>CO₂ Yield (mmol/g)</th>
<th>Yield (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>16.7</td>
<td>5.1</td>
<td>8.4</td>
<td>30.2</td>
<td>50.7</td>
<td>80.9</td>
</tr>
<tr>
<td>Glycerol</td>
<td>27.1</td>
<td>15.4</td>
<td>12.7</td>
<td>55.4</td>
<td>86.7</td>
<td>133.2</td>
</tr>
<tr>
<td>Glucose</td>
<td>13.4</td>
<td>14.2</td>
<td>17.6</td>
<td>45.6</td>
<td>96.6</td>
<td>125.3</td>
</tr>
<tr>
<td>Humic Acid</td>
<td>9.2</td>
<td>2.0</td>
<td>7.0</td>
<td>18.2</td>
<td>19.2</td>
<td>56.8</td>
</tr>
</tbody>
</table>

Table 3-2 Comparison between several model compounds for gasification in the presence of 0.22g of Raney nickel 4200 at 380°C for a 15 minute residence time (model compound loading: 0.3g, water loading: 9.7g)

3.3.3 Comparison to thermodynamics equilibrium

Equilibrium data predicted thermodynamically were found using Aspen process simulator (Aspen 2006.5, Aspen Technology Inc.). These data were calculated based on the minimization of the Gibbs free energy using Peng-Robinson equations of state. The findings along with the experimental data for the SCWG of glucose at 380°C at low and high catalyst loadings are summarized in Table 3-3. As can be seen from this table, hydrogen yield is much higher than the predicted thermodynamic value whereas methane and carbon dioxide experimental yields approach the equilibrium yields at high catalyst loading. The deviation of the experimental data from the predicted ones suggests that SCWG is kinetically driven.
<table>
<thead>
<tr>
<th></th>
<th>Experimental Low Loading</th>
<th>Experimental High Loading</th>
<th>Equilibrium Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Yield (mmol/g)</td>
<td>41.9</td>
<td>45.6</td>
<td>37.2</td>
</tr>
<tr>
<td>H₂ Yield (mmol/g)</td>
<td>20.1</td>
<td>13.4</td>
<td>3.9</td>
</tr>
<tr>
<td>CH₄ Yield (mmol/g)</td>
<td>7.2</td>
<td>14.2</td>
<td>15.6</td>
</tr>
<tr>
<td>CO₂ Yield (mmol/g)</td>
<td>14.6</td>
<td>17.6</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Table 3-3 Comparison of experimental data to equilibrium data for the gasification of glucose at 380°C at low (0.028g) and high (0.22g) catalyst loading

### 3.3.4 Binary mixtures of model compounds

Table 3-4 summarizes the results obtained for the gasification of individual model compounds at low catalyst loading (0.028g). These results along with the one summarized in Table 3-2 (for high catalyst loading) were used to determine the calculated yields and values of CGR and HGR at low and high catalyst loading respectively based on the rule of mixture.

<table>
<thead>
<tr>
<th></th>
<th>H₂ Yield (mmol/g)</th>
<th>CH₄ Yield (mmol/g)</th>
<th>CO₂ Yield (mmol/g)</th>
<th>Yield (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>18.0</td>
<td>2.9</td>
<td>7.1</td>
<td>28.1</td>
<td>37.7</td>
<td>71.7</td>
</tr>
<tr>
<td>Glycerol</td>
<td>42.7</td>
<td>9.4</td>
<td>15.5</td>
<td>67.8</td>
<td>77.1</td>
<td>141.6</td>
</tr>
<tr>
<td>Glucose</td>
<td>20.1</td>
<td>7.2</td>
<td>14.6</td>
<td>41.9</td>
<td>65.5</td>
<td>103.6</td>
</tr>
<tr>
<td>Humic Acid</td>
<td>1.1</td>
<td>0.1</td>
<td>4.3</td>
<td>5.5</td>
<td>9.3</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Table 3-4 Comparison between several model compounds for gasification in the presence of 0.22g of Raney nickel 4200 at 380°C for a 15 minute residence time (model compound loading: 0.3g, water loading: 9.7g)

In order to examine the extent of binary interactions of model compounds in SCWG, the yields, CGR, and HGR for mixtures of these compounds were found experimentally (summarized in Table 3-5) and compared to the calculated ones. Figure 3-6 shows plots of the experimental versus calculated total yields for binary mixtures B1 to B6 at high (0.22g) and low (0.028g) catalyst loadings. On this graph, the larger the deviation from the 45°-line, the more intense is the interaction between the components in the mixture. This deviation can be quantified by comparing the slopes of trend lines to unity. The summary of the slopes along with the statistical errors at a 95% confidence interval for the graphs that follow can be found in Table 3-6. The data
points in Figure 3-6 can be partitioned into two groups: mixtures not containing humic acid (B1, B2 and B4) and those containing humic acid (B3, B5 and B6). At low catalyst loading, experimental yields were significantly lower than the calculated ones. However, the mixtures containing humic acid not only had a lower yield but also had a larger negative interaction (larger negative deviation from 45°-line) than the other binary mixtures. The total yield in this case was only about 64% of the calculated values. The lower total yield is likely due to the competition of various components in the mixture for active catalyst sites. However, at a high catalyst loading, the presence of excess amount of catalyst reduced the extent of such adverse interactions and the experimental data fell on the calculated values. In this case, the effect of humic acid was also less pronounced.

<table>
<thead>
<tr>
<th></th>
<th>Yield (mmol/g)</th>
<th>H₂ Yield (mmol/g)</th>
<th>CH₄ Yield (mmol/g)</th>
<th>CO₂ Yield (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>B1</td>
<td>42.3</td>
<td>41.9</td>
<td>21.7</td>
<td>17.2</td>
<td>7.3</td>
<td>12.8</td>
</tr>
<tr>
<td>B2</td>
<td>30.2</td>
<td>36.1</td>
<td>11.4</td>
<td>11.0</td>
<td>6.8</td>
<td>11.6</td>
</tr>
<tr>
<td>B3</td>
<td>10.6</td>
<td>25.5</td>
<td>4.0</td>
<td>12.0</td>
<td>0.9</td>
<td>4.6</td>
</tr>
<tr>
<td>B4</td>
<td>51.0</td>
<td>50.7</td>
<td>23.6</td>
<td>17.7</td>
<td>9.6</td>
<td>15.2</td>
</tr>
<tr>
<td>B5</td>
<td>24.4</td>
<td>38.6</td>
<td>14.0</td>
<td>15.6</td>
<td>1.8</td>
<td>9.9</td>
</tr>
<tr>
<td>B6</td>
<td>13.5</td>
<td>33.5</td>
<td>5.3</td>
<td>12.0</td>
<td>0.7</td>
<td>8.1</td>
</tr>
</tbody>
</table>

Table 3-5 Summary of the experimental yields for the gasification of binary mixtures B1 to B6 at 380°C for a 15 minutes residence time at low (0.028g) and high (0.22g) Raney nickel 4200 loading (model compounds loading: 0.3g, water loading: 9.7g)

Figure 3-7 and Figure 3-8 show similar plots for CGR and HGR, respectively. Once again, at low catalyst loadings and in the presence of humic acid, both CGR and HGR were considerably smaller and on average were only about 60% of their calculated values. Without humic acid, there is an increase of about 20% in CGR and a decrease of about 10% in HGR compared to the rule of mixtures, indicating a higher methane production at the expense of hydrogen likely due to an increase in methanation reaction. At high catalyst loading, the CGR and HGR approached the calculated values and were within 10% of predicted values based on the rule of mixtures. This figure also shows that the adverse effects of humic acid on the CGR and HGR diminished at high catalyst loadings.
Figure 3-6 Experimental versus calculated total yields for the gasification of binary mixtures without humic acid (solid symbols) and with humic acid (hollow symbols) at 380°C for 15 minutes at low catalyst loading (0.028 g) (triangles), and high catalyst loading (0.225 g) (squares).

