Catalytic Gasification of Pretreated Activated Sludge Supernatant in Near-critical Water

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Abstract:

Pretreatment of waste activated sludge (WAS) and the subsequent near-critical water gasification (NCWG) is a potential avenue to convert WAS into value added products. Part one of the research investigated thermal and thermochemical pretreatments. No difference was observed in the percentage of sludge liquefied beyond 10min between 200°C to 300°C. It was found that pretreated activated sludge supernatant (PASS) doubled the gas yield compared to untreated sludge when gasified. The order of effectiveness for sludge treatment was thermo-alkali > thermal > thermo-acid for hydrogen production in NCWG. Part two investigated NCWG parameters to identify optimal conditions. High gasification yields were obtained using a commercial catalyst (Raney nickel), with hydrogen content of 65-75% of the gas phase products. Thermo-alkali treated PASS was found to perform well at subcritical temperatures with 25% higher yields than thermally treated PASS. Increased catalyst loading had little additional effect on gas yields above 0.075g.
Acknowledgements

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Thank you to my friends and family for all of you support

  To my mom and dad thanks for being there and giving me the push I needed to get things done
  To my partner Jess you’re awesome, and you’re always there to support me :D
  To my Friends there are so many of you, thank you for your kind ear while I more than likely bounced radical ideas off of it
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<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>SCW</td>
<td>Super Critical Water</td>
</tr>
<tr>
<td>SCWO</td>
<td>Super Critical Water Oxidation</td>
</tr>
<tr>
<td>SCWG</td>
<td>Super Critical Water Gasification</td>
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<tr>
<td>NCWG</td>
<td>Near-critical Water Gasification</td>
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<tr>
<td>$Y_{H_2}$</td>
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<td>$Y_{CH_4}$</td>
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<td>Carbon Monoxide Yield</td>
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<tr>
<td>$Y_{CO_2}$</td>
<td>Carbon Dioxide Yield</td>
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<tr>
<td>CGR</td>
<td>Carbon Gasification Ratio</td>
</tr>
<tr>
<td>HGR</td>
<td>Hydrogen Gasification Ratio</td>
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<tr>
<td>AD</td>
<td>Anaerobic Digestion</td>
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<tr>
<td>TS</td>
<td>Total Solids</td>
</tr>
<tr>
<td>VSS</td>
<td>Volatile Suspended Solids</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>SCOD</td>
<td>Soluble Chemical Oxygen Demand</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>ML</td>
<td>Mixed Liquor</td>
</tr>
<tr>
<td>WAS</td>
<td>Waste Activated Sludge</td>
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<tr>
<td>PASS</td>
<td>Pretreated Activated Sludge Supernatant</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Background

The activated sludge process is used to remove organic contaminants from wastewater. To do this, microorganisms, air and wastewater are mixed together in the biological reactor at a wastewater treatment plant. The microorganisms degrade the organic matter and multiply. Since the reactor can only sustain a certain amount of the organisms there is a need to remove and dispose of the excess. This excess is referred to as waste activated sludge or WAS. The WAS is water laden (up to 98%) and contains a large amount of organic material, giving it the potential as a fuel feedstock. However heavy metal contamination and pathogens within the WAS pose many environmental and health issues [1,2]. As such the WAS must be treated before disposal with costs amounting to as much as 50% of the total process cost [3,4].

With an increase in urban populations and demand for better treatment of effluent there has been a large increase in WAS generation. Sludge production in the European Union increased to 10-11 million tons in 2005 and the United States has seen an increase from 7.6 million tons in 2005 to 8.3 million tons in 2010 [5,6]. Typical disposal methods include landfilling, and incineration. Landfilling requires that sludge be dewatered before application. The incineration of sludge requires the drying of the sludge, and risks liberating harmful pollutants and particulate matter to the environment. Increasingly stringent environmental regulations and a decreased social acceptance have led to a decline in these disposal methods. Other disposal methods, particularly ones that transform the waste into value added products are receiving attention. Notable products include fuels, biopolymers, and fertilizers. One such process is the gasification of sludge; a process where organic matter in the sludge is directly converted to a gas with a high heating value. However, due to the large amount of water in sludge, current gasification technologies require pre-drying of the sludge leading to an increase in energy/process and disposal costs.

In recent years it has been suggested that to avoid the high costs associated with drying sludge, a process which utilizes the high water content of the sludge should be used. Disposal techniques that utilize supercritical water (SCW), water above its critical point of 374°C and 22.1 MPa, demonstrate good potential. This is mainly due to the vast difference in properties between water under standard conditions and SCW. The latter is able to completely dissolve organics and gases, making it an excellent...
medium for organic conversion reactions [7]. One technology making use of SCW is supercritical water gasification (SCWG). SCWG of sludge is hydrothermal conversion of organic matter; sometimes in the presence of catalyst, to value added products such as methane and hydrogen.

SCWG is a promising alternative for conventional WAS treatment and disposal. Previous studies have demonstrated that WAS can be gasified with near completion in SCW at high temperature and pressure [8,9] far above the critical point of water. However, these process conditions are extreme and present various engineering issues such as high rates of corrosion. The extreme conditions combined with the large energy input required, significantly increase the operating costs and limit the feasibility of this process for practical use.

To address this issue, research has focused on catalyst development to facilitate gasification at substantially lower temperatures and pressures, while maintaining high yields. Literature shows that many active metals have been identified for this purpose [10]. Raney nickel, a commercially available hydrogenation catalyst, has shown to be effective for this process. However its stability in SCW conditions is of concern as it rapidly deactivates [11]. One way to prolong catalyst life under SCW conditions is to reduce the amount of available material that may poison the catalyst by sludge pretreatment. Although there is a large body of work on pretreatment of WAS for subsequent anaerobic digestion [4,12,13] little is done in the area of WAS pretreatment for the purpose of SCWG.

It is the aim of this research to develop a better understanding of thermochemical pretreatment of WAS in terms of parameters pertinent to gasification, and to elucidate insight into what role pretreatment of WAS may play in its subsequent near-critical water gasification.

1.2 Objectives

The primary objective of this thesis is to develop an understanding of how pretreating municipal waste activated sludge influences gasification under near critical water conditions, as an alternative method for sludge treatment and disposal. Specific objectives for this research are:

- To examine the effectiveness of hydrothermal and thermochemical treatments for liquefaction of municipal waste activated sludge.

  In this study, the effects of temperature, residence time, pH, and sludge concentration on the concentration of liquor produced from the liquefaction of sludge were investigated. Additionally
the effects of these pretreatment conditions on the product distribution and gasification yields were investigated with attention paid to hydrogen production.

• To systematically examine the performance of near-critical water gasification of supernatant from treated municipal sludge using Raney nickel as a catalyst.

In this study the effect of temperature, residence time and catalyst loading on the product distribution and gasification yields were investigated to determine optimal conditions for hydrogen production.

1.3 Thesis Outline

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

• Chapter 2 contains an in-depth literature review. The activated sludge process is discussed and the relevant properties of waste activated sludge are presented. Discussion shifts to cover current disposal methods, their advantages and drawbacks. Supercritical water is looked at insofar as it sets the stage for understanding the thermodynamics involved and the properties that make it a good medium for the gasification of sludge. Some of the early works are covered to give context for this work. Beyond this other common pretreatment methods are discussed along with their advantages and disadvantages compared to hydrothermal and thermochemical pretreatment.

• Chapters 3 and 4 focus on the objectives of the research identified above. In each chapter the experimental setup and methodology is introduced followed by a presentation of the results. The focus then shifts to a discussion of the results and conclusions drawn from them.

• Chapter 5 presents key conclusions from the works presented. Recommendations for how the research can be continued and areas that require more investigation are discussed.
1.4 References


2 Literature Review

2.1 Activated Sludge

2.1.1 Biological Treatment Process

Wastewater treatment plants world-wide utilize the activated sludge process to treat municipal and industrial wastewater. The purpose is to reduce the organic content of the wastewater before discharge to the environment. Microorganisms consume the organic content and nutrients (nitrogen and phosphorous), converting them into biomass and metabolic products in what is typically an aerobic process.

Figure 2.1 shows a typical activated sludge process. Incoming wastewater is mixed with activated sludge creating Mixed Liquor (ML), which is fed to the biological reactor. This ML is a mixture of microorganisms, biodegradable organics, non-biodegradable organics, and various inorganic materials. Effluent from the biological reactor is sent to the secondary clarifier, where the suspended solids settle out of the treated clean water on top. The clean water is sent for disinfection while the activated sludge is recycled. Only a fraction of sludge is recycled as return activated sludge (RAS), while the rest is waste activated sludge (WAS) and is sent to be dewatered and stabilized before disposal.
### 2.1.2 Activated Sludge Characteristics

Activated sludge is a mixture of microorganisms, organic and inorganic matter. Typically water content of AS is greater than 95wt%. Compositional information is located in table 2.1 [1]. Volatile solids make up 60-80% of activated sludge total solids (TS), giving a good indication of the organic content of the material. The balance is either fixed carbon or ash (inorganics). There are also many trace heavy metals such as arsenic, mercury, and nickel found in activated sludge [1-4]. Activated sludge is typified by a diverse microbial community that contains pathogenic organisms [5,6].

### 2.2 Sludge Disposal and Reuse

Activated sludge is the largest component of solid waste produced by municipal wastewater treatment plants. Disposal of the sludge can account for as much as 50% of the total operating cost of the plant [7]. With increasing urban populations the amount of sludge that must be disposed of is increasing as well. Sludge production in the European Union increased to 10-11 million tons in 2005 and the United States has seen an increase from 7.6 million tons in 2005 to 8.3 million tons in 2010 [8,9]. This large increase in output is mainly attributed to increasingly stringent environmental regulations for water quality.

The water content of the sludge, the pathogenic nature of some of the microorganisms and the trace heavy metals translate into a need for the WAS to be treated before it is disposed of. Typically the WAS is thickened and dewatered to reduce volume and mass. Dewatering is accomplished using mechanical or thermal means and greatly increases disposal costs. Methods employed include: centrifugation, filtration, and thermal drying. Additionally biological stabilization may be used to reduce the potential health hazard associated with pathogens in WAS. Heavy metals are typically dealt with upon disposal and not at the wastewater treatment plant. Here, methods for sludge disposal along with their advantages and drawbacks are briefly discussed.

