OPERATION OF SOLID OXIDE FUEL CELLS ON
ANAEROBICALLY DERIVED WASTEWATER TREATMENT
PLANT BIOGAS

by

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Abstract

Solid Oxide Fuel Cells (SOFCs) have been researched for operation on anaerobic digester (AD)-derived biogas at wastewater treatment plants (WWTPs). SOFCs have been shown to perform well on light hydrocarbon fuels and the use of AD-derived biogas would provide an opportunity for the CH$_4$ produced in anaerobic digestion to be used as a renewable fuel.

Tests were conducted at different levels of H$_2$ dilution (using N$_2$, Ar and CO$_2$ as diluent gases, plus H$_2$O) at the Fuel Cell Research Centre (FCRC) to examine the performance of tubular SOFCs. When gases that are inert in SOFC reactions are used there is a decrease in cell performance, but when CO$_2$ was used as a diluent a decrease in cell performance was higher due to the reverse water-gas shift reaction (WGS reaction) reducing the partial pressure of H$_2$ in the gas mixture. A computer simulation was developed to model the dilution test results and predict SOFC system efficiency and GHG emissions. The simulation indicated that the system electrical efficiency is higher for a steam to carbon ratio of 2 then a steam to carbon ratio of 1 due to the increased partial pressure of H$_2$ in the reformate that results from the increased H$_2$O from the WGS reaction going towards equilibrium. The increase in fuel cell efficiency from the higher H$_2$ partial pressure can offset the decrease in efficiency that can be caused by the need to raise steam for the fuel processor/reformer. The reduction in GHG emissions is estimated to be approximately 2,400 tonnes CO$_2$, 60 kg CH$_4$ and 18 kg N$_2$O, annually.

Testing was conducted using a simulated biogas reformate mixture that was developed based on an average biogas composition for North America, determined through a research initiative in which urban areas with populations over 150,000 in the United States and 50,000 in Canada were solicited to participate in a survey of biogas composition. The biogas reformate composition was determined to be 66.7% H$_2$, 16.1% CO, 16.5% CO$_2$ and 0.7% N$_2$, which was
then humidified to 2.3 and 20 mol% H_2O. The reformate tests conducted at the higher humidification level yielded a better performance than those at the lower humidification because the WGS reaction produced more H_2 when additional H_2O was provided, resulting in higher cell performance. The cell was found to perform more efficiently during the reformate tests than the dilution tests, indicating that the WGS reaction had an impact on the fuel utilization by producing more H_2 when H_2O and CO were present in the gas mixture.

It was concluded that WWTP AD-derived biogas, when cleaned effectively to remove H_2S, Si compounds, halides and other contaminants, could be reformed to provide a clean, renewable fuel for SOFCs. Biogas/SOFC systems could provide electricity and heat to WWTPs, as well as reduce GHG emissions, thus reducing their energy costs and environmental impact.
Co-Authorship

Chapter 3 through 6 of this thesis will be submitted for publication in peer reviewed scientific journals. The presented work was carried out by Jillian Lackey, with the assistance of the indicated co-authors who provided valuable comments, suggestions and revisions to the manuscripts.

CHAPTER 3
A Review of Biogas Composition and Uses in North America
Jillian Lackey, Allison Maier, Pascale Champagne, Brant Peppley
Manuscript will be submitted to Renewable and Sustainable Energy Reviews

CHAPTER 4
The Performance of Anode Supported Tubular Solid Oxide Fuel Cells on Dilute Hydrogen Gas
Jillian Lackey, Pascale Champagne, Brant Peppley
Manuscript will be submitted to the Journal of Hydrogen Energy

CHAPTER 5
Biogas as a Renewable Fuel at WWTPs: A Modeling Approach to Determining Efficiency and Environmental Impact
Jillian Lackey, Stephen Wartman, Pascale Champagne, Brant Peppley
Manuscript will be submitted to the Journal of Power Sources
CHAPTER 6

Performance of an Anode-Supported Tubular Solid Oxide Fuel Cell on Simulated Biogas Reformate

Jillian Lackey, Pascale Champagne, Brant Peppley

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Chapter 1

Introduction

1.1 Background Overview

Solid oxide fuel cells (SOFCs) operating on biogas produced through the anaerobic digestion (AD) process can present an opportunity to utilize the readily available fuel produced at wastewater treatment plants (WWTPs) to generate ‘clean’ electricity and heat. Harmful greenhouse gas (GHG) emissions form the facility would also be reduced as utilizing the biogas would prevent it from being flared and released to the atmosphere because a SOFC produces lower emissions of NOx, SOx, hydrocarbon pollutants (Ormerod, 2003; Skok & Eschbach, 2005; Kordesch & Simader, 1995). Flaring biogas does not capture energy and is intended only to serve as a means of reducing the GHG emissions from the facility by converting CH4 to CO2, which 23 times less environmentally potent (Peppley, 2006). Research by Jiang & Virkar (2003) reported that cell performance of SOFCs operating on dilute H2 decreases when the diluent is an inert gas in fuel cell reactions; but, when CO is used as a diluent the cell performance is similar to that of pure H2 fuel because of the water-gas shift (WGS) reaction. It was expected that the anode-supported tubular SOFC tested at the FCRC would display similar results when operated on dilute H2 and from this we were confident that operation on AD-derived simulated biogas reformate would also show positive results.

SOFCs typically operate on pure H2 fuel but have shown the potential to operate on light hydrocarbon fuels (such as CH4) that can be reformed to H2-rich fuel. This H2-rich fuel can be derived from biogas produced through the AD-process. AD-derived biogas is typically composed of CH4 and CO2 with smaller concentrations of CO, N2, H2, H2S and Si compounds, but can be
cleaned-up to improve the quality and H$_2$ component (Wheeldon, Caners, Karan, & Peppley, 2007). The cleaned biogas can be reformed to increase the H$_2$ partial pressure and decrease the proportion of other constituents to increase cell performance.

It is important to understand the cell performance that can be expected when SOFCs are operating on dilute H$_2$ because biogas produced through AD can contain varying partial pressures of H$_2$. Due to this variance in H$_2$ partial pressure in AD-derived biogas, it is necessary to study SOFC cell performance on different partial pressures of H$_2$ with different diluent gases that can cause changes in cell performance due to diluent effects and the forward or reverse WGS reactions. Typically H$_2$ is the desired fuel to use in SOFCs, but H$_2$ does not occur naturally in the environment and requires energy to be created. The use of AD-derived biogas could provide a renewable source of H$_2$ for electrical generation.

1.2 Research Objectives

The research conducted and presented in this thesis will present an overview of the possibility of the utilization of AD-derived biogas in a SOFC.

The main objectives of this research were to:

1) Understand the variability of biogas composition and production at WWTPs and determine variations that occur at various sites throughout Canada and the United States. A voluntary survey was conducted soliciting data from urban areas with populations over 150,000 in the United States and 50,000 in Canada.

2) Determine the cell performance of SOFCs operating on dilute H$_2$ fuels using CO$_2$, N$_2$ and Ar as diluents.
3) Develop a simulation in UniSIM to model the performance of a SOFC system operating on the dilute H₂ fuel gas mixtures (for which data was collected during the diluent tests) to determine the system efficiency, GHG emissions and expected system performance.

4) Determine the cell performance of SOFCs operating on simulated biogas reformate. The simulated biogas reformate composition is based on the results of a UniSIM simulation that models reformation reactions based on an initial biogas composition of 60% H₂ and 40% CO₂.

1.3 Thesis Organization

This thesis is composed of seven chapters. Chapter 1 is an introduction to introduce the background information, the objectives of the research and the organization of the remainder of the thesis. A survey of biogas composition in North America is presented in Chapter 2. Experimental results of dilution testing and operation on simulated biogas reformate are presented in Chapters 4 and 6. Chapter 5 presents the results of a simulation developed in UniSIM to model the dilution testing results to determine system efficiency, system performance and GHG emissions. The four manuscripts presented in Chapters 3 to Chapter 6 will be submitted for publication to peer-reviewed journals. Chapter 7 concludes the thesis with recommendations for future work.

Chapter 2 is a review of literature that examines the different variations of SOFCs that are operable on AD-derived biogas as well as the production and optimization of AD-derived biogas at WWTPs. The performance of different types of fuel cells at WWTPs is examined through the inclusion of case studies to serve as examples of where AD-derived biogas has been used as a renewable fuel.
A survey was conducted to determine the AD-derived biogas composition from urban areas with populations over 150,000 in the United States and 50,000 in Canada that utilize AD technologies. The results of the survey are presented in Chapter 3. The biogas composition and production data obtained through this survey provided a basis for the reformation simulation in UniSIM that was used to determine the composition of the simulated biogas reformate. It is important to understand the composition and variance in composition of AD-derived biogas in order to design appropriate biogas conditioning systems and operate SOFC systems effectively at WWTPs.

SOFC cell performance data was collected using diluted H$_2$ as a fuel, with N$_2$, Ar and CO$_2$ as diluents at H$_2$ concentrations of 10%, 25% and 65% H$_2$, which was humidified to 2.3 mol% H$_2$O. The results of the dilution tests are reported in Chapter 4. Dilution testing was required because AD-derived biogas is predominately CH$_4$ and CO$_2$ that is reformed to a H$_2$ rich fuel mixture, but the resulting fuel mixture is not 100% H$_2$ so it was necessary to analyze the SOFC performance when fuels that were not 100% H$_2$ were used.

Chapter 5 presents the results of a UniSIM simulation that was developed to model the SOFC system performance, system efficiency and GHG emission reductions that could be expected if a biogas/SOFC system was implemented at the Utilities Kingston Ravensview facility. The empirical model that was implemented into UniSIM was developed based on the results of the dilution testing that was conducted.

Chapter 6 presents the results of the lab testing conducted with the SOFC operating on the simulated biogas reformate mixture. The results presented are reflective of an anode-supported tubular SOFC operating at 800°C and atmospheric pressure and using air as a cathode fuel. Cell performance (voltage) was recorded for the current density range of 0-500 mA/cm$^2$. 

4
Chapter 7 concludes the thesis by providing recommendations for future work and summarizing the findings of the studies conducted.

### 1.4 References


Chapter 2

Review of Advances in Biogas Applications for Solid Oxide Fuel Cells

2.1 Abstract

Solid oxide fuel cells (SOFCs) can be considered a carbon neutral electricity source when operated on biogas produced at wastewater treatment facilities through anaerobic digestion (AD). Typically, SOFCs consist of a nickel and yttria-stabilized zirconia (Ni-YSZ) anode, strontium-doped lanthanum manganite (La$_{0.84}$Sr$_{0.16}$)MnO$_3$ (LSM) cathode and solid yttria-stabilized zirconia (YSZ) electrolyte materials. SOFCs can take on a planar or tubular geometry. There are many different anode, cathode and electrolyte combinations and varieties that are being investigated for different cell geometries. Ideally, SOFCs operate on H$_2$, but it does not occur naturally in the environment and therefore energy is required to convert H$_2$, which is not ideal when attempting to use fuel cells to generate electricity.

When combining AD-derived biogas and fuel cells there are many factors that need to be considered such as the effects of lower partial pressures of H$_2$ in the fuel gas mixture on cell performance, contaminant partial pressures in the biogas and their removal, and biogas reforming to increase the H$_2$ partial pressure. At wastewater treatment plants (WWTPs), the composition of the biogas can also be adjusted through chemical or mechanical processes to increase the H$_2$ partial pressure and reduce undesirable constituent concentrations. Further research and investigation into the various materials that can be used to reduce the cost and increase the durability of SOFCs would enable AD-derived biogas fueled SOFCs to become more commercially available and financially viable. Producing a cleaner and SOFC-friendly biogas
would also allow SOFCs at WWTPs to become a more desirable technology to reduce the electrical and heating needs of the facility.

2.2 Introduction

Biogas can provide a fuel source for solid oxide fuel cells (SOFCs) that is both environmentally sustainable and electrically and thermally efficient. Biogas is a renewable energy source produced through the anaerobic digestion (AD) process. It can be produced from a number of substrates and is generally primarily composed of methane, carbon dioxide, water vapour, and trace quantities of hydrogen sulfide (Egger, Sutter, & Wellinger, 1985). Biogas is the result of the conversion of biomass to a renewable fuel source through combustion, pyrolysis, hydrogasification, or anaerobic digestion (Larminie & Dicks, 2003; IEA International Energy Agency, 2006). For the purpose of this study biogas production from anaerobic digestion at municipal wastewater treatment plants (WWTPs) will be reviewed.

A fuel cell converts energy stored in a fuel source into electrical energy through electrochemical reactions between a fuel, oxidant, electrodes and an electrolyte (DOE, 2004; Larminie & Dicks, 2003; Ormerod, 2003). A fuel cell produces lower emissions of nitrogen oxides, hydrocarbon pollutants and reduced concentrations of carbon dioxide compared to typical combustion types of energy production (Ormerod, 2003; Skok & Eschbach, 2005; Kordesch & Simader, 1995). Fuel cells operating on biogas are specifically advantageous because the conversion from CH$_4$ to H$_2$ offers a significant reduction in greenhouse gases, as CH$_4$ is considered to have 23 times more greenhouse gas potential than CO$_2$ (Peppley, 2006). Fuel cells can also convert energy from renewable biogas sources at wastewater treatment facilities that can be used to power and heat the facility (Fetters, 2007; Ormerod, 2003). WWTPs are seen as
advantageous locations because the biogas is produced on-site, which can reduce the cost of implementing an energy system and the energy that would be required to transport the fuel.

2.3 Solid Oxide Fuel Cells

Fuel cells convert energy stored in fuel to electrical energy. This electrochemical conversion occurs in a cell, which consists of an electrolyte layer that is in contact with an anode and cathode on either side. Fuel is fed to the anode and the oxidant is fed to the cathode (DOE, 2004). Passing through the electrolyte layer, the oxygen ions react with hydrogen at the anode, releasing water and electrons (Bove, Lunghi, & Sammes, 2005).

A SOFC utilizes an oxide ion-conducting ceramic material as its electrolyte, as displayed in Figure 2-1.

![Figure 2-1: Separate anode and cathode reactions for the Solid Oxide Fuel Cell when utilizing hydrogen fuel (Larminie & Dicks, 2003).](Image)

2.3.1 Cell Properties

SOFCs operate at high temperatures, typically between 600-1000°C (DOE, 2004). They utilize a solid electrolyte enabling them to be constructed in two different configurations: planar or tubular (Lymeropolous, 2005).
Tubular SOFCs have the same electrochemical reactions as planar SOFCs, but have a different electrode and electrolyte arrangement. The anode of a tubular SOFC can be on the outside or the inside of the tube depending on whether it is anode or cathode supported (DOE, 2004).

2.3.1.1 Anode Materials

A typical anode material for the SOFC is nickel-yttria-stabilized zirconia (Ni-YSZ) (Ormerod, 2003; Brandon, Skinner, & Steele, 2003). Anode materials are typically a cerment of Ni and the electrolyte material, configured to achieve the necessary electrical performance and stability of the anode (Brandon et al., 2003). The addition of YSZ to the Ni lowers the thermal expansion coefficient of the nickel (Zhou & Singhal, 2009). The anode must have a similar coefficient of thermal expansion as the electrolyte and interconnect material, as well as have chemical stability with the electrolyte and interconnect (Zhou & Singhal, 2009). A significant drawback of the Ni-YSZ anode is that it is sensitive to sulphur, H₂S, halides, etc. (DOE, 2004). Ni-YSZ can also be susceptible to re-oxidation of the Ni, particularly when exposed to air at high temperatures (DOE, 2004; Zhou & Singhal, 2009). A benefit of the Ni-YSZ anode is that it can act as a catalyst for the oxidation of hydrogen and is highly active in the steam reforming of methane making it useful in biogas applications (Zhou & Singhal, 2009).

There are alternative anode materials and configurations that are being researched to enable alternative fuel use and to reduce carbon deposition or sulphur poisoning effects. A diffusive barrier was tested with methane as a fuel and was designed to be non-coking by limiting the methane to the anode, thus increasing product partial pressures across the anode (Lin, Zhongliang, & Barnett, 2006). The barrier was shown to reduce the power density of the cell, but was effective at preventing coking of the anode. Thinner or more porous barriers could be used to
increase the power density, but that could also hinder the effectiveness of the barrier at reducing coking (Lin, et al., 2006). A tubular SOFC with a double-layer anode comprised of NiO-YSZ as a supporting layer and CoO-NiO-SDC as a reforming layer was also tested for the conversion of methane at 800°C (Li, Wang, Nie, & Wen, 2007). The results of this investigation showed that no carbon was deposited on the surface of the anode and a maximum power density of 350 mA/cm² was reached (Li, et al., 2007). This technology could eventually aid in the utilization of biogas in SOFCs without additional reforming steps.

2.3.1.2 Cathode Materials

The cathode material of a SOFC is typically strontium-doped lanthanum manganite (La₀.₈₄Sr₀.₁₆)MnO₃ (LSM) (Larminie & Dicks, 2003; DOE, 2004) (Brandon, et al., 2003; Hart, Bandon, Day, & Shemilt, 2001). Cathode materials must have high thermal and chemical stability, low interactions with the electrolyte, possess electronic and ionic conductivity, and a thermal expansion that is compatible with the cell components (DOE, 2004; Zhou & Singhal, 2009). They must be porous to enable oxygen to diffuse through the cathode layer to reach the electrolyte and to enable the electrochemical reactions that support SOFC power production (Zhou & Singhal, 2009). Cathode current collectors, in tubular configurations are typically comprised of Ag material (Brandon, et al., 2003).

Doped LaMnO₃ (LSM) is a common cathode material because it has a good thermal expansion compatibility with YSZ electrolyte materials, offers stability in the SOFC operating environment, and possesses excess oxygen (Zhou & Singhal, 2009). There are drawbacks to the LSM cathode including low ionic conductivity and low surface area kinetics (Zhou & Singhal, 2009). In order for SOFC technology to be optimized alternate cathode materials must be investigated. Shao and Halle presented Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋ (BSCF) as a cathode material to be
combined with a thin-film doped ceria fuel cell (Shao & Haile, 2004). When tested, the BSCF cathode reached a maximum power density of 1010 mW/cm² when operated at 600°C and 402 mW/cm² at 500°C on humidified hydrogen and air (Shao & Haile, 2004). At higher temperatures the diffusion rate was determined to be higher (7.3x10⁻⁵ cm²/s at 775°C to 1.3x10⁻⁴ cm²/s at 900°C). More common cathode materials have oxygen diffusion rates that are significantly lower (2 to 200 times lower) (Shao & Haile, 2004). This was determined to be the factor that resulted in higher power densities.

Alternative means of constructing cathode electrodes are also being considered. Functionally graded materials (FGMs) are employed to connect materials that are not similar by grading the transition from one material to the next. This enables the effects of abrupt changes in material composition to be avoided, lessening the effects of thermal expansion (Hart, et al., 2001; Brandon, et al., 2003). In a study by Hart et al. (2001), an YSZ/LSM graded microstructure with four screen-printed layers was utilized. The graded structures resulted in consistently lower polarization resistance when compared to an ungraded structure. This is advantageous as a decreased polarization resistance enables an increased cell performance (DOE, 2004). This advancement, and ones like it, could lead to increased cell performance using alternate, potentially more cost-effective production methods.

Research by Matsuzaki and Yasuda (2000) discussed the possibility of utilizing alloys as separators by lowering the operating temperature of the cell. Metallic interconnects are desirable due to reduce costs, higher thermal conductivity and strength (Matsuzaki & Yasuda, 2000). In this experiment the cathode material was La₀.₆Sr₀.₄MnO₃⁺/YSZ, and it was determined that an increase in cell overvoltage was due to an increase in charge-transfer resistance and diffusion resistance (Matsuzaki & Yasuda, 2000). A lower cell operating temperature that does not result in
a decreased cell performance would be advantageous because it would increase the efficiency of the system by requiring less energy to heat the fuel cell system. There would also be more materials that would be available for use as cell components that are not applicable at higher temperatures because of their properties.

2.3.1.3 Electrolyte Materials

Electrolyte materials are typically perovskites, specifically stabilized zirconia’s, which conduct ions at a specific temperature range (DOE, 2004). The opportunity for SOFCs to be operated at lower temperatures can be influenced by the materials selected. Currently, yttrium stabilized zirconia (YSZ) is the most common electrolyte material (DOE, 2004; Larminie & Dicks, 2003; Ormerod, 2003; Ball, Stevens, & Luo, 2004). YSZ electrolyte provides the required oxygen ion conductivity, maintains good stability under oxidizing and reducing operating conditions, and is unreactive with other SOFC components (Ormerod, 2003). YSZ electrolyte fuel cells utilize nickel chromium alloys to withstand the high operating temperatures required for the use of YSZ, but these alloys increase the total fuel cell cost (Ball, et al., 2004). The use of electrolyte materials that are operational at lower temperatures could result in the use of other less expensive interconnect materials. Two alternatives to YSZ have recently been investigated: gadolinia-doped ceria (GDC) and lanthanum gallate based structures (Ormerod, 2003; DOE, 2004).

GDC provides a higher ionic conductivity, compared to YSZ, and allows greater oxygen flow through the electrolyte structure (Ball, et al., 2004). Ball reported that although GDC enabled an electrolyte to experience higher ionic conductivities, disadvantages of the material included a reduced strength, as well as lower stability at certain oxygen partial pressures (Ball, et al., 2004). GDC (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$) and 3% yttria stabilized zirconia (3Y-TZP) were used to
determine the characteristics of composite electrolytes. As the quantity of gadolinia doped ceria added to the zirconia increased, a gradual decrease in ionic conductivity and activation energy was observed (Ball, et al., 2004). These decreases were thought to be the result of the formation of a solid solution of ceria in zirconia. GDC electrolyte was shown to be a successful innovation for low-temperature, anode-supported planar SOFC stacks (Liu, Khor, Chan, & Chen, 2006). A disadvantage of using doped ceria as an electrolyte is often reduces when the partial pressure of oxygen is low (Ball, et al., 2004).

Strontium and magnesium doped lanthanum gallate (LSGM), when compared to standard YSZ, provides better oxide-ion conductivity and has good chemical stability. The ionic conductivity of LSGM at 800°C has been reported to be similar to that of YSZ at 1000°C (Man, Goodenough, Kegin, & Milliken, 1996; Bergman, Li, & Li, 2010). A study by Feng (1996) presented results for LSGM tests utilizing two different anode materials (doped ceria mixed with NiO and LSGM mixed with NiO) and a doped lanthanum cobaltite cathode. The tests, performed between 600-800°C, demonstrated that the cells could reach approximately 40% of their theoretical power density (Man, et al., 1996). The Ni/ceria anode supported cell showed an increase in performance with time, whereas the Ni/LSGM anode supported cell showed a decrease. The Ni/LSGM cell had a small increase in OCV, suggesting a reduction in the overpotential, which was related to the possibility of higher lattice compatibility between the Ni/LSGM and higher oxide-ion conductivity (Man, et al., 1996). The research conducted concluded that a suitable anode material is the key to a successful SOFC with LSGM electrolyte material (Man, et al., 1996).

It has been reported by Guo and Liu (2010) that at higher temperatures there is a reaction between LSGC and the nickel anode (Guo & Liu, 2010). A composite of LSGM and doped ceria
(CSO) was investigated as an electrolyte material for a SOFC (Bergman, et al., 2010). It was reported that the conductivity of the LSGM-CSO composite was the highest in at 350-600˚C (Bergman, et al., 2010). To prevent the reaction between LSGM and the nickel anode at higher temperatures, it was proposed that LDC be used as an interlayer between the LSGM electrolyte and the anode (Guo & Liu, 2010). Research conducted by Guo and Liu (2010) suggested that utilizing a tri-layer electrolyte of yttria-doped bismuth oxide (YDB), LSGM and lanthanum-doped ceria (LDC) could provide higher OCV values, as well as higher power densities than a cell that was tested with a LSGM/LDC electrolyte film. The higher values were attributed to the lower polarization resistance of oxygen reduction between the cathode and electrolyte layers, as well as a lower ohmic resistance (Guo & Liu, 2010). Guo and Liu concluded that the tri-layer composite electrolyte investigated is a promising material for IT-SOFC technologies (Guo & Liu, 2010).

Innovative electrolyte materials are crucial to the performance of the SOFC. Advanced electrolyte technologies should continue to be investigated to further increase the performance of the SOFC whilst decreasing the cost to allow the technology to become more commercialized.

2.3.1.4 Effects of Operating Parameters

There are a number of factors that cause changes in fuel cell performance, including fuel and oxidant utilization, system pressure and the operating temperature.