Figure 3-7 Experimental versus calculated values of CGR for the gasification of binary mixtures without humic acid (solid symbols) and with humic acid (hollow symbols) at 380°C for 15 minutes at low catalyst loading (0.028 g) (triangles), and high catalyst loading (0.225 g) (squares).
Figure 3-9 and Figure 3-10 show the hydrogen and methane yields compared to the rule of mixtures. Hydrogen yield in the SCWG of binary mixtures was consistently lower than calculated values. This could be explained by the fact that some model compounds are easier to gasify (such as glycerol) and result in a “quick” release of hydrogen. The released hydrogen reacts with available carbon source to produce more methane. At a high catalyst loading, hydrogen yield was about 85% of the calculated value. In comparison, HGR was similar to the calculated value under similar conditions, suggesting that lower hydrogen yield was offset by higher production of methane. This explanation is further confirmed by higher methane yield under similar conditions that was about 11% more than its calculated value.

Similar to CGR and HGR, the deviation from calculated yields for hydrogen and methane was generally larger at low catalyst loadings and the presence of humic acid further enhanced this deviation. The adverse effect of humic acid was particularly dramatic for methane production where methane yield was only 33% of its calculated value. For mixtures not containing humic acid, hydrogen yield remained lower than the calculated values, whereas methane yields (and CGR values) were about 20% greater than the calculated ones.
Figure 3-8 Experimental versus calculated values of HGR for the gasification of binary mixtures without humic acid (solid symbols) and with humic acid (hollow symbols) at 380°C for 15 minutes at low catalyst loading (0.028 g) (triangles), and high catalyst loading (0.225 g) (squares).

Figure 3-9 Experimental versus calculated hydrogen yields for the gasification of binary mixtures without humic acid (solid symbols) and with humic acid (hollow symbols) at 380°C for 15 minutes at low catalyst loading (0.028 g) (triangles), and high catalyst loading (0.225 g) (squares).
Figure 3-10 Experimental versus calculated methane yields for the gasification of binary mixtures without humic acid (solid symbols) and with humic acid (hollow symbols) at 380°C for 15 minutes at low catalyst loading (0.028 g) (triangles), and high catalyst loading (0.225 g) (squares).

<table>
<thead>
<tr>
<th></th>
<th>High Loading</th>
<th>Low Loading</th>
<th>Low Loading + Humic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Yield</td>
<td>1.0 (±0.04)</td>
<td>0.9 (±0.08)</td>
<td>0.64 (±0.13)</td>
</tr>
<tr>
<td>( \text{H}_2 ) Yield</td>
<td>0.85 (±0.09)</td>
<td>0.71 (±0.16)</td>
<td>0.59 (±0.26)</td>
</tr>
<tr>
<td>( \text{CH}_4 ) Yield</td>
<td>1.1 (±0.08)</td>
<td>1.2 (±0.18)</td>
<td>0.33 (±0.2)</td>
</tr>
<tr>
<td>CGR</td>
<td>1.1 (±0.07)</td>
<td>1.19 (±0.07)</td>
<td>0.6 (±0.22)</td>
</tr>
<tr>
<td>HGR</td>
<td>1.03 (±0.06)</td>
<td>0.89 (±0.06)</td>
<td>0.61 (±0.39)</td>
</tr>
</tbody>
</table>

Table 3-6 Summary of the slopes (and errors at 95% confidence interval) of experimental versus calculated values

In addition to binary mixtures, higher order mixtures (mixtures containing more than 2 model compounds) were also examined in this study. These mixtures exhibited similar trends compared to the binary mixtures and therefore they are not discussed in here.
3.4 Conclusion

In this paper, SCWG of glucose, glycine, glycerol, and humic acid at 380°C in 15 minute batch tests was investigated. Catalyst loading generally increased CGR and HGR however decreased the hydrogen yield. In addition, glucose and glycerol generally had higher yields than glycine and humic acid.

Binary interactions between the above model compounds were investigated. It was found that at low catalyst loadings CGR and HGR are generally smaller than the calculated values. Furthermore, hydrogen yields were found to be consistently lower than the calculated ones. Finally, the presence of humic acid in the mixture resulted in a larger deviation from calculated values determined based on the rule of mixtures. Humic acid inhibited hydrogen and methane production in binary mixtures.

3.5 References

4 Catalytic Gasification of Activated Sludge in Supercritical Water

4.1 Introduction

In the recent years, concerns over global warming have led to the search for new technologies in order to produce clean and renewable energy and to reduce our reliance on fossil fuels. One of such technologies is the conversion of biomass to biofuels. Considering various sources of biomass, conversion of activated sludge to valuable fuels provides an attractive opportunity since it is not only considered a renewable energy resource but also its disposal as a solid waste presently poses a major environmental challenge.

Activated sludge is a by-product of the biological treatment of wastewater. It has high water content (up to 98wt% water) and can contain toxic compounds. Current sewage sludge treatment and disposal methods, such as landfilling, incineration and gasification require drying the sludge, a costly pre-treatment step, and risk contaminating the environment.

Supercritical water (SCW), i.e. water above 374°C and 22.1MPa, has unique properties that render it a suitable medium for organic chemical conversion. SCW acts as a non-polar solvent and therefore, high water content biomass and wastes such as sludge can be readily treated in SCW without the need for drying. Among various supercritical water technologies, supercritical water oxidation (SCWO) for sewage sludge treatment has been studied extensively by various researchers. This process is mainly used as a means of eliminating the total organic carbon (TOC) from water. In SCWO, the organic matter in the sludge reacts with an oxidizing agent (usually O₂ or H₂O₂) to reduce the TOC in the sludge to smaller molecules in the aqueous phase, and CO₂, water and N₂ in the gas phase [1]. An alternative approach to SCWO is supercritical water gasification (SCWG) of biomass that is used to convert the wet biomass to combustible gases. During this process, the organic matter reacts with water, decomposes into smaller molecules and may also undergo steam reforming, water-gas shift and methanation reactions. Products of catalytic SCWG are mainly H₂, CO₂ and CH₄ with trace of CO and some other hydrocarbons.
Due to the complexity of real biomass, model compounds are often used to investigate the SCWG of biomass under various operating conditions. Among such compounds, glucose is widely used as a representation for cellulosic biomass. Minowa et al. [2-7] showed that gasification of glucose in SCW was essentially similar to that of cellulose. Lee et al. [8] studied the catalyst-free gasification of glucose in SCW in a continuous reactor. They found that complete gasification of glucose was only achieved at 700°C and that below 650°C the major product is the gas phase is CO. Kersten et al. [9] investigated the SCW gasification of glucose and glycerol at 550°C to 800°C and confirmed that CO was the main product in the gas phase at below 600°C. It was only at 800°C that the H₂ and CO₂ yields increased and near complete gasification was achieved for dilute feeds. However, these high temperatures result in high reactor cost and severe operational issues such as corrosion and scaling.