#### Table 2.1 Activated sludge composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>2.0-8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dry solids (TS)%</td>
<td>2.0-8.0</td>
</tr>
<tr>
<td>Volatile solids % TS</td>
<td>60-80</td>
</tr>
<tr>
<td>Grease and fats % TS</td>
<td>15-35</td>
</tr>
<tr>
<td>Protein % TS</td>
<td>20-30</td>
</tr>
<tr>
<td>Nitrogen % TS</td>
<td>1.5-5.0</td>
</tr>
<tr>
<td>Phosphorous % TS</td>
<td>0.28-11</td>
</tr>
<tr>
<td>Cellulose % TS</td>
<td>8.0-15.0</td>
</tr>
</tbody>
</table>
2.2.1 Agricultural Reapplication

Since sludge is composed of organic matter and contains up to 5% nitrogen, and up to 11% phosphorus. This makes it attractive for use in agricultural applications [2]. Prior to use WAS must be stabilized and dewatered to remove pathogens and ease shipping requirements. During the 1970’s large amounts of WAS were used as fertilizer in the United Kingdom. However the practice has subsided in more modern times due to issues with soil contamination by heavy metals, as well as degradation of soil quality in regard to local microorganism communities and nutrients [10].

2.2.2 Landfilling

Landfilling is the burial of sludge. In the 1990’s approximately 40% of waste activated sludge was disposed of by landfilling in the European Union [11]. WAS needs to be well stabilized and dewatered for this application due to concerns over ground water pollution from leachate and runoff. Where suitable land is available this method of sludge disposal is inexpensive when compared to incineration. However with the availability of suitable land diminishing the cost gap between the two methods is narrowing. Environmental regulations, public awareness, and increasing amounts of sludge to be disposed of are quickly limiting disposal of activated sludge in this manner [12].

2.2.3 Incineration & Co-incineration

Incineration & co-incineration can be used to attain complete oxidation of the organic matter in WAS, and to significantly reduce the volume of solid waste. Incineration is the combustion of sludge as the sole fuel source, whereas co-incineration is the combustion of sludge with another fuel source, usually coal, or municipal solid waste. Heat integration is more important for incineration as the sludge must be dewatered or dried before to less than 20% moisture content before use, adding to the cost of operation [13,14]. Co-incineration can tolerate a larger moisture content of WAS since sludge is used in limited amounts with another fuel source. Upon combustion sludge is converted to gases, heat and ash. Of environmental concern are the heavy metals and emissions. Literature shows that heavy metals are well immobilized in the ash produced [15], with the exception of mercury, cadmium and arsenic which are completely vaporized [13]. Appropriate emission scrubbing is employed to deal with SO$_x$ and NO$_x$ formation, again this is an added cost for an incineration plant, whereas for co-incineration the required infrastructure is typically already in place [16].
2.2.4 Anaerobic Digestion

Anaerobic digestion is a process that utilizes microorganisms called methanogens to ferment organic matter into a product called biogas. The major benefit of this process is that the pathogens in the sludge are destroyed and that the solid residue is easily dewatered. The quantity of solids and the volume of sludge requiring disposal is greatly reduced [17]. The biogas is mainly composed of methane with various impurities and it can be burned on site for energy recovery, or upgraded and sold as higher quality methane. The effectiveness of this process depends of the quality of the incoming sludge stream. Fluctuations in organic and nutrient content greatly influence the ability of the microorganisms to hydrolyze the sludge. Literature shows that hydrolysis is the rate limiting step in anaerobic digestion of WAS [18,19]. As such there is a large amount of literature investigation focusing on pretreatment methods to improve WAS degradability by anaerobic digestion [7,20-23]. These methods provide a basis for this thesis and a more extensive review will be presented later on.

2.2.5 Thermal Conversion Technologies

Gasification

Gasification is a process where carbonaceous material such as sludge, is reacted with air, oxygen or steam to produce syngas a mixture of carbon monoxide, carbon dioxide, hydrogen and methane [24]. Typical operating temperatures are above 700°C. Typically the syngas has a high heating value and is used as a utility stream in the gasification plant, or it may be converted to liquid fuel via the Fisher-Tropsch process. For gasification to be successful, the incumbent sludge must have less than 20% moisture content, which adds to the cost of the process. The only by-product is ash at 1-5% of the initial wet sludge loading [13].

Pyrolysis

Pyrolysis is process in which sludge is pressurized and heated to 350–500 °C in the absence of oxygen, by doing so the sludge is converted to char, ash, pyrolysis oils, water vapor, and combustible gases [25-27]. The major advantage to the process is that it allows for the production of value added gases and oil which can either be used as base chemicals or directly as fuels. However the major drawback is that like most other sludge disposal methods, sludge first must be dried.
SCWO
Supercritical water oxidation is a process that utilizes the unique properties of supercritical water, and an oxidizing agent (O\textsubscript{2} or H\textsubscript{2}O\textsubscript{2}) to convert sludge to carbon dioxide and water. With this process, the total organic carbon content of a wastewater stream can be reduced to near zero [28]. Also, unlike many other disposal methods, this process relies on high water content of WAS, since water participates in the reaction. Requiring relatively severe operating conditions (above 374°C and 22.1MPa), there is an increased operating cost and a need for expensive materials to deal with corrosion problems. However to offset the energy cost, the hot exhaust gases may be brought into contact with incoming feed to recover heat.

SCWG
Supercritical water gasification is an emerging technology that has potential to convert WAS into value added products such as fuel oils and gases. Like SCWO, it makes use of the properties associated with SCW, and relies on the high water content of the WAS feedstock. It also does not require pathogen destruction as a pretreatment since the conditions used biologically stabilize the material. Unlike SCWO there is no oxidizing agent, and as such the carbonaceous material in the sludge is converted primarily to syngas, tar and char in the liquid effluent. This gas is mainly composed of hydrogen, methane, carbon dioxide and carbon monoxide. Since this is a topic covered in this thesis a more extensive literature survey will be presented.

2.3 Pretreatment of Activated Sludge
As discussed earlier, anaerobic digestion is widely used to stabilize and reduce activated sludge mass while producing biogas. The limiting factor in the process is sludge hydrolysis. To this end, a wide variety of research into different WAS pretreatment methods have been investigated [7,18-20,22,23,29-32]. Pretreatment of WAS for use in SCWO and to a lesser extent SCWG have not had the same level of investigation as that for anaerobic digestion. Notably Matusmura \textit{et al.} had investigated hydrothermal pretreatment (a common form of pretreatment for anaerobic digestion) as a means to ease biomass slurry deliver to a gasifier [33,34]. This idea of borrowing technologies from anaerobic digestion for use in SCWG is relatively new and un-studied. It is the aim of this thesis to elucidate more practical treatments prior to SCWG of WAS.
2.3.1 Thermal Pretreatment

Thermal treatment involves applying heat in excess of 100°C to sludge. Hot compressed water facilitates floc degradation and the release of water. Literature shows that digestibility of the sludge increases as pretreatment temperature increases [29], with the optimal treatment temperatures in the range of 160°C - 180°C at residence times of 30 to 60 min [22, 29, 35]. It is also reported that there is little benefit to increasing temperatures beyond the above range for subsequent anaerobic digestion. This is likely due to the formation of Maillard reaction products, which are known to inhibit microbial growth [37-39]. Maillard products are the result of reactions between carbohydrates and amino acids to form melanoidins which are extremely recalcitrant for enzymatic processes. The result of thermal treatment is a sludge that is easier to degrade with a higher output of methane. This increase in output has been linearly correlated to increased COD solubilization [36].

2.3.2 Acid/Alkaline Pretreatment

Literature shows that the addition of alkali increases solubilization, Alkali treatment is used to increase sludge solubilization and degradability of sludge. The effect increases with increasing amounts of alkali and the optimal pH for degradation have been found to be in the range of 10-12 [21, 41-47]. The effectiveness of alkaline pretreatment depends on the type of alkali materials and has been reported to decrease in the following order: NaOH > KOH > Mg(OH)₂ and Ca(OH)₂ [40]. Ray et al. investigated the effect of low level alkali addition on sludge degradation and anaerobic digestion. The process involved the addition of 20ml alkali per litre of sludge followed by mixing for 24 hours under anoxic conditions. Digestion was improved by 25-35% [31]. Stuckey et al. investigated the combined thermal-alkali pretreatment of WAS. It was demonstrated a maximal degradability of 61% was achieved at 175°C with a 27% increase in methane production and that the addition of 300ml 15 molar NaOH preserved this maximal degradability up to 275°C [30]. Acid treatment has also been investigated as a pretreatment method to a lesser extent than alkali treatment. Reducing sludge pH in the range of 2-2.5 has been reported to increase hydrolysis and mineralization of the organic matter in the sludge, which reduces residual solids by increased solubilization [42, 48-50].
2.3.3 Oxidative Pretreatment

The use of ozone as an oxidative pretreatment method for WAS before anaerobic digestion is one of the most widely used chemical methods [32]. This chemical treatment increases sludge solubilization and methane output with increasing ozone dose; a 20% increase was found to be typical for an ozone loading of 0.055g/g [51,52]. Literature shows an optimal ozone dosage of 0.1-0.2g/g [53-55]. Increasing the dose beyond 0.2g/g has been reported to result in direct oxidation of organics to carbon dioxide and to reduce methane output [53].

During the ozone treatment process the high molecular weight compounds are converted to smaller molecules via the oxidation process, as well a decrease in pH was reported to take place due to the formation of organic acids. Hydrogen peroxide has also been investigated as an oxidative pretreatment method for WAS [41]. Mild thermal treatment combined with 2g/g VSS hydrogen peroxide addition provided enhanced COD removal upon anaerobic digestion [56]. Recently Yawei et al. improved sludge solubilization by combining hydrogen peroxide treatment with microwave treatment [57]. These experiments were the equivalent of a combined mild heating and oxidative treatment. The result was that increased peroxide dosage (0.1-1g/g) enhanced the SCOD and TOC content of the produced supernatant by 10 fold.

2.3.4 Ultrasound Pretreatment

Ultrasonic treatment mechanically disrupts the cell structure and floc matrix of WAS through cavitation and chemical reactions from radical formation [32]. Degradability by sonication is a function of treatment time and the specific energy input, i.e. amount of energy per unit mass of sludge [58]. Huan et al. demonstrated that sonication with low energy density; 0.4W/ml for 10 min, increased WAS solubility to nearly 40% whereas high density; 4W/ml for 1 minute, resulted in only 10% solubilization [59]. The degree of disintegration of WAS has been found to increase with increasing specific energy input [60,61]. Akin et al. demonstrated that ultrasonic pretreatment with densities of 0.67, 1.03 and 0.83W/ml were effective in achieving a 6.5 fold reduction in particle size for 2%, 4% and 6% TS, respectively. For the same WAS, SCOD was found to be 320 mg/g, 160mg/g and 90 mg/g for 2%, 4% and 6%, respectively, at 5kWs/g power input [62].