Fuel utilization refers to the percentage of fuel supplied that is reacted by the cell. To maintain a high efficiency the fuel utilization should be high, yet a higher fuel utilization results in a lower cell voltage, leading to a decrease in cell efficiency (Larminie & Dicks, 2003). A lower voltage is generally due to a decreased fuel partial pressure as the concentration of fuel decreases across the cell. Figure 2-2 displays the variation in cell voltage as fuel utilization is changed.
The utilization of fuel leads to mass transport losses as the concentration of reactants changes at the electrodes (Larminie & Dicks, 2003). When pure oxygen is used, as opposed to air, there is an expected increase in cell potential due to the increase in the partial pressure of oxygen (Blomen & Mugerwa, 1993; Larminie & Dicks, 2003). The proportion of oxygen in air is approximately 21%, as such the availability of oxygen increases when pure oxygen is used (DOE, 2004). Some systems that are specifically designed for use with pure oxygen as oxidant cannot be utilized with air, as they cannot operate with the other inert gases present (i.e. N₂), whereas systems that are designed to operate using air often experience increases in performance when operated on pure oxygen (Blomen & Mugerwa, 1993). The utilization of fuel and oxygen results in a drop in system pressure. Oxidant utilization can also have a significant effect on the efficiency of the fuel cell system because it is generally provided by a compressor that can consume a significant amount of power (Kang, Koh, & Lim, 2002).
The effects of the increased system pressure are higher than predicted by the Nernst equation at lower temperatures (Larminie & Dicks, 2003). Figure 2-3 shows the results obtained by Siemens Westinghouse and Ontario Hydro Technologies (2004) that describe the effects of different cell pressures when tested at different current density values (DOE, 2004). It can be noted that at higher system pressure, the cell performance is greatly increased across a range of current densities.

![Figure 2-3: Effect of Pressure on Air Electrode Supported Cell Performance at 1000°C (2.2cm diameter, 150cm active length) (DOE, 2004).](image)

2.3.2 Commercialization of Fuel Cells

The commercialization of SOFCs is particularly advantageous because it converts electrical energy and can provide useful heat by-product that can be utilized in cogeneration (Rayment & Sherwin, 2003). But, fuel cell technologies are often considered too expensive for a number of applications. A benefit associated with the use of gas from the AD process is that there
are fewer additional costs associated with implementing the technology for biogas capture (Peppley, 2006). For many municipalities, fuel cell technologies are still out of reach due to the high capital cost associated with their installation, and since available grants and incentives vary between regions. There are, particularly in parts of the United States, funding opportunities for green energy projects that can reduce the capital cost of environmentally responsible technologies such as fuel cells. The commercialization of fuel cells could be influenced by the automotive industry because if fuel cells are used in widespread automotive applications the production of the required materials will enable the manufacturing of fuel cells for alternative applications to become more affordable. (PriceWaterhouseCoopers, 2008). The automotive industry can employ lower cost materials and benefit from an increased production capacity. The increased capacity impacts the capital cost and availability of product.

SOFCs are often less expensive than other fuel cell technologies because they have lower cost components, such as the electrodes and electrolyte. SOFCs commonly utilize YSZ as an electrolyte material, which is abundant, easy to fabricate and relatively low in cost (Ormerod, 2003). Alternative technologies are being considered to replace components of SOFCs to further decrease the cost. Barium-zirconium-cerium-yttrium-ytterbium oxide BZCYYb was researched at Georgia Tech and could tolerate higher sulfide concentrations (50ppm) (Toon, 2010). It does not promote carbon accumulation on the anode and can operate at lower temperatures than the standard SOFC (500°C), therefore reducing operating costs (Toon, 2010). (BZCYYb) could be used as a coating for cell anodes or as a replacement for the YSZ electrolyte (Toon, 2010).

Until recently it had not been cost-effective to invest in alternative energy sources. The capital investment required often exceeded the expected return on investment (Appleby, 1996). With fossil fuels having a lower cost and higher availability, alternative technologies for energy
production, such as fuel cells are often not considered. Efficiency is not always a high priority when the cost of the required fuel is low (Appleby, 1996). It has been stated that fuel cell technologies will be competitive with other power generation technologies when the price per kW of energy production is reduced (Peppley, 2006). These economic factors have greatly hindered the commercialization of fuel cell technology. Fuel cells will become more of a mainstream technology as the importance of lower or zero GHG emissions becomes more prevalent and regulated, and as their ability to operate on inexpensive hydrocarbon fuels becomes more clearly understood (Appleby, 1996).

2.3.3 Alternative Fuels for Use in Solid Oxide Fuel Cells

Hydrogen is the most common fuel used in SOFC technologies. It is ideal because it is highly reactive and its oxidation produces water (Larminie & Dicks, 2003). The disadvantage to hydrogen is that it does not occur naturally in the environment as a gas and, therefore, must be generated from an alternate fuel source, which can increase the cost of fuel cell operation (Larminie & Dicks, 2003; Peppley, 2006). Utilizing alternate fuels could reduce the requirement to generate hydrogen and aid in reducing operating costs for SOFCs. An important alternate fuel to be further researched for use in SOFC applications is AD-derived biogas.

2.3.3.1 Effects of Dilute Hydrogen Gas on SOFCs

When SOFCs are operated on dilute hydrogen gas the cell performance is typically affected. In a study by Jiang and Virkar (2003) utilizing a Ni-YSZ anode substrate, Ni+YSZ anode interlayer, YSZ-SDC bilayer thin-film electrolyte, LSC+SDC cathode interlayer and a LCS cathode current collector layer, describes the changes in cell performance (Jiang & Virkar, 2003). The tests were conducted using button-cells, as well as helium, nitrogen, carbon dioxide, and water as hydrogen diluents. They reported that the maximum power density obtained at the
highest concentration of the diluent (approximately 71-81%) was the highest for the hydrogen-helium gas mixture (approximately 0.75 W/cm²) and lowest for the hydrogen-carbon dioxide mixtures (approximately 0.3 W/cm²). The results generated from the data collected are presented in Figure 2-4.

![Figure 2-4: Voltage and Current Density vs. Power Density for (A) as received H₂ and H₂ diluted with He; (B) H₂ and H₂ diluted with N₂; (C) H₂ and H₂ diluted with CO₂; and (D) H₂ and H₂ diluted with CO as fuel (Jiang & Virkar, 2003).](image)

It is interesting to note that for H₂ diluted with CO, there is a distinct difference between the voltages produced at concentrations above and below about 50% H₂ concentration (Jiang & Virkar, 2003). This is a result of water-gas shift (WGS) reaction introducing additional H₂. The
tests conducted utilizing He and N\textsubscript{2} as diluents showed less substantial differences than the tests conducted using CO\textsubscript{2} as a diluent because He and N\textsubscript{2} are inert gases and therefore do not react in the cell.

A study by Madsen and Barnett (2005) examines effects of composite SOFC anodes when operated using different hydrocarbon fuels. Madsen and Barnett conducted tests of hydrocarbon fuels using La\textsubscript{0.8}Sr\textsubscript{0.2}Cr\textsubscript{0.98}V\textsubscript{0.02}O\textsubscript{3} anodes (which also contained GDC and a small amount of NiO) GDC electrolytes (Madsen & Barnett, 2005). The cathodes were made from La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3-δ} and the test used a single cell apparatus. The results with different hydrocarbon fuels are shown in Figure 2-5, where it can be seen that some of the hydrocarbon fuels performed similarly in terms of the cell potential at specific current densities.

![Figure 2-5: Voltage vs. Current Density for a composite anode SOFC when operated on varied humidified (3% H\textsubscript{2}O) hydrocarbon fuels at 700°C. Anode is a cerment of Ni and yttria-stabilized zirconia (YSZ, Zr\textsubscript{0.92}Y\textsubscript{0.08}O\textsubscript{2}). Cathode was La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3-δ}. (Madsen & Barnett, 2005) ](image)

From Figure 2-5, it can be seen that the maximum current density appears to vary slightly with the molecular weight of the hydrocarbon, which Madsen and Barnett suggested was due to degradation of the cell with increased operating time, concluding that all hydrocarbon fuels tested displayed similar results (Madsen & Barnett, 2005). As knowledge regarding the adaptability of
SOFC technologies operating on hydrocarbon fuels increases the practicality of establishing SOFC-biogas or hydrocarbon fuel systems may come to fruition.

2.4 Biogas from Anaerobic Digestion at Wastewater Treatment Facilities

Biogas from the anaerobic digestion of crop residues, lignocellulosic biomass and wastes can be used to provide a renewable source of energy, as biogas can help to relieve some of the pressures currently associated with the global fossil fuel supply (Appels, Baeyens, Degreve, & Dewil, 2008).

2.4.1 Anaerobic Digestion Process

Anaerobic digestion is a biological treatment process in which solids are metabolized and solubilized (Droste, 1997). AD primarily produces CH₄ gas that can aid in offsetting the substantial amount of heat energy required in the AD process, as heat can be recaptured and employed to heat the digesters (Spiegel, Thorneloe, Trocciola, & Preston, 1999). Since there is no oxygen consumed in the AD process the reduction in chemical oxygen demand (COD) is done through the conversion of organic compounds to CH₄ (Droste, 1997). In biogas production the concentration of hydrogen is quite low and is increased through the reformation process, which occurs before biogas can be used in a SOFC and converts CH₄ to H₂.

In AD, the quantity of CH₄ produced from a waste is proportional to the concentration of organics (COD) in the waste (Droste, 1997). The maximum theoretical yield of methane from waste is 0.35 m³ CH₄/kg COD (5.6 ft³/lb) removed (Droste, 1997). The energy content associated with the gas is from CH₄ (which has an energy content of 37 MJ/m³) (Droste, 1997). Carbon dioxide reduces the energy content to about 22-26 MJ/m³ (Droste, 1997).

2.4.2 Biogas Composition
Typical biogas in WWTPs in Ontario is primarily composed of CH$_4$ and CO$_2$ (Wheeldon, Caners, Karan, & Peppley, 2007; Appels, et al., 2008; Droste, 1997; Larminie & Dicks, 2003; Spiegel, et al., 1999). The composition of biogas can vary with location and time, which can present difficulties when preparing a system for its use in conjunction with fuel cells (Singhal & Kendall, 2003). Wheeldon et al. (2007) reported that, in Ontario, biogas is typically comprised of 60.8% CH$_4$ and 34.8% CO$_2$.

The sulphur compounds found in biogas are typically sulphides and oxidized sulphur is corrosive in the presence of H$_2$O (Appels, et al., 2008). In Ontario, the average concentration of H$_2$S ranges from 2.5 to 3450 ppm with an average of 78 ppm in biogas (Wheeldon, et al., 2007). Siloxanes were noted to be the second most concentrated contaminant with concentrations up to 2500 ppm (Wheeldon, et al., 2007).

In Ontario, the average amount of biogas produced is 57.4 ± 17.7 m$^3$ per 1000 m$^3$ of wastewater treated (Wheeldon, et al., 2007). The energy from the biogas produced at WWTPs could be extracted in a combined heat and power system that could include (but not be limited to) a fuel processing system for biogas cleanup and reforming and the fuel cell system to generate electricity and heat (Wheeldon, et al., 2007).

### 2.4.3 Biogas Optimization

Biogas produced from the AD process is an environmentally responsible fuel. To make biogas more available for use as a fuel, the methane content must be increased to increase the energy content of the gas (Appels, et al., 2008). To achieve this goal the partial pressures of CO$_2$ and other constituents must be reduced, which will be a great advantage for biogas use in fuel cells.
There are different approaches to optimize biogas production and quality in the AD-process. The biogas yield from anaerobic digestion can be increased because only about half of the organic material present is converted to biogas (Ahring, 2003). Research by Ahring (2003) reported that biogas production could be improved in the AD-process including increasing the digestibility of the waste, optimizing the reactor configuration, optimizing the process control and stability, and improving the microbial process and its efficiency. The digestibility of the waste can be increased through mechanical, chemical or biological methods (Ahring, 2003; Angelidaki & Ahring, 2000). Treatment with acids or bases or treatment with enzyme mixtures have been shown, to generally increase the conversion to biogas, although these practices have also been reported to have a high financial costs (Ahring, 2003; Angelidaki & Ahring, 2000). The mechanical process of decreasing particle size was found to increase the biogas production and the increase in biogas production out weighed the capital cost of implementing a macerating unit (Ahring, 2003; Angelidaki & Ahring, 2000). It was reported that a two-phase system with a short hydrolysis phase performed at 70°C followed by a methane production phase, conducted at 55°C, in a continuous stirred tank reactor would increase the conversion of organics in manure.

Full-scale studies conducted by Alatriaste - Mondagen et al. (2006) reported on the enhancement of gas production through the addition of co-digestates. Co-digestion is particularly useful because a co-substrate is used to improve biogas yield via the addition of missing nutrients. It was reported that mixing slaughterhouse wastes with municipal wastewater sludge (MWS) and co-digestion of kitchen waste with MSW increases biogas production by 60% and 27%, respectively (Alatriste-Mondragon, Samar, Cox, Ahring, & Iranpour, 2006). The increase in gas production was correlated with the organic loading associated with the addition of the co-digestate. The combination of FOG (Fats, Oils, and Gases) with MWS also resulted in an increase
in gas production of up to 21%, but the FOG addition did not increase the digestion in the reactor. The addition of organic waste (kitchen waste from grocery stores and hospitals) to MWS can lead to an increase in the gas produced and surplus of heat and electrical energy can be provided (Edelmann, Engeli, & Gradenecker, 2000). A disadvantage in using co-digestion to develop biogas as a fuel in SOFCs could be the possibility of introducing more toxic contaminants and inorganic compounds into the sludge that could alter the quality of the output biogas (Rulkens, 2008).

The primary advantage to increasing the CH$_4$ production is the corresponding increase in the energy that can be produced through the conversion of CH$_4$ into energy and/or electricity (Alatriste-Mondragon, et al., 2006). The use of co-digestion to increase the biogas production has other advantages, which include the reduction in GHG effects during composting of organic wastes and it is a viable option in communities where there is not sufficient MSW to warrant the construction of solid waste digestion facilities (Edelmann, et al., 2000). The design of the anaerobic digester reactor can greatly influence CH$_4$ production. Biogas produced, after reformation and contaminant removal, can be fed through fuel cell technologies to produce electricity, and therefore research into the improvement of CH$_4$ partial pressure and biogas optimization should be continued.

2.5 Biogas for Fuel Cells

Fuel cell and AD biogas applications are being developed all over the globe. The US Environmental Protection Agency (USEPA) established a design for a fuel cell energy recovery system for an AD at a WWTP, which utilized a phosphoric acid fuel cell (PAFC), manufactured by ONSI, in Yonkers, NY (Spiegel & Preston, 2003). The Yonkers, NY fuel cell installation represents the first fuel cell installation at a WWTP in North America. The use of a fuel cell in
conjunction with biogas from WWTPs will reduce emissions to the atmosphere that affect global warming, acid rain and other health and environmental concerns. In addition, fuel cells emit less CO\textsubscript{2} into the atmosphere per kW than any other heat recovery or electricity generation equipment (Sandelli, Troccoli, & Spiegel, 1994).

In general, as a fuel, biogas has a low heating value, which makes it unsuitable for use in gas engines but is not a problem for technologies such as the SOFC and MCFC (Larminie & Dicks, 2003). The low heating value is caused by high concentrations of carbon oxides and nitrogen in biogas.

2.5.1 Limitations of Solid Oxide Fuel Cells to Biogas Applications

Although SOFCs are recognized as a technology that can be adapted to generate electricity and heat but there are still a number of limitations that are barriers to the large-scale application of this technology. A primary reason that fuel cell technologies are not commonly employed in biogas applications is the potential for poisoning the cell with certain biogas contaminants and the effects of varying H\textsubscript{2} dilutions on SOFC performance. This is particularly critical, as these factors are likely to arise given the biogas variability. There is a distinct need for further research into the response of fuel cells to biogas contaminants to further the use of this technology.

2.5.1.1 Fuel Cell Poisoning

Previous research has shown that there is a distinct relationship between the impurities found in gas mixtures and the performance of the cell. The fuel requirements for fuel cells are somewhat narrow. Alternative fuels often require reforming and pretreatment to remove contaminants before they can be processed by the fuel cell. An advantage of SOFC technology is
that since it operates at higher temperatures the cell can tolerate higher concentrations of impurities than lower temperature cells (Omosun, Bauen, Brandon NP, Adjiman, & Hart, 2004).

2.5.1.1.1 Sulphur Compounds

Sulphur present in gas streams can poison catalytic sites in fuel cells, as well as metal catalysts in fuel reformers (DOE, 2004; Larminie & Dicks, 2003). This indicates that the H$_2$S must be removed to an acceptable level before the gas is fed to the reformer. In SOFCs the sulphur tolerance, by percent volume in the cleaned reformate gas is less than 1 ppm of sulphur as H$_2$S (DOE, 2004). H$_2$S has been shown to cause an immediate drop in cell performance when introduced to a gas mixture, followed by a linear degradation (DOE, 2004; Haga, Shiratori, Adachi, Sasaki, & Itoh, 2008). It has been shown that at low concentrations of sulphur-containing compounds, the adsorption of sulphur onto nickel is reversible when the cell is switched back to sulphur free fuel, which would indicate a tolerance to sulphur in the gas mixture (Singhal & Kendall, 2003). The potential to reverse the effects of sulphur deposition on nickel is particularly possible at high temperatures, since the tolerance of the anode and reforming catalyst to sulphur increases with temperature (Singhal & Kendall, 2003).

H$_2$S can act as a poison for steam reforming and the WGS reaction catalysts (Wheeldon, et al., 2007). H$_2$S can be removed through the use of an activated carbon bed, which has been shown to be very effective at H$_2$S loadings of less than 200 ppm (Wheeldon, et al., 2007). The carbon absorbent material used is a commercially available potassium-hydroxide-impregnated activated carbon that has previously been tested in landfill gas cleanup applications (Spiegel, et al., 1999; Appels, et al., 2008). Other means of reducing the H$_2$S concentration in biogas have also been reviewed, including conditioning the sludge that is fed to the digester to minimize H$_2$S
content (Appels, et al., 2008). The addition of salts in the sludge can also reduce H₂S concentration in the biogas generated.

2.5.1.1.2 Hydrocarbons & Carbon Formation

When fuel cells are operating on hydrocarbon fuels, there is the possibility of carbon deposition (coking) if the fuel processor is not adequately designed and operated (DOE, 2004). Nickel is particularly known for its affinity to promote the coke formation, which can result in catalyst deactivation (Singhal & Kendall, 2003). Hydrocarbons can react on the surfaces of the anode, interconnect plates, tubing leading to the anode, as well as in the gas phase through free-radical cracking and polymerization creating tars that can then deposit on the anode surface as the fuel flows through (McIntosh & Gorte, 2004).

The use of hydrocarbon fuels that are larger then CH₄ will be more likely to result in carbon deposition (Singhal & Kendall, 2003). In order to use fuel gas mixtures containing higher hydrocarbons it is necessary to have a lower-temperature pre-reforming stage in which the fuel can be further conditioned (Singhal & Kendall, 2003). Strategies to reduce the impact of coking with hydrocarbon fuels include the addition of dopants to anode materials (including gold, copper, ruthenium and molybdenum), which has been shown to improve the resistance of the nickel/zirconia and nickel/ceria anodes to carbon deposition (Singhal & Kendall, 2003).

2.5.1.1.3 Silicon Compounds

Silicon has also been researched as a contaminant and it is believed to accumulate on the anode as silica (SiO₂) and this deposition of silica has been shown to be heightened by a high H₂O partial pressure in the fuel gas mixture (DOE, 2004). This is important for biogas applications because, as CH₄ reforms to CO and H₂, H₂O is consumed, which favours the deposition of SiO₂ (the reverse reaction shown in Equation (2-1)) (DOE, 2004):
$\text{SiO}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Si(OH)}_4(\text{g})$  \hspace{1cm} (2-1)

Haga et al. (2008) conducted research to determine the effects of siloxanes on SOFC performance. The impact of $[\text{SiO(CH}_3)_2]_3$ (a major siloxane in ADG) was shown to decrease cell performance with time at 10ppm siloxane in 3%-humidified H$_2$ at 800°C, 900°C and 1000°C resulting in a fatal degradation of cell performance that is associated with the formation of SiO$_2$(s) in porous cermet anodes. This research supports the need for further advancements in biogas conditioning.

2.5.1.2 Biogas Reformation

Biogas can be reformed through steam or dry reforming in which alternative fuels are converted into a H$_2$-rich fuel (Wheeldon, et al., 2007; Singhal & Kendall, 2003). Reforming of biogas is necessary because the direct feed of CH$_4$ to a SOFC anode can cause fouling of the anode catalyst due to coking (Wheeldon, et al., 2007). In steam reforming, the highest amount of H$_2$ is converted per mole of carbon when compared to dry reforming; this is shown in Equations Steam Reforming (2-2) and Dry Reforming (2-3) (Wheeldon, et al., 2007; Larminie & Dicks, 2003). The steam reforming reaction works in conjunction with the water gas shift reaction, therefore the product gas generated through these two reactions taking place is a mixture of CO, CO$_2$, and H$_2$ with any remaining unconverted CH$_4$ and steam (Larminie & Dicks, 2003).

$\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$  \hspace{1cm} \text{Steam Reforming (2-2)}

$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$  \hspace{1cm} \text{Dry Reforming (2-3)}

As shown in Equations Steam Reforming (2-2) and Dry Reforming (2-3), steam reforming has the potential to convert more H$_2$, while producing less CO than the dry-reforming reaction.

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(DOE, 2004). Although less H₂ is converted the dry reforming reaction is often desired because it allows a SOFC to operate on a wide compositional range of CH₄ and CO₂ partial pressures without the addition of steam (Singhal & Kendall, 2003; Wheeldon, et al., 2007). Direct biogas reformation on the SOFC anode is a challenge because of the susceptibility of the anode materials to the contaminants in typical WWTP AD biogas and since dry-reforming reactions are catalyzed by nickel, deactivation due to carbon formation and nickel sintering can be a problem (Larminie & Dicks, 2003).

2.5.2 Performance of SOFCs Operating on Biogas

The opportunity to further develop SOFC technologies and practices to optimize the use of biogas and biogas reformate in fuel cell systems has been recognized and is being further developed.

Dietrich et al. (2011) demonstrated the feasibility of using biogas derived from a sugar plant WWTP as a fuel for a SOFC. The WWTP produced approximately 120,000-230,000 m³/d of biogas, of which 4,000-15,000 m³/d was fed to a 1.5-MW CHP unit. In 2010, the biogas composition at the plant was in the range of 62-73% CH₄, 28-36% CO₂, and 4-53 ppmv H₂S; the H₂S partial pressure was too high to be used in the CHP unit at start-up but consistently decreased throughout the year to a lower level (Dietrich, et al., 2011). To accommodate biogas variability, a reformer module was designed consisting of a reformer/burner reactor, an evaporator and superheater to prepare the biogas mixture to be used in the cell (Dietrich, et al., 2011). A two Mk200 stack module was used to illustrate the variation in cell performance with different partial pressures of CH₄ in the biogas and it was shown that fluctuating biogas composition does not affect the stack power significantly because it is mitigated by the water addition upstream of the reformer. In summary, the study by Dietrich showed that a fuel cell plant comprising of a sulphur
trap, reformer module and SOFC was developed with the ability to reduce the H$_2$S concentration in the biogas to below 1 ppmv and produce a stack efficiency of 37.6% and no degradation within 1,300 hrs. of operation.

LaBarbera et al. (2011) conducted a study on the performance of SOFCs operating on ADG (55% CH$_4$ and 45% CO$_2$ by volume) based on an analysis of ADG generated at the Penn State WWTC after sulphur removal. The tests were conducted using button cells with a porous 50 µm nickel-YSZ cerment anode, 50 µm LSM cathode and 150µm YSZ membrane (cell active area of 1.256 cm$^2$ (LaBarbera, et al., 2011). The maximum power densities generated in the SOFC system with H$_2$ as a fuel were 0.325 W/cm$^2$ observed at 0.65 A/cm$^2$ and 0.5 V, compared to 0.14 W/cm$^2$ observed at 0.375 A/ cm$^2$ and 0.4V with the biogas (LaBarbera, et al., 2011). LaBarbera et al. attributed the reduced performance of the cell with ADG to the partial pressure of CO$_2$ in the fuel gas mixture, which is consistent with the results obtained by Jiang et al. (2003). The review concludes that desulphurized ADG can be used to generate electrical power with only moderate performance losses (LaBarbera, et al., 2011).