In order to avoid the above issues, the use of catalysts has been suggested to reduce the reaction temperature. Elliott et al. [10] studied the gasification of 10% p-cresol in water at 350°C using several metal catalysts on different supports. They found that nickel and ruthenium are active metals for SCW gasification. Raney nickel had the best activity among other nickel based catalysts with 93% carbon conversion and a methane-rich gas was obtained. Finally, comparison of several industrial catalysts for near-critical gasification of glucose have shown that Raney nickel 4200 has a good activity under these conditions [11-13].

Numerous studies have been conducted to examine the SCWG of sewage sludge. Sludge is mainly a mixture of carbohydrates, proteins and fattiness. Gasification of individual model compounds, representing various components of sludge, has been reported in the literature [14]. In the previous section, we studied the SCWG of four model compounds to examine the gasification yields of the individual model compounds as well as their binary mixtures. Several studies have used real sludge as the feedstock for SCWG [15-19]. Xu et al. [15] used Coconut Shell activated carbon catalyst to gasify sewage sludge in a continuous reactor at 600°C and 34MPa and reported a total gas yield of 77%. Xu et al. [16] also gasified a mixture of sewage sludge and corn starch in SCW at 650°C and 28MPa using the same catalyst. Near complete gasification of the organic in the feed was achieved and a hydrogen-rich (42%) gas was obtained. Zhang et al. [17] who tested the catalyst-free gasification of several types of sludge at
temperatures ranging from 400 to 550°C. At 500°C and for the secondary activated sludge used, they obtained a gas yield of 18% containing high amounts of CO₂. Yamamura et al. [18] studied the SCW gasification of sewage sludge in the presence of RuO₂ as catalyst at 375°C to 500°C. At 450°C, 47.1MPa and 120 minutes reaction time, a total gas yield of 11% based on carbon was achieved (23.1% based on hydrogen). The gas product was a hydrogen rich gas but also contained a high fraction of methane. Schmieder et al. [19] used K₂CO₃ as a homogeneous catalyst for the SCW gasification of sludge at 450°C and 330bar. The use of the catalyst increased the gas yield from 55.2% to 85.3%, while it did not change the gas composition significantly where a hydrogen-rich (48%) gas was obtained in both cases.

Despite the wide range of studies on the SCWG of sludge, no systematic work has been reported to examine the suitability of Raney nickel for SCWG of real sludge. Raney nickel has been shown to be an effective catalyst in supercritical water gasification processes. This porous catalyst is composed of nickel-aluminum alloy and is commonly used for hydrogenation reactions. However, its thermal stability under SCW conditions has been of concern.

In this work, we examine the catalytic gasification of activated sludge from 320°C to 410°C (with corresponding pressure range of 113 to 280 bar) using Raney nickel in a batch reactor. Effects of catalyst loading, temperature, residence time, and ash content on the SCW gasification of activated sludge are addressed. The deactivation of Raney nickel catalyst during the process is also studied and possible mechanisms for catalyst deactivation are discussed.

### 4.2 Experimental Setup

The experimental setup used in this work is illustrated in Figure 4-1. The reactor used was made of 316SS with 50ml volume. Activated sludge was obtained from Ashbridges Bay sewage treatment plant in Toronto, Ontario, Canada. Raney nickel was obtained from Sigma Aldrich (Canada) as a slurry with 50wt% solid content. In order to inject a consistent amount of feed to the reactor, the activated sludge was concentrated by removing water to obtain a thick paste followed by drying at 80°C overnight. For each run, 9.7g water was added to 0.3g of dried activated sludge to obtain a total weight of 10g at a 3wt% dry sludge. The desired amount of
catalyst was then added to the slurry and the mixture was loaded to the reactor. The reactor was immersed in a molten salt bath maintained at the desired temperature and kept for the desired reaction time. The molten salt bath consists of a mixture of potassium nitrate, sodium nitrate and sodium nitrite with a high heating rate (~500°C/min). The salt bath temperature was measured using a K-type thermocouple (Omega) and controlled by a PID controller (Hanyoung NX4). At the end of the experiment, the reactor was quickly quenched to room temperature by immersing it in a cold water bath. The final pressure inside the reactor was measured using a digital pressure gauge (Cecomp Electronics) and was used to calculate the total gas yield. The produced gas was collected in a gas bag and analyzed using a Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector. Based on the total gas yield and gas composition, the specific yield of each compound was calculated. Since the sludge can be highly heterogeneous, at least 3 replicates were done for each reaction condition. Their average is reported in the result section below.

Volatile organic compounds (VOC), fixed carbon (FC) and ash content of the dried sludge were determined using Thermo-gravimetric Analysis (TGA Q500 apparatus from TA instruments). The analysis consisted of a ramp 20°C/min from room temperature to 100°C, then the sample was maintain at 100°C for 5 minutes and then it was subject to another 20°C/min ramp to 800°C. The TGA analysis was performed both in nitrogen and in air environment. Also, elemental analysis of the dry sludge was done using the 2400 Series II CHNS Analyzer from Perkin Elmer operating at the C-H-N mode.

To test the thermal deactivation of Raney nickel in SCW, 0.34 g of catalyst was added to 9.7 g of water and the mixture was introduced to the reactor. The reactor was immersed in the molten salt bath and after a certain period of time (referred to as the pre-exposure time), activated sludge was added to the reactor. The mixture was allowed to react for 15 minutes, after which the gaseous products were collected and analyzed as described above.
4.3 Results and Discussion

In this study, the effects of catalyst loading, temperature and residence time on the SCW gasification of activated sludge are examined. Results are reported in terms of gas yield, carbon gasification ratio (CGR) and hydrogen gasification ratio (HGR). Gas yield is the amount of gas produced (in mmol) per gram of dry sludge initially loaded to the reactor. CGR is the ratio of the amount of carbon in the gas phase to the amount of carbon in the sludge. Similarly, HGR is the ratio of the amount of hydrogen in the gas phase to the amount of hydrogen in the sludge.

4.3.1 Sludge Characterization

Figure 4-2 shows the results obtained by TGA analysis of sludge both in an inert (nitrogen) and reactive (air) environment. In the inert environment, no combustion occurs and therefore the loss in mass is attributed to the loss of volatiles (VOC). As can be seen from the figure, the sample decreased in weight by 63% from 21.8 to 8.05mg in this environment. Following the analysis in
nitrogen, the remaining of the sample on the TGA pan was cooled down and then analyzed in an air environment. The weight loss at around 500°C (Figure 4-2) is due to the combustion of fixed carbon. The weight dropped from 37% to 25% of the initial weight; the dried sludge contains 12% fixed carbon. The remaining, i.e. 25%, is ash that cannot be combusted or gasified in SCW.

Figure 4-2 Change in weight of dried activated sludge versus temperature for TGA in nitrogen (black line) followed by air (gray line) to determine VOC, FC and ash content.

Elemental analysis of the dry sludge showed that the sludge contains 36.7% carbon, 6.2% hydrogen and 6.8% nitrogen. The sludge characteristics are summarized in Table 4-1. Oxygen content was calculated using the following formula assuming negligible sulfur content:

Oxygen content=100%-C%-H%-N%-Ash%.

However, activated sludge typically contains some sulfur. The range of sulfur content reported in literature varies from 0.5 to 1wt% on a dry sludge basis [17].