Ultrasound frequency is an important parameter in determining the effectiveness of this pretreatment method. Lower frequency ultrasound creates large cavitation bubbles that exert strong shear forces in
the liquid upon collapse. At higher frequencies the bubbles are smaller reducing the effectiveness of the treatment [63]. The impact of different ultrasound intensities was investigated by Tiehm et al., frequencies ranged from 41 to 3217 kHz. Sludge disintegration was most significant at low frequencies (80% at 41 kHz, compared to 2% at 3217 kHz).

### 2.4 Supercritical Water Gasification

#### 2.4.1 Characteristics

Supercritical water is water above its critical point of 374°C and 22.1 MPa. The properties of water change drastically near and above this point as functions of temperature and pressure. Density decreases significantly above the critical point resulting in a decreased in the static relative dielectric constant. It drops from 80 under normal conditions to 5 under SCW conditions [71]. This makes SCW a non-polar solvent, the solubility of salts decreases [72] while the solubility of organics and permanent gases increases. Above the critical point water can be mixed in any ratio with the aforementioned substances [73,74]. SCW has low viscosity and consists of a single phase; this removes heat transfer limitations and results in large diffusion coefficients and reactions rates in the medium. There is also a noted drop in ion product, indicating a shift from an ionic reaction mechanism to a free radical mechanism [73].

During SCWG, water suppresses tar and char intermediate formation from pyrolytic processes. It readily dissolves complex molecules (i.e. those containing multiple double bonds) at low concentrations, reducing the likelihood of polymeric char formation. SCW also facilitates hydrolysis of biomass and acts as an acid catalyst for gasification reactions. It is perceived as an ideal medium for chemical conversion reactions [75]. The viability of the method relies on having high organics feed concentrations, and from heat recovery, due to the large heat capacity of water and the severe conditions.

#### 2.4.2 Early Work

In 1970’s, thermodynamic analysis of SCWG of cellulose by Antal et al. and Modell et al. suggested the formation of a gaseous product rich in hydrogen and containing methane, carbon dioxide and carbon monoxide [64-66]. Antal et al. also predicted complete gasification for temperatures above 600°C and demonstrated that under atmospheric pressure biomass does not react with steam [67]. Later, it was demonstrated that the liquefaction and gasification of forest products in SCW was feasible [68]. Sawdust
from maple wood was decomposed to tars and gases, with little char formation reported. It was suggested that cellulose decomposes rapidly in water at temperatures well below the supercritical temperature of water, with rapid solvolysis of lignin and hemicellulose occurring at temperature at 190°C and above [68-70].

2.4.3 Thermodynamic Analysis

Since the pioneering work of Antal’s in 1978, several thermodynamic studies have been carried out to determine the effect of temperature, pressure and concentration on the products of SCWG. Lu et al. [76] modeled the impact of temperature and biomass concentration on the equilibrium of SCWG. To examine the effect of temperature, a 5wt% biomass concentration was considered at a pressure of 25MPa. The result predicted that hydrogen would be the dominant product above 425°C and represent almost 90% of the gas yield above 625°C. At 25MPa, and 600°C, Lu et al. found that at biomass concentrations below 10% hydrogen was the favoured product constituting more than 60% of the total yield, while at higher biomass concentrations methanation was favoured. Using a similar approach, Yan et al. [77] studied the gasification of glucose in SCW. Their findings with respect to temperature and feed concentration were in agreement with the earlier observations of Lu et al. However, the predicted conversion values were systematically lower than the measured ones, emphasizing that SCWG is a kinetically driven process.

Key reactions in SCWG include, steam reforming, water gas shift and methanation. Equation 1 shows the steam reforming of cellulose, 2 is the water gas shift reaction, 3 and 4 are potential methanation reactions.

\[
\begin{align*}
\text{Steam Reforming:} & \quad \text{C}_6\text{H}_{10}\text{O}_5 + 7 \text{H}_2\text{O} \rightarrow 6 \text{CO}_2 + 12 \text{H}_2 \quad (1) \\
\text{Water gas shift:} & \quad \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (2) \\
\text{Methanation:} & \quad \text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (3) \\
& \quad \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \quad (4)
\end{align*}
\]
2.4.4 SCWG of Model Compounds

Biomass is a general classification for carbonaceous matter typically derived from plant matter, and now more prevalently animal wastes, and microorganisms. Biomass is a complex mixture of compounds, and for plant derived biomass it is composed of cellulose, lignin and hemicellulose. Biomass from microorganisms differs in that the cell walls are made up of peptidoglycan. WAS is typically composed of biomass derived from all the aforementioned sources. Due to the complexity of biomass composition, model compounds are often used to elucidate the basic mechanisms involved in biomass gasification. Minowa et al. studied the gasification of cellulose and glucose over temperatures ranging from 200°C to 350°C. It was found that cellulose rapidly hydrolyzed to water soluble sugars, above 250°C, producing gas, oil, char, and other water soluble compounds. They reported that decomposition of cellulose and glucose resulted in similar product distribution [78-81]. Hence, glucose is often used as a model compound for cellulose.

Aside from cellulosic materials, biomass may also contain proteins and fat. Kang et al. investigated the behaviour of protein decomposition to amino acids in near-critical water using silk fibroin as a model compound. It was determined that at low temperatures the decomposition products consisted of many complex amino acids. However as the temperature was increased beyond 300°C these complex amino acids were decomposed further into glycine and alanine [82]. A similar trend was observed with increased residence time [82]. As such, glycine and alanine have been used to represent protein in the SCWG of biomass [83]. These model compounds are simple amino acids and do not contain any sulfur, which is known to be a catalytic poison and thus of industrial concern. Hydrolysis to ammonia and decarboxylation of protein are competing reactions during the gasification process of amino acids that reduce the efficiency of SCWG. The model compound used to represent fats is glycerol which has been shown to produce a gas rich in hydrogen during SCWG, it has also been shown to be completely gasified under SCW conditions [83].
2.4.5 SCWG of Activated Sludge

Studies involving activated sludge as a feedstock for SCWG are few in number due to the complexity of the material. Xu et al. studied the gasification of sewage sludge in the presence of an activated carbon catalyst derived from coconut shells at 600°C and 34.5 MPa in a continuous reactor. Complete conversion of the sludge was achieved with a total gas yield of 77%, the major component was carbon dioxide [84]. To improve reactor performance cornstarch was used to suspend the sewage sludge in a slurry so as to minimize fouling. The gasification of this mixture was also studied by Xu et al. near complete conversion was observed with a hydrogen rich product gas (42%) [85]. Schmieder et al. studied the SCWG of sewage sludge at 450°C and 330 bar with K$_2$CO$_3$ as a homogeneous catalyst. The total gas yield increased from 55% without catalyst to 85% with catalyst. A hydrogen rich (48%) was obtained in both cases [86]. Yamamura et al. reported that sewage sludge was not completely decomposed after SCWG at 450°C, 47.1 MPa and 120 min in the presence of RuO$_2$ catalyst. Although the product gas was rich in hydrogen it contained a large fraction of methane and total yield was low, 11% based on carbon and 23% based on hydrogen [87].

2.4.6 Catalysts in SCWG

Alkali, and alkali salts have been shown to exhibit a catalytic effect for the SCWG of model compounds and biomass. These alkali salts include NaOH, KOH, K$_2$CO$_3$, and Na$_2$CO$_3$, to name a few. Minowa et al. demonstrated that the presence of alkali salts had a catalytic effect on the SCWG of cellulose [78, 80, 88]. It was noted that the addition of sodium carbonate lowered the degradation temperature of cellulose to below 180°C. This is due to the peeling reaction of carbohydrates, which is the conversion of polysaccharide end groups and monosaccharaides to carboxylic acids in the presence of alkali. The reaction proceeds via the cleavage of the 1-4 glycosidic bond, isomerization of the end group to a ketose, which under goes further transformation to form a carboxylic acid [89]. Sinag et al. investigated the effect of K$_2$CO$_3$ on the SCWG of biomass, it was reported that carbon monoxide yield was minimal while hydrogen and carbon dioxide yields increased, likely due to the promotion of the water gas shift reaction by alkali salts [34,90]. Recent studies have shown the tar formation is suppressed in the presence of NaOH, combined with enhanced gasification of biomass and hydrogen production [91,92]. Since homogeneous catalysts are soluble in water under ambient conditions and relatively insoluble under SCW conditions [72], catalyst recovery is difficult. Also do to the reduced solubility of these salts in SCW, reactor fouling is a key concern [85]. To avoid these challenges, heterogeneous catalysts have been investigated to enhance SCWG of biomass [34,80,84,93-97]. Special attention has been paid to
Raney type catalysts, due to their extremely large surface areas. Azadi et al. investigated the activity of several Raney type catalysts for SCWG of glucose, reporting that Raney Nickel gave the highest gasification yield [96,97].

2.4.7 Advantages of SCWG

SCWG has the potential to be a useful technology for energy production from biomass. Since SCWG relies on water as the reaction medium, the costly step of drying of feedstock is not required. This is a significant advantage for the conversion of water laden waste streams including but are not limited to agricultural waste, waste from the food and beverage industry, pulp and paper wastewater and WAS. The operation at high pressure ensures that the product gas does not require compression for storage. The high pressure also facilitates the separation of carbon dioxide from hydrogen and methane, as its solubility is greatly enhanced under SCW conditions. Carbon monoxide content is generally low as it is converted to carbon dioxide via the water gas shift reaction producing hydrogen as a byproduct.

2.4.8 Challenges

There are many challenges associated with SCWG. Most notable are those associated with materials of construction. SCWG involves high temperature, pressure and extreme corrosion as environmental conditions. Expensive specialty materials are typically utilized in reactor construction which can reduce the economic viability of the process depending on the scale of operation. Another limitation is that of sludge delivery, Xu et al., reported severe reactor fouling due to suspended solids in sewage sludge feed settling out of suspension, their workaround was to suspend the sludge in a cornstarch slurry [85]. However, these challenges can be addressed if gasification can be achieved at sub-critical conditions.
2.5 References


3 Thermal and Thermo-chemical Pretreatment of Activated Sludge

3.1 Introduction

Global warming has fueled the search for new ways to produce energy from renewable resources. The conversion of biomass to biofuel presents an interesting opportunity. There are many sources of biomass among which waste activated sludge (WAS) has drawn increasing attention in recent years. With rising urban populations and demand for better treatment of effluent there has been a large increase in WAS generation. The United States produced 8.3 million tons in of sewage sludge in 2010, with that amount expected to rise in the future [1]. The conversion of waste activated sludge to value added products is attractive as it is considered a renewable resource, it is plentiful and its current disposal is of environmental concern.