From research by Kendall et al. (2002) it was reported that carbon deposition was occurring on the nickel cermet anode (5% cerium oxide) of a cell with a LSM cathode. This was concluded because the electrodes became blocked within 30 minutes of operation. The CH$_4$ gas was mixed with He to examine the effects of dilution with an inert gas and it was shown that when the fuel gas mixture was 10% NH$_4$ and 90% He only a small amount of carbon deposition was occurring above 800°C (Kendall, Finnerty, Saunders, & Chung, 2002). Kendall et al. (2002) concluded that the dilution of CH$_4$ caused a change in the reaction mechanism from partial oxidation with significant carbon deposition to complete oxidation with minimal carbon deposition. When CO$_2$ was used as the diluent gas, it was shown that the results almost perfectly
fit the model of full oxidation with a slight negative slope, which could indicate H₂ or CO oxidation (Kendall, et al., 2002). The addition of CO₂ resulted in almost no carbon deposition suggesting that the addition of CO₂ to CH₄ can prevent the partial oxidation of CH₄ that causes carbon deposition (Kendall, et al., 2002). Kendall explains that when CH₄ is adsorbed on the nickel sites it does so at adjacent sites, producing carbon layers, where as the diluent gas will co-adsorb to separate the carbon atoms allowing oxygen to diffuse from the nickel/zirconia boundary to give full oxidation. The research concluded that pure CH₄ is an inferior fuel to biogas with a composition of 60% CH₄ and 40% CO₂ (Kendall, et al., 2002).

2.5.3 Case studies

There are a number of locations where fuel cell systems are operating on biogas produced at WWTPs has been demonstrated. Most of these systems use phosphoric acid or molten carbonate fuel cell stacks rather then SOFCs. The basic operating principles are, however, basically the same. The principal attraction of SOFCs is the possibility of significantly reducing their capital cost below that of all other fuel cell types. This will, however, require substantial effort in materials research and development of low cost manufacturing methods.

2.5.3.1 Los Angeles, California

The Sanitation District of Los Angeles commissioned a 250 kW Molten Carbonate Fuel Cell (MCFC) system at their Palmdale Water Reclamation Plant (WRP) in 2004 (California Stationary Fuel Cell Collaborative, 2010; Skok & Eschbach, 2005; Western Area Power Administration, 2005). The installation was part of a demonstration project that ended in 2009. The Palmdale WRP generates about 2.27 m³/min of biogas (55% methane) to fuel the 250 kW MCFC and generate a maximum of 225 kW of power for use at the facility; not all biogas produced is used in the fuel cell (Clean Water, Clean Energy: Palmdale's Water Treatment Plant, 2010).
The coproduct heat in the exhaust gas from the fuel cell was used to heat the digestion process, increasing the fuel cell system’s combined electrical and thermal efficiency to 73% (Clean Water, Clean Energy: Palmdale’s Water Treatment Plant, 2005) (McDannel, 2010). As expected with fuel cell applications, the fuel cell system achieved low emissions during operation (Clean Water, Clean Energy: Palmdale's Water Treatment Plant, 2005).

The capital cost of the project was $2.4 million before being subsidized and $1.3 million after a rebate from Self-Generation Incentive Program covered the other 40-50% (Western Area Power Administration, 2005; Western Area Power Administration, 2005; McDannel, 2010). Over its lifetime the project was able to achieve a savings of $298,000, which was 31% of the targeted savings, and had paid back 24% of its subsidized capital cost and 12% of the unsubsidized cost (Los Angeles County Sanitation Districts, 2009). The expected simple payback period was 9 years and the length of the project was only 5 years, therefore resulting in a financial loss.

The Palmdale WRP fuel cell project demonstrated that a low-emission, high efficiency fuel cell could be successfully operated on anaerobic digester biogas but the system did not achieve the performance goals set at the beginning of the project. The total downtime of the fuel cell system was 11,059 hrs. and major reasons for outages included the an undersized chiller for high summer temperatures (requiring redesign and replacement in 2005), an unavailable fuel skid due to digester gas supply and chiller issues, and four stack replacements (two due to stack issues and two due to sulphur poisoning) (Los Angeles County Sanitation Districts, 2009). The demonstration was finally decommissioned after the last sulphur poisoning in 2009. The lessons learned in the Palmdale demonstration project by FCE and the Sanitation District of Los Angeles have resulted in design improvements and increased reliability for other fuel cell installations (Los Angeles County Sanitation Districts, 2009).
2.5.3.2 Eastern Municipal Water District

The Moreno Valley Facility in the Eastern Municipal Water District (EMWD) has a wastewater treatment capacity of approximately 53,000 m$^3$/d, with 5 ADs producing 4,250 to 5,700 m$^3$/d of biogas (Eastern Municipal Water District, 2011). Moreno Valley began with three 250 kW FCE 300MA MCFC units and will upgrade those existing units to 300 kW versions by 2012 and intends to add additional 300 kW units to have and ultimate fuel cell capacity of 1,200 kW (Mossinger, 2010; Eastern Municipal Water District, 2011). Fuel Cell Energy announced that due to the good performance of the fuel cell power plants at the Moreno Valley site the EMWD purchased two 300 kW DFC300 fuel cell power plants for another site (Parris Valley). The fuel cell installation and cogeneration project help to produce enough energy to meet approximately 40% of the plants power needs (Eastern Municipal Water District, 2011).

The total cost of the Moreno Valley fuel cell project was approximately $9 million with a SGIP grant of $3.4 million decreasing the net project costs to $5.7 million and the expected payback period is 8.5 years (Eastern Municipal Water District, 2011). The estimated annual electricity purchase savings are $700,000 (Eastern Municipal Water District, 2011).

Perris Valley has a wastewater treatment capacity of approximately 15 mgd and a proposed expansion capacity of 22 mgd, which would allow for an increase in the quantity of biogas produced (Eastern Municipal Water District, 2011). The current fuel cell capacity of the plant is 600 kW, utilizing two 300 kW MCFC power plants and a facility ultimate capacity of 1,500 kW with up to five 300 kW units (Eastern Municipal Water District, 2011). The heat recovery unit exhaust provides hot water at a temperature of 180°F to the digesters (Eastern Municipal Water District, 2011).
The approximate cost of the project was $9.9 million, with a SGIP grant of $2.7 million to reduce the net cost to $7.3 million with a estimated payback period of 8 to 10 years (based on the addition of another 300 kW unit within the next few years) (Eastern Municipal Water District, 2011). The estimated annual savings to the EMWD are $670,000 to $856,000.

2.5.3.3 New York, New York

The New York Power Authority (NYPA) uses the methane from the biogas as an energy source at some of the City’s wastewater treatment facilities. The biogas is used in engines to produce electricity and heat, as well as in fuel cells at four of the city’s water pollution control plants (as of 2003) (New York City Department of Environmental Protection, 2010). Fuel cells are installed at the following water pollution control plants: 26th Ward, Red Hook, Oakwood Beach and Hunts Point (New York City Department of Environmental Protection, 2010; Chuck, 2008). The NYPA operates nine fuel cells powered by ADG in total (including eight at the previously mentioned four sites) and one at the Westchester County Yonkers WWTF (Kishinevsky & Zelingher, 2003). The NYPA has installed PAFC’s.

The Yonkers fuel cell installation was the first fuel cell installation in the Western Hemisphere to be powered directly by ADG (Kishinevsky & Zelingher, 2003). The system was installed at the facility in 1997 (Chuck, 2008). The installation contains a 200 kW PC25C PAFC, which were modified to operate on ADG. Modifications included changes to the stack assembly, reformer, thermal management system, etc. to accommodate the use of ADG (Kishinevsky & Zelingher, 2003). Modifications were designed to accommodate higher fuel flow rates that are required because ADG has only about a 60% partial pressure of NH$_4$ as well as accommodate for the pressure drops that result of the flow rate increases (Spiegel & Preston, 2003). The fuel cell
The Yonkers facility produces approximately 493 m$^3$/h of ADG of which about 70% is used in boilers and engines (the remainder is flared) (Kishinevsky & Zelingher, 2003; Chuck, 2008). The Yonkers fuel cell underwent stack and ILS replacements in 2004 and further refurbishment and replacement of parts in 2006 (Chuck, 2008). From the Yonkers project it was learned that a number of changes could be incorporated into the plant design to increase the performance of the fuel cell system. A smaller reformer with a lower pressure drop and a lower pressure drop across the condenser, and reformer burner and cell stack manifolds should be incorporated (Chuck, 2008). Changes are also recommended to allow for a higher flow rate through the cells; additional acid in the cells can allow for a higher evaporation rate and more rugged manifolds are required to accommodate the higher pressures and flow rates (Chuck, 2008). An external gas-processing unit (GPU) was added to convert hydrogen sulfide into elemental sulphur and water and a halide absorber was added to remove mostly chlorine (Kishinevsky & Zelingher, 2003).

The other facilities in New York that have fuel cell technologies in place all are aiding in the energy demand that WWTPs put on the electrical grid. The 26th Ward WWTP has an output capacity of 200 kW, as does the Oakwood Beach WWTP (Kishinevsky & Zelingher, 2003). The 26th Ward WWTP treats about 6.6 m$^3$/d of wastewater and the Oakwood Beach WWTP treats approximately 1.7 m$^3$/d (Kishinevsky & Zelingher, 2003). The Oakwood Beach system has been operational since May of 2004 (Chuck, 2008). The fuel cells in the 26th Ward have been in operation since 2003 (Chuck, 2008). The Red Hook WWTP has a capacity of 400 kW (two 200 kW units) and Hunts Point WWTP has a capacity of 600 kW (operating three units) (Kishinevsky
& Zelingher, 2003). The Red Hook WWTP treats approximately 2.6 m$^3$/d (New York City Department of Environmental Protection, 2010) and the fuel cell system was commissioned in January of 2004 (Chuck, 2008). The Hunts Point WWTP is the largest plant utilizing biogas fuel PAFCs, treating 8.8 m$^3$/d of wastewater has been operating since January of 2005 (New York City Department of Environmental Protection, 2010; Chuck, 2008).

There is a significant potential for energy production from ADG in the City of New York. In New York City there are 14 WWTPs with a sewage design capacity of 78.8 m$^3$/d and a biogas production of 10MM scf (Chuck, 2008). Chuck reported that over $2 million in energy is recovered per year and the ADG that is flared is believed to be sufficient to generate an additional 10-MW. In 2003 a publication by Kishinevsky and Zelingher reported that with eight fuel cells operating in New York City’s WWTPs would ensure that the NYPA (New York Power Authority) would meet its goal of zero net emissions.

2.5.3.4 King County, Washington

In 2004, King County, Washington began a two-year project to test a 1 MW MCFC operating on ADG from its South Treatment Plant in Renton Washington. This was the first MCFC operating on ADG in the United States (King County Department of Natural Resources and Parks, 2009; Skok & Eschbach, 2005). At the King treatment plant the fuel cells also produce heat that is used to heat the anaerobic digester to convert sludge into additional biogas (Skok & Eschbach, 2005). King County’s South WWTP produces enough sludge to power 4mW of DFC (Direct Fuel Cell) systems (Skok & Eschbach, 2005). The U.S. EPA, by means of a $12.5 million grant, subsidized this project and King County and FuelCell Energy (the manufacturer of the MCFC system) divided the remainder of the $19 million cost (Skok & Eschbach, 2005).
The King County fuel cell installation required adaptation from FuelCell Energy’s standard DFC model to accommodate the equipment to pretreat and utilize un-scrubbed digester gas (Skok & Eschbach, 2005). The project was conducted for two years. The second year there was no digester gas used in the system due to excess moisture in the digester gas delivery system and when the biogas was not conditioned enough to be utilized in the fuel cell system the natural gas was engaged (King County Department of Natural Resources and Parks, 2009). The system operated on digester biogas for 2,401 hrs. and generated 2.1 million kWh and the system had an electrical efficiency of approximately 43-44% and a thermal efficiency of about 59-64% (King County Department of Natural Resources and Parks, 2009).

Overall the King County fuel cell installation operated on biogas for only about 100 days. After the two-year trial was completed King County determined that it would not continue with the operation of the system (King County Department of Natural Resources and Parks, 2009). The fuel cell system would require additional changes to its configuration (stack replacement and modifications to integrate the power plant with the operation of the treatment plant), which would not be ideal since the repairs would be expensive and the FCE plant designs had significantly improved since the King County fuel cell plant was designed (King County Department of Natural Resources and Parks, 2009). King County considered replacing the 1-MW system with a smaller 300 kW power plant but decided against it. The biogas generated at the plant is currently being scrubbed and sold to a local gas utility.

2.5.3.5 Portland, Oregon

Portland, Oregon has developed a strategy to reduce climate change through the reduction of contamination due to the combustion of fossil fuels – they aim to do this by utilizing the ADG produced at the Columbia Boulevard Wastewater Treatment Plant (CBWTP) (U.S.)
Department of Energy, 2010). The City of Portland installed a 200 kW ONSI fuel cell system at a cost of $1.3 million (U.S. Department of Energy, 2010). The cost of the installation was reduced when the facility received a $200K Department of Defense grant, a $247K Green Power Credit from Portland General Electric, and a $10K grant from the Oregon Department of Environmental Quality as well as receiving a credit through the Oregon Building Energy Tax for $194K, reducing the project cost to $645K (U.S. Department of Energy, 2010). In a case study prepared by the U.S. Department of Energy, it was reported that the fuel cell installation at the CBWTP has an estimated annual savings of $60K in operating costs.

The CBWTP treats approximately 3.5-3.9 m$^3$/d of sewage per day (U.S. Department of Energy, 2010). The 320 kW PAFC installation began operation in 1998 and the system provided enough power for the facility and the waste heat was used to aid in maintaining the process heating requirements. A four-pack 30 kW microturbine system was installed as an additional power supply in 2003 (U.S. Department of Energy, 2010).

The greatest challenge reported in the case study prepared by the U.S. Department of Energy was the cleaning of the biogas. The ADG was saturated with moisture, and contained hydrogen sulfide, chlorine compounds, and siloxanes that can damage the components of the power plant (U.S. Department of Energy, 2010). There were also a number of issues with the desiccant bed, which was unable to provide adequate of drying the gas and a gas dryer was added to the system (U.S. Department of Energy, 2010). It was deemed that the fuel cell was too costly to maintain and the system was decommissioned in 2005 (Ott, 2008).

2.5.3.6 Case Study Conclusions

The case studies presented highlight recent applications of biogas operating in fuel cells. Some of the projects highlighted display successful applications, whereas others show a less
attractive outcome with the projects being decommissioned due to lacking performance. What can be concluded from the unsuccessful fuel cell initiatives as well as initiatives that are currently operating but have required upgrades and refurbishment is that much research and improvement must be performed to allow fuel cells to operate on AD-derived biogas without decreased cell performance or fouling of the associated systems. The unsuccessful attempts at operation have provided researchers with needed information about improvements and advancements that can be made to further the capabilities of fuel cells operating on AD-derived biogas. Although there are a number of locations where the use of biogas as a renewable source for fuel cells has been demonstrated, there are many more locations that could benefit from the technology. There are other locations throughout North America that are considering the implementation of a fuel cell system. A study in 2005 found that there are more than 400 wastewater facilities in the U.S. that generate enough digester gas to fuel a 1-MW fuel cell power plant, with even more facilities producing enough biogas to power 250 kW fuel cell power plants (Skok & Eschbach, 2005; Scroppo, Laurens, Bush, & Reynolds, 1999).

2.6 Conclusions

Applications of fuel cell technologies operating on ADG show a promising means of clean energy production. Although the technology has been shown to be adaptable to biogas utilization there are still hurdles that must be overcome before fuel cells can become more common. Problems with the operation of fuel cells include the high capital costs remaining high as well as higher the anticipated installation costs (Chuck, 2008). Much research is being conducted to further develop new materials and material properties that can result in a more durable, less expensive SOFC, which will assist with the lowering of the cost of the installation of a biogas fuel cell system as well as reduce the maintenance/operating cost. The installation of fuel
cells at WWTPs can also require additional trained staff members to be employed at the WWTP in preparation for system maintenance, leading to the creation of additional jobs within municipality. The environmental impact of reducing CO$_2$ emissions that would have resulted from flaring of the biogas can be avoided by reforming the CH$_4$ rich biogas to increase the H$_2$ partial pressure and utilizing it as a renewable, readily available fuel source. Using the biogas on-site can reduce the electricity costs to the facility and use on-site would not require additional transport of the gas to another location. This is a technology that once proven could lead to installations at other types of facilities where AD technologies are used such as large agricultural farms, breweries and vineyards.

2.7 References


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Chapter 3

A Review of Biogas Composition and Uses in North America

3.1 Abstract

A study was conducted to determine the current state of knowledge on biogas production and its use at municipal wastewater treatment plants (WWTPs) across North America. Information was voluntarily provided by municipal WWTPs across Canada and the United States, including how the biogas was used as well as any available data on biogas composition and/or production. The compositional analysis indicated that insufficient data is currently collected and available to identify trends or causes in the observed fluctuations. It was determined that hydrogen sulphide ($H_2S$) and silicon (Si) compounds had sufficient variability to be of concern, whereas methane ($CH_4$) did not. The only biogas production trend that could be identified was a possible seasonal relationship with sludge input and biogas production. A secondary analysis was performed to observe trends in biogas usage in urban areas larger than 150,000 in the United States and 50,000 in Canada; 66% of facilities had anaerobic digestion (AD) systems and, of those, only 35% had an energy recovery system. Of these systems, heat generation was the most prevalent and fuel cells the least. Other options included power generation, combined heat and power or selling of the biogas. Climatic, population and socio-political influences on the trends were considered. Fuel cells were identified as a promising new technology and case studies on fuel cells currently employed were presented; at present only phosphoric acid (PAFC) and molten carbonate fuel cells (MCFC) have been used. The primary conclusion of the study was that more data is required in order to perform significant analyses on biogas production and composition.
variation, which are important characteristics for the further development of energy recovery systems.

3.2 Introduction

Municipal wastewater treatment plants (WWTPs) commonly employ anaerobic digestion (AD) systems to treat activated sludge. The digestion process uses bacteria to reduce the mass of sludge as a first step in a biosolids management program. A by-product of this process is a gas composed mainly of CH$_4$ and CO$_2$, commonly referred to as biogas. As the biogas is primarily CH$_4$ (approximately 60%), it can serve as an alternative energy source (Rasi, Veijanen, & Rintala, 2007; Walsh, Ross, Smith & Harper, 1989). Different types of systems are currently being employed or investigated for deployment at WWTPs to utilize this green energy source (direct combustion, internal combustion engines, pipeline sales (can be upgraded to natural gas)) (Walsh et al., 1989). Fuel cells are also being investigated in many urban areas. In addition to CH$_4$, and CO$_2$ and N$_2$, biogas is composed of a number of compounds that can be toxic when the gas is used as a fuel source in fuel cells. These contaminants, primarily H$_2$S, Si (generally in the form of siloxanes) and halides, have different impacts on the equipment required in energy recovery systems.

There is currently considerable discussion in both public and academic forums regarding the expansion of biogas systems. Research shows that there are major concerns associated with variability in the composition and production of biogas even within individual facilities, and little is known of the effect of this variability on energy recovery systems. Wheeldon, Caners, Karan, & Peppley (2007) studied 58 WWTPs across Canada and found significant ranges in biogas contaminant composition. This study expands upon the research compiled by Wheeldon et al. (2007) by targeting facilities across North America. The objective was to determine the current
state of knowledge on biogas production and composition and to identify areas where more data and research are required. This included attempting to identify trends within the variability of the data and factors that could affect this variability at individual WWTPs, as well as between facilities.

This work also reviews various technologies employed across North America and assesses the potential for development and application in North America. Special attention is given to fuel cell systems because of their high efficiencies and potential for lower maintenance costs relative to other biogas energy recovery systems.

3.3 Methodology

3.3.1 Data Acquisition

Lists of urban areas in Canada and the United States were compiled from the most recent census data – 2000 in the USA (United States Census Bureau, 2000) and 2006 in Canada (Statistics Canada, 2007). The minimum population considered in Canada was 50,000 and 150,000 for the US, although smaller urban areas surrounding the study origin (Kingston, Ontario) were also included. In US states where high numbers of biogas systems were observed (i.e. California, Oregon and Colorado), the search was expanded to include all urban areas over 50,000. For states without urban areas with populations above 150,000, the urban area with the largest population was considered. Urban area was selected as the unit of analysis because many American and some Canadian municipalities (i.e. Edmonton and Vancouver) have independent agencies responsible for the operation of their WWTPs. Urban area was found to be a better representation of the scale of industry present in the region.

Official agency websites were searched for references to wastewater treatment. Agencies were classified into three categories: those that (1) mentioned specific biogas end use associated
with the AD of their sludges; (2) mentioned the use of AD in their sludge management; or (3) made no reference to AD in their sludge treatment. Those agencies with specific biogas production systems were contacted electronically. Requests were made for any available data on biogas composition and/or production for use in the study conducted at Queen’s University in Kingston, Ontario.

Finally, the United States database was augmented by including sites found through the 2004 Clean Watersheds Needs Survey (CWNS) Database as compiled by the Environmental Protection Agency (EPA) and individual states, in a report on the Opportunities for and Benefits of Combined Heat and Power at Wastewater Treatment Plants (Eastern Research Group 2006). In this report, it was noted that data was voluntarily self-reported and did not include biogas usage by individual facilities. The CWNS data was reported using a treatment facility unit of analysis. To incorporate the CWNS data in our study, the urban area was first identified for each facility. Where the CWNS list of ADs included urban areas not found in our initial survey, but with populations above the 150,000 minimum, these were added to the United States database, which added 50 urban areas for a total of 139 American and Canadian urban areas.

Some urban areas have multiple agencies and/or multiple treatment plants. For the biogas usage analysis, technologies used (either ADs or biogas systems) were included based on the data found. Where an urban area included multiple treatment plants, different biogas systems were included as reported, otherwise a single anaerobic digester or biogas system was used to represent the entire urban area.

3.3.2 Compositional Analysis

The composition data provided from the facilities and agencies contacted was compiled for the major constituents of biogas (CH₄, CO₂ and N₂₂) and potentially toxic compounds (H₂S and
Si). Oxygen ($O_2$) was included as an indicator of possible air contamination. The original objective included carbon monoxide and halogens/halides, however, as these constituents were not routinely monitored at a number of facilities there was not sufficient data to provide a statistically significant analysis.

The format and breadth in which the data was provided was generally not consistent. Some urban areas provided a number of compositional analyses taken over regular intervals (weekly or monthly) for periods of up to 10 years (City of Ottawa, 2010; City of Philadelphia, 2010; Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010). Other facilities provided one or two reports commissioned to detail the properties of their biogas (OSB Services, 2009b; City of Olympia, 2010; City of Corvallis, 2010).

All the agencies that provided information on their testing procedures reported that the gas was analyzed at independent laboratories. Two limitations were noted, including: the maximum frequency of samples that could be taken due to cost and accessibility, as well as the high potential for sample contamination in transit. In the data provided there were a number of weeks where the samples were noted to be lost or discounted. It was also suggested that extreme data could generally be attributed to air contamination in gas sampling (City of Ottawa, 2010).

Typically, the same protocols were repeated at individual facilities when collecting multiple samples, however, little information was available to report on the similarities or differences between protocols at different sites, which would suggest possible variations in sampling method, number of samples taken, type of gas sampling bag, time between collection and analysis, and different testing methods, leading to challenges in data comparisons and the identification of trends. Accurate and precise sampling protocols and analytical methods are essential for future analysis and application.
Si compounds are particularly challenging to analyze and compare because they are reported in a number of different forms: mg/m\(^3\) or ppm; Si equivalence (equivalent to total Si) or concentration of individual siloxane constituents. For the purpose of this study, Si equivalence was used as it is possible to calculate Si equivalence from siloxane concentrations but it is not possible to back-calculate from Si equivalence. Si equivalence is calculated from individual siloxane concentrations as shown in (3-1):

\[
\text{Silicon Equiv} = \sum \left[ \left( \frac{\text{MW Silicon} \times \frac{\text{Silicon Atoms}}{\text{Molecule}}}{\text{MW Molecule}} \right) \times \text{(Molecule Concentration)} \right]
\]  

(3-1)

Trends and factors that could affect biogas composition variability at individual sites were investigated where enough data were provided (Ottawa, Boston and Philadelphia). Not enough data was available to perform seasonal analysis on Si.

Multivariate statistical analysis using the ProSensus Multivariate statistical software package was conducted for compositional analysis as well as seasonal trend analysis, and production trend analysis. Multivariate statistical analysis examines the observations and analysis of more than one variable simultaneously. Principal component analysis was the multivariate analysis used in the research. Principal component analysis uses orthogonal transformations to convert variables into linearly uncorrelated variables to attempt to explain where the variance in data comes from. These original observations can possibly be correlated or uncorrelated and when transformed to uncorrelated variables are referred to as principal components (there are less principal components than the number of original variables and the first principal component accounts for the greatest amount of variance in the data). The data collected contained some outliers, which were determined to be from gas sampling error in most instances, and were therefore removed from the data sets. ProSensus Multivariate has embedded models to handle
missing data, which are adjusted to better model the data as more data is added. In cases where there was a lot of missing data, such as only having 1-5 data points, the data was not included in the analysis because a model would not be reflective of the variation over an extended time period.