<table>
<thead>
<tr>
<th>Elemental Analysis</th>
<th>TGA analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>36.7%</td>
<td>6.2%</td>
</tr>
</tbody>
</table>

Table 4-1 Summary of the dried activated sludge characteristics
4.3.2 Effect of catalyst loading

Figure 4-3 shows the effect of catalyst loading on the total gas yield for the SCW gasification of activated sludge at 380°C and a residence time of 15 minutes. Yields of individual gaseous products, CGR and HGR as a function of catalyst loading are also shown in Figure 4-4 and Figure 4-5, respectively.

From Figure 4-3, it is apparent that the addition of Raney nickel had a positive effect on the total gas yield up to a certain point. The total yield increased almost linearly from 3.5mmol/g for the catalyst-free gasification to 33mmol/g at a catalyst loading of 0.45g after which the total yield reached a plateau level. In the absence of catalyst and at very low loadings, the major gasification product was carbon dioxide accounting for more than 60% of the product composition (Figure 4-4). However, the higher initial slope of hydrogen yield indicates that hydrogen production was more sensitive to the catalyst loading than the other products. In fact, as Raney nickel loading increased above 0.08 g, hydrogen became the dominant component in the gas phase. However, beyond a catalyst loading of about 0.45g, hydrogen yield started decreasing likely due to increase in the methanation rate. In contrast to hydrogen, methane production showed a linear correlation with Raney nickel loading, increasing monotonically from 0.3mmol/g in the absence of catalyst to almost 12mmol/g at a catalyst loading of 0.56g. It is worthy to note that small amounts of carbon monoxide were also produced in this process; however, CO yield was less than 0.1mmol/g for all conditions.

Figure 4-5 shows that both CGR and HGR were positively affected by Raney nickel loading. CGR increased from 10% for catalyst-free conditions to about 70% at the catalyst loading of 0.58 g whereas HGR increased from 4% to 113% over the same range. An HGR higher than 100% indicates that the decomposition of water molecules as a result of steam reforming and water-gas shift reactions contributes to the production of hydrogen. Also, a portion of hydrogen is produced by partial oxidation of nickel catalyst during the initial stage of the gasification reaction. Interestingly, even though the total gas yield remained constant at high catalyst loadings
(i.e. >0.45g), CGR, HGR and methane yield showed an increasing trend. These trends were accompanied by decrease in hydrogen yield, suggesting that high Raney nickel loadings favor methanation reactions.

Figure 4-3 Total gas yield versus catalyst loading for the SCW gasification of activated sludge at 380°C for 15 minutes (dry sludge loading: 0.3g, water loading: 9.7g)
Figure 4-4 Gas yields of hydrogen (squares), methane (triangles) and carbon dioxide (crosses) versus catalyst loading for the SCW gasification of activated sludge at 380°C for 15 minutes (dry sludge loading: 0.3g, water loading: 9.7g)

Figure 4-5 CGR (squares) and HGR (triangles) versus catalyst loading for the SCW gasification of activated sludge at 380°C for 15 minutes (dry sludge loading: 0.3g, water loading: 9.7g)
4.3.3 Effect of Residence Time

Figure 4-6 illustrates the effect of residence time on the total gas yield at 380°C for a catalyst loading of 0.22g. This figure shows that the total yield increased rapidly with increasing residence time and approached a plateau level of about 25mmol/g after 30 minutes.

According to Figure 4-6, 63% of the maximum yield was achieved after only 4 min whereas after 15 minutes, 87% of the maximum yield was reached. Similar trends were observed for the hydrogen, methane and carbon dioxide yields as well as for CGR and HGR (Figure 4-7 and Figure 4-8). After 30 minutes, the gas product consisted of 50% hydrogen, 22% methane and 27% carbon dioxide, while the maximum CGR and HGR under these conditions were 45% and 75%, respectively. The above results suggest that the SCW gasification of activated sludge under these conditions reached equilibrium after 30 minutes.

![Figure 4-6 Total gas yield versus residence time for the SCW gasification of activated sludge at 380°C (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.22g)](image-url)
Figure 4-7 Gas yields of hydrogen (squares), methane (triangles) and carbon dioxide (crosses) versus residence time for the SCW gasification of activated sludge at 380°C (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.225g)

Figure 4-8 CGR (squares) and HGR (triangles) versus residence time for the SCW gasification of activated sludge at 380°C (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.225g)
4.3.4 Effect of Temperature

Figure 4-9 illustrates the effect of varying temperature from subcritical (320°C) to supercritical (410°C) conditions on the total gas yield for the 15 minute SCW gasification of activated sludge at a catalyst loading of 0.225g. The total gas yield increased linearly from 17.8mmol/g to 27.5mmol/g by increasing the temperature from 320°C to 380°C. However, the total yield obtained at 410°C was similar to the one obtained at 380°C. As can be seen from Figure 4-10, the hydrogen yield increased initially from 6.5 at 320°C to 12.6mmolH\textsubscript{2}/g at 380°C, but then dropped to 11mmolH\textsubscript{2}/g at 410°C, however, this decrease is not statistically significant and it can be argued that hydrogen production also reached a plateau at temperatures above 380°C. In comparison, methane yield increased continuously from 4.6mmolCH\textsubscript{4}/g to 7.5mmolCH\textsubscript{4}/g over the same range. Temperature had also a positive effect on CGR and HGR. HGR achieved a maximum plateau level of 84% at temperatures above 380°C while CGR reached 55% at 410°C compared to 37% at 320°C.
Figure 4-10 Gas yields of hydrogen (squares), methane (triangles) and carbon dioxide (crosses) versus temperature for the SCW gasification of activated sludge for 15 minutes (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.34g)

Figure 4-11 CGR (squares) and HGR (triangles) versus temperature for the SCW gasification of activated sludge for 15 minutes (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.34g)
4.3.5 Effect of Ash Addition

To quantify the effect of ash content on the SCWG of sludge, known amounts of ash were added to the sludge biomass. Earlier studies showed that ash content in the biomass plays a role in the final gasification yields [20, 21]. For the catalyst-free gasification of several types of biomass, it was shown that low ash content biomass resulted in lower hydrogen yields and higher CO yields [19, 22].

The ash was obtained by combusting the dried activated sludge in a furnace at 550°C for 1 hour. Here, three samples were tested: the original sludge sample (with no extra ash) and two modified sludge samples with 0.075g and 0.15g of added ash. Table 4-2 shows the effect of ash addition on the total yield, on the yields of individual gasification products as well as CGR and HGR. Based on this table, the total yield dropped from 27.5mmol/g for original sludge to 23mmol/g for samples containing 0.15g of added ash. Methane and carbon dioxide yields also dropped from 6.4 and 8.4mmol/g to 2.6 and 5.4mmol/g, respectively. Interestingly, ash addition had a positive effect on hydrogen yield from 12.6 to 15mmol/g. Both CGR and HGR decreased linearly with the addition of ash. CGR went down from 49% to 26% and HGR from 82% to 65%. The drop in total yield and CGR can be attributed to catalyst poisoning by ash. Ash contains elements (such as sulfur) that showed to poison catalysts [23]. On the other hand, the increase in hydrogen yield can be attributed to the presence of alkali metals (such as potassium and sodium) in the ash which facilitate tar cracking reactions. These alkali metals have been also shown to be effective in catalyzing the water-gas-shift reaction [24].