Activated sludge is a mixture of microorganisms, organic and inorganic matter. It is a by-product of wastewater treatment. It has water content greater than 95wt% and trace amounts of heavy metals such as arsenic, mercury, and nickel [2-4]. Typical disposal methods of landfilling, incineration, and gasification require dewatering or drying of sludge feed which is prohibitively expensive. Anaerobic digestion is widely used to stabilize and reduce activated sludge mass while producing a value added product (biogas) it also does not require the sludge to be dried. The limiting step in anaerobic digestion of sludge is hydrolysis. Researchers have investigated numerous pretreatment methods to increase the bioavailability of WAS for hydrolysis [5-9]. Thermal and thermo-chemical treatments have been found to be quite effective. Literature shows that optimal treatment occurs in a temperature range of 160°C - 180°C and residence times of 30 – 60 min [9-11]. It is also reported that there is little benefit to increasing temperatures beyond this range, likely due to the formation of Maillard reaction products, which are known to be enzymatically recalcitrant and inhibit microbial growth [12-14]. However, this is not a likely constraint on the gasification of pretreated WAS.

Sludge pretreatment with alkali compounds is shown to significantly enhance the bioavailability of sludge. Sodium hydroxide is the preferred compound for thermo-alkali treatment [15]. Stuckey et al. investigated the thermal-alkali pretreatment of WAS. It was demonstrated that the addition of strong alkali preserved the maximal degradability of 61% from 175°C up to 275°C [6]. Literature shows that the addition of alkali increases solubilization with increasing loading. Optimal conditions for degradation
were found to be in the range of pH 10-12 [16-19]. Acid treatment has also been investigated as a pretreatment method to a lesser extent than alkali treatments. Reducing sludge pH in the range of 2-2.5 has been found to be optimal for increasing solubilization [18, 20].

In comparison, little is known in terms of the pretreatment of WAS for use in SCWG. Notably Matusmura et al. had investigated hydrothermal pretreatment as a means to ease biomass slurry delivery [21]. This idea of borrowing technologies from anaerobic digestion for use in SCWG is relatively new and un-studied.

Supercritical water (SCW), water above the critical point of 374°C and 22.1 MPa, is able to completely dissolve organics and permanent gases, making it an excellent medium for organic conversion reactions [22]. Literature shows that the direct gasification of sewage sludge produces a hydrogen rich gas stream [23-25]. Pretreatment of activated sludge is also expected to be beneficial for the SCWG of activated sludge. However, the use of thermal and thermo-chemical pretreatment for SCWG has not been done before. It is the aim of this study to elucidate the effect of thermal and thermo-chemical pretreatments of WAS on the composition of pretreated activated sludge supernatant.

3.2 Experimental Setup

The apparatus used in this research is depicted in Figure 3.1. The reactor is made of 316 SS and has a volume of 50ml. Activated Sludge was obtained from Ashbridges Bay Waste Water Treatment Plant in Toronto Ontario Canada. The collected sludge was concentrated by removing water to form a thick paste it was then dried at 80°C for 24hrs and stored for subsequent experiments. For each test, the dried sludge was ground in a Hamilton beach coffee grinder. Sludge samples were prepared by adding 0.3g of dried sludge to 3g of water and allowed to rehydrate for a period of 24hrs. In a typical experiment, 6.7g of distilled water was added to each sludge sample to achieve a 3wt% sludge suspension. Other sludge concentrations were prepared in a similar manner.

Prepared sludge samples were loaded into the reactor and immersed into a molten salt bath at the target temperature for the desired residence time. The salt bath was a mixture of potassium nitrate, sodium nitrate, and sodium nitrite and had a heating rate of ~500°C/min. Temperature was measured and controlled using a K-type thermocouple (Omega, Laval, Canada) and a NX4 PID controller (Hanyoung USA, FL,). Quenching was performed rapidly in a cold water bath. After each test, the reactor pressure was measured using a digital pressure gauge (Cecomp Electronics, API Inc., IL, USA). In addition, any gas
evolved during the process was collected in a 0.3L gas bag and analyzed in a Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector (Hewlett Packard, USA). Gasification of pretreated sludge was performed using the same reactor system described above. Gas yields

The amount of sludge solubilized was determined through centrifugation and drying of the sludge residue after pretreatment. Centrifugation was accomplished at 4000 RPM for 15 min. The pretreated activated sludge supernatant (PASS) was decanted and the residue was dried for 24 hours at 80°C. The mass of the residue was then measured. The difference between the initial dry sludge mass and the residue was assumed to be the mass of sludge solubilized. The concentration of PASS was determined by dividing the solubilized sludge mass by the total mass of the liquid phase and the solubilized sludge. The percentage liquefied was determined by dividing the solubilized mass by the initial dry sludge mass.

Elemental Analysis of the dried sludge and solid residues were determined using a 2400 Series II CHNS analyzer (Perkin Elmer, USA) operating in C-H-N mode. Prior to the CHN analysis, solid residue was dried at 80°C for 24 hours. The results of the CHN analysis were used to determine the carbon and hydrogen content of the PASS through a difference calculation (i.e. the amount in the residue was subtracted from the amount in the dry sludge and the difference was assumed to be in the PASS). Ash content of the dried sludge was determined by heating a known quantity of sludge at 550°C for 1 hour. The remnant was assumed to be ash. Total organic carbon (TOC) was measured using a (TOC-VWP, Shimadzu, Japan). Sulfur content in the sludge and in the supernatant was determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP AES) (Optima 7300 DV, Perkin Elmer, USA). All experiments were run at least in triplicate. The percentages extracted of carbon and sulfur were calculated by using the measured amount of carbon and sulfur in PASS and dividing by the measured amount in the dry sludge. Mathematically these quantities are defined as:

\[
\text{% Liquefied} = \frac{\text{sludge mass} - \text{sludge residue mass} - \text{gas mass}}{\text{sludge mass} - \text{ash}\% \times \text{sludge mass}} \times 100
\]

\[
\text{% Extracted} = \frac{\text{mass carbon or sulfur in PASS}}{\text{mass of carbon or sulfur in sludge}} \times 100
\]

\[
\text{PASS Concentration} = \frac{\text{solubilized sludge mass}}{\text{solubilized sludge mass} + \text{mass of water}} \times 100
\]

\[
\text{CGR} = \frac{Y_{CO} + Y_{CH4} + Y_{CO2}}{\text{mmol C/g solubilized sludge}} \times 100
\]

\[
\text{HGR} = \frac{2Y_{H2} + 4Y_{CH4}}{\text{mmol H/g solubilized sludge}} \times 100
\]
3.3 Results and Discussion

In this study the effects of temperature, residence time, pH and sludge loading on the liquefaction of activated sludge are examined, as well as the effects of pretreatment pH and temperature on the subsequent gasification of the PASS. Pretreatment results are reported on an ash free basis as percent liquefied (i.e. the difference in mass between the dry sludge loaded in the reactor and the sludge residue after pretreatment (less the mass of any gas formed) divided by the mass of dry sludge loaded in the reactor), percent extracted (i.e. the ratio of carbon or sulfur in the liquid phase to that of the sludge), and PASS concentration (i.e. the mass of solubilized organics divided by the mass of PASS (water + organics)). Gasification results are reported in terms of gas yield (i.e. amount of gas produced (in mmol) per gram of sludge initially loaded to the reactor), carbon gasification ratio (CGR) which is the ratio of carbon in the gas phase to the amount of carbon in the PASS, and hydrogen gasification ratio (HGR) which is the ratio of hydrogen in the gas phase to hydrogen in the PASS).
3.3.1 Sludge Characterization

Elemental analysis of the dry sludge found the composition to be 33.3wt% carbon, 5.94wt% nitrogen and 6.01wt% hydrogen. Table 3.1 summarizes the sludge characteristics. From ICP AES of the sludge, the sulfur content was found to be 0.75wt%, which is typical for activated sludge as reported in literature [27]. Oxygen content of sludge was estimated according to:

\[
\text{Oxygen Content} = 100\% - C\%-N\%-H\%-S\%-\text{Ash}\%
\]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>H</th>
<th>S</th>
<th>O*</th>
<th>Ash%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>33.3%</td>
<td>5.9%</td>
<td>6.0%</td>
<td>0.75%</td>
<td>28.9%</td>
<td>25.1%</td>
</tr>
</tbody>
</table>

3.3.2 Effect of Temperature & Residence Time

Figure 3.2 illustrates the effects of temperature (200°C–300°C) and residence time (2-30 min) on the liquefaction of activated sludge in near-critical water. The figure demonstrates that the extent of liquefaction increased rapidly with increasing residence time to a plateau of approximately 80% after 10 min.

There is no significant difference between liquefaction amounts for the three temperatures at residence times of 10 min or longer. Treatment at 300°C for residence times of 2 and 5 min yielded in 72% and 81% liquefaction, respectively, while at 250°C the corresponding yields were 39% and 65%. At 200°C the results were similar to that of 250°C, 36% and 63%. These findings suggest that saturation is achieved, or that conversion of WAS to non-soluble products becomes dominant after a residence time of 10 min regardless of temperature. The liquefaction is almost independent of temperature between 200°C – 300°C, for residence times greater than 10min. However at residence times lower than 10 min thermal treatment at 300°C achieved a greater degree of liquefaction.

The figure also depicts the amount of activated sludge that was gasified during the treatment process; this amount increases as residence time increases. At 300°C and 250°C there was a measureable amount of gas produced after 5, and 10 min respectively. After 30 min 8.8% of the sludge was gasified at 300°C whereas 5.1% was gasified after the same period of time at 250°C. There was no measureable amount of gas produced at 200°C. Table 3.2 summarizes the analysis of the gaseous products.
The effect of temperature on TOC, carbon and sulfur extraction in the PASS was also investigated. The trend mirrored that of liquefaction, increasing temperature increased TOC as well as carbon and sulfur extraction for a fixed residence time (Table 3.3).

No statistical difference was found between 250°C and 300°C treatments in terms of these parameters.