3.3.3 Seasonal Trend Analysis

Trends in CH\(_4\) were tested using one-way Analysis of Variance (ANOVA) in MATLAB. CH\(_4\) is inversely correlated with CO\(_2\) and therefore it was not necessary to run ANOVA testing on CO\(_2\); this correlation was validated using multivariate statistical analysis software. Analysis was first run by season where Winter was defined as December through February, Spring was March through May, Summer was June through August and Fall was September through November; the data from all of the years was divided into these four groups. When sample groups were defined by season, a p value less than 0.0001 was found, indicating some of the samples were statistically significant. Using the Tukey method, with a p value of 0.05, the methane partial pressures in the Tukey method is a statistical test used with ANOVA to determine which means are statistically different from one another; it was used to determine what seasons were statistically different from one another.

In the seasonal analysis there were instances where extreme outliers were reported that were uncharacteristic of the other data reported. It is likely that extreme values observed were the result of sampling errors (i.e. air contamination) or major changes on-site (i.e. maintenance). These outliers were removed from the data set.

3.3.4 Geographical Trend Analysis

ANOVA tests were conducted to determine if the data from each urban area was statistically significant. Only the three sites with extensive data sets were included in the primary
ANOVA tests (Ottawa, Boston and Philadelphia). For the major components (CH$_4$, CO$_2$ and N$_2$) and H$_2$S concentrations both parametric and non-parametric tests were conducted. Parametric tests assume that the data to be modeled comes from a type of probability distribution (for example, that assumption that the data follows a normal distribution) and non-parametric analysis does not assume that the data has a fixed structure. Parametric tests conducted include analysis in the Microsoft Excel software package and non-parametric tests include those done in ANOVA.

3.3.5 Production Trend Analysis

Multivariate analysis was conducted using the data provided for cities across North America and no strong trends in biogas production could be identified using ProSensus Multivariate statistical software. This would indicate that none of the East, West or Central urban areas studied reported having similar biogas compositions at a specific time of the year as other areas in their region. Western urban areas that were included were Washington and Oregon. Eastern areas were Pennsylvania and Massachusetts. And Central areas were: Ontario, Illinois and Ohio. Only areas that provided enough annual biogas composition data were included in the study.

3.4 Biogas Composition and Production Results and Discussion

3.4.1 Biogas Composition Trends

Analysis was first completed on a location-by-location basis where possible. Averages, medians, maxima and minima were found. The data was then compared between urban areas by averaging the data obtained from individual facilities, as shown Table 3-1. The number of urban areas that provided data on each compound is included for perspective. The overall average was calculated using the averages from each location. The minimum and maximum columns represent
the extreme values from any data point from any site. Variability was calculated on an individual facility basis (where multiple data points were provided). Variability at a specific facility within an urban area was deemed critical in determining the feasibility of implementing waste-to-energy systems at a particular site and would affect the performance of the waste-to-energy system.

Table 3-1: Macro analysis of biogas composition variability

<table>
<thead>
<tr>
<th>Compound</th>
<th># Urban Areas</th>
<th>Average</th>
<th>Standard Deviation</th>
<th>Median</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average Variability</th>
<th>Max Variability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH$_4$)</td>
<td>16</td>
<td>63%</td>
<td>2%</td>
<td>63%</td>
<td>50%</td>
<td>69%</td>
<td>9%</td>
<td>28%</td>
</tr>
<tr>
<td>Carbon Dioxide (CO$_2$)</td>
<td>15</td>
<td>37%</td>
<td>4%</td>
<td>38%</td>
<td>24%</td>
<td>45%</td>
<td>14%</td>
<td>38%</td>
</tr>
<tr>
<td>Nitrogen (N$_2$)</td>
<td>13</td>
<td>1%</td>
<td>2%</td>
<td>0.3%</td>
<td>0.0%</td>
<td>9%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Oxygen (O$_2$)</td>
<td>12</td>
<td>0%</td>
<td>0.7%</td>
<td>0%</td>
<td>0%</td>
<td>3%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Hydrogen Sulphide (H$_2$S)</td>
<td>14</td>
<td>134ppm</td>
<td>186ppm</td>
<td>18ppm</td>
<td>0ppm</td>
<td>855ppm</td>
<td>258%</td>
<td>651%</td>
</tr>
<tr>
<td>Si Equivalence</td>
<td>11</td>
<td>12ppm</td>
<td>10ppm</td>
<td>10ppm</td>
<td>0.2ppm</td>
<td>38ppm</td>
<td>137%</td>
<td>340%</td>
</tr>
</tbody>
</table>

*(City of Ottawa, 2010; City of Philadelphia, 2010; Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010; OSB Services, 2009b; City of Olympia, 2010; City of Corvallis,2010; OSB Services, 2009a; City of York, 2010; City of Hamilton, 2010; City of Columbus, 2010; Town of Cobourg, 2010; King County Department of Natural Resources and Parks, 2009; Regional Municipality of Niagara, Ontario, 2010; Metropolitan Water Reclamation District of Greater Chicago, 2007)*

The most frequently measured compounds in biogas are generally CH$_4$ and CO$_2$. They are measured most regularly because they are an indication of the energy value of the gas and are the primary constituents of biogas. Overall, little variation was found in CH$_4$, the more important of the two. The smallest partial pressure reported, approximately 50%, was above the generally accepted value required for fuel cells (Peppley 2006). Ottawa, where this low value was reported also exhibited one of the lowest average values (60%) and the highest variability (28%). The next lowest average CH$_4$ composition of 57% was noted in Seattle; and the next highest variability was approximately 18% in Boston. The summary median and average values were very similar, which would suggest the data was normally distributed for CH$_4$. The distribution of the values can be seen in Figure 3-1.
Similarly, a less than 1% composition difference in the three statistical measures was also reported in Boston, Welland, Grimsby and Philadelphia. As such, the CH$_4$ variability was not considered to be of significant concern for the operation of biogas-to-energy conversion technologies such as fuel cells. More relevant was the potential for the systems to operate continuously at the concentrations produced in the biogas via anaerobic digestion. When analyzed using multivariate statistical analysis using ProSensus Multivariate software CH$_4$ and CO$_2$ were consistently reported to have opposing principle component loadings, indicating that they are generally oppositely contributing to the loadings and this is confirmed when reviewing the biogas production data; as the CH$_4$ production increases, the CO$_2$ production decreases. For Ottawa, it was possible to account for almost all variation in data using 2 principal components.

The larger standard deviations indicate significant variability for N$_2$ and O$_2$. The variability value appears small due to the scale of the average concentrations but the deviation
indicates otherwise. It has been suggested that the higher concentrations of these two compounds are likely from sample contamination with air (City of Philadelphia, 2010; Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010; Regional Municipality of Niagara, Ontario, 2010). The high values for both compounds were observed at Olympia, Washington, which suggests their sampling procedure may have allowed for air contamination (City of Olympia, 2010).

The variability is considerably more significant for \( \text{H}_2\text{S} \) and sulphur compounds. For \( \text{H}_2\text{S} \), the average (134ppm) was considerably different than the median (18ppm) and the standard deviation (186ppm) was larger than both of these values. For individual sites the distribution was generally less variable with the maximum difference between means, medians and averages on the order of 10ppm. Many facilities exhibited extreme concentrations that may be of concern for biogas systems susceptible to sulphur poisoning. The maximum variability was observed for the Ottawa facility, where consistently higher concentrations of \( \text{H}_2\text{S} \) were reported in the last year of data provided (City of Ottawa, 2010). Omitting the extreme values from the Ottawa data set, the average variability remained greater than 200%, which is of concern for treatment systems.

Philadelphia’s \( \text{H}_2\text{S} \) concentrations were significantly lower than many other facilities, ranging from 0 to 9ppm with an average of approximately 4ppm (±3ppm). This was attributed to the use of ferric chloride as a coagulant, where the iron was reported to bond with the sulphur in the sludge preventing it from forming \( \text{H}_2\text{S} \) gas (City of Philadelphia, 2010). The addition of ferrous sulphate (\( \text{FeSO}_4 \)) has also been reported to precipitate phosphorus from sewage, and can also precipitate \( \text{H}_2\text{S} \) under anaerobic conditions (Rasi et al. 2007). In groupings of average concentration observations, 3 cities were noted to have averages below 10ppm, 6 cities had average between 10ppm and 21ppm, and 5 cities had averages greater than or equal to 150ppm. It
would be essential for a city to determine its biogas H$_2$S concentration prior to biogas use particularly for sensitive technologies, as well as consider possible variances in biogas components when considering biogas-to-energy system applications. For Ottawa, using multivariate analysis, with 2 principal components, it was shown in the variable importance plot that H$_2$S was the most variable.

The variability in Si compounds is not as extensive as for H$_2$S, but is sufficient to be of concern. Most technologies are sensitive to Si at low concentrations. In this study, the number of concentration values provided was smaller, which would imply that less information is available and, hence, less is known regarding the Si concentration variability. The maximum number of data provided from a single site was 12, compared to up to 480 for other compounds. This is likely due to the sampling procedures required for Si testing (City of Philadelphia, 2010). The summary average (12.0ppm) and median (9.895ppm) were found to be on the same scale. On an individual site basis, the averages, approximate modes and medians were generally similar (within 1-2ppm) for the 4 locations where this data was available and provided. A variation in Si would be expected, but not enough data was available to accurately identify any trends or extremes. Including Si testing in the regular testing of biogas conducted at a number of biogas generating sites would greatly improve the state of knowledge on the composition and variability of Si in biogas.

The average composition and variability for biogas found in this study was comparable to the other studies (Wheeldon et al., 2007; Rasi et al., 2007; Spiegel, Thorneloe, Trocciola, & Preston, 1999).
Table 3-2: Comparison of biogas composition in literature

<table>
<thead>
<tr>
<th>Research</th>
<th>CH$_4$ (%)</th>
<th>CO$_2$ (%)</th>
<th>O$_2$ (%)</th>
<th>N$_2$ (%)</th>
<th>H$_2$S (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogas Survey Data</td>
<td>50-69</td>
<td>24-46</td>
<td>0-3</td>
<td>1-9</td>
<td>0-855</td>
</tr>
<tr>
<td>Wheeldon et al., 2007</td>
<td>58-70</td>
<td>30-43</td>
<td>0.1-2</td>
<td>1.2-7.1</td>
<td>2.5-3450</td>
</tr>
<tr>
<td>Rasi et al., 2007</td>
<td>61-65</td>
<td>36-38</td>
<td>&lt;1.0</td>
<td>&lt;2.0</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Spiegel et al., 1999</td>
<td>57-66</td>
<td>33-39</td>
<td>&lt;0.5</td>
<td>1.0-4.0</td>
<td></td>
</tr>
<tr>
<td>Balat, M., Balat, H., 2009*</td>
<td>55-65</td>
<td>35-46</td>
<td>0-2</td>
<td>0-3.0</td>
<td></td>
</tr>
</tbody>
</table>

*Research was conducted in the UK, yet shows similar results to North American data

All the compositional analysis studied is within a similar range for the major constituents of CH$_4$ and CO$_2$. Greater variation is reported for H$_2$S, which is often the contaminant that can cause the most significant impact when used in waste-to-energy systems such as fuel cells.

3.4.2 Seasonal Trends

No trends were observed for CH$_4$ concentration as a function of time. This is demonstrated in Figure 3-2 and Figure 3-3. In Ottawa the lowest concentrations occurred in the Winter and the highest concentrations were reported in the Summer. Summer was found to be statistically different from those noted in Winter and Spring. The analysis was then repeated for samples based on month; methane concentrations in July were found to be statistically different from January, April and December. Similar trends were not observed in Philadelphia and Boston, where Spring and Fall were found to have the greatest variability and no seasons or months were found to have statistically significantly different methane concentrations based on ANOVA, which would suggest that the behaviour noted at the Ottawa facility is site-specific. Cites of
Boston and Ottawa provided samples from multiple days per month (typically, at least 4 samples per month).

**Figure 3-2**: Annual Ottawa CH$_4$ composition (City of Ottawa, 2010).

**Figure 3-3**: Annual Boston CH$_4$ composition (Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010).
Using ProSesnus Multivariate statistical analysis these observations were confirmed and it can be concluded that no strong trends can be reported that are attributed to seasonal analysis.

In the multivariate analysis for Boston, using a model with three principal components (R2 =0.99, Q2=1), the T-scores outside the 95% confidence region are the dates in the winter of 2005 that are shown in Figure 3-3 as the green line and appear to have no trend, which can be attributed to fluctuations in the CH₄ and CO₂ production reported.

No relationships were observed for H₂S concentrations in Ottawa and Philadelphia (data was not available for Boston). Since the variation in H₂S concentrations at individual sites was substantial, other factors not represented by season were thought to be prevalent. Multivariate analysis indicated that H₂S was an important variable and contributed to the variation in T-scores for the Ottawa annual data, showing that in 2009 elevated H₂S production was uncharacteristic of the other annual data provided. The model used had 2 principal components R2 was approximately 0.83. T-scores, or the t-statistic, can be used to assess the statistical significance of the difference between to data sample means. The presence of sulphur is thought to be dependent on the feed composition and wastewater treatment process (Arnold, 2009). Additional data including variables for both sludge composition and digester process conditions are required to analyze additional possible trends with respect to H₂S and sulphur concentrations.

Statistically significant (defined as p=0.05) differences were found between all sites for all components, indicating that each urban area exhibits differences in biogas composition that would be an important consideration in implementing waste-to-energy systems that are sensitive to differences in biogas composition. Waste-to-energy systems that utilize biogas must be specifically designed (the fuel conditioning systems in particular) to meet the needs of the biogas
being fed to the system or risk potential failure of the system. Hence, each urban area would require a system to be designed to specifically meet their gas conditioning needs.

More definitive conclusions regarding important factors can be drawn from ANOVA tests on the data from the 4 sites from the Niagara Region (Grimsby, Niagara Falls (Ontario), St. Catherine’s and Welland). Each site had 12-13 data points. The sites have comparable climates and some similar socio-economic factors. Non-parametric conservative analysis (referring to statistical analysis that does not assume that the structure of the statistical model is fixed) was conducted on CH$_4$, CO$_2$, H$_2$S and Si equivalence. For CH$_4$, Grimsby and Welland were found to be significantly different. No pairs were significantly different for CO$_2$. Niagara Falls was found be significantly different from both Grimsby and Welland for both H$_2$S and Si. It could be concluded that climatic factors alone were not the likely cause of differences in biogas composition since the sites are within a 50km radius of each other and therefore share similar climates. The weather in the area consists of 4 seasons with average daily temperatures of 5-19°C in spring, 21-25°C in summer, 8-22°C in the fall and -1-2°C in the winter.

3.4.3 Production Trends

In order to optimize biogas usage at WWTPs, a detailed understanding of the variation in its production is required. Besides the deviation in biogas composition, there is also variability in biogas production over time. Based on the data from the four sites that provided extensive data sets (Welland, Ontario; two plants in Niagara Falls, Ontario; and Boston, Massachusetts), CH$_4$ variability at a single facility was found to range between 61% and 98% (m$^3$/d) (Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010; Regional Municipality of Niagara Ontario, 2010). Within the compositional range of this variation, systems designed to use biogas could either be starved of fuel or produce excess fuel that would require flaring.
There are numerous factors that can be related to biogas production variability. Source-based factors could include: source population and characteristics, percentage and type of industry, restrictions or additions to the sanitary system and seasonal variation. Treatment plant process-based factors could include digester volume, temperature, standard residence time and type of pre-treatment processes. A critical factor is system size - either enough systems of equivalent size or a wide range of sizes would be required to quantify the relationship between volume and production before variation based on other factors could be properly analyzed. With the data available only a preliminary analysis was possible. For example, in Cobourg, Ontario it was noted that the closing of the Kraft Canada plant in 2007 resulted in a reduction in biogas production of 50% (Town of Cobourg, 2010). This decrease was likely a combined effect of the loss of organic waste from the food processing plant (primary cause), and the effect of food organic waste effectively serving as a co-digestate (secondary cause). Had information on the specific decrease in loading been available, the effect of the secondary factor could have been preliminarily quantified. Both Boston and Ottawa utilize mesophilic ADs, which operate between 30-35°C to maintain optimal living conditions for mesophilic bacteria that assist in the formation of biogas. Overall, mesophilic reactors are the most commonly used in anaerobic digestion of sewage (Balat, 2009). Analysis was conducted to compare different cities against each other, but it would be very interesting to have multiple WWTPs in the same city provide data so that further conclusions regarding trend within the same wastewater source location be identified.

The City of Boston’s Deer Island Treatment Plant, operated by the Massachusetts Water Resources Authority, provided comprehensive data on biogas production from July 2000 to June 2009 (Deer Island Treatment Plant, Massachusetts Water Resources Authority 2010). While this data cannot be used as a representative analysis of production across North America, it is a
preliminary step to identifying some major trends and factors in biogas production variability at a single site. The data of primary interest was the monthly biogas production and sludge input (also divided into primary and secondary sludge input values).

The biogas production data was plotted on a monthly basis to allow for visual observation of any seasonal patterns. None were observed, nor was any significant correlation found. Plotting sludge input monthly resulted in the same absence of observable or statistical relationships. A positive linear trend was observed between sludge input and biogas production, but the $R^2$ value of 0.3677 shows many other factors influenced the biogas production. This trend between sludge input and biogas production could also be visually observed by plotting both the sludge input and the biogas production over the time period reported as seen in Figure 3-4.

![Figure 3-4: Biogas production and sludge input from Boston (Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010).](image)

From Figure 3-4, it can be seen that an increase or decrease in sludge input generally resulted in a corresponding change in biogas production. Sludge input versus biogas production was plotted as four distinct seasonal data sets to discern if different trends could be identified during different periods of the year. In Figure 3-5, the seasons are defined as: Spring (March,
April, May), Summer (June, July, August), Fall (September, October, November), and Winter (December, January, February).

![Figure 3-5: Seasonal trends between sludge input and biogas production from Boston (Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010).](image)

From Figure 3-5 the most significant difference could be seen for winter. This might suggests that a fundamental difference in the relationship between sludge input and biogas production in Winter. The $R^2$ value of 0.662 was relatively low, however, the range of data variability and other influential factors in biogas production, also need to be considered. The Summer trend line also exhibited a similar correlation ($R^2=0.599$). The trend lines for Spring and Fall had comparatively low correlation values suggesting that other factors may have had primary influence. In Spring and Fall there are typically more fluctuating weather patterns, which influence the wastewater entering the treatment plant, thus altering the biogas production and quality. Seasonal analysis using multivariate statistical analysis indicated that there were no
seasonal trends for Boston. A model with 2 principal components had an R2=0.99 and Q2=0.99. Data that was outside the 99% confidence region had abnormally high CH4 partial pressures contributing to p-scores and occurred in winter months (there were only two data points outside the 99% confidence region).

Relationships between biogas production and other factors were examined: primary versus secondary sludge, average monthly temperature, average monthly temperature variation, and precipitation. No significant trends were noted.

3.5 Biogas Use at WWTPs in North America

Biogas generated via AD at municipal WWTPs has been utilized in a number of applications. Often the gas is flared to convert the CH4 into CO2, lessening the greenhouse gas effect (Deer Island Treatment Plant, Massachusetts Water Resources Authority, 2010). Biogas can also be considered a commodity for its energy potential. The practices employed across North America were categorized based on technological complexity and end products. The simplest method being the selling of the raw gas for usage elsewhere (Farhad et al., 2010). Another practice is to burn the biogas in boilers or similar equipment for the direct production of heat that is often employed to maintain the temperatures of the digesters, or to heat dryers used to dry the sludge during biosolids processing. At some sites, all of the biogas can be utilized as heat during the winter months, however, during the summer, excess gas is flared (City of Mount Vernon, Washington, 2010). In this study, systems that were found to have an anaerobic digester but did not report biogas use, or where biogas usage was reported but specified, usage was categorized as “Unknown” during analysis. Cogeneration, also known as combined heat and power (CHP), is a single system (often a generator), which generates both electricity and heat to be used on-site.
The technology may be similar to that employed in electricity production, but the end products are different.

![Pie chart showing biogas end use distribution for the United States and Canada.](image)

**Figure 3-6**: Biogas end use distribution for the United States and Canada. Only known biogas systems, with no restrictions on minimum population size, are included. Where cities report multiple type of system, equal weighting is given to each. The total weighting for each city is one regardless of the size or the number of treatment plants with units. 210 locations are used.

From Figure 3-6, heat production was most prevalent, representing 44% of all the biogas use in the study. This is due in part to its popularity in smaller communities because it is the easiest to install and operate. Systems that produce electricity can have a high capital cost, which can be difficult for smaller WWTPs to implement and the high cost may have a longer payback period given the relative amount of biogas produced at these site, which would provide for limited electricity production. Fuel cell applications are relative limited. Currently, the capital cost of installation of a fuel cell system (approximately $3000/kW) is high and expensive gas conditioning systems must be in place to enable the cells to work effectively (Spiegel et al., 1999). This, combined with limited research in large-scale applications, has prevented fuel cells from becoming more commercially viable. It is anticipated that as the automotive industry adopts
fuel cells as a viable power source, parts required for the systems will become less expensive and more readily available (PriceWaterhouseCoopers, 2008).

3.5.1 Biogas End-Use Trends

In order to visually observe any trends associated with biogas usage as a function of location, the locations of all facilities with known biogas systems or ADs were added to a Google Earth© map as shown in Figure 3-7. Urban areas that were known to have digesters but reported no biogas-to-energy systems were included on the map, as indicated by the navy blue makers.
Figure 3-7: Geographical Distribution of Systems on Google Earth Map. The map shows all urban areas with populations above 150,000, colour-coded based on type of end use. Sites with populations below 150,000 were added only if they had a known system. Where multiple types of systems are reported, only the most technologically advanced was shown.

3.5.1.1 Climatic Trends

Figure 3-7 indicates that no climatic trends could be identified for the presence of ADs or biogas systems. It may appear as though coastal climates have a greater prevalence for these systems; however, this can be accounted for by the larger population densities and in coastal regions. From Figure 3-7, no correlations could be found that would suggest that anaerobic digester use decreases as regional temperature decreases due to higher energy requirements in maintaining digester temperature. There may be a relationship between heating systems and increasing latitude as seen by the general absence of heating systems below Nashville, Tennessee. This is likely because cooler climates require a larger fraction of the biogas generated to maintain digester temperature.

3.5.1.2 Socio-Political Trends

Based on Figure 3-7, there would appear to be a greater prevalence of biogas-to-energy systems along the west coast of the United States, implying that socio-political relationships may exist in this region. These socio-political relationships can be developed through the implementation of green legislation, etc. The presence of ADs appears fairly random with regard to state boundaries, although they are more concentrated in the eastern United States, where as biogas-to-energy systems are more prevalent on the west coast. For the three west coast states (Washington, Oregon and California) only 7 (out of a total of 28) sites were found to have ADs without a waste-to-energy system. In the eastern states only approximately 20% of the ADs were associated to waste-to-energy systems.
Any state-based trends observed in Figure 3-7 should be adjusted based on the number of urban areas within each state. In order to compare the different states, the number of sites with digesters and biogas systems were found as a percentage of the number of urban areas above 150,000 for the United States. For analysis, states were categorized as ‘larger’ if they had five or more urban areas above 150,000 for the United States.

Within the grouping of larger states, California was observed to have the highest percentage of biogas-to-energy systems (55%) and digesters (73%). It was followed by Pennsylvania (33% biogas systems and 78% digesters), Ohio (33% biogas systems and 67% digesters) and Illinois (40% biogas systems and 80% digesters). This trend was further supported by Figure 3-7, examining the cities with populations below 150,000, especially within California where 5 additional biogas systems and 8 additional digesters were found (out of 29 cities). California’s higher number of waste-to-energy system installations may be related to the status of green legislation within the state. California was the only state identified in a 2009 World Bank report on the carbon market; both the California Global Warming Solutions Act and the California Climate Action Reserve were included in a list of five major carbon market initiatives (DOE, 2004). Four states: Texas (no waste-to-energy systems and 64% digesters), Florida (6% waste-to-energy systems and 53% digesters), Michigan (no waste-to-energy systems and 43% digesters) and Connecticut (no waste-to-energy systems and 50% digesters) were observed to demonstrate a low affinity towards the implementation of higher-level wastewater treatment and the application of waste-to-energy systems.

Colorado, with 3 sites, has 67% biogas-to-energy systems and 100% digesters. All urban areas within Colorado with populations above 150,000 were found to have digesters, with only one not having a biogas-to-energy system. Idaho, Kansas and New Hampshire each had only 1
urban area above 150,000, but reported the use of a biogas-to-energy system. Many states had no biogas-to-energy systems. Mississippi (with 2 cities) did not report the use of AD at its wastewater treatment plants. Louisiana (25% digesters) and Alabama (50% digesters), each with 4 sites, were identified as states with minimal affinity towards the installation of biogas-to-energy systems. Oregon and Washington appear significant on the map because both have many cities between 50,000 and 150,000 with ADs and biogas-to-energy systems.