<table>
<thead>
<tr>
<th>Ash Addition (g)</th>
<th>Total Yield (mmol/g)</th>
<th>H₂ Yield (mmol/g)</th>
<th>CH₄ Yield (mmol/g)</th>
<th>CO₂ Yield (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27.5</td>
<td>12.6</td>
<td>6.4</td>
<td>8.4</td>
<td>48.7</td>
<td>82.1</td>
</tr>
<tr>
<td>0.075</td>
<td>23.9</td>
<td>13.6</td>
<td>4.2</td>
<td>6.1</td>
<td>33.7</td>
<td>70.0</td>
</tr>
<tr>
<td>0.15</td>
<td>23.1</td>
<td>15.0</td>
<td>2.6</td>
<td>5.4</td>
<td>26.2</td>
<td>65.3</td>
</tr>
</tbody>
</table>

Table 4-2 Summary of the effect of Ash Addition on gas yields, CGR and HGR for the SCW gasification of activated sludge for 15 minutes at 380°C (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.34g)
4.3.6 Catalyst deactivation

Results of catalyst deactivation tests as a function of catalyst pre-exposure time are given in Table 4-3. This table shows that following a catalyst pre-exposure of 8 minutes, the total gas yield drops by 50% from 27.5mmol/g to 13.5mmol/g. This effect was more pronounced for a pre-exposure time of 15 minutes, where the total yield decreased to 9mmol/g, i.e. a reduction of 67%.

Table 4-3 also shows that methane yield was affected dramatically by the SCW pre-treatment process. This yield dropped from 6.5mmol/g for a fresh catalyst to 0.3mmol/g after a catalyst exposure of 15 minutes. It is worth mentioning that the level of methane produced for pre-exposed Raney nickel was similar to the methane yield obtained for a catalyst-free reaction. Hydrogen yield also dropped significantly; though not as dramatically as methane, from 12.5 to 3.6mmol/g (compared to 0.6mmol/g for the catalyst free reaction). Carbon dioxide was affected the least by pre-exposure of catalyst; its yield dropped by 40% from 8.5 to 5mmol/g.

<table>
<thead>
<tr>
<th>Pre-Exposure Time (min)</th>
<th>Total Yield (mmol/g)</th>
<th>H\textsubscript{2} Yield (mmol/g)</th>
<th>CH\textsubscript{4} Yield (mmol/g)</th>
<th>CO\textsubscript{2} Yield (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27.5</td>
<td>12.6</td>
<td>6.4</td>
<td>8.4</td>
<td>48.7</td>
<td>82.1</td>
</tr>
<tr>
<td>8</td>
<td>13.4</td>
<td>5.9</td>
<td>1.1</td>
<td>6.3</td>
<td>24.3</td>
<td>26.0</td>
</tr>
<tr>
<td>15</td>
<td>8.9</td>
<td>3.7</td>
<td>0.3</td>
<td>4.9</td>
<td>17.2</td>
<td>13.6</td>
</tr>
<tr>
<td>Catalyst Free</td>
<td>3.6</td>
<td>0.6</td>
<td>0.3</td>
<td>2.5</td>
<td>10.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 4-3 Summary of the gas yields, CGR and HGR as function of catalyst pre-exposure time to SCW for the SCW gasification of activated sludge for 15 minutes at 380°C (dry sludge loading: 0.3g, water loading: 9.7g, catalyst loading: 0.34g).

Both HGR and CGR also showed a continuous decrease with increasing the pre-exposure time. Figure 4-12 shows the X-Ray diffraction plots of three catalyst samples: fresh catalyst (A), catalyst maintained at 380°C in nitrogen gas for 15 minutes (B) and catalyst exposed to SCW for 15 minutes at 380°C (C). The XRD patterns were obtained using a Philips XRD system at 0.015°/s. Using the XRD patterns and the Scherer equation, the average nickel crystallite sizes were calculated to be 10.7, 11.8 and 69nm for fresh (sample A), nitrogen treated (B) and SCW
treated (C) catalysts respectively. Although sintering of Raney nickel in an inert gas at 380°C was found to be negligible, the dramatic increase in nickel crystallite size for the catalyst exposed to SCW at the same temperature implies that Raney nickel lost a significant portion of its active sites in SCW. This is consistent with the findings of Watanabe et al. [25]. They studied the deactivation of Raney nickel during the hydrogenation reaction using XRD analysis. They concluded that the deactivation of Raney nickel was due to the increase in average nickel crystallite size, but this increase was not as dramatic as the one found in this work. Therefore, in addition to chemical deactivation processes; such as oxidation and poisoning by ash, the drop in the number of active sites is a key contributor to the decline in the activity of Raney nickel in SCW.

![Figure 4-12 XRD pattern for Raney nickel catalysts. Fresh catalyst (A), N2-treated catalyst at 380°C for 15 minutes (B) and SCW-treated catalyst at 380°C for 15 minutes (C)](image)

### 4.3.7 Comparison with previous works

Table 4-4 is a comprehensive account of published literature on SCWG of activated sludge. A key distinction of the present work is the operating temperature. Previous research in this area was limited to temperatures higher than 450°C. Xu et al. achieved near complete gasification at 650°C using a carbon catalyst bed at a flowrate of 2g/min and a concentration of 2.8wt% [16]. Schmieder et al. obtained a relatively high yield (CGR = 55%) for the catalyst-free gasification
of activated sludge [19]. However, the reaction temperature (450°C), reaction time (120 min) and feed concentration (0.23%) were significantly more favorable than those used in the present study. Zhang et al. also studied the catalyst-free gasification of 4.5wt% activated sludge solution at 500°C [17]. Compared to this work, longer residence time was used and the CGR was about 16%, i.e. 1.6 times higher than the one obtained in this work at 380°C.