Table 3.3 Summary of the effect of temperature on TOC, carbon & sulfur extraction at a residence time of 10 min (dry sludge loading 0.3g water loading 9.7g).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>TOC (ppm)</th>
<th>% Carbon Extracted</th>
<th>% Sulfur Extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7 Temp 200</td>
<td>3106</td>
<td>30.4</td>
<td>43.5</td>
</tr>
<tr>
<td>pH 7 Temp 250</td>
<td>4257</td>
<td>41.7</td>
<td>55.6</td>
</tr>
<tr>
<td>pH 7 Temp 300</td>
<td>4112</td>
<td>40.3</td>
<td>49.3</td>
</tr>
</tbody>
</table>
3.3.3 Effect of pH

Figure 3.3 shows the effect of pH on the liquefaction of activated sludge at 250°C for a residence time of 10 min. The effects of pH on TOC, carbon and sulfur extraction are illustrated in Figures 3.4 and 3.5 respectively. At pH 7, nearly 80% of sludge was liquefied after 10 min. From Figure 3.3, both acidic and alkaline conditions increased the yield of sludge liquefaction. Decreasing pH to 1.5-2 increased the liquefaction to nearly 83% with an apparent maximum solubilization of 86% at pH 4. However, this maximum value is within the measurement variability for acidic conditions. On the other hand increasing the pH had a large effect on the liquefaction of sludge as noted in literature [16-19]. A maximum solubilization of 95% was achieved at a pH of 13.5. Hence, deviation from a neutral pH will increase the amount of sludge liquefied, however alkaline pH is preferred over acidic pH for its higher solubilization of activated sludge due to the peeling reaction of carbohydrates, as described in section 2.4.6.

![Figure 3.3 Effect of pH on activated sludge liquefaction at 250°C for a residence time of 10 min](image)

Figure 3.4 illustrates the effect of pH on TOC of PASS. At pH 4, TOC was about 30% higher than TOC under neutral condition. However, there was little difference in TOC at pH below 4. Increasing alkalinity also had a positive effect on the TOC present in the PASS. Strong base is known to promote the effects of hydrolysis in proteins, cellulosic materials, sugars, and lipids [15]. Treatment at pH 13.5 more than
doubled the TOC content over that of treatment at neutral pH, i.e. 9440ppm versus 4260ppm. A comparison of the theoretical carbon content of the PASS (calculated from CHN analysis on the residual solid in the reactor) and the measured carbon content obtained by TOC analysis is given in Table 3.4. The estimated carbon content of PASS was obtained by mass balance using the carbon content of the sludge, solid residue and gaseous products. The average deviation between calculated and measured carbon in the PASS is 20%. This discrepancy is partly due to weight loss from drying of the solid residue [28].

![Figure 3.4 Effect of pH on TOC for PASS at 250°C for a residence time of 10 min](image)

<table>
<thead>
<tr>
<th>pH</th>
<th>1.5</th>
<th>2</th>
<th>4</th>
<th>7</th>
<th>10</th>
<th>12</th>
<th>13</th>
<th>13.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Content Calculated (CHN)</td>
<td>34.0%</td>
<td>34.1%</td>
<td>34.1%</td>
<td>35.7%</td>
<td>37.9%</td>
<td>36.9%</td>
<td>38.8%</td>
<td>38.8%</td>
</tr>
<tr>
<td>Carbon Content Measured (TOC)</td>
<td>28.2%</td>
<td>28.3%</td>
<td>29.1%</td>
<td>23.1%</td>
<td>21.1%</td>
<td>30.0%</td>
<td>37.8%</td>
<td>42.8%</td>
</tr>
</tbody>
</table>

Table 3.4 Comparison of carbon content: measured vs calculated for PASS at different pHs

The presence of sulfur compounds in PASS is of concern as these materials are known to poison catalysts and hence reduce the gasification yield of liquefied activated sludge [25]. Figure 3.5 illustrates the effect of pH on the carbon and sulfur content of PASS. Acidic conditions resulted in the least amount of sulfur extracted in PASS ranging from about 44% to 48% compared to 56% for the neutral and alkali conditions. Increasing the pH beyond 10 caused a rapid increase in the fraction of carbon and sulfur extracted. However above pH 12, sulfur extraction was relatively constant 80-82%. Accordingly, sulfur
content of PASS increased from 102 ppm at pH 1.5 to 189 ppm at pH 12. The results suggest that supernatant from alkaline treated sludge above pH 10 may cause premature deactivation in catalytic gasification of sludge due to increased sulfur content. However, acidic conditions favor the formation of sulfides, and sulfides are known to be a stronger poison than sulfates for catalytic reactions [29].

![Figure 3.5 Effect of pH on the extraction of carbon and sulfur at 250°C and a residence time of 10 min](image)

### 3.3.4 Effect of Sludge Loading

Figure 3.6 shows the effect of sludge loading on PASS concentration, percentage liquefied and percentage gasified at 250°C and pH 7 for a residence time of 10 min. There is a linear trend between sludge feed concentration and the corresponding concentration of solubilized organic matter. PASS concentration increases from 1.8wt% for 3wt% sludge to 7.6wt% for 15wt% sludge. The function that describes this relationship is as follows:

\[
\text{PASS concentration (wt%)} = M \times \text{Feed concentration (wt%)}
\]

Where M is the proportionality constant and equal to 0.53, the R² value is 0.99. As sludge concentration in the feed increases, nearly a fixed percentage of it is liquefied, represented by the slope of the line. This suggests that a quick way to estimate the concentration of organics in supernatant from hydrothermally treated activated sludge is to multiply the initial feed concentration by 0.53. *Goto et al.*
observed a similar trend in the SCWO of sludge [30]. Figure 3.6 also depicts the amounts of sludge liquefied and gasified during the treatment process. Increasing the sludge loading decreases the percentage of dry sludge that is liquefied; 80% at 3wt% sludge to 63% at 15wt% sludge. This is in contrast to the effect on the amount of sludge gasified, as it increased with increasing sludge loading; 2.8% at 3wt% sludge to 5% at 15wt% sludge. This is due to the total sample mass being kept constant at 10g. To change the concentration of the sludge, both the mass of water and sludge were adjusted accordingly, hence the apparent contradiction with the above result.

Table 3.5 summarizes the analysis of the gaseous products after thermal treatment. The observed trends in the gas composition can be explained by the ever increasing amount of carbon dioxide that is produced. Since it is the dominant gas produced it lessens the percentage of the other components even though their amounts stay relatively constant.

Table 3.5 Summary of gas analysis for different sludge loadings at 250°C for a residence time of 10 min

<table>
<thead>
<tr>
<th>Sludge wt %</th>
<th>Total Gas Yield (mmol/g)</th>
<th>H₂ (%)</th>
<th>CO (%)</th>
<th>CH₄ (%)</th>
<th>CO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.82</td>
<td>38.4</td>
<td>6.9</td>
<td>2.4</td>
<td>52.2</td>
</tr>
<tr>
<td>5</td>
<td>0.57</td>
<td>23.1</td>
<td>4.6</td>
<td>1.4</td>
<td>70.9</td>
</tr>
<tr>
<td>10</td>
<td>0.83</td>
<td>9.1</td>
<td>1.9</td>
<td>0.6</td>
<td>88.3</td>
</tr>
<tr>
<td>15</td>
<td>0.92</td>
<td>6.3</td>
<td>1.5</td>
<td>0.4</td>
<td>91.7</td>
</tr>
</tbody>
</table>
3.3.5 Direct Gasification Vs Pretreatment & Gasification

Figure 3.7 illustrates the comparison in the gasification yields of sludge at 3wt% and PASS with organics loading of 1.47wt%. Thermal pretreatment of sludge was conducted at neutral pH, 250°C and a residence time of 10 min. Gasification of PASS was performed at 380°C with 0.1g catalyst loading, and 5 min residence time. The total yield of produced gases for PASS was 16.5mmol/g compared to 8.2mmol/g for direct sludge gasification. The product gas in both cases was rich in hydrogen, containing about 63% H$_2$. Hydrogen yield for PASS was 10.3mmol/g which is nearly twice that of the corresponding value for untreated sludge. Similarly, methane yield of 2.3mmol/g for PASS was 3 times higher than that of untreated sludge. Finally, the yield of carbon dioxide for PASS and sludge were 3.7mmol/g and 2.2mmol/g, respectively. The results suggest the potential for greater gas yields from the SCWG of PASS over the direct gasification of the sludge itself, particularly at low gasification residence times.
3.3.6 Gasification of PASS

Figure 3.8 shows the effect of pretreatment pH on the gasification yield of PASS. It should be noted that all yields reported in this section are based on the feed to the gasification reactor. At pH 7, the total yield was 40mmol/g. By lowering the pH to acidic conditions, total yield decreased to 25mmol/g at pH 4 and subsequently increased again to 32mmol/g at pH of 1.5. Lower gasification yield at lower pH is likely due to increase in sulfide concentrations under acidic conditions. It is known that sulfides are nickel poisons, and it was expected that the acid regime would accumulate more of these species [29]. On the other side, mildly alkaline conditions appear to have no effect on the total gas yield. Table 3.6 shows the effect of sulfur poisoning on total gas yield for the gasification of activated sludge and PASS. Thermochemical pretreatment significantly decreases the amount of sulfur present in the feed compared to the original sludge and increased the total gasification yield. This figure suggests there is no advantage to pretreatment of sludge with acidic conditions, since the total gas yield for these treatments were the lowest.

Figure 3.8 Effect of pretreatment pH on total gas yield for NCWG of PASS at 350°C, 30 min residence time and 0.075g catalyst loading
Table 3.6 Comparison of the effect of S on gasification of Sludge vs PASS

<table>
<thead>
<tr>
<th>Feed</th>
<th>Sulfur content (g)</th>
<th>Sulfur content (wt%)</th>
<th>Total gas yield (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PASS</td>
<td>0.0005</td>
<td>0.70</td>
<td>39.7</td>
<td>This work</td>
</tr>
<tr>
<td>Sludge</td>
<td>0.002</td>
<td>0.75</td>
<td>27.5</td>
<td>Afif et al [25]</td>
</tr>
<tr>
<td>Sludge + added Sulfur</td>
<td>0.005</td>
<td>1.73</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.008</td>
<td>2.70</td>
<td>20.2</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.9 illustrates the effect of pH on the product gas yields. Methane and carbon dioxide yields followed a similar trend; they were highest at neutral pH and decreased under acid and alkali conditions. On the other hand, by increasing pH hydrogen yield appeared to decrease to a minimum at pH 4 and steadily increase afterwards. These results suggest that hydrogen is produced from the water gas shift reaction at an increased rate since NaOH is known to catalyze the water gas shift reaction via CO$_2$ capture through carbonate formation [31]. This is evident from the decrease in CO$_2$ in the gas phase with increasing H$_2$ and decreasing CH$_4$.