A similar analysis in Canada is challenging due to the small number of urban areas above 50,000. Ontario has the highest number of biogas-to-energy systems, but this may be entirely accounted for by the density of urban areas within Ontario. Canada has 20 urban areas above 50,000 (that information regarding AD-technology was available for); 45% of them have waste-to-energy systems and 60% of them have ADs. In the United States, of the 185 cities surveyed, 21% had waste-to-energy systems and 45% had ADs.

In Canada heat has a greater prevalence (62%) and electricity generation is lower (13%) in WWTPs. Cogeneration is similar at 25%. In urban areas with populations above 50,000, fewer AD have been implemented without waste-to-energy systems in Canada. The study observed that cultural differences existed between the two countries regarding WWTPS.

A relationship between carbon market and/or emissions organizations and a state/province’s affinity towards biogas systems was considered. Three major North American initiatives have been implemented: The Regional Greenhouse Gas Initiative (Regional Greenhouse Gas Initiative, 2010), the Midwestern Gas Reduction Accord (Regional Greenhouse Gas Initiative, 2010) and the Western Climate Initiative. The membership of these three American initiatives was reviewed. Only the Western Climate Initiative membership was found to correspond to states with a high rate of installation of biogas-to-energy systems; it was
expected that a states participation in these initiatives would increase the likelihood that it would have a higher chance of installing biogas-to-energy systems at WWTPs, but this was not the case.

California, Oregon and Washington are all members of this organization, with Colorado, Idaho and Kansas being observers. The other state members (Arizona, Montana, New Mexico and Utah) or observers (Alaska, Wyoming or Nevada) were found to have some affinity towards the installation of waste-to-energy systems (Western Climate Initiative, 2010). Further investigation is required to determine the motivations exerted by some states toward a greater prevalence of waste-to-energy systems compared to others, as it cannot simply be directly related to the carbon market or emissions initiative present in a given state.

3.5.1.3 Population Trends

When determining any trends in population, the analysis of waste-to-energy systems in place in a particular urban area was limited to urban areas with a population above 150,000. A histogram of the data, categorized by end use, is shown in Figure 3-8.
Figure 3-8: Biogas usage population histogram for the United States and Canada. The histogram bin range doubled with population as the number of sites decreases with population; the number of urban areas within each bin is included.

Generally, the use of ADs at WWTPs increases with increasing population. The percentage of ADs without a known waste-to-energy system (classified as Unknown) was relatively common below populations of 4 million. Known waste-to-energy systems slowly increase, with the exception of populations of 1 million and 4 million, where rapid increases were observed. These trends were better represented in Figure 3-9.

Very few biogas to fuel cell energy system trends as a function of population could be identified with the exception that most fuel cell systems tended to be located in urban areas with populations greater than 1 million. This is likely due to two factors: larger communities have greater financial support available for demonstration and pilot facilities, which is the status of most current fuel cell operations, and the types of fuel cell systems currently applied require
larger scale operations to be financially viable (Peppley, 2006). Expansion into fuel cell systems that can be operated cost-efficiently on a smaller scale could change this trend.

For ADs, 50% of urban areas above a population of 150,000 had ADs; 75% of urban areas above 533,000 and 100% of cities above 3.9 million reported having ADs. For known biogas usage, 25% of urban areas above 187,000, 50% of cities above 1.3 million, 75% of cities above 4.0 million and 100% of urban areas above 5.1 million reported having a biogas energy recovery system.

![Graph showing biogas population trends](image)

**Figure 3-9:** Biogas population trends in anaerobic digester installations and waste-to-energy biogas end usage. Percentage of usage corresponds to the population that typically has anaerobic digestion technology installed and a known waste-to-energy use for biogas produced. 210 urban areas were included.

A tangential function pattern for both ADs and biogas systems is shown in Figure 3-9. Both lines have a stable region between populations of approximately 2 million and 4 million, which would suggest that population size is not the primary factor within this range for influencing the usage of ADs or biogas systems. Outside of this range an increase in population corresponds to an increase in the likelihood that a facility will be equipped with ADs and consequently employ the biogas in an energy recovery system. The difference between the two
lines is relatively consistent throughout the population range until anaerobic digester use reaches 100%. For example, at a population of 193,000 the difference is 45%. Within the stable region, at a population of 1.5 million, the difference is 36% and when digesters reach 100% at 3.9 million the difference is 40%. This would suggest the relationship between ADs and biogas usage is consistent for all population ranges.

The application of various biogas energy recovery systems, as seen in Figure 3-8, over the range of populations considered suggests that implementation of biogas-to-energy system is feasible for all urban areas with ADs identified in the study. This could result in an additional 90 cities where energy could be obtained from biogas, almost twice the current number of cities (49). If the quantity of biogas produced at each WWTP was known it would be possible to estimate the potential energy produced when a specific waste-to-energy system (such as cogeneration or a fuel cell system) was implemented. This information was not available as many urban areas flare their biogas and therefore do not need to measure the quantity produced. For example, the Yonkers, NY 200 kW fuel cell installation produces 1,565,000 kWh of electricity over 11,959 hrs. and treats approximately 90-100 million gallons of sewage daily (Spiegel, & Preston, 2003). The potential for electricity generation at WWTPs is high.

There are a few factors that limit some sites with ADs from harvesting energy from the biogas produced. The first major factor is a time delay, the time required between adoption of a technology and its widespread implementation, particularly in the public sector. Anaerobic digesters are an older technology and therefore more established within the wastewater treatment community. Our study identified a number of cities including: Baltimore; Phoenix; Raleigh, North Carolina; Norwich, Connecticut; and Modesto, California, that were at various stages of studying or implementing biogas to energy systems (City of Baltimore, 2010; City of Phoenix,
This requires an accurate estimate of the composition and production of biogas based on-site characteristics.

Currently, electricity generation through the use of fuel cell waste-to-energy systems at WWTPs is generally only economical for capacities greater than 200 kW due to maintenance costs (Peppley, 2006). The energy produced from the fuel cell system could provide a decrease in the operational costs of the WWTPs by reducing energy costs, making the lifecycle cost of anaerobic digester/biogas energy systems reasonable and it has been reported that as the costs of electricity from the grid become higher, electricity generation from fuel cells becomes more economically advantageous (Spiegel et al., 1999). It has been proposed that fuel cells, notably solid oxide fuel cells (SOFCs), could be economical at lower capacities due to higher energy efficiency and lower maintenance costs (Peppley, 2006). Their inherent modular design is also beneficial, as they can be easily scaled for site-specific use.

3.6 Biogas Use in Fuel Cells

Consideration of biogas composition variability is especially relevant for those studying the application of biogas to fuel cell energy systems because fuel cells are one of the technologies most susceptible to contamination. Fuel cells have many advantages, including: being modular; having a higher electrical efficiency than traditional electricity generation systems and combined heat and power systems. It is important that the current data on biogas composition variability be increased because fuel cell systems depend on high quality biogas, free of contaminants such as H₂S, and compositional changes can cause decreases in cell performance. Understanding and being able to estimate biogas production variability, both in terms of volume and composition,
could allow for future system designs where modular systems are turned on and off based on estimated biogas production quality and quantity.

Despite their advantages, fuel cells are currently the least implemented of the major biogas systems (6%) at municipal WWTPs, though there has also been expansion of the technology into non-municipal biogas sources (i.e. breweries) (Peppley, 2006). Case studies involving municipal fuel cell installations were compiled to determine the current status of the technology and are summarized in Table 3-3. Special focus was given to the size and type of system implemented, as well as any available results or issues encountered.

**Table 3-3: Comparison of fuel cell biogas waste-to-energy system installations**

<table>
<thead>
<tr>
<th>Location</th>
<th>Type of Fuel Cell</th>
<th>Biogas Produced at Site</th>
<th>Years of Operation</th>
<th>Contaminants/ Lessons Learned</th>
<th>Biogas Cleanup System</th>
<th>Energy Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yonkers, New York</td>
<td>200 kW PAFC</td>
<td>95mgd of sewage treated</td>
<td>Still in operation</td>
<td>Removal of sulphur and chlorine compounds necessary System was altered to accommodate increased fuel flow rates since biogas is typically ≈ 60% CH₄ which is converted to H₂ and high flow is required so the cell does not starve Additional acid was necessary in the cells to match the higher fuel flow rate.</td>
<td>Fuel processor removes O₂, sulphur and halides (carbon beds used), and converts fuel to H₂ using a reformer</td>
<td>In a 2-year research period the system operated 11,959 hrs. and produced 1,565,000 kWh of electricity.****</td>
</tr>
</tbody>
</table>
Dual fuel capability was implemented to enable a back-up fuel to be used when fuel conditioning needs were not met.

<table>
<thead>
<tr>
<th>Location</th>
<th>Power</th>
<th>Wastewater capacity</th>
<th>Demonstration period</th>
<th>Fuel Conditioning Issues</th>
<th>Fuel Conditioning Solutions</th>
<th>Run Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Treatment Plant, Renton, King County, Seattle, Washington</td>
<td>1MW MCFC</td>
<td>115 mgd wastewater capacity</td>
<td>2 year demonstration project</td>
<td>Issues with mechanical routes of getting biogas to the fuel cell system and cleanup</td>
<td>Carbon media to remove H\textsubscript{2}S</td>
<td>Run time of 2,401 hrs. produced 2.14 million kWh with an electrical efficiency of 44% and thermal efficiency between 59-64%</td>
</tr>
<tr>
<td>Columbia Blvd. WWTP, Portland, Oregon</td>
<td>320 kW PAFC</td>
<td>80-90mgd of sewage treated</td>
<td>Air flow in fuel stream sensitivities – unable to remove air though because it was required in carbon beds. Very low concentrations of</td>
<td>Gas processing unit to remove H\textsubscript{2}S and halogens Carbon beds to remove H\textsubscript{2}S Additional drying required</td>
<td>Power for the facility and waste heat used to heat facility Decommissioned in 2005</td>
<td></td>
</tr>
</tbody>
</table>
The re are additional PAFC installations at various WWTPs in New York City, NY, at the 26th Ward WWTP (200 kW), the Red Hook WWTP (two 200 kW), the Oakwood Beach WWTP (200 kW) and the Hunt’s Point WWTP (three 200 kW units) (Kishinevsky, 2003, New York City Department of Environmental Protection). Also, the City of Santa Barbara operates two 250 kW MCFCs using renewable digester gas at its El Estero Wastewater Treatment Plant (California Stationary Fuel Cell Collaborative, 2010). The Dublin San Ramon Services District in California’s San Ramon Valley has installed two 300 kW MCFC’s (Gunn, 2009). The Sanitation District of Los Angeles has installed a 250 kW MCFC system at their Palmdale Water Reclamation Plant (WRP) as part of a demonstration project (California Stationary Fuel Cell Collaborative, 2010). The Palmdale WRP generates about 80 cfm of digester gas, with about 60-80% of it being used to produce electricity for the facility (California Stationary Fuel Cell Collaborative, 2010; Western Area Power Administration, 2005). To date, these studies have not published extensive data with regards to their performance, as they are newer installations.

The successful installation and operation of biogas powered fuel cells is encouraging for the future of fuel cell systems at municipal WWTPs. Using biogas for fuel cell installations is entirely feasible, as the highlighted case studies have shown. Yet, there is considerable research that remains to be conducted to further the effectiveness of biogas to fuel cell applications. To date only two types of fuel cells have been tested at WWTPs (MCRCs and PAFCs) while

*(U.S. Department of Energy)*
**(King County Department of Natural Resources and Parks, 2009)**
***Kishinevsky, 2003***
****Hermann, 2008****
******Spiegel, & Preston, 2002******
research suggests other types (such as SOFCs) could be just as effective if not more so (Peppley, 2006). As such, fuel cells are well suited to meet the high-energy demands of a WWTP in an environmentally and financially sustainable manner.

3.7 Summary

The primary objective of this study was to determine the current state of knowledge on biogas in North America. The goals were to both characterize the composition and production rates, and to determine the extent of biogas systems across the continent. Data analysis was performed to identify trends within the compiled data, the variability and typical values of the biogas and any areas where available data is inadequate.

Results from the biogas composition analysis were inconclusive. Prior to analysis, the study outlined differences in testing protocols between sites and the potential for sample contamination. A table of ranges and averages was developed for common compounds and from this it was noted that CH₄ variability is not a significant concern, but small quantities of H₂S and Si in the biogas could be of concern. H₂S (ppm) was found to vary significantly between sites (0-855ppm). H₂S can vary drastically depending on the quality of wastewater entering the WWTP. When examining single-site variability, biogas production trends or relationships as a function of date or season could not be readily identify. Data on process or feed changes would be essential in determining causes for the fluctuation in H₂S concentration. The data acquired through the survey was insufficient to perform analyses on possible factors influencing the differences in composition between sites. It would be difficult to compile data for some of the factors hypothesized factors, notably socio-economic ones. It was determined that there were statistically significant differences in composition between sites, even within the same geographic region.
It was not possible to conduct a comprehensive analysis on biogas production due to the limited number of cities providing data. It was found to be highly variable for each site, which can be accounted for through a combined relationship between anthropological seasonal patterns and sludge input. To establish any trends between sites the relationship between production and treatment facility size would first have to be quantified before other relationships could be identified.

In urban areas, greater than 150,000, 66% of sites reported having digesters and of these digesters 35% had an associated energy recovery system. Heat generation is the most employed technology (44%), with fuel cells being the least employed on-site technology (6%). The only climatic trend observed was the higher prevalence of heat generation as the chosen end use with increasing latitude. Stronger socio-political trends were observed, with California appearing as the most active state in terms of AD and biogas usage systems. Detailed analysis was not possible in Canada, due to the limited number of facilities that were able to provide data to the study.

Trends in the type of biogas system employed in urban areas were observable; fuel cells primarily located in urban areas with populations greater than 1 million. The largest potential market for further implementation of biogas systems resides in smaller urban areas and as more systems are manufactured and successfully demonstrated, capital costs will decrease. Based on the number of ADs already employed in North America, an additional 90 urban areas exist where biogas can be utilized as a renewable energy. Many smaller urban areas are already in the process of designing new systems, which include digesters and biogas recovery systems could be implemented simultaneously. The most promising technology for smaller communities is SOFCs, which with future research can be made modular for small-site implementation. Currently, the successful biogas-to-fuel-cell systems have been primarily PAFC or MCFCs.
Acquiring sufficient data to perform significant analyses on the variation in composition and production of biogas at WWTPs is essential in implementing biogas systems. This data must come from communities across North America with a dedicated effort to expand and share information.

3.8 References


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City of Hamilton, O. (2010). *Biogas Data from Hamilton's Anaerobic Digesters*.


City of Tampa, F. (2010). *Anaerobic Digesters*.


King County Department of Natural Resources and Parks. (2009). *King County Fuel Cell Demonstration Project*. Retrieved August 13, 2010, from King County:


Town of Cobourg, O. (2010). *Biogas Data from Cobourg's Anaerobic Digesters*.


Chapter 4

The Performance of Anode Supported Tubular Solid Oxide Fuel Cells on Dilute Hydrogen Gas

4.1 Abstract

Commercially available anode supported tubular solid oxide fuel cells (SOFCs) with Ni-YSZ (nickel and yttria-stabilized zirconia) anodes, LSM (lanthanum strontium manganite) cathodes and an YSZ electrolytes were tested with dilute H\textsubscript{2} fuel to determine the effects on cell performance. Diluents used in the testing procedure were N\textsubscript{2}, N\textsubscript{2}+H\textsubscript{2}O, Ar+H\textsubscript{2}O and CO\textsubscript{2}+H\textsubscript{2}O at mole fractions of 65% H\textsubscript{2}, 25% H\textsubscript{2} and 10% H\textsubscript{2}, respectively. All tests were conducted at 800°C and 1 atm with air as the oxidant. N\textsubscript{2}, N\textsubscript{2}+H\textsubscript{2}O and Ar+H\textsubscript{2}O diluted fuel performed similarly for all H\textsubscript{2} partial pressures studied. CO\textsubscript{2}+H\textsubscript{2}O as a diluent exhibited a decrease in cell voltage performance in comparison to the other diluents, and through computation, it was determined that the reverse water gas shift reaction reduced the mole fraction of H\textsubscript{2} in the fuel gas mixture, which caused the decreased performance.

4.2 Introduction

Recent studies in fuel cell technologies have shown that solid oxide fuel cells (SOFCs) have the ability to operate dilute hydrogen gas mixtures, while still maintaining high performance (Jiang & Virkar, 2003; Ormerod, 2003; Kendall, Finnerty, Saunders, & Chung, 2002). Hydrogen gas mixtures can be in the form of hydrogen mixed with diluent or biogas produced through anaerobic digestion of municipal wastewater sludge. A limitation of SOFC’s is the need to operate with hydrogen (or hydrogen-rich fuels) (Atkinson, et al., 2004). The intermediate
operating temperatures and resilience to poisoning by a number of impurities in fuel gas mixtures makes SOFCs a more flexible technology for use with a variety of different fuels (Ormerod, 2003; Jiang & Virkar, 2003). Because of the required operating temperature for SOFCs, it is possible to internally reform fuel gases within the cell, without the use of an external reforming catalyst (DOE, 2004). This allows for the use of methane and other light hydrocarbons to be used successfully within the cell.

Anode-supported SOFCs could potentially exhibit reduced cell performance as a result of the resistance to the transport of fuel gas mixtures through the anode to the electrolyte layer (Jiang & Virkar, 2003). Concentration polarization losses can occur when there is not a high enough partial pressure of reactants diffusing through the porous anode and cathode to react and, thereby, maintain cell performance.

This paper will investigate the effects of H₂ diluted with humidified N₂, CO₂ and Ar at various partial pressures to determine diluent effects on the performance of a tubular-SOFC. The overall goal of this research was to formulate a better understanding of the characteristics of fuel cell performance when operating on biogas generated at municipal wastewater treatment facilities.

4.3 Experimental

4.3.1 Test Procedure

The cells used for all experiments were fabricated the Acumentrics Corporation and constructed with a Ni-YSZ (nickel-yttria stabilized zirconia) anode, LSM (lanthanum strontium manganite) cathode and an YSZ electrolyte. The approximate thickness of the Ni-YSZ anode was 1mm, LSM cathode thickness of 10µm, and YSZ electrolyte area of 18µm. The cell active area was between 134cm² and 137cm². The cathode region determines the active are of the cell. Figure
4-1 shows the characteristics of the cell’s construction; fuel flows down the centre of the cell and oxidant surrounds the cell.

![Diagram of Anode-Supported SOFC](image)

**Figure 4-1: Construction of Anode-Supported SOFC. Fuel flows inside the tubular cell, while oxidant is supplied externally (Song & Sammes, 2010).**

Acumentrics manufactured the fuel cell test stand used in the research. Suitable modifications were made to accommodate the test stand in the laboratory. The test stand was designed to measure the performance of up to three cells simultaneously. However, only one cell holder was modified for the dilution experiments. The other two cell holders were not used. The cell was operated in a test stand heated to 800°C. Fuel gas mixtures were provided to the cell at varying flow rates to maintain an approximate fuel utilization of 80% for specified current densities. Oxidant utilization was maintained at 20% and air was used as an oxidant.

Test fuel mixtures were 10%, 25% and 65% (by volume) hydrogen partial pressure with humidified and non-humidified N₂, humidified CO₂, and humidified Ar. The calculated open circuit voltages were 1.032V, 1.013V and 0.994V, for 65%, 25% and 10% H₂, respectively, as determined by the Nernst equation. Humidity was maintained at 2.3 mol% of the total flow of fuel gas when used, which was the humidification level used in other research (Jiang & Virkar, 2003). Tests were also conducted with both humidified and non-humidified flows of 100% H₂, to compare the effects of diluents to ensure an adequate comparison between diluent mixtures and the standard hydrogen fuel gas. At current densities (below 100 mA/cm²) cell performance was
unstable at low fuel and oxidant flow rates due to accuracy and stability of the mass flow controllers. To overcome this problem and to prevent complications that could arise in the cell if it were to be starved of fuel or oxidant, the fuel and oxidant flow rates were maintained at a constant flow rate below 100 mA/cm$^2$. The selected flow rates for the low current densities was determined by using the settings for the fuel and oxidant flow rates calculated to maintain 80% fuel and 20% oxidant utilization at 100 mA/cm$^2$. This current density corresponds to the lowest flow rates that the mass flow controllers could accurately control to ensure 80% fuel utilization. This is not expected to significantly change the results since the cell is primarily controlled by activation and ohmic losses in this region. However, as can be seen in a number of polarization curves this caused a small jump in the polarization curve as the flow controller became active.

4.3.2 Measurement of Cell Performance

Individual tubular cells were mounted on a test stand using cell holders that discharge excess fuel from within the cell into the cathode region. A blower forces air into the heated area where the cell is contained.

![Modified Acumentrics SOFC Test Stand](image)

Figure 4-2: Modified Acumentrics SOFC Test Stand. Cells are contained in a furnace, which allows for controlled high temperature tests.
Cell performance was measured, for each dilution test to determine current-voltage
curves. Current densities are based on the cathode area of the cell of this tubular SOFC. Flow
rates for both the oxidant and fuel were predicted using Equation Oxidant Utilization (4-1) and
Fuel Utilization (4-2). \( U_{OX} \) is the oxidant utilization and \( U_f \) is fuel utilization. F is Faraday’s
constant and I is the current at which the utilization is being predicted. The molar flow rate is
denoted by ‘n’ for a given component.

\[
U_{OX} = \frac{I}{4F} \frac{n_{O_2}}{n_{O_2}} \rightarrow \frac{n_{O_2}}{U_{OX}} = \frac{4F}{I}
\]

\[
U_f = \frac{I}{2F} \frac{n_{H_2} + n_{CO}}{n_{H_2}} \rightarrow \frac{n_{H_2}}{U_f} = \frac{2F}{I}
\]

Oxidant Utilization (4-1)

Fuel Utilization (4-2)

It was necessary for the flow rate of both the fuel gas mixture and the oxidant be
controlled for each current density to maintain the desired 80% and 20% fuel and oxidant
utilizations, respectively.

Two replicate experiments were completed for each diluent to ensure the reproducibility
of the test results. Cell potential was measured at different fuel partial pressure combinations,
including: 100% \( H_2 \), 97.7% \( H_2 + H_2O \) (this will be referred to as humidified \( H_2 \)), \( H_2+N_2+H_2O \)
mixtures, \( H_2+N_2 \) mixtures, \( H_2+CO_2+H_2O \) mixtures, and \( H_2+Ar+H_2O \) mixtures. Humidification
was performed via a water pump that provided a specified amount of liquid water to the gas
mixture for each fuel mix flow rate. It was assumed that this liquid water would become vapour
once contact was made with the higher temperature gases in the furnace chamber.
4.4 Results

Voltage vs. current density and cell power density vs. current density results are displayed in Figure 4-3 to Figure 4-6 for H₂ diluted with partial pressures of CO₂, N₂ and Ar.

Figure 4-3: 100% H₂ voltage and power density vs. current density (800°C, 1 bar) with high purity H₂ and H₂O as fuel.

The maximum power density reached using 100% H₂ was 0.194 W/cm², and 0.185 W/cm² for humidified H₂ (as shown in Figure 4-3). The maximum power density observed when diluent fuels were used in the fuel mixture was 0.148 W/cm², which occurred when N₂+H₂O was utilized at a H₂ partial pressure of 65% (Figure 4-5). The lowest observed maximum power density was noted when CO₂+H₂O was the diluent, as shown in Figure 4-4, and was approximately 0.129 W/cm² (this will be further examined later with an analysis of the water-gas shift (WGS) reaction).
Figure 4-4: Voltage and power density vs. current density (800°C, 1 bar) with H₂ diluted with CO₂ and H₂O as fuel.

Figure 4-5: Voltage and power density vs. current density (800°C, 1 bar) with high purity H₂ diluted with N₂/H₂O as fuel.
Figure 4-6: Voltage and power density vs. current density (800°C, 1 bar) with high purity $\text{H}_2$ diluted with $\text{Ar}$ and $\text{H}_2\text{O}$ as fuel.

Table 4-1: OCV values for fuel mixtures used in dilution testing.

