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THESIS

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by

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DEDICATION

To my parents for all of their love and support….

Thanks mom for always understanding and letting me leave the nest to experience new things even though it hurts to let go. And thanks dad for sharing your vast knowledge and guidance on just about everything important in life. You guys helped shape me into the proud person I am today.
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LIST OF ACRONYMS

ADG – Anaerobic Digester Gas
CEA – Chemical Equilibrium with Applications
CNG – Compressed Natural Gas
EES – Engineering Equation Solver
EHS – Electrochemical Hydrogen Separation
FCE – Fuel Cell Energy
GC – Gas Chromatography
HSU – Hydrogen Separation Unit
HTS – High Temperature Shift
LFG – Landfill Gas
LTS – Low Temperature Shift
MCFC – Molten Carbonate Fuel Cell
OCSD – Orange County Sanitation District
PEM – Proton Exchange Membrane
PSA – Pressure Swing Adsorption
RNG – Renewable Natural Gas
SMR – Steam Methane Reformation
SOFC – Solid Oxide Fuel Cell
TCD – Thermal Conductivity Detectors
WGS – Water Gas Shift
WGSR – Water Gas Shift Rector
WWTP – Waste Water Treatment Plant
I would first like to thank my advisor, Dr. Jacob Brouwer. I first joined the lab with an interest in fuel cells but with no real experience and you gave me the opportunity to pursue my passion. I admire your great enthusiasm and leadership that continued to inspire me and guide me along the way. I also want to thank you for being not just an advisor but a friend. Being easy to talk to, discussing basketball, and even playing music together made my experience here at UCI that much more enjoyable.

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ABSTRACT OF THE THESIS


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The growing market for clean, sustainable energy systems has opened to door for many technologies in both the power generation and transportation sectors. Fuel cell technology has provided a means to produce power and heat more efficiently and with fewer emissions than traditional power generation systems. The emergence of hydrogen fuel cell vehicles has demonstrated the use of fuel cells for transportation that use hydrogen fuel to achieve comparable performance to traditional vehicles while achieving greater efficiency and zero emissions. This thesis focuses on a system that brings the two sectors together by utilizing fuel cell technology to tri-generate three useful products from a renewable biogas stream: power, heat, and hydrogen. The hydrogen produced is then directly used at a fueling station to refuel hydrogen fuel cell vehicles. A fully operational system has successfully demonstrated this technology at the Orange County Sanitation District which provided the inspiration for this work. A dynamic tri-generation system has been modeled with investigation of electrochemical hydrogen separation to produce high purity hydrogen necessary for fuel cell vehicles. Results from this analysis show a wide range of design and operational values to characterize the performance under many conditions. Electrochemical separation has unique operation compared
to other separation methods and can improve system performance especially in sub megawatt systems. It is shown that tri-generation systems have great promise as an energy system because of their efficient operation, near zero emissions, ability to run on renewable biogas, and the ability to produce the hydrogen fuel for fuel cell vehicles.
1 INTRODUCTION

1.1 Overview

Biogas is a relatively untapped resource that is quickly gaining interest as an energy resource. A vast majority of current biogas-to-energy projects utilize boilers, reciprocating engines, or turbines to produce heat and electricity from a resource that would otherwise be wasted and flared to produce and emit greenhouse gases and criteria pollutants. A handful of projects now incorporate high temperature fuel cell systems to harvest the energy at higher efficiencies and lower emissions, but why stop at just electricity and heat?

The concept of tri-generation has been developed to generate hydrogen, electricity, and heat as products from a fuel cell system that can use bio methane as fuel. This sustainable technology can now be used to promote hydrogen fuel cell vehicles and assist in the transition from fossil fuels to renewable fuels in the transportation and stationary power sectors. The widespread implementation of fuel cell tri-generation systems around the U.S. could provide a solid initial resource base and expand hydrogen infrastructure which is all derived from renewable natural gas (RNG).