Figure 3.9 Effect of pretreatment pH on product gas yields for NCWG of PASS at 350°C, 30 min residence time and 0.075g catalyst loading

Figure 3.10 shows the CGR and HGR as a function of pH. Increasing pH increased HGR up to a maximum of 101% at pH 13. However, CGR was maximal (about 50%) at neutral condition and decreased when pH was either decreased or increased. These figures suggest that the preferred order of pretreatment for
hydrogen production is Thermo-alkali > Hydrothermal (treatment under neutral conditions) > Thermo-acid. Hydrothermal treatment is preferred over thermo-acid due to higher total gas yields, and the requirement of extremely low pH to achieve similar hydrogen yields. Thermo-alkali is preferred over both of the other treatments due to increased hydrogen yields, and increased total gas yields.

The effect of varying pretreatment temperature on the total gas yields, product gas yields, and on CGR and HGR for the NCWG of PASS at a catalyst loading of 0.075g and residence time of 30 min are shown in Figures 3.11-3.13. As temperature increased a shorter pretreatment residence time resulted in a higher total yield. Above 250°C, total yield for 2 min treatment was about 30% greater than that for 10 min treatment. A similar trend is observed for the measured product gas yields at temperatures above 250°C for both pretreatment times (Figure 3.12). Hydrogen was by far the major product above 250°C. Yields at 200°C were substantially lower than those at 250°C and 300°C for the 2 min treatment time. CGR and HGR for the gasification of PASS followed a similar trend to the total yield (Figure 3.13). These results suggest that there is no benefit to pretreatment at temperatures above 250°C, and that the optimum conditions for thermal pretreatment of PASS were 2 min and 250°C.
Figure 3.11 Effect of pretreatment temperature on total gas yield for NCWG of PASS at 350°C, 30 min residence time and 0.075g catalyst loading

Figure 3.12 Effect of pretreatment temperature on product gas yields for NCWG of PASS at 350°C, 30 min residence time and 0.075g catalyst loading
3.3.7 Comparison to previous works

Table 3.7 provides an account of some of the published literature on thermo and thermo-chemical pretreatment of activated sludge. It should be emphasized that the published literature on this topic is limited to sludge pretreatment for anaerobic digestion, whereas this work utilizes pretreatment prior to gasification. Comparison of pretreatment methods listed in Table 3.7 show that thermal pretreatment of sludge with or without addition of alkali or acid improved the subsequent anaerobic digestion by 14 to 75%. In comparison, thermal pretreatment of sludge increased the total yield by a factor of two.
Table 3.7 Comparison of Pretreatment of activated Sludge with previous works

<table>
<thead>
<tr>
<th>Substrate/feed for secondary treatment</th>
<th>Pretreatment Conditions</th>
<th>Secondary Treatment</th>
<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated Sludge (4.3% total solids)</td>
<td>175°C 60 min</td>
<td>Anaerobic Digestion: Batch 34 days 35°C</td>
<td>COD solubilization of 55% Increase in methane yield of 27%</td>
<td>Stuckey et al. [6]</td>
</tr>
<tr>
<td>Activated Sludge (7g/L)</td>
<td>0.3g NaOH/g VSS, 130°C, 5 min</td>
<td>Anaerobic Digestion: Batch, 10 days, 37°C</td>
<td>WAS solubilization of 70-80 % Increase in CH₄ production from 32- 42%</td>
<td>Tanaka et al. [9]</td>
</tr>
<tr>
<td>Industrial Activated Sludge (7g/L)</td>
<td>7g NaOH/g VSS, 121°C 30 min</td>
<td>Anaerobic Digestion: Batch 7 37°C</td>
<td>COD solubilization of 86.5% Increase in biogas production from 3657 – 5037 L/m³</td>
<td>Kim et al. [15]</td>
</tr>
<tr>
<td>Activated Sludge (17g/L)</td>
<td>KOH, pH 10, 130°C, 60 min</td>
<td>Anaerobic Digestion: Batch 24 days 35°C</td>
<td>40% WAS solubilization with 60% COD solubilization Increased biogas production of 30 %</td>
<td>Valo et al. [16]</td>
</tr>
<tr>
<td>Activated Sludge (17g/L)</td>
<td>pH 2, 24 hours refrigerated</td>
<td>Anaerobic Digestion: Batch 21 days, 35°C</td>
<td>COD solubilization of 12% Increase in biogas production of 17 %</td>
<td>Devlin et al. [20]</td>
</tr>
<tr>
<td>Activated Sludge (5% total solids)</td>
<td>121°C, 20 min</td>
<td>Anaerobic Digestion: Batch 30 hours, 35°C</td>
<td>SCOD extraction of 56.5% Increase in hydrogen from 1.34mg/g COD to 4.44mg/g COD</td>
<td>Guo et al. [26]</td>
</tr>
<tr>
<td>Activated Sludge (14.6g/L)/ filtrate (same as PASS)</td>
<td>250°C, 10 min</td>
<td>Supercritical water gasification: Batch 380°C 5 min, 0.1g catalyst loading</td>
<td>Was solubilization of 80%. 2x and 3x increase in yield for H₂ and CH₄ compared to direct gasification of activated sludge</td>
<td></td>
</tr>
<tr>
<td>Activated Sludge (3wt%) / PASS (15g/L)</td>
<td>250°C, 10 min</td>
<td>Near-critical water gasification: Batch 350°C 30 min, 0.075g catalyst loading</td>
<td>WAS solubilization of 80% total gas yield of 39.7mmol/g, H₂ yield of 24.8mmol/g</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>6.7ml 0.127M NaOH, pH 13, 250°C, 10 min</td>
<td></td>
<td>Was solubilization of 91% total gas yield of 42.8mmol/g, H₂ yield of 31mmol/g</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Conclusion

Gasification of PASS suggests the potential for greater gas yields compared to the direct gasification of activated sludge, particularly at low gasification residence times. Hydrogen yield for PASS was 10.3mmol/g; nearly twice that for untreated sludge. Methane yield of 2.3mmol/g for PASS was 3 times higher than that of untreated sludge. For gasification of thermally pretreated sludge, results suggest that there is no benefit to pretreatment at temperatures above 250°C, and that the optimum condition for thermal pretreatment of PASS was 2 min and 250°C. The order of effectiveness for sludge treatment as a means for hydrogen production was found to be Thermo-alkali > Thermal > Thermo-acid. Of the thermo-alkali conditions investigated, treatment at 250°C and pH 13 for 10 min was found to perform optimally for hydrogen production with total gas yield of 42.8mmol/g, hydrogen yield of 31mmol/g.

Liquefaction of WAS over 200°C to 300°C and for residence times longer than 10 min was relatively independent of temperature. Thermo-alkaline treatment increased WAS solubilization to 90% at pH 13. Pretreatment reduces the amount of sulfur available to poison the catalyst. Thermo-acidic treatment extracted the least sulfur and thermo-alkali the most however gasification was more effective for the later treatment. Pretreatment feed concentration is linearly correlated to the solubilized sludge concentration in the range of 3-15wt% sludge. This demonstrates that as feed concentration increases, a fixed percentage is solubilized.
3.5 References


4 Near-critical Water Gasification of Pretreated Activated Sludge Supernatant (PASS)

4.1 Introduction

Concerns over global warming have led to the search for new technologies for the production of energy from renewable resources. One such technology is that of biomass conversion to biofuels. There are many sources of biomass and most tend to be derived from plant matter. However, with increasing prevalence of biomass from animal wastes, and wastewater treatment is gaining interest. The conversion of waste activated sludge to value added products is attractive as it is considered a renewable energy source, and its current disposal is of great environmental concern.

Activated sludge is a mixture of microorganisms, organic and inorganic matter. It is a by-product of wastewater treatment. It has water content greater than 95 wt% and trace amounts of heavy metal such as arsenic, mercury, and nickel [1-3]. Typical disposal methods of landfilling, incineration, and gasification require a dry sludge feed which is very expensive. There is also concern over environmental contamination.

Supercritical water (SCW), water above the critical point of 374°C and 22.1 MPa, is able to completely dissolve organics and permanent gases, making it an excellent medium for organic conversion reactions [4]. This is because of a substantially reduced static relative dielectric constant. This makes it an ideal medium for the conversion of wet biomass. Supercritical water gasification (SCWG) converts organic matter to value-added products such as methane and hydrogen. Typically, steam reforming, water gas shift and methanation reactions are thought to take place. Product gases are hydrogen, methane and carbon dioxide with trace amounts of carbon monoxide.

Biomass is complex necessitating the use of model compounds to investigate SCWG under varying operating conditions. Minowa et al. studied the gasification of cellulose and glucose concluding that the decomposition of these substrates were essentially the same [5-8]. Lee et al. studied the catalyst-free gasification of 0.6 M glucose in supercritical water at a temperature range from 480°C to 750°C and 28 MPa. The yield of hydrogen among gaseous products increased with increasing temperature above 660°C. The yield of carbon monoxide decreased with temperature, most probably due to the role of a water-gas shift reaction. Carbon gasification efficiency reached 100% at 700 °C [9].
Catalysts have been investigated to reduce the severity of the operating conditions, and to facilitate the SCWG of real biomass. *Muangrat et al.* studied NaOH as a homogeneous catalyst for biomass gasification with the result of increased methane and hydrogen yields. Further to this it was shown that the presence of NaOH catalyzed the water gas shift reaction through carbon dioxide capture [10]. *Garciajarana et al.* investigated the SCWG of industrial organic wastes using KOH at 450°C. It was found that KOH promoted the water gas shift reaction and produced a hydrogen rich gas [11]. Since homogeneous catalysts are hard to recover, heterogeneous catalysts have also been investigated.

*Takuya et al.* studied the SCWG of lignin and cellulose, and found that gas yields increased with increasing catalyst loading over a reduced nickel catalyst [12]. Literature shows a diverse collection of active catalysts for SCWG [7, 13-19]. Special attention has been paid to Raney type catalysts, due to their extremely large surface areas. *Azadi et al.* investigated the activity of several Raney type catalysts for SCWG of glucose. Raney Nickel had the highest activity [18,19].