For the catalytic gasification, Schmieder et al. used K₂CO₃ to obtain a CGR of 85%. Once again, the higher value compared to this work can be attributed to more favorable reaction conditions. Yamamura et al. used RuO₂ catalyst to gasify 3.2wt% activated sludge at 450°C. However, the CGR was significantly less than the one obtained in this work. This result is expected since RuO₂ is partially oxidized and hence is less active than Raney nickel.
<table>
<thead>
<tr>
<th>Feed</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Reactor type</th>
<th>Time/Flowrate</th>
<th>Catalyst</th>
<th>CGR (%)</th>
<th>H₂ (%)</th>
<th>CO (%)</th>
<th>CH₄ (%)</th>
<th>CO₂ (%)</th>
<th>C₂+</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Sludge (2.8wt%)</td>
<td>600</td>
<td>34.5</td>
<td>Continuous</td>
<td>2g/min</td>
<td>Coconut Shell Activated Carbon</td>
<td>77</td>
<td>38</td>
<td>4</td>
<td>2</td>
<td>47</td>
<td>9</td>
<td>Xu et al. [15, 16]</td>
</tr>
<tr>
<td>Activated Sludge (2.8wt%) + Corn Starch (5.1wt%)</td>
<td>650</td>
<td>28</td>
<td>Continuous</td>
<td>2g/min</td>
<td>Coconut Shell Activated Carbon</td>
<td>100</td>
<td>42</td>
<td>1</td>
<td>17</td>
<td>39</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Activated Sludge (0.23wt%)</td>
<td>450</td>
<td>33</td>
<td>Batch</td>
<td>120min</td>
<td>-</td>
<td>55</td>
<td>49</td>
<td>3</td>
<td>17</td>
<td>31</td>
<td>-</td>
<td>Schmieder et al. [19]</td>
</tr>
<tr>
<td>Activated Sludge (3.2wt%)</td>
<td>450</td>
<td>33</td>
<td>Batch</td>
<td>120min</td>
<td>K₂CO₃</td>
<td>85</td>
<td>47</td>
<td>1</td>
<td>15</td>
<td>37</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Activated Sludge (3.2wt%)</td>
<td>450</td>
<td>47.1</td>
<td>Batch</td>
<td>120min</td>
<td>RuO₂</td>
<td>11</td>
<td>56</td>
<td>7%</td>
<td>37%</td>
<td>7%</td>
<td>-</td>
<td>Yamamura [18]</td>
</tr>
<tr>
<td>Activated Sludge (4.5wt%)</td>
<td>500</td>
<td>37</td>
<td>Batch</td>
<td>60min</td>
<td>-</td>
<td>16</td>
<td>22</td>
<td>15</td>
<td>17</td>
<td>46</td>
<td>-</td>
<td>Zhang et al. [17]</td>
</tr>
<tr>
<td>Activated Sludge (3wt%)</td>
<td>380</td>
<td>23</td>
<td>Batch</td>
<td>15min</td>
<td>-</td>
<td>10</td>
<td>16</td>
<td>6</td>
<td>9</td>
<td>69</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>Activated Sludge (3wt%)</td>
<td>380</td>
<td>23</td>
<td>Batch</td>
<td>15min</td>
<td>Raney nickel</td>
<td>58</td>
<td>46</td>
<td>0.1</td>
<td>25</td>
<td>29</td>
<td>-</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 4-4 Comparison of SCW gasification of activated sludge with previous works
4.4 Conclusion

In this paper, Raney nickel catalyst was used to gasify activated sludge in supercritical water at different operating conditions. Total gas yield increased initially by increasing catalyst loading but attained a maximum value at a loading of 0.45g. The major component of the gasification products was hydrogen accounting for 45.7% of the total gas. A further increase in the catalyst loading did not result in any increase in the total yield, but decreased hydrogen yield and increased the methane yield. At a heating rate of approximately 500°C/min, the catalytic SCW gasification of activated sludge at 380°C reached equilibrium within 30 minutes and no noticeable change was observed at higher reaction times. While temperature had a positive effect on the carbon gasification ratio, Raney nickel catalyst lost half of its activity after being exposed to SCW for 8 minutes. After 15 minutes exposure to SCW, the catalyst did not catalyze the methanation reaction. The loss of activity is likely due to the growth of nickel crystallite size.

4.5 References


5 SCWG of Activated Sludge using Alumina-supported Nickel Catalysts

5.1 Introduction

In chapters 3 and 4, the SCWG of several model compounds and activated sludge were studied using a commercial catalyst (Raney nickel). Also in Chapter 4, it was shown that Raney nickel was unstable in supercritical water after a relatively short exposure time (less than 8 minutes).

One way to enhance the stability of nickel catalysts is to use a catalyst support. High throughput catalyst screening in our lab at the University of Toronto showed that alumina supported nickel catalysts had good activity in SCWG applications [1].

In this chapter, preliminary results regarding the activity of alumina-supported nickel catalysts (prepared in our laboratory) for the SCWG of model biomass and real sludge is examined. Performance of this catalyst is then compared to those of three commercial catalysts; i.e. Raney nickel, ruthenium on carbon and ruthenium on alumina.

5.2 Experimental Setup

The experimental setup used in this work consisted of a batch reactor made of 316SS with 50ml volume, similar to Figure 4-1. The feeds gasified in this study were: Glucose (Aldrich), Glycine (Mallinckrodt U.S.P), Glycerol (ACP Montreal), Humic acid (Aldrich) and activated sludge (obtained from the Ashbridge Bay wastewater treatment plant in Toronto). Sludge composition is given in Table 4-1. Several commercial and laboratory-made catalysts were used to catalyze the reaction. The catalysts used along with some of their characteristics are summarized in Table 5-1. For each run, 9.7g water was added to 0.3g of feed to obtain a total weight of 10g at a 3wt%. The desired catalyst was then added and the whole mixture was loaded to the reactor. The reactor was immersed in a molten salt bath maintained at the 380°C and kept for 15 minutes. The molten salt bath
consists of a mixture of potassium nitrate, sodium nitrate and sodium nitrite and has an extremely high heating rate (\~500°C/min). The salt bath temperature was measured using a K-type thermocouple (Omega) and controlled by a PID controller (Hanyoung NX4). At the end of the experiment, the reactor was quickly quenched to room temperature by immersing it in a cold water bath. The final pressure inside the reactor was measured using a digital pressure gauge (Cecomp Electronics) and was used to calculate the total gas yield. The produced gas was collected in a gas bag and analyzed using a Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector. Based on the total gas yield and gas composition, the specific yield of each compound was obtained.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Active Metal</th>
<th>Catalyst Loading (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raney Nickel 4200</td>
<td>93</td>
<td>0.11</td>
</tr>
<tr>
<td>Ru/C</td>
<td>5</td>
<td>0.11</td>
</tr>
<tr>
<td>Ru/Al</td>
<td>5</td>
<td>0.11</td>
</tr>
<tr>
<td>5%Ni/Al2O3</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>10%Ni/Al2O3</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>15%Ni/Al2O3</td>
<td>15</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 5-1 Commercial and formulated catalysts used in this work

### 5.3 Results and discussion

In this study, the effects of several commercial and formulated catalysts on the SCWG of model compounds and activated sludge are examined. Results are reported in terms of gas yields, carbon gasification ratio (CGR) and hydrogen gasification ratio (HGR). Gas yield is the amount of gas produced (in mmol) per gram of organic matter loaded to the
reactor. CGR (or HGR) is the ratio of the amount of carbon (or hydrogen) in the gas phase to the amount of carbon (or hydrogen) of the organic matter in the feed.

### 5.3.1 Model compounds

Table 5-2 provides a summary of experimental results for the gasification of model compounds at 380°C and 15 minutes using various commercial and formulated catalysts. For comparison, gasification results in the absence of catalyst are also given in this table.

Based on Table 5-2, regardless of the catalyst type, glycerol was the easiest to gasify and had the highest yield compared to other model compounds while humic acid had the lowest yield. Glycerol also generally produced more hydrogen and methane than other model compounds for all the catalysts examined in this work. On the other hand, comparing gasification yields of glucose and glycine was dependent on the catalyst type. For example, glucose had 50% higher total yield but lower hydrogen than glycine when using Raney nickel. This trend was reversed in the presence of Ru/Al, where glycine produced slightly more gaseous products but less hydrogen.