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Calculated OCV (V)</th>
<th>Experimental OCV Run 1 (V)</th>
<th>Experimental OCV Run 2 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$65% \text{H}_2/\text{CO}_2 + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>$25% \text{H}_2/\text{CO}_2 + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>0.87</td>
<td>0.88</td>
</tr>
<tr>
<td>$10% \text{H}_2/\text{CO}_2 + \text{H}_2\text{O}$</td>
<td>0.99</td>
<td>0.82</td>
<td>0.83</td>
</tr>
<tr>
<td>$65% \text{H}_2/\text{N}_2 + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td>$25% \text{H}_2/\text{N}_2 + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$10% \text{H}_2/\text{N}_2 + \text{H}_2\text{O}$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$65% \text{H}_2/\text{Ar} + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$25% \text{H}_2/\text{Ar} + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$10% \text{H}_2/\text{Ar} + \text{H}_2\text{O}$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{H}_2\text{O}$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 4-5 and Figure 4-6 demonstrate the cell performance when N₂ and Ar were used as diluents. It was expected that N₂ and Ar would act only as diluents. This was done to verify that the reverse WGS reaction did cause a significant reduction in the performance of the cell when H₂ was diluted with CO₂ by comparing the performance of the cell when the H₂ with an inert gas of similar molecular weight was tested. Overall, the general trend in the test results indicated that with increasing diluent partial pressure there was a distinct decrease in cell potential and power density for a given current density, as was expected.

4.5 Discussion

4.5.1 Open Circuit Voltage (OCV)

The experimental OCV of the fuel cell for pure un-humidified hydrogen was approximately 1.023V and the OCV of 100% H₂ (humidified) was approximately 1.008V. These values are lower than the calculated expected value for 100% H₂ (humidified) of 1.040V. The calculated and experimental OCV values for each test conducted (humidified only) are displayed in Table 4-1. The calculated OCVs were determined using Equation (4-3).

\[
E = E^0 + \frac{RT}{nF} \cdot \ln \left( \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right) \quad (4-3)
\]

There was a discrepancy between the estimated OCV values and the actual values that were observed during testing. These observations were consistent with the results obtained by Jiang et al., who also reported that the experimental results observed during dilution testing were lower than the estimated values.
As expected, the OCV was highest for the pure hydrogen (DOE, 2004). Equation (4-3) depends on temperature and fuel composition, which is consistent with the trend in OCV with the hydrogen partial pressures in the gas mixtures (Bove, Lunghi, & Sammes, 2005).

4.5.2 Water-Gas Shift Reaction

It was suspected that the WGS reaction was the major factor in the observed reduction in cell performance when reactive CO₂ was used as a diluent. To test this hypothesis the performance of the cell with non-reactive Ar as the diluent gas for the same hydrogen partial pressures was compared to the tests conducted using a non-reactive N₂ gas mixture. The maximum power densities for each test are summarized in Table 4-2. The results between N₂ and humidified N₂ were well correlated. Humidified N₂ was used in the comparisons to humidified Ar.

Table 4-2: Maximum power densities determined through experimental procedure. Two experimental runs of each test were conducted.

<table>
<thead>
<tr>
<th>Fuel Mixture</th>
<th>Maximum Power Density (W/cm²)</th>
<th>Maximum Power Density (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65% H₂/CO₂ + H₂O</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>25% H₂/CO₂ + H₂O</td>
<td>0.060</td>
<td>0.051</td>
</tr>
<tr>
<td>10% H₂/CO₂ + H₂O</td>
<td>0.029</td>
<td>0.028</td>
</tr>
<tr>
<td>65% H₂/N₂ + H₂O</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>25% H₂/N₂ + H₂O</td>
<td>0.094</td>
<td>0.097</td>
</tr>
<tr>
<td>10% H₂/N₂ + H₂O</td>
<td>0.061</td>
<td>0.062</td>
</tr>
<tr>
<td>65% H₂/Ar + H₂O</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>25% H₂/Ar + H₂O</td>
<td>0.094</td>
<td>0.093</td>
</tr>
<tr>
<td>10% H₂/Ar + H₂O</td>
<td>0.062</td>
<td>0.063</td>
</tr>
<tr>
<td>H₂ + H₂O</td>
<td>0.18</td>
<td>0.14</td>
</tr>
<tr>
<td>H₂</td>
<td>0.19</td>
<td>0.19</td>
</tr>
</tbody>
</table>
The power densities calculated from the cell potentials obtained through experimental testing for humidified Ar and humidified N\textsubscript{2} were consistently similar. These power densities are shown in Figure 4-7 to Figure 4-9.

Figure 4-7: Voltage and power density vs. current density (800°C, 1 bar) with a gas mixture of 10\% H\textsubscript{2} with diluent gases.
Figure 4-8: Voltage and power density vs. current density (800°C, 1 bar) with a gas mixture of 25% H2 with diluent gases and high purity H2.

![Graph showing voltage and power density vs. current density](image)

Figure 4-9: Voltage and power density vs. current density (800°C, 1 bar) with a gas mixture of 65% H2 with diluent gases and high purity H2.

A discrepancy was noted when the maximum power densities of Ar and N2 diluent tests were compared directly to the test when CO2 was utilized as the diluent. The molecular weight of the diluent gas did not have a significant impact on the performance of the cell and the decrease in cell performance observed when using CO2 must have been caused by an additional reaction. It is expected that the reverse WGS reaction was the cause. The WGS reaction is an exothermic reaction that can move in the forward or backward direction at high temperatures and favours equilibrium (Bustamante, et al., 2002; DOE, 2004). The WSR reaction is stated in Equation (4-4):

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]  

(4-4)

The presence of CO2 in the fuel gas mixture can cause the reverse WGS reaction to occur at high temperature. The reverse WGS reaction leads to a decrease in the mole fraction of H2 and CO2 in the fuel gas mixture, consequently increasing the production of CO and H2O (Aguiar, Chadwick, & Kershenbaum, 2002). The effects of the WGS reaction can be determined through a
series of calculations and the results of each test conducted (10%, 25% and 65% H₂) are summarized in Table 4-3 to Table 4-5. Calculations were conducted using an equilibrium constant of K=1.024 (DOE, 2004). The temperature dependent equilibrium constant can be determined by calculating \( K_p \):

\[
K_p = e^{\left( \frac{4276}{T} \right)}
\]  

(4-5)

The partial pressures in brackets in Equation (4-6) are equal to the mole fractions of the components at equilibrium, but because the WGS reaction is occurring, the mole fractions provided by the inlet gas composition do not represent the mole fractions at equilibrium (DOE, 2004).

\[
K_p = \frac{[CO_2][H_2]}{[CO][H_2O]}
\]  

(4-6)

\[
K = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[0.50 + x][0.125 + x]}{[0.0 - x][0.375 - x]} = 1.024
\]  

(4-7)

\[
K[CO-x][H_2O-x]=[CO_2+x][H_2+x]
\]  

(4-8)

\[
(1-K)x^2 + \{[CO_2]+[H_2]+K([CO]+[H_2O]))\}x + \{[CO_2][H_2]-[CO][H_2O]\}K = 0
\]  

(4-9)

The prediction of the effects of the WGS reaction was conducted using the method suggested in the Fuel Cell Handbook (DOE, 2004, p. 9-8). The value of \( K_p \) is calculated using (4-5), which is substituted into (4-7), in which ‘x’ is used to represent the extent to which the reaction occurs to the right. (4-7) is expanded to (4-8), which is expanded and solved algebraically to give (4-9). (4-9) is a quadratic, which can be solved to obtain the value of ‘x’, which can then be used to predict the equilibrium gas composition. All computations were conducted using a temperature of 800°C. The fuel flow rates used in the calculations of the spent fuel (to obtain “Mol Percent” at the “FC Outlet”) were the flow rates calculated for the required
flows at 100 mA/cm$^2$, which represents the 80% fuel utilization that was maintained at specified current densities throughout the experiments. The negative ‘Mol Percent’ in the 10% H$_2$ studies indicate that H$_2$ is in a deficit and that there is not enough H$_2$ to provide adequate fuel flow to the SOFC. This is occurring due to the effects of the WGS reaction.

**Table 4-3: Fuel Gas Composition considering the effects of the water gas shift reaction at an initial H$_2$ partial pressure of 10%.

<table>
<thead>
<tr>
<th>Gas</th>
<th>FC Inlet Mol Percent</th>
<th>FC Inlet μmol/s</th>
<th>FC Reaction</th>
<th>FC Outlet Mol Percent</th>
<th>FC Outlet μmol/s</th>
<th>Effect of Shift Reaction</th>
<th>FC Outlet in Shift Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H$_2$</td>
<td>10%</td>
<td>5.4</td>
<td>-28</td>
<td>-28</td>
<td>-28%</td>
<td>-278</td>
<td>8.8</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>88%</td>
<td>47</td>
<td>28</td>
<td>76</td>
<td>92%</td>
<td>92</td>
<td>-8.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.3%</td>
<td>1.2</td>
<td>28</td>
<td>29</td>
<td>36%</td>
<td>36</td>
<td>-8.8</td>
</tr>
<tr>
<td>CO</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>8.8</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>54</td>
<td>82</td>
<td>100%</td>
<td>100</td>
<td>0.0</td>
<td>100</td>
</tr>
</tbody>
</table>

**Table 4-4: Fuel Gas Composition considering the effects of the water gas shift reaction at an initial H$_2$ partial pressure of 25%.

<table>
<thead>
<tr>
<th>Gas</th>
<th>FC Inlet Mol Percent</th>
<th>FC Inlet μmol/s</th>
<th>FC Reaction</th>
<th>FC Outlet Mol Percent</th>
<th>FC Outlet μmol/s</th>
<th>Effect of Shift Reaction</th>
<th>FC Outlet in Shift Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H$_2$</td>
<td>25%</td>
<td>2.65</td>
<td>-2.12</td>
<td>0.53</td>
<td>4.2%</td>
<td>4.2</td>
<td>18</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>73%</td>
<td>7.70</td>
<td>2.12</td>
<td>9.8</td>
<td>77%</td>
<td>77</td>
<td>-18</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.3%</td>
<td>0.24</td>
<td>2.12</td>
<td>2.4</td>
<td>19%</td>
<td>189</td>
<td>-18</td>
</tr>
<tr>
<td>CO</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>18</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>10</td>
<td>0.13</td>
<td>100%</td>
<td>100</td>
<td>0.0</td>
<td>100</td>
</tr>
</tbody>
</table>
Table 4-5: Fuel Gas Composition considering the effects of the water gas shift reaction at an initial H\textsubscript{2} partial pressure of 65%.

<table>
<thead>
<tr>
<th>Gas</th>
<th>FC Inlet Mol Percent</th>
<th>FC Inlet µmol/s</th>
<th>FC Reaction</th>
<th>FC Outlet Mol Percent</th>
<th>FC Outlet µmol/s</th>
<th>Effect of Shift Reaction</th>
<th>FC Outlet in Shift Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH\textsubscript{4}</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>65%</td>
<td>5.4</td>
<td>-4.3</td>
<td>1.1</td>
<td>8.6%</td>
<td>8.6</td>
<td>21</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>33%</td>
<td>2.7</td>
<td>4.3</td>
<td>7.0</td>
<td>56%</td>
<td>56</td>
<td>-21</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>2.3%</td>
<td>0.19</td>
<td>4.3</td>
<td>4.5</td>
<td>36%</td>
<td>36</td>
<td>-21</td>
</tr>
<tr>
<td>CO</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>21</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
<td>8.3</td>
<td>1.23</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

As the initial partial pressure of H\textsubscript{2} increased (from 10% to 65%) the outlet partial pressures of CO and H\textsubscript{2} increased, whereas the partial pressure of CO\textsubscript{2} decreased due to the reverse WGS reaction. The effects of the reverse shift reaction are evident when compared to the cell performance obtained from experiments. The tests using CO\textsubscript{2} had a significantly reduced cell potential. The decrease in cell performance observed during the 10% H\textsubscript{2}/CO\textsubscript{2} test can be explained by the starvation of the cell that occurs (mole fraction of -18.89%), as shown by the fuel gas mole fractions. The negative value of H\textsubscript{2} indicates that more H\textsubscript{2} is required to produce a greater cell potential, which is representative of the drop in cell potential in Figure 4-4 and Figure 4-7. Typically, biogas reformate contains greater than 10% H\textsubscript{2}, and therefore it is unlikely that there will be an instance where it is required that the mole fraction of H\textsubscript{2} be so low.

### 4.5.3 Electrochemical and Mass Transfer Limitations

Diffusion polarization includes losses that can occur due to the diffusion of reactants through the anode (Hall & Colclaser, 1999). A diffusive flux (driven by Knudsen flow and continuum flow) and a viscous flux (driven by pressure gradients) contribute to mass transport in
porous electrodes (Jiang & Virkar, 2003). The Knudsen diffusion coefficient indicates that the diffusivity of an element (H₂, Ar, N₂, H₂O, CO₂, etc.) is affected by its molecular dimensions (i.e. the diffusivity of H₂O will be less than that of H₂) (Cannarozzo, Grosso, Agnew, Del Borghi, & Costamangna, 2007; Jiang & Virkar, 2003). Jiang & Virkar (2003) compared the diffusivities of N₂ and CO₂ as diluents and concluded that H₂ diluted with either N₂ or CO₂ will lower the partial pressure of H₂ and reduce the effectiveness of the H₂ diffusion coefficient; both of which would lower the cell performance. The review by Jiang & Virkar (2003) corroborates with the experimental findings of this study – that the maximum power density was lower when CO₂ was used as a diluent then when N₂ was employed (at the same diluent partial pressure).

Generally, at low current densities and high reactant partial pressures mass transfer limitations are not significant, whereas at high current densities and low fuel partial pressure mass transport losses are more significant. The latter was the situation in the tests conducted utilizing dilute fuels (DOE, 2004). As the H₂ is being consumed at the anode there will be a reduction in the partial pressure in the anode region. This results in a pressure drop, which will correspondingly result in a reduction in voltage (Larminie & Dicks, 2003; DOE, 2004; Arpino & Massarotti, 2009). When there is adequate H₂ flowing across the anode at the active boundary, the electrochemical oxidation reactions can continually occur. This causes a continuous change in the molar fraction of H₂. As the inlet mole fractions of H₂ are decreased, the active boundaries are starved of fuel and the reaction rates slow. This leads to a reduction in the cell voltage (Grew, Joshi, Peracchio, & Chiu, 2010). A study by Mollayi et al. (2009) showed the gradients of decreasing mole fraction of H₂ across the length of a tubular cell and increasing mole fraction of water vapour due to consumption of H₂ and production of water vapour on the anode. The starvation of the cell that can occur as the partial pressure of H₂ at the active site decreases could
be the cause of the significant voltage decreases observed when there is only 10% H₂ in a diluent gas (as shown in Figure 4-4 to 4-6). This starvation of the cell is a result of concentration polarization losses across the cells that are caused by spatial variations in reactant partial pressure at active sites.

4.6 Conclusions

From the experimental data obtained through tests conducted with H₂ diluted with various humidified and non-humidified gases, it was determined that diluent fuels impact cell performance for all mole fractions of H₂. The diluents used, N₂, N₂/H₂O and Ar/H₂O had similar effects on cell performance, producing identical results for each test. This was expected, as they are inert gases in fuel cell reactions. However, CO₂/H₂O as a diluent exhibited significantly different results, caused by the reverse shift reaction. The reverse shift reaction resulted in a decrease in the mole fraction of H₂ in the fuel gas mixture, which lead to a reduced availability of H₂ to produce high cell performance. It would be advantageous for the effects of the reverse shift reaction to be minimized, possibly through the addition of CO and H₂O to the fuel mixture to encourage the forward shift reaction at high temperature or by reducing the CO₂ partial pressure in the gas. It is not recommended that fuel cells be operated on such CO₂ rich fuels. The diffusivity of the varying fuel gas mixtures can also cause limitations in cell performance in terms of electrochemical and mass transfer limitations.

4.7 References


Chapter 5

Biogas as a Renewable Fuel at Wastewater Treatment Plants: Modeling Efficiency and Greenhouse Gas Emissions

5.1 Abstract

A model has been developed at the Queen’s-RMC Fuel Cell Research Centre (FCRC) to simulate the cell performance of a solid oxide fuel (SOFC) cell system operating on simulated anaerobic digestion (AD) derived biogas reformate. When used as a renewable fuel for SOFC’s AD-derived biogas provides clean electrical, carbon neutral, power. The fuel cell model created predicts cell stack performance and, when incorporated in a process simulator, system efficiency for operation on AD-derived biogas from a wastewater treatment plant (WWTP). This study uses experimental data to validate the cell model. A greater decrease in performance was observed when CO$_2$ was used as a diluent, compared to dilution with inert N$_2$ and Ar. This may be attributed to the reverse water-gas shift (WGS) reaction consuming H$_2$. Experimental data for the cell performance at different dilutions of H$_2$ (H$_2$+CO$_2$, H$_2$+Ar and H$_2$+N$_2$ at varying H$_2$ partial pressures) was collected. From the experimental data the empirical cell model was developed and used with a process simulator developed using the software package on UniSIM™ to determine the effect of the decreased cell performance on system efficiency when using biogas as a fuel. It was determined that the CO$_2$ effect reported in the experimental dilution data would not be as significant when operating on AD-derived biogas due to the reduced CO$_2$ partial pressure after reformation, which was not expressed in the dilution tests. It was shown that the installation of
the biogas/SOFC system could significantly reduce the GHG emissions from the Kingston
Ravensview WWTP.

5.2 Introduction

SOFCs operating on anaerobic digester (AD) derived biogas from wastewater treatment
plants (WWTPs) represent an opportunity to produce clean electricity that can be used on-site to
reduce the electricity cost to WWTP operations (with the potential to feed electricity back to the
grid with a large enough system) as well as offset the emissions from the facility that generally
result from flaring the biogas. An understanding of the operation of the biogas/SOFC system will
allow researchers to estimate the emissions reduction and electricity savings that can result from
an adequately scaled SOFC.

Research conducted at the Queen’s-RMC Fuel Cell Research Centre (FCRC) has produced
experimental data that represents the performance of a commercially available tubular SOFC
when operating on dilute H\textsubscript{2} fuel. The diluents used were CO\textsubscript{2}, Ar and N\textsubscript{2} and the partial pressures
studied were 65% and 25% H\textsubscript{2} with 2.3 mol% H\textsubscript{2}O (as steam) for humidification and the
remainder of the gas mixture was the diluent gas. It was noticed in the experimental data that the
tests conducted with CO\textsubscript{2} as the diluent showed a greater decrease in cell performance compared
to the N\textsubscript{2} and Ar tests, relative to pure H\textsubscript{2}. FCRC and its project partners plan to design a
biogas/SOFC pilot scale demonstration and; therefore, it is desirable to develop a computer model
that will simulate the efficiency and performance of the system. In order to use the experimental
data to calibrate a reasonable model for the system it was necessary to first fit an empirical model
to the experimental dilution data that could account for the $\Delta V$ CO\textsubscript{2}, which is the change in
voltage when CO\textsubscript{2} is used as a diluent. There was a dilution effect that was shown in the dilution
data for CO\textsubscript{2} that was not covered by the simulations WGS reaction calculations and therefore the
ΔV CO₂ was required to account for the decreases in cell performance when CO₂ was used as a
diluent, compared to N₂ and Ar, which displayed similar dilution effects. The empirical model
was then incorporated into the UniSIM™ simulation, which was able to calculate the system
efficiency, stack efficiency, output gas composition, etc. for a range of current densities. The
model was run at S/C ratios of 1 and 2 to determine the impact of the ΔV CO₂ when operating on
biogas that had an initial composition of 60% CH₄ and 40% CO₂.

5.2.1 Background Information

Research being conducted at the FCRC at Queen’s University, Kingston is analyzing the
effects of AD-derived biogas from WWTPs on SOFC performance. A SOFC system operating on
AD-derived biogas can be considered a renewable energy source. A WWTP generally represents
the highest electricity demand in a municipality and; therefore, the energy savings that can result
from the installation of a fuel cell system will be beneficial in terms of both reduced operating
costs of the plant and reduced GHG emissions.

5.3 Literature Review

Two major components to the implementation of an integrated biogas/SOFC system are
an understanding of biogas production and variability, and the operation of a fuel cell on dilute
hydrogen fuels.

5.3.1 Biogas Production & Variability

Biogas is produced at WWTPs through the AD process. The primary constituents in
biogas are methane (CH₄) and carbon dioxide (CO₂). There are four main phases of methane
fermentation: hydrolysis, acidogenesis, acetogenesis/dehydrogenation, and methanation
(Weiland, 2010). In stage 1, in Figure 5-1, hydrolyzing and fermenting bacteria break down
monomers and polymers in the waste to produce acetate and hydrogen (as well as small concentrations of volatile fatty acids (VFAs)) (Ahring, 2003). In stage 2, hydrogen and acetate are produced through conversion from VFAs (Ahring, 2003). Methane and carbon dioxide are produced from acetate and/or hydrogen in stage 3/4.

Figure 5-1: AD Process (Ahring, 2003).

AD-derived biogas is considered one of the most energy efficient and environmentally beneficial technologies for the production of renewable biofuels (Weiland, 2010). Biogas produced from properly operating ADs should contain approximately 65% methane and 35% carbon dioxide, with trace concentrations of other gases (Taricska, Long, Chen, Hung, & Zou, 2007). A study conducted by Wheeldon, Caners, Karan & Peppley (2007) confirmed that biogas composition at WWTPs in Ontario with populations over 100,000 people (when data was available) was about 61% methane and 35% carbon dioxide, as shown in Table 5-1.
Table 5-1: WWTP Biogas Composition (Wheeldon, at al., 2007).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane (CH₄)</td>
<td>%</td>
<td>60.8</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>%</td>
<td>34.8</td>
</tr>
<tr>
<td>Hydrogen Sulphide (H₂S)</td>
<td>ppm</td>
<td>78 (579)</td>
</tr>
<tr>
<td>Oxygen (O₂)</td>
<td>%</td>
<td>1.5</td>
</tr>
<tr>
<td>Nitrogen (N₂)</td>
<td>%</td>
<td>2.4</td>
</tr>
<tr>
<td>Moisture (H₂O)</td>
<td>%</td>
<td>0.01</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>ppm</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Hydrogen (H₂)</td>
<td>ppm</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Silicon Compounds</td>
<td>ppm</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*All but two sites had H₂S concentration ranging 2.5 – 200 ppm; two sites with higher concentrations had 350 and 3,450 ppm of H₂S.
*The average value of H₂S excluding the highest concentration.
*The average value of H₂S calculated by including all data.

For the gas compositions used in developing Table 5-1 there were also trace concentrations of toluene, methyl chloride and CFC’s (all below 10ppm) (Wheeldon, et al., 2007). The quantity of biogas produced was reported to be approximately 57±18 m³/1000 m³ of wastewater treated (Wheeldon, et al., 2007). Ideally, biogas that would be used in a biogas/SOFC system would be predominately CH₄ and CO₂ so that it could be internally or externally reformed to a H₂ rich fuel. A study on the variability of biogas at municipal WWTPs across North America in 2010 confirmed these compounds dominate with an average composition of: 63% CH₄, 37% CO₂, 1% N₂ and the remainder consists of trace amounts of O₂, H₂S, and Si compounds.

The quality of biogas can be enhanced through steps that occur before AD as well as gas cleanup before it is fed to a SOFC system. The quality and quantity of biogas produced can be increased by increasing the digestibility of the waste, optimizing the anaerobic reactor configuration, optimizing process control and stability, and improving the microbial process and its efficiency (Ahring, 2003). If the gas contains constituents such as H₂S, these can be removed using an activated carbon bed (Wheeldon, et al., 2007). The sulfur tolerance typical of a SOFC is less than 1ppm, and therefore sulfur compounds must be removed (DOE, 2004).
5.3.2 Solid Oxide Fuel Cells (SOFCs)

A SOFC is an electrochemical device that directly converts fuel to electricity and byproduct heat. The most common electrolyte in SOFCs is the solid ceramic material \( \text{Y}_2\text{O}_3-\text{stabilized ZrO}_2 \) (YSZ), the anode is typically Ni-YSZ and the cathode is Sr-doped LaMnO3 (DOE, 2004). SOFCs operate at temperatures between 600-800°C. Fuel, typically \( \text{H}_2 \), flows past the anode and reacts with \( \text{O}_2^- \) ions that have been transported through the electrolyte from the cathode side of the cell where oxygen in air is used as the oxidant (DOE, 2004).

SOFCs are able to effectively use hydrocarbon fuels because they produce waste heat at sufficiently high temperature to support steam reformation of hydrocarbons into \( \text{H}_2 \) rich fuel, which can then be reacted in the cell. Reformation of fuels can be done directly on the cell anode (direct internal reforming) or externally through the addition of steam and optionally air to the fuel stream resulting in \( \text{CO} \) and \( \text{H}_2 \) (Ormerod, 2003). Problems can arise with direct internal reforming because of the possibility of forming carbon deposits form on the anode.