The first in the world tri-generation system running on a biogas feedstock has been installed and operational over the past couple years at the Orange County Sanitation District (OCSD) in Fountain Valley, CA. The overall scheme of the plant takes a small portion of the biogas produced by the waste water treatment plant via anaerobic digestion and produces power, heat, and hydrogen from the novel fuel system while the hydrogen is compressed, stored, and eventually used to fuel hydrogen fuel cell vehicles at the on-site fueling station. The purpose of this pilot plant is to demonstrate the feasibility of a tri-generation system while promoting
research activities and outreach for both the system itself and the transportation aspect for fuel cell vehicles and fueling stations. Further details regarding the system and individual components will be explained throughout this thesis but here is an overview of what is contained in the full system:

- Fuel cleanup skid – removes unwanted compounds from the incoming fuel
- Fuel cell stack – high temperature molten carbonate fuel cell that generates power and heat
- Mechanical balance of plant – contains flow recirculation, fuel and air preheat heat exchangers, and anode off-gas oxidizer
- Electrical balance of plant – converts DC signal to AC signal and establishes connection with the electrical grid
- Hydrogen booster – utilizes two stage water gas shift reactors to increase hydrogen composition
- Hydrogen separation unit – uses pressure swing adsorption technology to separate a pure hydrogen stream from the anode off-gas
- Hydrogen processing – compression, storage, and pipeline transport for use at the hydrogen fueling station
- Hydrogen fueling station – additional compression and storage with the capability to refuel hydrogen fuel cell vehicles at 35 MPa and 70 MPa

Modeling efforts will focused on the hydrogen booster and hydrogen separation unit with major emphasis on full system performance.
1.2 Goal and Objectives

The goal of this thesis is to:

Optimize the design and performance characteristics of large scale tri-generation systems coupled with novel hydrogen separation methods.

The major objectives outlined below will guide research efforts to fulfill the overall goal:

1. Conduct literature review
2. Develop dynamic tri-generation system model
3. Simulate the particular tri-generation system representative of the OCSD system
4. Gather operational data from the site to verify the model
5. Develop dynamic models of three potential hydrogen separation techniques
6. Modify and integrate the component models to represent second generation large scale tri-generation systems
7. Run simulations with varied parameters to determine system performance
2 BACKGROUND

2.1 Bio Methane Fuel

The current status of bio methane technology and utilization has been conducted at Argonne National Laboratory in 2009 and again in 2012. Harnessing landfill gas (LFG) and producing biogas from anaerobic digestion are old technologies that have been implemented at landfills, wastewater treatment plants (WWTP), farms, and food waste facilities to make beneficial use from waste resources [1]. Using fuel cell systems is one method that can be used to generate power, heat, and other products from these resources.

The EPA updates a database for landfills that collect landfill gas (LFG) and farm sites that collect biogas from anaerobic digestion, but not for WWTPs and food waste facilities that have anaerobic digestion. Information was gathered via previous databases, the EPA, internet searches, journal articles, etc. to find sites utilizing biogas and provide more detailed information. Each database provides information such as project size, gas flow rates, organizations involved, biogas use, and more. Many of the projects use the biogas either as a heat source from a boiler or for electricity production using engines, turbines, or fuel cells that could be used on site or sold to the grid. A smaller percentage of interesting projects cleaned the raw biogas to about 95% methane so it could be injected into a natural gas pipeline or used as vehicle fuel mostly for compressed natural gas (CNG) vehicles. Overall, there has been an increase in the number of these unique projects over the last couple years that are operational, in construction, or in the planning stages with a total of at least 77 project sites. The continued future interest is apparent in this technology because 24 of those projects are under construction
or being planned for the near future. These projects make up a small fraction of total projects that harness biogas around the U.S. which shows the potential for biogas utilization to substantially increase [1]. Tri-generation is a revolutionary technology that can capture the benefits of this biogas resource in an efficient and clean manner to produce renewable energy across the country.

2.2 Tri-Generation System

2.2.1 The Tri-Generation Concept

Tri-generation is a term used to describe a system that produces hydrogen, power, and heat. High temperature fuel cells such as molten-carbonate fuel cells (MCFC) and solid-oxide fuel cells (SOFC) present the opportunity for tri-generation because of the high operation temperatures that allow for a variety of fuel inputs and internal reformation in the fuel cell stack [2]. This thesis will focus on MCFC technology because an existing 300 kW system from Fuel Cell Energy (FCE) is operational at the Orange County Sanitation District (OCSD) that can be used to verify models and there is an interest in larger scale MCFC systems for tri-generation. The diagram below displays this process of tri-generation [3].
Figure 1: The tri-generation concept

With an operational temperature of 550-650 °C, a MCFC doesn’t require pure hydrogen fuel because of its ability to internally reform methane with water to produce hydrogen [2]. This steam methane reformation (SMR) combined with the simultaneous water-gas shift reaction (WGS), which further reacts carbon monoxide with water to produce more hydrogen and carbon dioxide, produces the hydrogen necessary for the fuel cell. The endothermic nature of this reformation helps cool the fuel cell stack to offset the exothermic nature of the overall hydrogen and oxygen reaction in the stack [4]. This provides a great improvement in system efficiency, cost, and complexity over external reformation techniques since the heat can be directly used from the stack without transferring it to a separate reformer. The cost and complexity are reduced because additional equipment isn’t necessary with internal reformation [5].