Figure 5-1, Figure 5-2 and Figure 5-3 provide comparison of various catalysts for the gasification of model compounds in terms of total yield, CGR, and HGR respectively. In general, regardless of the model compound, Raney nickel had the highest total yield and HGR followed by alumina-supported nickel catalysts. However, catalyst performance in terms of CGR and individual product yields were dependent on the model compound. For glucose, significantly more hydrogen, methane and carbon dioxide were produced in the presence of the nickel based catalyst than Ru-based catalysts. CGR was almost double that obtained in the presence of Ru/C and Ru/Al. In contrast, for glycine and glycerol; Raney nickel exhibited the lowest CGR and methane yield but the highest hydrogen yield. The highest CGR for glycine and glycerol was obtained in the presence of Ru/Al. It is worth to note that both Ru-based and alumina-supported catalysts resulted in complete gasification of glycerol at 380°C.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Catalyst</th>
<th>Total Yield (mmol/g)</th>
<th>H(_2) (mmol/g)</th>
<th>CH(_4) (mmol/g)</th>
<th>CO(_2) (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>None</td>
<td>9.1</td>
<td>3.6</td>
<td>0.1</td>
<td>4.8</td>
<td>16.5</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>Raney Nickel</td>
<td>44.5</td>
<td>15.3</td>
<td>11.6</td>
<td>16.8</td>
<td>87.5</td>
<td>115.5</td>
</tr>
<tr>
<td></td>
<td>Ru/C</td>
<td>22.2</td>
<td>6.4</td>
<td>4.0</td>
<td>11.4</td>
<td>47.6</td>
<td>43.0</td>
</tr>
<tr>
<td></td>
<td>Ru/Al</td>
<td>27.3</td>
<td>11.7</td>
<td>3.4</td>
<td>11.7</td>
<td>47.1</td>
<td>55.4</td>
</tr>
<tr>
<td></td>
<td>5%Ni/Al(_2)O(_3)</td>
<td>37.2</td>
<td>15.3</td>
<td>6.3</td>
<td>15.3</td>
<td>65.7</td>
<td>83.6</td>
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<td></td>
<td>10%Ni/ Al(_2)O(_3)</td>
<td>36.1</td>
<td>15.5</td>
<td>5.4</td>
<td>15.0</td>
<td>61.8</td>
<td>78.6</td>
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<td>15%Ni/ Al(_2)O(_3)</td>
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<td>15.6</td>
<td>4.8</td>
<td>14.3</td>
<td>58.4</td>
<td>75.7</td>
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<td>Glycine</td>
<td>None</td>
<td>7.3</td>
<td>1.3</td>
<td>0.1</td>
<td>5.8</td>
<td>22.5</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>Raney Nickel</td>
<td>31.0</td>
<td>17.0</td>
<td>5.2</td>
<td>8.9</td>
<td>52.6</td>
<td>81.9</td>
</tr>
<tr>
<td></td>
<td>Ru/C</td>
<td>22.6</td>
<td>7.6</td>
<td>8.2</td>
<td>6.7</td>
<td>56.3</td>
<td>72.0</td>
</tr>
<tr>
<td></td>
<td>Ru/Al</td>
<td>28.8</td>
<td>9.6</td>
<td>8.1</td>
<td>10.9</td>
<td>72.1</td>
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</tr>
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<td>5%Ni/Al(_2)O(_3)</td>
<td>28.1</td>
<td>12.8</td>
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<td>75.3</td>
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<td>15%Ni/ Al(_2)O(_3)</td>
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<td>7.6</td>
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<td>71.0</td>
<td>80.7</td>
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<td>Glycerol</td>
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<td>5.8</td>
<td>0.1</td>
<td>1.2</td>
<td>5.6</td>
<td>13.9</td>
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<td></td>
<td>Raney Nickel</td>
<td>54.7</td>
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<td>13.4</td>
<td>14.2</td>
<td>85.1</td>
<td>123.7</td>
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<td></td>
<td>Ru/C</td>
<td>45.6</td>
<td>12.9</td>
<td>17.8</td>
<td>14.2</td>
<td>100.2</td>
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<td>15.0</td>
<td>102.0</td>
<td>106.9</td>
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<td>5%Ni/Al(_2)O(_3)</td>
<td>55.8</td>
<td>23.3</td>
<td>14.9</td>
<td>17.4</td>
<td>99.6</td>
<td>122.1</td>
</tr>
<tr>
<td></td>
<td>10%Ni/ Al(_2)O(_3)</td>
<td>53.6</td>
<td>19.8</td>
<td>16.9</td>
<td>16.6</td>
<td>103.7</td>
<td>123.3</td>
</tr>
<tr>
<td></td>
<td>15%Ni/ Al(_2)O(_3)</td>
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<td>18.9</td>
<td>16.2</td>
<td>16.1</td>
<td>100.0</td>
<td>118.4</td>
</tr>
<tr>
<td>Humic Acid</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Raney Nickel</td>
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<td>0.6</td>
<td>5.5</td>
<td>14.2</td>
<td>26.8</td>
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<td></td>
<td>Ru/C</td>
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<td>0.2</td>
<td>4.5</td>
<td>10.0</td>
<td>3.1</td>
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<td></td>
<td>Ru/Al</td>
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<td>0.2</td>
<td>0.0</td>
<td>3.8</td>
<td>8.2</td>
<td>1.0</td>
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<tr>
<td></td>
<td>5%Ni/Al(_2)O(_3)</td>
<td>5.5</td>
<td>1.8</td>
<td>0.1</td>
<td>3.6</td>
<td>7.9</td>
<td>8.4</td>
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<tr>
<td></td>
<td>10%Ni/ Al(_2)O(_3)</td>
<td>5.1</td>
<td>1.1</td>
<td>0.1</td>
<td>3.8</td>
<td>8.5</td>
<td>5.4</td>
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<td>15%Ni/ Al(_2)O(_3)</td>
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<td>1.1</td>
<td>0.1</td>
<td>3.9</td>
<td>8.5</td>
<td>5.2</td>
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</table>

Table 5-2 Comparison of the results obtained for the SCWG of model compound at 380°C and 15 minutes using various catalysts.
Figure 5-1 Effect of catalyst type on the total gasification yield for model compounds. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.

Figure 5-2 Effect of catalyst type on the CGR for model compounds. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.
Figure 5-3 Effect of catalyst type on the HGR for model compounds. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.

Compared to Raney nickel, alumina-supported catalyst in general had lower total yield and lower CGR and HGR. However, their performance was equal or better than ruthenium-based catalysts.

The effect of nickel concentration in alumina-supported catalysts on the SCWG of model compounds are summarized in Figure 5-4, Figure 5-5, Figure 5-6 and Figure 5-7 for glucose, glycine, glycerol and humic acid respectively. It should be noted that the nickel loading to the reactor was maintained constant by adjusting the total catalyst loading.
Figure 5-4 Effect of nickel concentration on total yield, CGR and HGR for glucose. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.

Figure 5-5 Effect of nickel concentration on total yield, CGR and HGR for glycine. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.
Figure 5-6 Effect of nickel concentration on total yield, CGR and HGR for glycerol. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.

Figure 5-7 Effect of nickel concentration on total yield, CGR and HGR for humic acid. Reactor temperature 380°C, catalyst loading: as per Table 5-1. Feed concentration: 3%.
Comparing various alumina-supported catalysts, 5% nickel on alumina had a better overall performance. In general, increasing the nickel concentration caused a monotonic decrease in the total yield and HGR, except for glycine where the total yield had an increasing trend and HGR first decreased and then increased. No general trend was obvious for CGR, hydrogen yield, methane yield.

### 5.3.2 Activated Sludge

Table 5-3 shows a comparison of the results obtained for the SCWG of activated sludge at 380°C and 15 minutes using various commercial and formulated catalysts.