5.3.3 SOFCs Operating on WWTP Biogas

A publication by Fuel Cell Energy published in 2009 estimated that the average WWTP in the United States process about 100gallons of wastewater per person served per day and generates approximately 1 ft\(^3\) of biogas. If a fuel cell electrical efficiency of 47% is used and assuming the average methane content of the gas is 60%, then approximately 3.2J/s/person would be generated (Fuel Cell Energy, 2009). Worldwide, it is estimated that the electrical power output from WWTPs is 13GW (Spiegel & Preston, 2003). Peppley (2006) reports that if all of the wastewater in Ontario were treated by AD there would be the potential to produce 1.51 GWh per day from \( \text{CH}_4 \). Exploitation of biogas with conventional engines is only practical for very large WWTPs because the operation and maintenance costs do not scale linearly. SOFC power plants,
however, have lower operation and maintenance costs that decrease for smaller units and; therefore, can be used for much smaller WWTPs. Although there are few examples of SOFC systems running directly on biogas, other high types of fuel cells have been employed to produce electricity at WWTPs by means of utilizing biogas. The Yonkers WWTP in Yonkers, NY was an assessment site for the use of a commercially available 200 kW phosphoric acid fuel cell (PAFC) unit. A gas-processing unit (GPU) in which the biogas (predominately CH\(_4\)) is converted to H\(_2\) and CO\(_2\) and removes sulfur and halide compounds from the gas is an integral part of the system (Spiegel & Preston, 2003). From the Yonkers, NY demonstration is was concluded that fuel cells could be modified to adapt better to the use of biogas by enhancing the high-volume flow capacity required for biogas, removing condensate from the system more effectively, being equipped for variations in H\(_2\)S variability (assisted by being familiar with gas quality at the site), and incorporating the possibility of operation with a fuel back-up system (such as natural gas) when the biogas quality is limited (Spiegel & Preston, 2003). In total, NY has nine such 200 kW systems in operation.

5.3.4 Greenhouse Gas Emissions at WWTPs

It is currently common practice for WWTPs to flare biogas in order to convert the CH\(_4\) to CO\(_2\) since CH\(_4\) is considered to be 23 times more potent than CO\(_2\) (Peppley, 2006; Monteith, Sahely, MacLean, & Bagley. 2005).

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (5-1)
\]

Based on Equation (5-1) the combustion of CH\(_4\) to CO\(_2\) and H\(_2\)O in the presence of O\(_2\), 2.75kg of CO\(_2\) is produced per 1kg of CH\(_4\) combusted, hence flaring is very beneficial for reducing GHG emission (Monteith, et al., 2005).
5.4 Method & Procedure

5.4.1 Experimental Testing Apparatus & Procedure

Experimental data was obtained at the FCRC using commercially available anode supported tubular SOFCs. The tests were conducted on single cells using a test stand (commercially available, built by the Acumentrics Corporation, but modified at the FCRC). The cells have a YSZ electrolyte, a Ni-YSZ anode and Sr-doped LaMnO$_3$ YSZ cathode. All tests were conducted at 800°C and 1atm. The fuel utilization was maintained at 80% for current densities above 100 mA/cm$^2$. It was not possible to maintain 80% fuel utilization below 100 mA/cm$^2$ as the flow rate was less than the minimum flow of the mass flow controller. CO$_2$, N$_2$ and Ar were used as diluent gases and were mixed with H$_2$, using a gas mixer that was developed at the FCRC, and H$_2$O. The test stand is shown in Figure 5-2.

![Tubular SOFC test stand at the FCRC.](image)

**Figure 5-2: Tubular SOFC test stand at the FCRC.**

The gas mixture compositions tested were 65% H$_2$/32.7% CO$_2$/2.3% H$_2$O, 65% H$_2$/32.7% N$_2$/2.3% H$_2$O, 65% H$_2$/32.7% Ar/2.3% H$_2$O as well as 25% H$_2$/32.7% CO$_2$/2.3% H$_2$O, 25% H$_2$/32.7% N$_2$/2.3% H$_2$O and 25% H$_2$/32.7% Ar/2.3% H$_2$O.
5.4.2 Fitting a Mathematical Model to Experimental Data

An empirical model was used with the UniSIM™ model to predict system performance. The parameters of the empirical model were adjusted to fit the experimental polarization curves for diluted H₂ fuel mixtures.

The empirical model fit is displayed in Figure 5-3 and Figure 5-4. It was required to develop a model that would accurately suit both the N₂/Ar diluent tests and the CO₂ diluent tests. The accuracy of the empirical model for the 65%H₂ in diluent tests was within approximately 6% error for all data points, and was within 11% error for the 25%H₂ tests (ignoring the data point that was an outlier when CO₂ was used as a diluent fuel in one test run). It was necessary to determine the average partial pressures after the hypothesized effects of the water-gas shift reaction had occurred to ensure that an accurate representation of the partial pressure of CO₂, H₂, H₂O and CO was obtained. A ΔV term was added to represent the decreasing H₂ partial pressure as the partial pressure of CO₂ increased and to account for the decrease in cell performance that could not be attributed to the dilution effects as recorded when N₂ and Ar were used as diluents.

Equations (5-2) to (5-7) represent the process of developing the empirical model that was implemented in the simulation. The equations are in sequential order with (5-2) being the starting point, (5-3) to (5-6) showing the intermediate steps in which the equation was simplified, and (5-7) is the final model.
\[ V = E_{OC} + \frac{RT}{2F} \ln \left( \frac{p_{H_2}P_{O_2}^{0.5}}{p_{H_2O}} \right) - \frac{RT}{2aF} \ln \left( \frac{i}{i_o} \right) - rT \ln \left( 1 - \frac{i}{i_L} \right) \]  
\[ (5-2) \]

\[ V = E_{OC} + \frac{RT}{2F} \ln \left( \frac{p_{H_2}P_{O_2}^{0.5}}{p_{H_2O}} \right) - r \]  
\[ (5-3) \]

\[ V = E_{OC} + \frac{RT}{2F} \ln \left( \frac{p_{H_2}P_{O_2}^{0.5}}{p_{H_2O}} \right) \]  
\[ (5-4) \]

\[ V = E_{OC} + \frac{RT}{2F} \ln \left( \frac{1 - \frac{p_{CO_2}}{p_{Total}}}{p_{H_2O}} \right) - r \]  
\[ (5-5) \]

\[ V = E_{OC} + \frac{RT}{2F} \ln \left( \frac{p_{H_2}P_{O_2}^{0.5}}{p_{H_2O}} \right) - r + \frac{RT}{2F} \ln \left( 1 - \frac{p_{CO_2}}{p_{Total}} \right) \]  
\[ (5-6) \]

\[ V = C_1 + C_2 \ln \left( \frac{p_{H_2}P_{O_2}^{0.5}}{p_{H_2O}} \right) - C_3 i + C_4 \ln \left( 1 - \frac{p_{CO_2}}{p_{Total}} \right) \]  
\[ (5-7) \]

Where:
\[ E_{OC} = \text{The standard open circuit potential} \]
\[ F = \text{Faraday’s constant} \]
\[ a = \text{Charge transfer coefficient} \]
\[ i = \text{Current density} \]
\[ i_o = \text{The exchange current density} \]
\[ \tau = \text{The ohmic resistance} \]
\[ i_L = \text{The limiting current density} \]
\[ p_{H_2} = \text{H}_2 \text{ partial pressure averaged between the anode inlet and outlet} \]
\[ p_{O_2} = \text{O}_2 \text{ partial pressure averaged between the cathode inlet and outlet} \]
\[ p_{H_2O} = \text{H}_2\text{O partial pressure averaged between the anode inlet and outlet} \]
\[ C_1, C_2, C_3, \text{ and } C_4 = \text{Constants determined through the regression of experimental data to fit models most precisely to the experimental data using Equation (5-7).} \]

Parameter fitting to account for the \text{CO}_2 partial pressure changes were required and versions of the model were tested that included adjusting the average partial pressures with and
without the WGS reaction equilibrium. In the end, the model that displayed the average partial pressures that included the WGS reaction was most effective at representing cell performance. A least squares regression of the experimental data was conducted in Excel using Equation (5-5). The datum included in the regression were the experimental results obtained for the 65%H₂+2.3%H₂O+diluent and 25%H₂+2.3%H₂O+diluent gas data. The data were regressed against the results for the N₂ dilutions (N₂ and Ar had negligible differences between data sets). The minimized sum of squared residuals resulted in parameter values, displayed in Table 5-2.

**Table 5-2: Parameter values determined to fit empirical model to experimental data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.9130 V</td>
</tr>
<tr>
<td>C2</td>
<td>0.0168 V</td>
</tr>
<tr>
<td>C3</td>
<td>0.0016 kΩcm²</td>
</tr>
<tr>
<td>C4</td>
<td>0.0229</td>
</tr>
</tbody>
</table>

Assumptions were made to simplify the empirical model. Due to the high operating temperature (800°C), activation polarization was considered negligible and its corresponding term was omitted from the final polarization model (resulting in Equation (5-3)). The term describing the effects of concentration polarization was omitted because the limiting current density occurred beyond the range of current densities, which is reflected in (5-4). If these data points were to be accounted for more information regarding the diffusion coefficients and characteristics of the cell would be required.

The presence of CO₂ causes a drop in cell voltage, referred to as the ΔV CO₂. It can be assumed that ΔV CO₂ lowers the average partial pressure of H₂ seen at the anode by a factor, as shown in Equation (5-8). The ΔV CO₂ term can be removed from the brackets in Equation (5-5) to yield Equation (5-6).
The empirical models developed were plotted with the experimental data polarization lines (two separate plots are included to view the modeled data and experimental data more clearly).

Figure 5-3: 65% high purity H₂ with diluent experimental data and modeled data plot.
Figure 5-4: 25% high purity H₂ with diluent experimental data and modeled data plot.

Figure 5-3 and Figure 5-4 show how well the empirical model fits the experimental data. Using the constant parameter values determined through the data regression has permitted the capture of the effect of the CO₂ dilution, which was the more complicated part of the empirical modeling procedure. This is important to obtain the most accurate results from the UniSIM™ model.

5.4.3 Process Model

A simulation was developed using UniSIM™ at the FCRC to determine the characteristics of the fuel cell system. The flow diagram for the model is displayed in Figure 5-5.
5.4.3.1 General Model Description

The model begins with a stream of cool biogas being pre-heated in a heat exchanger and then fed to a mixer where it is combined with steam to the specified S/C ratio. The mixer exhaust is then pre-heated in a second heat exchanger and enters the reformer unit. The biogas reformer calculates the equilibrium composition of the product stream for the given reformer exit.

The reformer, in addition to steam reforming, takes into account dry reforming and the WGS reaction. After reformation the biogas reformate, made up of predominately H₂, CO, CO₂ and H₂O is fed to the SOFC. There is no built-in unit operation in UniSIM™ to simulate a SOFC so a user-defined fuel cell model was developed and programmed, by other researchers at FCRC, configured as a series of spreadsheet calculations. The fuel cell model consists of 64 tubular cells in 8 modules that are each made up of 2 rows of 4 cells each. Each cell has an active area of 135cm². The following describes the various spreadsheets in the cell model.
The *Electrochemical Reactions* spreadsheet calculates the anode and cathode exhaust component molar flow rates based on the anode and cathode feeds and amount of current drawn from the stack. The voltage calculations portion of the spreadsheet contains the inputs for a polarization model that will determine the system output voltage and power. The temperature, active cell surface area, pressure and current density, at which the system is operating, can be specified by the user in the *Control Panel* spreadsheet. The control panel spreadsheet also details the stack design (number of stacks per row, number of stack rows and the number of cells in the stack, and the stack output current). The *Hotbox Temperature and Pressure Distributer* spreadsheet exports the same temperature and pressure setting simultaneously to various material streams within the hotbox to enforce the assumption that the hotbox is isothermal and isobaric. The hotbox contains the reformer and fuel cell. Both the anode and cathode exhaust streams are fed to a tail gas afterburner where unutilized fuel (H₂ and CO) are combusted to produce a high-temperature exhaust stream that is re-circulated throughout the system and used to pre-heat the inlet streams. The first heat exchanger downstream from the afterburner pre-heats the inlet cathode air. The combustion exhaust stream then continues on through three subsequent heat exchangers where it is used to pre-heat the reformer feed, raise steam then pre-heat the inlet biogas. After pre-heating the inlet biogas, the stream exits the system as the exhaust stream.

Two adjusts are included in the model. These adjusts iteratively adjust operating inputs until a specified output is reached. Specifically, the “biogas flow adjust” adjusts the biogas feed molar flow rate until the number of H₂ equivalents produced by the reformer satisfies the user-specified fuel utilization (relative to number of H₂ equivalents consumed in the stack). The “Air Adjust” adjusts the inlet air molar flow rate until the steady state energy balance (calculated by the SOFC Energy Balance Calculations spreadsheet) is achieved around the hotbox. Recycle
points within the simulation recalculate and update component flows for each iteration of the 
adjusts until the solution achieves convergence.

A mass balance is used to double-check that the electrochemical reactions, programmed 
into the spreadsheets, are consistent with the overall conservation of mass. If the mass balance 
fails it is an indication in the fuel cell unit operation failed to properly converge. Generally the 
mass balance closed once the fuel cell parameters were set correctly.

The spreadsheets allow for a significant amount of control over the characteristics of the 
various operating parameters (such as controlling temperature, pressure, etc. in the hotbox as well 
as components that are specific to the SOFC stack design).

The modeled system was designed to maximize the integration of the various heat 
sources and sinks. The two most prevalent examples of heat recovery are the inclusion of the 
reformer in the hotbox and use of the tail gas burner exhaust stream throughout of the various 
heat exchangers to pre-heat the various streams. Thermal integration in a high temperature fuel 
cell system is very important to reduce the heating demand and maximize the overall system 
efficiency.

There were some assumptions that were required to ensure that the model operated 
effectively. These are assumptions made in the empirical model that were necessary because of it 
being input to UniSIM™. These assumptions include:

1. There is laminar and plug flow within the cells and composition is uniform.
2. The WGS reaction is fast within the cells at 800°C and instantly reaches equilibrium 
   (Mogensen, Grunwaldt, Hendriksen, Dam-Johansen, & Nielsen, 2011).
3. Only H₂ electrochemically reacts within the cells, but CO is considered a source of H₂ via 
   the WGS reaction.
4. All cells operate isothermally at 800°C.

Assumptions that were required for the system simulation were as follows:

1. The tail gas burner is located outside of the fuel cell hotbox.
2. System heat losses occur only through the fuel cell hotbox shell.
3. There is no heat transfer from the combustion zone back to the fuel cell hotbox, regardless of their proximity.
4. Pumping power is not significant (low-pressure system).
5. The hotbox is well designed with highly thermally-conducting materials such that all hotbox internals are isothermal and maintained at 800°C.
6. The residence time is large enough (or there is enough catalyst) to achieve equilibrium composition at the exit of both the reformer and the tail gas burner.
7. The entire model is isobaric (everything is at 1 atm).
8. An approach temperature of 50°C is always achieved at the exits of all heat exchangers.
9. The overall heat loss for the hotbox was set to 7.8W. This value ranged between 1.4 and 10% of the total electrical power output of the stack (operating between 10 and 150 mA/cm²).

5.5 Results & Discussion

The UniSIM™ system simulation was used to determine the overall efficiency, stack/cell efficiency and output gas composition at S/C ratios of 1 and 2. The simulation was run for current densities from 10-150 mA/cm². Initial trial runs showed that the cell voltage was less then 0.6V for current densities greater then 150 mA/cm². In later tests, following adjustment of the fuel cell model for experimental data higher current densities were acceptable. According to Van Herle et al. (2004) SOFCs are not typically operated below 0.65V. The lowest current density studied was 10 mA/cm² because the spreadsheet model had difficulty converging at very low current densities. The cell would not likely be operated at such low current densities and this was not considered a serious limitation.

The empirical model was able to represent the expected voltage that would be shown when the fuel cell system was operated on AD-derived biogas and the results are displayed in Figure 5-6.
ΔV CO₂ was investigated with different S/C ratios to determine if the CO₂ decreases recorded when CO₂ was used as a diluent would have an effect on the system output voltage. The S/C ratio and ΔV CO₂ do not appear to have a significant impact on the cell performance across current densities of 10-150 mA/cm². It is common to have an increased S/C ratio to ensure that coking is not occurring on the anode (Koh, Kang, Lim, & Yoo, 2001; Ihara, et al., 1999). Therefore, it may be beneficial to maintain the lower S/C ratio to increase the overall efficiency of the system.

It was important to investigate the ΔV CO₂ and therefore four test runs were conducted: S/C = 1 and ΔV CO₂ = ON, S/C = 1 and ΔV CO₂ = OFF, S/C = 2 and ΔV CO₂ = ON and S/C = 2 and ΔV CO₂ = OFF. ‘ON’ was used to represent the test runs in which the ΔV CO₂ was accounted for and ‘OFF’ was used when the ΔV CO₂ was set equal to zero. Changing the S/C
ratio changes the partial pressure of CO\textsubscript{2} in the fuel stream, thus changing the $\Delta V$ CO\textsubscript{2}, which could change the cell performance.

![Graph](image)

**Figure 5-7:** $\Delta V$ CO\textsubscript{2} comparison between S/C = 1 and S/C = 2. This plot shows only the $\Delta V$ CO\textsubscript{2} (dV) portion of the entire empirical model, and indicates that the $\Delta V$ CO\textsubscript{2} is very small, and almost negligible.

The results show that the $\Delta V$ CO\textsubscript{2} is not significant at either S/C ratio studied. This likely occurs because the partial pressure of CO\textsubscript{2} coming from the reformer to the cell is approximately 8.2\% at S/C = 1 and 10.6\% at S/C = 2. This is significantly lower than the partial pressure that was fed to the anode during the dilution tests, which was 32.7\% in the 65\% H\textsubscript{2} test and 72.7\% in the 25\% H\textsubscript{2} test. The $\Delta V$ CO\textsubscript{2} was necessary because when the empirical model was used without it there was a significant discrepancy in the results; the model was not accurately representing the data, which made is impossible to simulate the expected system performance results in UniSIM\textsuperscript{TM}.

The stack efficiency, which is correlated with the cell voltage, is displayed in Figure 5-8.
The stack and cell electrical efficiencies, when calculated using the lower heating value (LHV) are more meaningful than the cell efficiencies determined using Equation A1, in the Appendix, based on the theoretical voltages. The stack electrical efficiency appears much higher then when determined using the LHV, as shown in Figure A 1 and Figure A 2 in the Appendix. Relying on the method in Equation A1 could result in an inaccurate representation of cell or stack performance.
Figure 5-9: System Electrical Efficiency on a Lower Heating Value Basis.

The system electrical efficiency is calculated on a LHV because the water product of SOFCs is in the vapour phase (Larminie & Dicks, 2003). It can be shown in the results that the system electrical efficiency is higher for the at the higher S/C ratio. This increase in efficiency is likely due to the increased partial pressure of H$_2$ in the reformate that results from increased S/C ratio and the WGS reaction equilibrium. It is reported that the increase in fuel cell efficiency from the higher H$_2$ partial pressure can offset the decrease in efficiency that can be caused by the need to raise steam for the fuel processor/reformer (Blomen & Mugerwa, 1993).

5.5.1 Greenhouse Gas Emission Reduction

The installation of a biogas/SOFC system at Ravensview WWTP could reduce the GHG emissions at the facility in several ways. The GHG emissions would be reduced as biogas that is currently flared would be used to produce electricity that would otherwise be purchased from the grid, which uses coal to produce electrical power. Secondly, at times when heating of the digesters is required to maintain biogas production, waste heat from the SOFC unit could be co-generated while clean electricity is being produced.
Utilizing a S/C of 1 has higher N\textsubscript{2} and O\textsubscript{2} partial pressure in the output gas from the fuel cell system than when using S/C of 2. S/C=2 displayed a higher partial pressure of H\textsubscript{2}O (displayed in Figure A 3 to Figure A 6 in the Appendix). Both S/C ratios studied had comparable CO\textsubscript{2} partial pressures of ranging from approximately 0.23 atm at 10 mA/cm\textsuperscript{2} to 0.15 atm at 150 mA/cm\textsuperscript{2}. The CO\textsubscript{2} emissions released from the fuel cell system would range from 39.8 tonnes to 60.1 tonnes annually at Ravensview based on the 2007 biogas production if all biogas produced was fed to a SOFC system. Flaring biogas with a composition of 65% CH\textsubscript{4} and 35% CO\textsubscript{2} would release approximately 1429.5 tonnes CO\textsubscript{2} if 2.75 kg of CO\textsubscript{2} is formed for each 1 kg of CH\textsubscript{4} combusted. That reduction is from flaring the gas alone, additional reductions can occur from decreased electrical consumption.

The electricity use for 2009 at the Ravensview facility was 5.9 GWh, which was significantly greater than the electricity consumption for 2010. The energy equivalent is 21240 GJ. The cost of the electricity used in 2009 was $533,587.98.

Figure 5-10: Ravensview WWTP electricity consumption, by month, for 2010
Figure 5-10 shows the electricity consumption at Ravensview for 2010. There was a decrease from 2009 that was likely due to changes in electricity use practices at the facility or possibly that overall the temperatures were higher in 2010 resulting in reduced heating requirements. Heating requirements are a contributing factor to electricity use and a SOFC system could assist the heating demand because of its ability to provide cogeneration heat for the facilities buildings or anaerobic digester. Heating capability should be added to the model to determine the heating power output.

In applications at WWTPs where fuel cell systems have been installed it is common to see 200-250 kW per fuel cell unit, with some locations operating multiple units to increase their electrical generation capacity. It has been estimated that if all the biogas produced at the Yonkers, NY WWTP was fed to PAFC systems installed on-site the following GHG emissions reductions would be realized: 1,225 tonnes of CO₂, 309 tonnes of CH₄, 1.8 tonnes of CO, 1.8 tonnes of COₓ and 1.6 tonnes of SO₂ annually from reduced electrical consumption (of on grid electrical mix in the state of New York) and reduced flaring (Spiegel & Preston, 2003). The Yonkers WWTP treats approximately 359,000 m³ of wastewater and produces about 12,000 m³ of biogas daily. This is greater than the biogas produced at the Kingston Ravensview facility (73,000 m³ of wastewater treated and 1,900 m³ of biogas produced daily) and, therefore, Kingston should expect less GHG reduction than Yonkers, but the reductions displayed at Yonkers are promising.

Table 5-3 shows the GHG emissions that would result from the electricity required to power the Ravensview WWTP. Expected annual emissions, as based on the 2008 GHG intensities and 2009 Ravensview electrical data, are 944,254kg CO₂, 59kg CH₄ and 17.7kg N₂O.
Table 5-3: Ontario Electricity Intensity (Government of Canada, 2010).

<table>
<thead>
<tr>
<th></th>
<th>Greenhouse Gas Intensity (g GHG/kWh Electricity Generated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ontario</td>
<td>1990</td>
</tr>
<tr>
<td>CO(_2) Intensity</td>
<td>210</td>
</tr>
<tr>
<td>CH(_4) Intensity</td>
<td>0.002</td>
</tr>
<tr>
<td>N(_2)O Intensity</td>
<td>0.002</td>
</tr>
<tr>
<td>Overall intensity (g CO(_2) eq/kWh)</td>
<td>210</td>
</tr>
</tbody>
</table>

Expected annual GHG emissions at the Ravensview WWTP are about 2,400 tonnes CO\(_2\), 60 kg CH\(_4\) and 18 kg N\(_2\)O (assuming flaring biogas results in 1,400 tonnes of CO\(_2\) being emitted). Ideally, the use of a SOFC system scaled to utilize all biogas produced at the WWTP would reduce the CH\(_4\), CO\(_2\) and N\(_2\)O emissions that result from using grid electricity generation. If a 250 kW system, which would not necessarily use all the biogas produced on-site, was installed the expected reduction in emissions would be about 350,400 kg CO\(_2\), 22 kg CH\(_4\) and 7 kg N\(_2\)O annually from electrical generation if the system was operated continuously. A CO\(_2\) reduction of 1,779 tonnes could be recorded if all flaring of biogas could be stopped and biogas was used for electricity generation instead. SOFC systems are more environmentally responsible than flaring of biogas because not only do they produce electricity, but, they also emit no NO\(_X\), SO\(_X\), hydrocarbons, etc. that can result from the combustion of biogas through flaring because the gas cleanup process removes all contaminants that result in those harmful compounds forming.
5.6 Conclusions & Future Work

The installation of biogas fueled SOFC systems can potentially reduce GHG emissions and provide an environmentally responsible alternative to conventional thermal electricity generation. A predicted CO₂ emission reduction of 1,800 tonnes annually could be achieved if the system is operating constantly. The modeling results show that a reasonable cell performance and efficiency are possible when operating the SOFC system at a S/C ratio of 1 or 2. The ΔV CO₂ effect that was recorded during the dilution experiments do not present a problem for the cell performance when operating on biogas because the post-reformer biogas feed contains a lower partial pressure of CO₂ then experimentally tested.