The ideal thermodynamic behavior under internal reformation is just one synergy associated with running a fuel cell for the purpose of generating hydrogen. A typical fuel cell may run with a fuel utilization of 85% in the anode which leaves 15% of the fuel un-reacted at the anode outlet. It is necessary to run a fuel cell with utilization less than 100% since a concentration of the fuel
is required along the entire length of the cell to achieve a voltage difference. When run at higher utilization factors, more electricity can be produced and the remaining fuel can be recycled back or burned for heat. For tri-generation, fuel utilization is maintained around 65% by flowing excess fuel through the anode. Operating the fuel cell at this factor increases the performance of the cell because fuel is present at a higher concentration along the entire length of the cell to allow for less concentration polarization and generate a higher potential difference. This concept doesn’t make sense for non tri-generating systems since less electricity will be produced per unit of fuel and now there is even more excess fuel at the anode outlet to manage. However, for tri-generation systems, the excess hydrogen is separated and captured as a useful product to be used in hydrogen fuel cell vehicles. This capture of hydrogen as a useful product now requires a different methodology for efficiency calculations to determine purely electrical efficiency, hydrogen efficiency, and total system efficiency both with and without heat recovery. System efficiency calculations were developed by Margalef et al. to investigate such performance. By determining the amount of input fuel flow that is allocated to electricity and hydrogen production separately, efficiencies could be calculated for both electrical and hydrogen efficiency. This displayed that the electrical efficiency was increased compared to a standard fuel cell system because of the fuel cell operation. System efficiency values for combined electricity and hydrogen production can exceed 80% even without capturing heat as a third product [6]. Such results provide great promise for tri-generation technology.

2.2.2 Fuels and Cleanup

Natural gas is the first fuel that comes to mind when considering methane as the input to the fuel cell; however, utilizing bio sources such as landfill gas or anaerobic digester gas (ADG) allows the tri-generation system to produce renewable energy from waste sources. This concept of fuel
flexibility creates the opportunity for a wider range of applications that could benefit from a tri-generation system while also eliminating the dependence on fossil fuels. Utilizing bio methane has great potential but it is important to consider the challenges related to gas cleanup before it enters the fuel cell. Typical sources of biogas contain 45-63% methane while most of the remaining percentage is carbon dioxide [1]. However, it is the sulfur compounds and siloxanes that pose the greatest threat to poisoning the fuel cell so these compounds must be removed from the gas. Even ppm levels of sulfur will “stick” to the catalysts where the triple phase boundaries allow for electrochemical reactions meaning that the reactions cannot occur and the fuel cell performance is greatly reduced. Siloxanes pose a different problem to fuel cells. These silicon containing compounds resemble sand which essentially means that siloxanes in a fuel cell will cause blockage just like a buildup of sand would. Both phenomena should be avoided as much as possible to maximize performance and stack life. Since carbon dioxide is the charge carrier in an MCFC, its removal isn’t a necessity and a presence of it is actually required in the cathode stream [7]. Carbon monoxide isn’t an issue in the high temperature environment due to the ease of oxidation, but even natural gas requires sulfur removal to prevent poisoning of the fuel cell [8].

There are a number of technologies that can be used to remove sulfur and siloxane compounds including cryogenic removal, activated carbon beds, zinc oxide capture beds, and iron sponge beds. The typical mechanism for removing these compounds is based on an active catalyst bed that adsorbs the unwanted compound while the remaining gas flows through [9] [10]. Hydrogen sulfide is the easiest sulfur compound to remove with a capture bed but a variety of more complex sulfur compounds are present in biogas fuels. A novel method to deal with issue at the OCSD system was developed called hydro-desulfurization. This process reacts a small amount
of hydrogen with the other sulfur compounds to reduce all sulfur to hydrogen sulfide making the removal process easier. This process is feasible for this particular system since pure hydrogen is readily available. A combination of the techniques listed above is used at the OCSD system to remove nearly all of the sulfur and siloxane compounds before the fuel enters the fuel cell.

2.2.3 Hydrogen Separation Techniques

The hydrogen stream resulting from the reformation process isn’t pure hydrogen so purification is necessary for the hydrogen to be used as vehicle fuel. The typical gas composition contains 70-80% H₂ and up to 25% CO₂, 6% CH₄, and 3% CO before any gas cleanup [11]. Proton exchange membrane (PEM) fuel cells on hydrogen fueled vehicles are very sensitive to contaminant gases that can reduce the performance and poison the fuel cell. Even trace amounts of CO can poison the platinum catalyst which drastically reduces the fuel cell operation [12].