The first 3 rows in Table 5-3 summarize the results obtained for the SCWG of activated sludge using the commercial catalysts. Raney nickel was significantly more active than the ruthenium based catalysts. Ruthenium did not result in any significant hydrogen or methane formation. On the other hand, Raney nickel generated high amount of hydrogen and methane and the CGR was about three times as higher as the ones obtained in the SCWG of activated sludge with the ruthenium based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (mmol/g)</th>
<th>H₂ Yield (mmol/g)</th>
<th>CH₄ Yield (mmol/g)</th>
<th>CO₂ Yield (mmol/g)</th>
<th>CGR (%)</th>
<th>HGR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raney Nickel</td>
<td>27.5</td>
<td>12.6</td>
<td>6.4</td>
<td>8.4</td>
<td>48.7</td>
<td>82.1</td>
</tr>
<tr>
<td>Ru/C</td>
<td>6.9</td>
<td>2.0</td>
<td>0.2</td>
<td>4.4</td>
<td>15.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Ru/Al</td>
<td>4.0</td>
<td>0.6</td>
<td>0.1</td>
<td>3.2</td>
<td>11.2</td>
<td>2.3</td>
</tr>
<tr>
<td>5%Ni/Al₂O₃</td>
<td>10.1</td>
<td>4.2</td>
<td>1.1</td>
<td>4.7</td>
<td>19.3</td>
<td>20.5</td>
</tr>
<tr>
<td>10%Ni/Al₂O₃</td>
<td>9.3</td>
<td>3.6</td>
<td>0.5</td>
<td>5.0</td>
<td>18.8</td>
<td>14.5</td>
</tr>
<tr>
<td>15%Ni/Al₂O₃</td>
<td>8.5</td>
<td>3.3</td>
<td>0.8</td>
<td>4.3</td>
<td>17.1</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Table 5-3 Comparison of the results obtained for the SCWG of activated sludge at 380°C and 15 minutes using various catalysts

Results for the nickel-supported catalysts are given in rows 4 to 6 in Table 5-3. As nickel concentration increased, the total yield decreased. This was due to a decrease in hydrogen and methane as the metal concentration increased. The values of CGR also decreased with nickel concentration. The formulated catalysts had better activities than the
ruthenium-based catalysts but their activities were significantly lower than that of Raney nickel. The total gasification yield, CGR and HGR for 5% nickel on alumina were 37%, 40%, and 24% of those for Raney nickel, respectively. Additional work is required to better understand the source of variations in catalyst performance; however this can be due to diffusion limitations of the larger molecules in activated sludge inside the supported catalysts or due to different poisoning potential of each catalyst. As mentioned in the Chapter 4, sulfur and certain heavy metals typically present in the sludge poison the catalyst. This poisoning can be more pronounced for some catalysts (the formulated catalysts and the ruthenium based ones) compared to others (Raney nickel).

5.4 Conclusion

In this chapter, the catalytic activities of several formulated catalysts were compared to that of three commercial catalysts that were tested in SCW applications. The activity was tested for a wide variety of model compounds and for activated sludge. The formulated catalysts consisted of nickel on alumina. For the SCWG of glycine and glycerol, Raney nickel was less active than the formulated catalysts but exhibited higher hydrogen selectivity. The ruthenium based commercial catalysts had similar activities to alumina-supported nickel catalysts but were more selective towards methane. Both these catalysts resulted in complete gasification of glycerol at 380°C, compared to 85% for Raney nickel. On the other hand, when glucose, humic acid and activated sludge were used as feed for the SCWG, Raney nickel had a superior performance over the formulated catalysts. This can be due to diffusion limitations of these larger molecules inside the supported catalysts or due to the fact that Raney nickel could be less prone to poisoning than the formulated catalyst.

5.5 References

[1] Azadi et al., unpublished work
6 Conclusions and Recommendations

6.1 Conclusions

This thesis was the report of the research done on the near-critical water gasification (NCWG) as an application for activated sludge treatment. The research started with the use of model compounds as feeds for the SCWG. These model compounds represented complex biomass that constitutes activated sludge. Glucose was used as a model compound for carbohydrates, glycine for proteins, glycerol for fats and humic acid for humic substances. The research then shifted to the use of actual activated sludge samples and the search for novel catalysts for that application. Here is a summary of the key conclusions drawn during this project:

- Complete gasification of a 3% solution of glucose was achieved at high Raney nickel loading (0.22 g) to produce a methane rich gas at 380°C.

- Among other model compounds, glycine and humic acid were the hardest to gasify in the presence of Raney nickel. Glycerol was easier to gasify at low catalyst loadings, where mostly hydrogen was produced. However, glycerol was not completely gasified under the testing conditions used in this work.

- Consistent with previous literature, as the catalyst loading increased, more methane was produced but at the expense of a lower hydrogen yield.

- When binary mixtures of model compounds were used as feed for the catalytic SCWG in the presence of low amounts of Raney nickel, the experimental yields deviated from the calculated yields (as determined based on the rule of mixtures).

- The presence of humic acid in the binary mixtures of model biomass compounds resulted in a significant reduction of hydrogen and methane generation. This was attributed to the possible catalyst poisoning by humic acid. At higher catalyst
loadings, this deviation was less pronounced. But hydrogen yields were less than the calculated ones and methane yields were higher. This lead to the conclusion that during SCWG, there are interactions between different molecules that will form new intermediates. The gasification of these intermediates is different from that of pure model compounds therefore altered the final gas composition.

- For the SCWG of activated sludge using Raney nickel, a high catalyst loading (>1.5g catalyst / g of feed) is needed to achieve relatively high gasification efficiencies with high hydrogen content. In the batch test used, the yields obtained at 380°C were similar to the ones obtained at 410°C and the reaction reached equilibrium after only 30 minutes.

- The addition of ash increased hydrogen yields. The inorganics present in the ash catalyzed the water gas shift reaction.

- Raney nickel deactivated quickly after exposure to SCW. It lost half of its activity after 8 minutes of exposure to supercritical conditions. This loss in activity was attributed to the increase the average nickel crystallite sizes.

- Formulated catalysts showed improved activity compared to the commercial catalysts used for the SCWG of glycine and glycerol. High gasification efficiencies were obtained compared to Raney nickel, but the latter was more selective towards hydrogen. For glucose, humic acid and activated sludge, Raney nickel was more active than the formulated catalysts. This was attributed to diffusion limitation of the larger molecules inside the pores of the formulated catalysts.

### 6.2 Recommendations

During the scope of the project, there were limitations that were not addressed in this thesis and require additional work to come to significant conclusions.
• In this thesis, only the activities of the formulated catalysts were tested. In order to render this study complete, the stabilities of the formulated catalysts should be assessed. This could be done by means of XRD and SEM after the catalyst was exposed to supercritical conditions for a certain period of time.

• The effect of the promoters on the catalyst activity and stability should also be looked into. Promoters could not only improve the activity of the catalyst, they could also improve its stability. Therefore the search for the most stable promoter is crucial in order to make SCWG economical.

• It was concluded that the complex nature of the activated sludge and the presence of large particles contributed to diffusion limitations during the catalytic process. This problem can be solved by a pretreatment of the activated sludge were the complex molecules are broken down to smaller ones and the large particles reduced or solubilized. The effect of several sludge pretreatment techniques on the SCWG of sludge should be assessed to determine if the gasification efficiency could be improved.

• Solubilizing activated sludge also renders the continuous process more economical. Regular pumps could be used instead of the expensive sludge pumps to bring the process to high pressures.