Future developments planned for the model will enable the study of combined heat and power system efficiency as well as determine the thermal power that could be used to heat buildings and the digesters at the WWTP. Further experimental testing using biogas at range of fuel utilization factors will enable the validation of the model results, and dilution testing using CO as a diluent would improve the prediction of the shift reaction equilibrium. It is desirable to look at the ΔV CO₂ effects at lower CO₂ partial pressures (with H₂) to determine if it, in an experimental setting, is true that the decreased ΔV CO₂ was due to the decreased CO₂ partial pressure being fed to the cell after the reformation reactions occurred.

5.7 References


Chapter 6

Performance of an Anode-Supported Tubular Solid Oxide Fuel Cell on Simulated Biogas Reformate

6.1 Abstract

Biogas produced at wastewater treatment plants can provide a renewable energy resource when used as a fuel in solid oxide fuel cells (SOFCs). Research conducted at the Queen’s – RMC Fuel Cell Research Centre (FCRC) investigated the performance of commercially available anode supported, tubular SOFCs. Acceptable cell performance could be obtained at varying current densities when operating on simulated anaerobic digestion (AD)-biogas reformate. Based on a minimization of the Gibb’s free energy, the equilibrium composition for reformate produced from typical AD-derived biogas was found to be 66.7% H₂, 16.1% CO, 16.5% CO₂ and 0.7% N₂. SOFCs were fed this gas composition with steam at a level of 2.3% and 20% H₂O. All testing conducted was conducted at 800°C and it was assumed that the water-gas shift (WGS) reaction reached equilibrium in the cell. The increased cell performance in the test with the higher humidification level was attributed to increased H₂ partial pressures in the fuel gas mixture due to the forward WGS reaction converting CO and H₂O into additional H₂, providing additional fuel to be used producing electrons at the anode sites.

6.2 Introduction

Biogas is produced through the anaerobic digestion (AD) of municipal sewage waste at wastewater treatment plants (WWTPs) and is generally flared to prevent the release of CH₄ to the atmosphere. Biogas can be considered a renewable fuel that is readily available at WWTPs using
AD technology. Using biogas as a fuel for SOFC power plants could offset electricity costs by producing clean electricity on-site. In addition, heat from the SOFCs could be utilized to heat the digesters. Alternate types of fuel cells, such as the phosphoric acid fuel cell (PAFC) or molten carbonate fuel cell (MCFC), have generally been used in combination with biogas or biomass fuel sources in small-scale applications, such as commercial buildings, to provide clean and efficient power (McIlveen-Wright, McMullan, & Guiney, 2003). A series of tests were conducted to examine the effects of H₂ dilution and biogas reformate composition on the performance of anode-supported commercially available tubular SOFCs. Typical WWTP biogas contains approximately 61% CH₄, and 35% CO₂. Contaminants such as H₂S, O₂, N₂, CO and H₂O are also present in small concentrations (Wheeldon, Caners, Karan, & Peppley, 2007). The CH₄ partial pressure is advantageous because the biogas can be reformed into a H₂-rich fuel for use in the SOFC anode.

6.2.1 Biogas Reformate Mixture

The simulated biogas reformate mixture that was used in the biogas experiments was determined using Gibbs Free Energy minimization as implemented in the process software package UniSIM™. The reformer model flow diagram, as generated by UniSIM™, is displayed in Figure 6-1.
Figure 6-1: Flow diagram of the reformer model developed to calculate the biogas reformer outlet gas composition at 800°C.

The simulated biogas reformate mixture at 800°C was found to be: 66.7%H₂, 16.1%CO, 16.5%CO₂ and 0.7%N₂. Preblended compressed gas with this composition was used for testing. Water was added to the gas mixture. Prior testing was conducted to determine the cell performance on dilute H₂ fuel using N₂, Ar and CO₂ as diluents with 2.3%H₂O. It was determined that N₂ and Ar had very little impact on cell performance beyond the anticipated Nernst effects, as reported in Chapter 4. However, CO₂ was found to have a significantly greater negative effect on performance. It was expected that the simulated biogas reformate, with its higher proportion of CO₂, would also show a ‘greater than Nernst’ negative impact on cell performance.

6.3 Experimental

6.3.1 Test Apparatus
Tests were performed using a modified Acumentrics SOFC test station. The active cell area was approximately 135 cm². The cell consisted of a Ni-YSZ anode, LSM (lanthanum strontium manganite) cathode, YSZ (yttria-stabilized zirconia) electrolyte and silver wire interconnect material. An example of the cell used in the tests is displayed in Figure 6-2.
Figure 6-2: Anode-supported tubular SOFC. The silver wire is shown being attached to the current collector. The smaller silver wire wrapped region is an anode active site and the larger regions are cathode active areas.

The cell was connected to the current collector using silver wire and the bond was made stronger through the application of silver paste applied to all wire/current collector contact interfaces.

6.3.2 Testing Procedure

The cell test chamber was heater to 650°C. During heating the anode was fed a mixture of 97% H₂ in N₂ at a flow rate of 250 mL/min. When the temperature was stable at 650°C the feed was switched to pure H₂ at a flow of 150 mL/min and the temperature was increased to 800°C. During the entire period of heating, air was allowed to flow through the test area and, therefore, over the cathode of the cell. The airflow rate was 10 SLPM. Excess fuel was vented from the anode into the area where it was oxidized by the large excess of air. Baseline tests were conducted to ensure that the small amount of excess fuel had a negligible effect on cathode performance.

Steam was added to the dry gas mixture by means of a pump that provided water at a controlled flow rate to achieve the specified H₂O concentration. De-ionized water was used in the
testing. Cell performance was measured at two steam levels, (2.3% and 20% by mol%), and three different fuel utilization levels (80%, 70% and 60%).

6.4 Results

The results of the biogas testing for steam levels of 2.3% and 20% by mol% of the total flow rate are shown in Figure 6-3.

Figure 6-3: Comparison of results determined for 80% fuel utilization of biogas compared to the tests conducted on dilute H₂ fuel and 100%H₂. There are replicate runs of each test displayed on the plot.

This discontinuity in the polarization curves around 100 mA/cm² is due to the poor stability of the mass flow controller at flow rates below 100 mA/cm². Below 100 mA/cm² the flow was held constant at 254 sccm, and therefore, the fuel utilization was lower than the 80% target.

Overall, the cell performance when operating on biogas humidified to 20% of the total flow rate, was similar to pure H₂. This is shown in Figure 6-3. The biogas tests conducted at a
lower humidification rate did not produce as high cell voltages as the tests conducted at the higher humidification rate. Due to the higher partial pressure of CO₂, as well as the presence of CO as a diluent, it was expected that the biogas tests would perform similarly to the 65% H₂/CO₂/H₂O tests, as shown in Figure 6-3. However, this was not the case as the cell performance was much higher than expected.

6.5 Discussion

6.5.1 Cell Performance

It was hypothesized that the cell performance when operating on the simulated biogas reformate would be lower than that which was observed for the pure H₂ and H₂/H₂O baseline curves. Results reported in literature have shown an increase in cell performance when 14% CO is used as a diluent in H₂ fuel compared to pure H₂ (Jiang & Virkar, 2003). Our observation that CO₂ dilution results in a more significant decrease in cell performance then predicted by the Nernst equation for dilution alone and presents a challenge in developing a predictive model of this complicated effect is consistent with Jiang and Virkar (2003). The main question was to what extent the WGS reaction would promote H₂ production. The results would appear to indicate that the forward WGS reaction converted additional H₂, which improved the cell performance with increasing H₂O partial pressure in the feed mixture.

6.5.2 Water-Gas Shift Reaction

The WGS reaction is an exothermic reaction that is typically equilibrium-limited and favored at lower temperatures (Blomen & Mugerwa, 1993). The WGS reaction can lead to an increase in H₂ available for use as fuel in SOFCs by converting excess CO and H₂O to CO₂ and H₂ as shown in Equation (6-1).
\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]  

(6-1)

At lower temperatures, the WGS reaction does not reach equilibrium for kinetic reasons and the partial pressure of CO remains higher than that which can be observed at higher temperatures (Blomen & Mugerwa, 1993); therefore, at the high operating temperature of 800°C, it can be expected that more CO will be converted to H\(_2\), assuming the water partial pressure is sufficient. From literature, it is generally assumed that the WGS reaction reaches equilibrium (Mogensen, Grunwaldt, Hendriksen, Dam-Johansen, & Nielsen, 2011).

The estimated effects of the WGS reaction for humidification levels of 2.3% and 20% of the total flow rate have been calculated, as shown in Table 6-1 and Table 6-2. All calculations were conducted using fuel flow rates (mol/s) that maintain 80% fuel utilization at 100 mA/cm\(^2\) at 800°C.

Table 6-1: Effect of the WGS reaction at 2.3% \(\text{H}_2\text{O}\) of total biogas reformate flow rate calculated at 100 mA/cm\(^2\).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mol %</th>
<th>mol/s</th>
<th>Mol %</th>
<th>mol/s</th>
<th>Mol %</th>
<th>mol/s</th>
<th>Mol %</th>
<th>mol/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FC Inlet</td>
<td>FC Inlet</td>
<td>FC Reaction</td>
<td>FC Outlet (no WGS reaction)</td>
<td>FC Outlet without Shift</td>
<td>Effect of Shift Reaction</td>
<td>FC Outlet Shift Equilibrium</td>
<td>FC Outlet Shift Equilibrium</td>
</tr>
<tr>
<td>H(_2)</td>
<td>65.6%</td>
<td>8.8E-06</td>
<td>-7.2E-06</td>
<td>1.7E-06</td>
<td>12.3%</td>
<td>12.3</td>
<td>10.0</td>
<td>22.2</td>
</tr>
<tr>
<td>\text{CO}_2</td>
<td>15.8%</td>
<td>2.1E-06</td>
<td>0.0E+00</td>
<td>2.1E-06</td>
<td>15.8%</td>
<td>15.8</td>
<td>-10.0</td>
<td>5.9</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>2.3%</td>
<td>3.0E-07</td>
<td>7.2E-06</td>
<td>7.5E-06</td>
<td>55.6%</td>
<td>55.6</td>
<td>-10.0</td>
<td>45.7</td>
</tr>
<tr>
<td>CO</td>
<td>16.2%</td>
<td>2.2E-06</td>
<td>0.0E+00</td>
<td>2.2E-06</td>
<td>16.2%</td>
<td>16.2</td>
<td>10.0</td>
<td>26.2</td>
</tr>
<tr>
<td>Total</td>
<td>100.0%</td>
<td>1.3E-05</td>
<td>1.3E-05</td>
<td>100.0%</td>
<td>100.0</td>
<td>0.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Table 6-2: Effect of the WGS reaction at 20% H₂O of total biogas reformate flow rate calculated at 100 mA/cm².

<table>
<thead>
<tr>
<th>Gas</th>
<th>FC Inlet</th>
<th>FC Outlet (no WGS reaction)</th>
<th>FC Outlet without Shift</th>
<th>Effect of Shift Reaction</th>
<th>FC Outlet Shift Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>55.9%</td>
<td>3.3E-07</td>
<td>2.5%</td>
<td>2.5</td>
<td>7.7</td>
</tr>
<tr>
<td>CO₂</td>
<td>13.5%</td>
<td>1.7E-06</td>
<td>13.5%</td>
<td>13.5</td>
<td>8.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>16.8%</td>
<td>9.0E-06</td>
<td>70.1%</td>
<td>70.1</td>
<td>85.0</td>
</tr>
<tr>
<td>CO</td>
<td>13.8%</td>
<td>1.8E-06</td>
<td>13.8%</td>
<td>13.8</td>
<td>19.0</td>
</tr>
<tr>
<td>Total</td>
<td>100.0%</td>
<td>1.3E-05</td>
<td>100.0%</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 6-1, for 2.3 mol% humidification, shows that the estimated effects of the shift reaction result in a more significant increase in CO than the 20% humidification case in Table 6-2. However, the additional H₂O that is provided in the 20 mol% steam shifts the equilibrium to convert additional H₂. This would indicate that the fuel cell reaction was pushed further towards equilibrium, utilizing more H₂ to produce a higher cell potential for a given current density.

Equation (6-2) illustrates the equilibrium for the WGS reaction. If the reaction is less than Kₑq the forward reaction is favoured. As the reaction approaches equilibrium, more H₂ is converted, which improves cell performance.

\[
Kₑq ≥ \frac{P_{H₂}P_{CO₂}}{P_{H₂O}P_{CO}}
\]  

(6-2)

Figure 6-4 shows the difference between the cell performances on simulated biogas reformate fuel humidified at both 2.3 mol% and 20 mol% of the total fuel flow rate. It was expected that at higher humidification levels, the cell performance would be lower because the partial pressure of H₂ in the initial biogas mixture (before consideration of the WGS reaction) would be lower than that of the lower humidification level (since H₂O would be displacing the H₂ in terms of mol fraction). This was not the case and the WGS reaction provided additional H₂.
Computations also indicated that the forward WGS reaction was likely favoured. Consequently, possible decreases in cell performance due to localized cooling as a result of the endothermic reverse WGS reaction can be ignored as the forward WGS reaction is exothermic. Therefore localized heating effects on the catalyst could increase cell performance with the increased temperature. However, these effects are likely minimal.

Figure 6-4: Comparison of cell performance on simulated biogas reformate with the addition of H₂O for humidification and 80% fuel utilization. There are replicate runs of each test displayed on the plot.

The addition of an excess of water to the fuel gas mixture results in a greater conversion of CO by the WGS reaction, while also raising the heat capacity of the reaction stream (Blomen & Mugerwa, 1993). The partial pressure of H₂O will also reduce the tendency for carbon deposition on anodes sites in CO-rich fuels and it is therefore desired in the fuel gas mixture (Rostrup-Nielsen, 2001). Since the WGS reaction is rapid in the presence of Ni (which is the anode material in the cell used for this research), at high temperatures and with high
humidification of the gas mixture, it can be inferred that additional H$_2$ was produced (Blomen & Mugerwa, 1993).

6.6 Conclusion

The installation of a SOFC system operating on AD-derived biogas at a WWTP could provide clean electricity for use on-site as well as additional heat to maintain the temperature of the ADs. The electricity produced would be considered ‘clean’ energy as the initial fuel is biomass-derived and the fuel cell reaction predominately produces no harmful emissions. Tests have shown that an anode supported tubular SOFC can operate successfully on simulated biogas reformate from the AD-process. The removal of certain contaminants will, however, be crucial to the successful operation of a SOFC/biogas system at a WWTP. It was also determined that the WGS reaction is occurring in the forward direction and is providing additional H$_2$ to the anode fuel stream. The forward WGS reaction was favoured when the humidification level was increased from 2.3% to 20%. In previous diluted H$_2$ tests, CO$_2$ caused a negative impact to cell performance at moderately high partial pressures (i.e. 35% CO$_2$ in H$_2$). It was expected that the CO$_2$ would cause a reduction in the cell performance in the simulated biogas fuel tests as well. This was not the case and the cell performance improved because the WGS reaction produced additional H$_2$ in the anode feed. Overall, the performance of the fuel cell on the simulated biogas reformate was encouraging, especially at the increased humidification level (20% H$_2$O).

These results indicate that biogas is a promising fuel for SOFC systems that could be implemented in WWTPs. Although there are still contaminants that need to be removed, the composition of AD biogas provides a satisfactory fuel for SOFC operations. Power produced from an SOFC system offsets the power that needs to be supplied from the grid and the associated
carbon emissions from the grid. In addition, the SOFC has the benefit of monitoring supplemental heat to the AD system when it is required.

6.7 References


Chapter 7
Conclusions & Recommendations

Anaerobic digester (AD)-derived biogas produced at wastewater treatment plants (WWTPs) is a renewable fuel that can be used to generate electricity to offset energy costs by reducing the electrical demand of the WWTP on the local utility grid. Local biogas composition analysis must be acknowledged in the design of the system, but once an adequate gas cleanup system and gas-processing unit are applied the system can produce clean electricity and assist with the reduction of GHGs. The use of a SOFC system can also reduce the heating demand because waste heat produced by the SOFC can be used to assist with the heating of the ADs and facility buildings.

It was determined that the biogas composition in North America can be variable depending on facility. Overall, the CH$_4$ and CO$_2$ partial pressures were not as variable as the other, lower concentration, components of the biogas, such as H$_2$S and Si compounds. The fluctuations in H$_2$S and Si compounds can be detrimental to SOFC performance but if an in depth analysis of the site-specific variability is conducted a gas cleanup strategy can be designed to accommodate for fluctuations in composition. The average composition of AD-derived biogas was determined to be 64% (2%) CH$_4$, 37% (4%) CO$_2$, 1% (2%) N$_2$, 0% (0.7%) O$_2$, 144ppm (186ppm) H$_2$S and 12ppm (10ppm) Si equivalence. This average composition was based on research collected from urban areas that participated voluntarily in a survey conducted in 2010. Very few urban areas contacted that had ADs installed at WWTPs tested the composition or monitored the generation of the biogas produced at regular intervals. The lack of knowledge in biogas composition at many WWTPs throughout North America makes it more challenging to
determine relationships between biogas composition and factors such as climate, season, population, industry, etc. It is recommended that more localized analyses be completed at WWTPs to enable researchers and practitioners to determine the variability of the biogas generated more accurately. It would be beneficial for multiple WWTPs within the same urban area to provide composition data so that more conclusions can be made regarding relationships between production and geographic conditions. It is also recommended that research be conducted to determine whether a correlation exists between the source of drinking water in the urban area (aquifer, lake/river, etc.) and WWTP biogas composition. Different drinking water sources require specific treatment, which can introduce alternative compounds that can alter biogas composition. It was an interesting observation that states/provinces, such as California, that have a significant amount of environmental legislature in place typically have more advanced biogas end-use systems such as fuel cells. The social response to environmental preservation is evident in some states and this is often reflected in the types of ‘green’ energy systems that are present at the WWTPs as well as the funding initiatives available to assist with capital expenditures associated with the installation of novel technologies such as fuel cells.

The dilution testing confirmed that an SOFC can operate at lower H$_2$ partial pressures in the fuel gas mixture. Tests were conducted at dilutions of 10%, 25% and 65% H$_2$ with diluent fuel, as reported in Section 4.4. There was a significant difference between the results reported for the 100% H$_2$ baseline tests, the 65% dilutions and the lower H$_2$ partial pressures at the lower (10% and 25%) dilutions (shown in Figure 4-4 to Figure 4-6). The diluent gases that are inert in fuel cell reactions performed as expected, with only a slight decrease in performance from the H$_2$ baseline tests, where as the CO$_2$ diluent tests resulted in a significant decrease in cell performance, which was attributed to the occurrence of the reverse water-gas shift (WGS).
reaction occurring. It is recommended that diluent tests be conducted using CO as a diluent fuel. Testing using CO could demonstrate whether the increased cell performance is due to the WGS reaction occurring in the forward direction. Performing tests using CO as a diluent fuel were not possible using the test stand arrangement that was available at the FCRC due to the hazards associated with using high flow rates of CO in the laboratory.

The UniSIM™ simulation that was developed modeled laboratory data reasonably well. It was necessary to account for the decrease in cell performance that was recorded when CO₂ was used as a diluent gas in the fuel mixture by adding a term (referred to as the ΔV CO₂ effect) to the empirical model that was input into the simulation. This term was based on the partial pressure of CO₂ in the fuel gas mixture and therefore was not significant when Ar or N₂ were used as the diluent gases. The ΔV CO₂ term adjusted the empirical model to accommodate the decrease in cell performance in addition to the dilution effects that were noted for N₂ and Ar. The results of the UniSIM™ simulation predicted that the cell performance and efficiency of a biogas/SOFC system are good when a steam to carbon ratio of 1 or 2 is used. The UniSIM™ model used and input gas mixture of 60% CH₄ and 40% CO₂ to approximate the average composition of AD-derived biogas from WWTPs and S/C ratios of 1 and 2 to examine the effects of different levels of humidification in the fuel gas. System efficiency, stack efficiency, and output gas composition were computed through the simulation for a range of user-defined current densities. In the future, the model will be adapted to enable researchers to determine the combined heat and power system efficiency and the thermal power output from the system (waste heat) that could be used to offset heating requirements at the WWTP, which will provide a better representation of the overall biogas/SOFC system efficiency. The current model was compared to the cell performance results that were obtained when the SOFC was operated on simulated biogas reformate and the
model did not accurately predict the cell performance results. The UniSIM™ model should be adapted to also represent the simulated biogas reformate results and will have to consider the potential effects of the reverse-water gas shift reaction due to the presence of CO in the simulated biogas reformate mixture. The CO₂ emissions released from the SOFC system would be approximately 104,025 to 159,505 m³/yr at the Kingston Ravensview WWTP if the biogas production were comparable to the 2007 production. This is a significant reduction when compared to the GHG emissions for flaring, which are approximately 1,429 tonnes (794,810 m³) CO₂ if 2.75 kg of CO₂ is formed for each 1 kg of CH₄ combusted. The GHG emission reduction potential of biogas/SOFC systems is significant and if employed worldwide would have a positive environmental impact.

Tests conducted using simulated biogas reformate with a composition of 66.7% H₂, 16.1% CO, 16.5% CO₂ and 0.7% N₂ with 2.3% and 20% H₂O as steam, by volume, displayed results that indicated that a SOFC system operating on AD-derived biogas is a viable energy solution at WWTPs. Tests were conducted that humidified the biogas reformate fuel to 2.3 mol% H₂O (as steam) and the cell performance was better than when CO₂ was used as a diluent fuel, which was encouraging. Tests were then conducted at 20 mol% H₂O (as steam) and the cell performance was more on par with the H₂ baseline tests, indicating that the higher humidification level encourages the WGS reaction, increasing the H₂ production. In the 20% H₂O output gas the fuel mixture was approximately 7.7% H₂, 8.4% CO₂, 65% H₂O and 19% CO, compared to the 2.3% H₂O (22.2% H₂O, 5.9% CO₂, 45.7% H₂O, and 26.2% CO) this is positive because more H₂ is being consumed by the cell (lower percentage in output gas mixture) and the output of CO is lower at 20 mol% H₂O. Also, at the higher humidification level the dominant component of the output gas mixture is H₂O, which is not harmful to the environment. The simulated biogas
reformate tests indicated a region of cell starvation when the fuel utilization approached 80% (Figure 6-4). To avoid this, it is suggested that in future tests the excess fuel be provided to the cell until a current density of 100 mA/cm² because the mass flow controllers employed in this study could not provide the lower flow rate required at 100 mA/cm² for the biogas reformate.

The simulated biogas reformate used was free of typical biogas contaminants such as H₂S, siloxanes, halides, etc. and therefore the results obtained are to be reproduced on a larger scale system operating on non-simulated biogas it must be ensured that the biogas is cleaned to maintain a high quality gas mixture that is free of harmful contaminants to prevent decreases in cell performance due to the blocking of active anode sites by contaminants in the fuel gas. To ensure adequate gas cleanup a system must be designed to meet the specific biogas conditioning needs of the specific WWTP, which can often be difficult as biogas can vary significantly site-to-site in terms of contaminants. No biogas cleanup system will work for 100% of WWTPs and therefore research much first be conducted to determine the biogas variability on-site.

Overall, the operation of a biogas fueled SOFC system is an opportunity for WWTPs to reduce GHG emissions, electrical costs, and heating costs by producing electricity from the biogas produced on-site. It would be a novel research initiative to install the pilot-scale biogas/SOFC system at a WWTP, as many of the current WWTP fuel cell systems are molten carbonate or phosphoric acid fuel cells. The installation of a pilot scale system could assist with future design of biogas conditioning systems as well as identify advantages and disadvantages of using AD-derived biogas as a renewable fuel. It is recommended that a pilot-scale system be installed at the Ravensview facility in Kingston, ON as a research initiative that could greatly benefit biogas/SOFC system research and potentially validate the results from previous research, both in this project and in the literature. The global fossil fuel depletion is inevitable and novel
technologies, such as fuel cells, must be further investigated as alternatives to electricity and heat production, and considering that WWTPs are often a municipality’s largest electricity consumer, using biogas produced on-site at WWTPs as a renewable fuel is an excellent starting point.
Appendix

Experimental Cell Efficiency

The cell efficiency for the experimental data was calculated using (A 1):

\[ \eta = \frac{V_{\text{Actual}}}{V_{\text{Theoretical}}} \]  

(A 1)

The results are displayed in Figure A 1.

Figure A 1: Cell Efficiency from Experimental Data Calculated Using Theoretical Voltage.
Figure A 2: Cell Efficiency from Experimental Data Calculated Using Theoretical Voltage.

Fuel Cell System Emissions

Figure A 3: System Emissions from S/C=1, Considering V CO₂.
Figure A 4: System Emissions from S/C=1, Not Considering V CO₂

Figure A 5: System Emissions from S/C=2, Considering V CO₂
Figure A 6: System Emissions from S/C=2, Not Considering V CO$_2$. 