Three different hydrogen separation techniques will be investigated including pressure swing absorption, palladium membranes, and electrochemical hydrogen separation (EHS), which can produce a hydrogen rich and/or pure hydrogen product streams.

Pressure Swing Absorption (PSA) is one of the most widely used hydrogen separation techniques, especially in large scale applications. This process utilizes the ability of gases to adsorb and desorb from surfaces at different pressures. In the hydrogen separation case, unwanted compounds including CO₂, CO, and CH₄ are all adsorbed to surfaces such as carbon or zeolite while the hydrogen passes through. These compounds are then desorbed by depressurization and the cycle is repeated again [11]. The hydrogen recovery of this process is lower than other methods at 70-85% due to some purging of hydrogen, yet a purity of up to 99.999% can be obtained [13]. The input flow to a PSA apparatus requires high pressure and cool temperature which adds a significant load on the system because the flow leaving the fuel
cell stack is at low pressure and high temperature. This requirement coupled with consistent changes in pressure must be considered within the system.

A number of membrane separation techniques exist but the most promising method for hydrogen purification involves the use of palladium alloys. The basic principle is based on selective reactivity of hydrogen to certain materials such as palladium where only hydrogen will first adsorb to the surface and split into two hydrogen ions, permeate through the surface, and finally desorb from the surface at the other end into H₂ again [14]. This process can obtain ultra-pure product streams of >99.9999% hydrogen with up to 99% recovery without high pressure requirements or pressure variations [13]. The permeability of a pure palladium membrane can limit the flux of hydrogen that can pass through, but utilizing palladium alloys with other metals such as silver can greatly increase the flux. One method that has been tested involves two thin layers of palladium on the outer surfaces with a silver layer in the center to provide structure and allow the hydrogen ions to permeate through. This use of very thin layers of palladium decreases the cost of materials while also increasing the hydrogen flux [15]. The reasonable temperature range for these membranes is 573-873K so some heat needs to be provided [14]. However, with exhaust heat available at 550-650 °C from the fuel cell, heating the membrane is possible by using the waste heat.

Another hydrogen separation technique that isn’t as widely used is electrochemical separation, which is sometimes referred to as a “hydrogen pump” due to its operation. This form of separation is done by running a direct electrical current through a proton conducting electrolyte where the hydrogen ions are transported across and then discharged as hydrogen gas at the cathode. The process doesn’t require pressurization and can be effective in just one step [16]. High temperature operation also isn’t a requirement but increased temperature results in higher
hydrogen purity, flux, and efficiencies [17]. Providing these higher temperatures can be provided by the waste heat produced by the high-temperature fuel cell to further increase system efficiency. Using electrochemical techniques can obtain hydrogen purity of 99.8% with 95% hydrogen recovery [13]. Fuel Cell Energy is developing an electrochemical hydrogen separator (EHS) that could be integrated with their DFC300 system with the ability to produce up to 300 lb/day of hydrogen while also compressing the gas [18]. The details of this process are not available to the public, but the research and development conducted on the EHS shows that there is an interest in electrochemical hydrogen separation for hydrogen production. The combination of hydrogen purification and compression has been tested and proven by a number of previous experiments in the literature [19] [20] [21]. EHS has also been investigated via a system modeling approach that compared the system performance of a solid oxide fuel cell coupled with an EHS for hydrogen production. This configuration was compared to a similar system that modeled the use of PSA rather than EHS. This work provided performance comparisons such as power requirements of components, electrical power produced, pure hydrogen produced, available heat, and efficiency calculations. The overall analysis showed that a system with the EHS could provide more hydrogen with higher system efficiency but yields slightly lower electrical efficiency and heat production [22].

The tri-generation system at OCSD uses the produced hydrogen stream to fuel vehicles but hydrogen can be utilized in a vast variety of ways. Some current uses for hydrogen include: petroleum processing, production of methanol, fertilizer production, recycling of plastics, fuel for the aerospace industry, and fuel for hydrogen fuel cells [23]. The focus of this research is on the use of hydrogen as vehicle fuel, but the vast spectrum of hydrogen use across different
industries justifies hydrogen production even without a high demand for vehicle fuel in the immediate future.