Literature shows that the direct gasification of sewage sludge produces a hydrogen rich gas stream. *Xu et al.* studied the gasification of sewage sludge with an activated carbon catalyst at 600°C and 34.5 MPa. Complete conversion of the sludge was achieved with a total gas yield of 77%, the major component was carbon dioxide [13]. The gasification of sewage sludge suspended in cornstarch was also studied by *Xu et al.* near complete conversion was observed with a hydrogen rich product gas (42%) [20]. *Schmieder et al.* studied the SCWG of sewage sludge at 450°C and 330 bar with K₂CO₃ as a homogeneous catalyst. A hydrogen rich (48%) was obtained [21]. *Yamamura et al.* reported that sewage sludge was not completely decomposed after SCWG at 450°C, 47.1 MPa and 120 min in the presence of RuO₂ catalyst. Although the product gas was rich in hydrogen it contained a large fraction of methane and total yield was low, 11% based on carbon and 23% based on hydrogen [22]. *Afif et al.* used Raney nickel catalyst in near-critical water to gasify WAS. A hydrogen rich (46%) product gas was produced with moderate carbon conversion (58%) [16].

However, little is known in terms of the gasification of PASS. *Guo et al.* studied the anaerobic digestion of pretreated sewage sludge filtrate which increased hydrogen yield by a factor of three over sludge alone [23]. Although not the same process, applicability in terms of feed substrate is valid. There is no systematic examination of the performance of Raney nickel for SCWG of PASS. It is the aim of this study to elucidate the effect of SCWG parameters on the gasification of PASS using Raney nickel.
4.2 Experimental Setup

The apparatus used in this research can be found in Figure 3.1 of chapter 3. The reactor is 316 SS and has a volume of 50ml. Raney Nickel 4200 was obtained from Sigma Aldrich (Canada) in slurry form with 50wt% solid content. PASS was obtained from pretreating activated sludge under hydrothermal (250°C and pH 7) and thermo-alkali (250°C and pH 13) for a residence time of 10 min. The particulars of this process and the effects on the sludge are described in the previous chapter. PASS was diluted to 15g/L. The reactor was loaded with 5 ml of PASS and 5ml nano-pure water to obtain a constant organics loading of 0.075g in each experiment. The desired amount of catalyst was added prior to each experiment and the reactor was immersed in a molten salt bath for the desired residence time. The salt bath was a mixture of potassium nitrate, sodium nitrate, and sodium nitrite with a high heating rate (~500°C/min). Temperature was measured and controlled using a K-type thermocouple (Omega, Laval, Canada) and a NX4 PID controller (Hanyoung USA, FL.). After the prescribed reaction time, the reactor was rapidly cooled by immersion in a cold water bath. The internal pressure was measured using a digital pressure gauge (Cecomp Electronics, API Inc., IL, USA), and was used to determine total gas yield. Any gas evolved during the process was collected in a 0.3L gas bag and analyzed in a Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector (Hewlett Packard,USA). Specific yields were determined based on the total gas yield and the product distribution determined from the gas chromatograph analysis.

Elemental Analysis of solid residues from pretreated sludge was conducted using a 2400 Series II CHNS analyzer (Perkin Elmer, USA) operating in C-H-N mode. Prior to the CHN analysis, solid residue was dried at 80°C for 24 hours. Total organic carbon (TOC) was measured using a TOC analyzer (TOC-VWP, Shimadzu, Japan). The carbon and hydrogen content of the PASS was determined from the CHN and TOC information through a mass balance (i.e. the amount in the residue was subtracted from the amount in the dry sludge and the difference was assumed to be in the PASS. Carbon gasification ratio (CGR) and hydrogen gasification ratio (HGR) were determined by calculating the carbon and hydrogen content of the measured gas products, and dividing by the amount of carbon or hydrogen in the PASS as determined above. All experiments were run at least in triplicate. CGR and HGR are mathematically defined as follows:

\[
\text{CGR} = \frac{Y_{\text{CO}} + Y_{\text{CH}_4} + Y_{\text{CO}_2}}{\text{mmol C/g PASS}} \times 100
\]

\[
\text{HGR} = \frac{2Y_{\text{H}_2} + 4Y_{\text{CH}_4}}{\text{mmol H/g PASS}} \times 100
\]
4.3 Results and Discussion

In this study the effects of residence time, temperature and catalyst loading on the NCWG of PASS are investigated. Results are reported as gas yields, CGR and HGR. Carbon monoxide is not shown in the figures as its production was less than 0.3mmol/g for both conditions with respect to residence time, temperature and catalyst loading.

4.3.1 Effect of Residence Time

Figure 4.1 illustrates the effect of residence time on the total gas yield for PASS gasification at 350°C with a catalyst loading of 0.075g. Total yield increased rapidly to plateau around 42mmol/g after approximately 30 min for both pretreatments. This suggests that equilibrium was achieved after 30 min under these gasification conditions. Although total yield is approximately the same for both treatments this may not be the case for product gas yields. Nearly 41% of the maximum yield was obtained after 5 min, tripling the residence time increased yields by a factor of 2, illustrating that further increases in residence time have a reduced return on gas yield, this is consistent with the finding of Afif et al. for the gasification of WAS [16]. Similar trends were observed for hydrogen, carbon dioxide and methane yields, as well as for CGR and HGR, as seen in Figures 4.2 and 4.3 respectively.

Both neutral and alkaline pretreatments produced generally similar product yields with respect to residence time (Figure 4.2). Yields for \( \text{H}_2 \), \( \text{CO}_2 \) and \( \text{CH}_4 \) plateaued near 28mmol/g, 10mmol/g and 3mmol/g respectively after 30 min. However at a residence time of 30 min, noticeable differences in product gas yields were observed between alkali and neutral PASS: the alkali PASS yielded nearly 24% more hydrogen, and around 27% less carbon dioxide and methane than the neutral PASS. This could be due to \( \text{CO}_2 \) capture since sodium hydroxide is known to promote the water gas shift through reaction with \( \text{CO}_2 \) to form carbonate [10].

The data suggests that the carbonate forming reaction reached equilibrium after 30 min and beyond this point, methanation reactions resulted in a decrease in the hydrogen yield and an increase in \( \text{CH}_4 \) yields. Furthermore, the ratio between the reduction in hydrogen yield to the increase in the yield of methane between 30 min and 60 min residence times was 3.77, which is close to the stoichiometric value of 4 for the methanation reaction. CGR and HGR reached plateau values of around 45% and 92%, respectively, for the neutral and alkali conditions (Figure 4.3).
Figure 4.1 Effect of residence time on total gas yield for NCWG of PASS at 350°C and 0.075g catalyst loading

Figure 4.2 Effect of residence time on the product gas yields for NCWG of PASS at 350°C and 0.075g catalyst loading
4.3.2 Effect of Temperature

Figure 4.4 illustrates the effect of changing temperature from subcritical to supercritical conditions (i.e. from 320°C to 410°C) on the total gas yield. Catalyst loading and residence time were maintained at 0.075 g and 30 min. As can be seen from the figure, total gas yields reached plateaus at nearly 39mmol/g and 43mmol/g above 350°C for neutral and alkaline PASS. It is also interesting to note that alkaline pretreatment resulted in approximately 25% higher total yield than the neutral treatment at 320°C, while at 380°C the neutral PASS had about 10% more gas yield.

The effect of temperature on product gas yields for PASS can be seen in Figure 4.5. Hydrogen yield follows a similar trend to that outlined above since it is the major component of the gas phase constituting 60% to 73% of gasification products. For alkaline treatment, hydrogen yield first increased to a maximum of 31mmol/g at 350°C, then decreased to a plateau around 26mmol/g in the supercritical region (380°C -410°C). For neutral treatment, hydrogen yield increased monotonically to a plateau at nearly 29mmol/g above 350°C. This figure clearly shows that the lower total yield of neutral PASS under subcritical temperatures was mainly due to its lower hydrogen yield under these conditions. In
supercritical conditions, however, both hydrogen and methane production for neutral PASS were higher compared to those of alkali PASS, hence resulting in a higher total yield. The linear trend in methane and carbon dioxide production is consistent with the findings of Afif et al. [16]. The results suggest that alkaline treatment performs better at subcritical gasification temperatures.

CGR and HGR for neutral and alkali PASS followed similar trends to those for hydrogen. It is worthy to note that a maximum HGR of 101% was achieved under alkaline conditions at 350°C, while maximum HGR for neutral condition was 91%. Again the linear trends are consistent with literature.

Figure 4.4 Effect of temperature on total gas yield for pH 7 and pH 13 PASS, 30 minute residence time, 0.075g catalyst loading
Figure 4.5 Effect of temperature on product gas yield for pH7 and pH 13 PASS, 30 minute residence time, 0.075g catalyst loading

Figure 4.6 Effect of temperature on CGR & HGR for pH7 and pH 13 PASS, 30 minute residence time, 0.075g catalyst loading
4.3.3 Effect of Catalyst Loading

Figure 4.7 illustrates the effect of varying Raney nickel loading on the total gas yield from the gasification of PASS at 350°C and 30 min residence time. Figures 4.8 and 4.9 show the yields of product gases and CGR and HGR as functions of catalyst loading.

From Figure 4.7 it is evident that both pretreatment conditions appear to reach plateaus above catalyst loading of 0.075g or a 1:1 weight ratio of catalyst to solubilized sludge. The figure suggests that at catalyst to feed ratios less than 1, hydrothermal pretreatment produces approximately 25% more gas than thermochemical (alkaline) treatment. Increasing the catalyst loading ratio from 0.5 to 1 nearly doubled the total yield for alkali PASS while that of neutral PASS increased by 50% indicating that the alkali PASS is likely more sensitive to Raney Nickel loading. However, at higher catalyst to feed ratios the difference between the two pretreatment methods nearly vanished.

Increasing catalyst loading has a positive effect on the yields of hydrogen (Figure 4.8). For the alkali PASS the large slope of the hydrogen yield suggests that it is sensitive to catalyst loading up to 0.075g. Doubling the amount of catalyst to 0.15g had little effect on the yield. The plateau value was around 30mmol/g. The effect was more pronounced for the alkali treated PASS likely due to the reduced methanation and the promotion of the water gas shift reaction by sodium hydroxide at the lower catalyst loadings. Methane yield shows a linear correlation with respect to increasing Raney nickel loading, with little difference between the yields for both conditions, while carbon dioxide levels off above a catalyst loading of 0.075g.

Since carbon dioxide and hydrogen are the major gaseous products, the CGR and HGR in Figure 4.9 mirror the trends described above for these species. HGR plateau at nearly 100% for both types of PASS. CGR increased linearly to nearly 50% at a loading ratio of 1.5 for alkali PASS and plateaued around the same value at a ratio of 1 for neutral PASS.
Figure 4.7 Effect of Raney nickel loading on total gas yield for pH7 and pH 13 PASS, 30 min residence time, 350°C

Figure 4.8 Effect of catalyst loading on product gas yield for pH7 and pH 13 PASS, 30 min residence time, 350°C
4.3.4 Comparison to Previous Works

Table 4.1 provides an account of published literature on SCWG of activated sludge. The key distinction between this work and the literature is the nature of the feed. Previous research on this topic was limited to the gasification of a slurry of sludge and water. This work utilizes a pretreated activated sludge supernatant. The advantages of this work compared to previous literature for the conversion of WAS to value added products are ease of sludge delivery; a liquid feed stream is easily adapted for continuous operation over a slurry. The literature is dominated by high temperature high pressure catalytic gasification this creates an environment where special materials are needed for operation. Utilizing subcritical conditions avoids the corrosion issues and specialty materials required for supercritical conditions. This work demonstrates increased hydrogen yields with low yields of carbon dioxide and methane. Carbon conversion falls in the middle of the range provided in the literature, 11-100%.
Table 4.1 Comparison of SCWG of activated sludge with previous works

<table>
<thead>
<tr>
<th>Feed</th>
<th>Concentration (wt%)</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Reactor Type</th>
<th>Time/Flowrate</th>
<th>Catalyst</th>
<th>CGR (%)</th>
<th>HGR (%)</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</td>
<td>2.8</td>
<td>600</td>
<td>34.5</td>
<td>Continuous</td>
<td>2g/min</td>
<td>Coconut Shell Activated Carbon</td>
<td>100</td>
<td>-</td>
<td>2.2</td>
<td>3.3</td>
<td>1</td>
<td>61</td>
<td>9</td>
<td>Xu et al. [13,20]</td>
</tr>
<tr>
<td>Activated Sludge/Corn Starch</td>
<td>2.8/5.1</td>
<td>650</td>
<td>28</td>
<td>Continuous</td>
<td>2g/min</td>
<td>Coconut Shell Activated Carbon</td>
<td>100</td>
<td>-</td>
<td>42</td>
<td>1</td>
<td>17</td>
<td>39</td>
<td>-</td>
<td>Schmieder et al. [21]</td>
</tr>
<tr>
<td>Activated Sludge</td>
<td>2.3</td>
<td>450</td>
<td>33</td>
<td>Batch</td>
<td>120min</td>
<td>-</td>
<td>55</td>
<td>-</td>
<td>49</td>
<td>3</td>
<td>17</td>
<td>31</td>
<td>-</td>
<td>Yamamura [22]</td>
</tr>
<tr>
<td>Activated Sludge</td>
<td>3.2</td>
<td>450</td>
<td>47.1</td>
<td>Batch</td>
<td>120min</td>
<td>K₂CO₃</td>
<td>85</td>
<td>-</td>
<td>47</td>
<td>1</td>
<td>15</td>
<td>37</td>
<td>-</td>
<td>Zhang et al. [24]</td>
</tr>
<tr>
<td>Activated Sludge</td>
<td>4.5</td>
<td>500</td>
<td>37</td>
<td>Batch</td>
<td>60min</td>
<td>-</td>
<td>16</td>
<td>13</td>
<td>22</td>
<td>15</td>
<td>17</td>
<td>46</td>
<td>-</td>
<td>Afif et al. [16]</td>
</tr>
<tr>
<td>Activated Sludge</td>
<td>3.0</td>
<td>380</td>
<td>23</td>
<td>Batch</td>
<td>15min</td>
<td>-</td>
<td>10</td>
<td>13</td>
<td>6</td>
<td>9</td>
<td>69</td>
<td>-</td>
<td>-</td>
<td>This Work</td>
</tr>
<tr>
<td>PASS pH 7</td>
<td>0.75</td>
<td>350</td>
<td>20</td>
<td>Batch</td>
<td>30min</td>
<td>Raney Nickel</td>
<td>58</td>
<td>84</td>
<td>46</td>
<td>0.1</td>
<td>25</td>
<td>29</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PASS pH 13</td>
<td>0.75</td>
<td>350</td>
<td>20</td>
<td>Batch</td>
<td>30min</td>
<td>Raney Nickel</td>
<td>47</td>
<td>101</td>
<td>73</td>
<td>0.5</td>
<td>6</td>
<td>21</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
4.4 Conclusion

In this study, Raney nickel catalyst was used to gasify PASS in near critical water under different operating conditions. At a heating rate of approximately 500°C /min, the catalytic NCW gasification of PASS at 350°C reached equilibrium after 30 min for both neutral and alkaline conditions. No significant change was observed at longer reaction time. The major product gas was hydrogen, comprising 65-75% of total gas yield for each pretreatment. The total gas and hydrogen yields obtained at subcritical temperatures were 25% greater for alkali PASS than neutral PASS. Since total yields obtained between 350°C and 410°C were similar; approximately 40mmol/g, indicating that this pretreatment can be used to effectively lower the operating temperature of the process while maintaining high yields.

Total gas yields increased initially up to a catalyst loading of 0.075g. Increasing loading beyond this did not impart any further evolution of product gases for either treatment. Both treatments plateaued around 42mmol/g. Alkaline treated PASS has low gasification efficiency in terms of carbon conversion; this is likely due to carbon capture through a carbonate or bicarbonate formation pathway as described in literature. As a result of this PASS gas has a large hydrogen yield due to water gas shift promotion.
4.5 References


5 Conclusions & Recommendations

5.1 Conclusions

This thesis reports the research done on the pretreatment of activated sludge and the subsequent near-critical water gasification (NCWG) as a method for waste activated sludge (WAS) disposal. The research was split into two phases. Phase one dealt with pretreatment methods and began with thermal pretreatment of WAS to elucidate effective conditions in hot compressed water. It then moved to the assessment of thermochemical treatment. Several suitable treatments were identified and applied to sludge to generate pretreated activated sludge supernatant (PASS). The second phase of this work dealt with the gasification of PASS in near-critical water and the performance assessment of the pretreatment as applied to gasification. Here is a summary of the key conclusions developed over the course of this project:

- NCWG of PASS is favourable compared to the direct gasification of activated sludge, especially for short gasifier residence times in a batch operation mode. This is promising for the adaptation of this to a continuous process. It would allow for easy delivery to a continuous gasifier via a standard pumping apparatus since the sludge is solubilized and the gas yield for PASS is nearly double that for sludge on a mmol of gas/g feed basis.

- Results suggest there is no benefit for pretreatment above 250°C for NCWG of PASS, with the optimal thermal treatment being 2min at 250°C.

- The order of effectiveness for sludge treatment for hydrogen production was found to be Thermo-alkali > Thermal > Thermo-acid as quantified by NCWG. Although a different method of efficacy testing, the results are consistent with literature about the pretreatment of activated sludge for anaerobic digestion.

- Residence times longer than 10 min impart no additional benefit for the liquefaction of waste activated sludge in hot compressed water. There is also no apparent difference between the percentage of sludge liquefied at 200°C, 250°C or 300°C beyond a residence time of 10 min.
• Pretreatment reduces the amount of sulfur available to poison heterogeneous catalysts, such as the Raney Nickel used in this work, thermo-acidic treatment extracted the least sulfur and thermo-alkali the most, however gasification was more effective for the later treatment.

• Pretreatment feed concentration is linearly correlated to the solubilized sludge concentration in the range of 3-15wt% sludge. This demonstrates that as feed concentration increases, a fixed percentage is solubilized.

• For the NCWG of alkaline PASS using Raney nickel, a moderate catalyst loading (1g catalyst / g of feed) is needed to achieve high hydrogen content in the product gas.

• In the batch test used, the total gas and hydrogen yields obtained at subcritical temperatures were 25% greater for alkali PASS than neutral PASS. Total yields obtained between 350°C and 410°C were similar; approximately 40mmol/g, indicating that this pretreatment can be used to effectively lower the operating temperature of the process while maintaining high yields.

• Alkaline treated PASS has low gasification efficiency in terms of carbon conversion; this is likely due to carbon capture through a carbonate or bicarbonate formation pathway as described in literature. As a result of this PASS gas has a large hydrogen yield due to water gas shift promotion.

5.2 Recommendations

The scope of this project imposed limitations on the amount of work that could realistically be done, as such there are aspects to this project that were not addressed in this thesis and require supplementary work to draw further conclusions.

• In this thesis only two pretreatment methods were investigated, to make the study complete investigation of other thermochemical, mechanical, or combined pretreatments for WAS solubilization should be examined for suitability in application to NCWG.

• Characterization of liquid effluent before and after the gasification process should be carried out as this analysis could elucidate details on the pathway for the carbon capture and subsequent low carbon conversion in the gas phase. This could allow for manipulation of process variables to push equilibrium further in favour of hydrogen production.
• Use of a continuous reactor system would be advised complete the study on the effectiveness of waste activated sludge pretreatment, and subsequent gasification of PASS.

• Investigation of the effect of increased feed concentration at equivalent catalyst to feed ratios would help to complete the picture for NCWG of PASS. Increasing feed concentration tends to decrease the normalized gas yield. It would be interesting to see if the yields are similar as it could be relevant for industrial applications.

• Investigation of the effectiveness of the pretreatment methods for an industrial WAS source, i.e. pulp and paper mill WAS.
## 6 Appendix A

**Table 6.1 Comparison of pH before and after thermochemical and hydrothermal treatment**

<table>
<thead>
<tr>
<th>Pretreatment Conditions</th>
<th>Thermochemical Treatment pH</th>
<th>pH after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermochemical Treatment pH</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Acid treatment, 250°C 10 min</td>
<td>2</td>
<td>4.5</td>
</tr>
<tr>
<td>Acid treatment, 250°C 10 min</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Hydrothermal treatment, 250°C 10 min</td>
<td>7</td>
<td>6.5</td>
</tr>
<tr>
<td>Alkali treatment, 250°C 10 min</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>Alkali treatment, 250°C 10 min</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>Alkali treatment, 250°C 10 min</td>
<td>13.5</td>
<td>9</td>
</tr>
</tbody>
</table>

The above table shows how the adjusted pH changes after pretreatment. In all thermochemical treatments, pH is neutralized. For acidic treatment this is likely due to alkali salts present in the sludge. For the Alkali treatment it is likely due to carbon dioxide reacting to form carbonic acid during the pretreatment.