2.3 Water Gas Shift Reactors

2.3.1 Water Gas Shift Reaction

The water gas shift (WGS) reaction describes the chemical reaction that reacts carbon monoxide with water to create carbon dioxide and hydrogen. The equilibrium state of the reaction is based on two major factors being temperature and the steam to carbon ratio (S/C). At lower temperatures, more of the carbon monoxide will react at the equilibrium state to produce hydrogen, however, the kinetics of the reaction are slower at these lower temperatures. The water gas shift reaction becomes useful when the carbon monoxide content in a gas stream is undesirable and hydrogen is the product needed. Because of the temperature dependence, reactors that facilitate the WGS reaction are typically designed in two stages with a high temperature reactor at about 350 °C followed by a low temperature reaction near 200 °C. This takes advantage of the faster kinetics first at the higher temperature but allows more of the carbon dioxide to be reacted when it reaches the lower temperature reactor. This allows a maximization of hydrogen production without waiting for the entire reaction to occur at the lower temperature with slow kinetics [24].

2.3.2 Systems Containing Water Gas Shift Reactors

Steam methane reformation plants exist today to produce pure hydrogen streams that are used for a number of industrial processes. These plants use natural gas as the fuel stream that reacts with steam to reform the fuel into a hydrogen rich stream. The chemical reaction is an endothermic process that reacts the methane with the steam which produces hydrogen and carbon monoxide.
The carbon monoxide is then further reacted in WGS reactors to produce a gas stream of mostly hydrogen and carbon dioxide. By a process called pressure swing adsorption a series of adsorption beds are pressurized and depressurized to separate the hydrogen from the other gas constituents. This process generates the high purity hydrogen stream that is then used throughout industry. The introduction of hydrogen fuel cell vehicles and the idea of a hydrogen economy have provided another use for a pure hydrogen stream that could significantly increase the demand for hydrogen as more vehicles are produced.

The primary application of research efforts pertains to a novel high temperature fuel cell system stationed at the Orange County Sanitation District. This system is the first one in the world that operates on a biogas feedstock and tri-generates three useful products: heat, power, and hydrogen. The biogas is generated by anaerobic digestion from the wastewater treatment process which makes the system a renewable process that doesn’t use fossil fuels. The heat and power generated are used on site while the pure hydrogen stream produced is used to fuel hydrogen fuel cell vehicles at the fueling station also on site. The system contains water gas shift reactors much like the large SMR plants to boost the hydrogen and reduce the carbon monoxide compositions. This occurs in two stages with a high temperature reactor followed by a low temperature reactor because of the equilibrium state and kinetics of the reaction chemistry discussed previously. Modeling work corresponding to the water gas shift reactors represents a piece of the overall goal to develop a model of a fuel cell tri-generation system and other related novel energy systems.

2.3.3 Gas Chromatography

Gas Chromatography (GC) is a method that is used to determine the constituent gas species contained in a gas mixture and generate the percent composition of each. This process can be
useful for determining the performance of a system, testing for purity levels of a sample, and conducting research for a number of applications. A GC machine works by injecting a stream of the sample gas through a sample loop where the gas enters a column. The gas travels through the column and specific gas species are released from the mixture after a certain residence time because of the unique properties of each species. The type and amount of the gases are measured by thermal conductivity detectors (TCD) that compare the sample with a reference gas that is supplied such as helium or nitrogen. The results of a GC analysis show peaks in a graph where the area under the curve shows the amount of each gas species and a complete analysis displays the percent composition of all measured gases. These peaks are calibrated to determine the type and amount of each gas by using known calibration gases with specific compositions.

2.4 Summary

The literature contains a number of experiments and modeling work in the areas related to tri-generation including reforming and water gas shift kinetics, gas cleanup technology, PSA for separation, membrane separation, and EHS. There is also great interest shown in the use of biogas for renewable energy which could include sources such as WWTP, landfills, farms, and other waste facilities. Only a select few papers are on the topics of hydrogen separation techniques and full tri-generation system performance. This thesis will focus on furthering research on EHS and the effects it has on complete tri-generation system performance using an MCFC fuel cell stack. This analysis along with a description and comparison to an operating tri-generation plant at the Orange County Sanitation District will provide a new perspective on the technology and help facilitate further research.
3 APPROACH

The following steps will be taken to accomplish the objectives outlined before:

Task 1. Conduct literature review
   a. Conduct literary research on fuel cells, tri-generation, hydrogen separation techniques, and biogas resources

Task 2. Develop a dynamic tri-generation system model
   a. Obtain previous high-temperature fuel cell models and learn their operation
   b. Compile all components of the system
   c. Complete system balance (thermal, electrical, flow rates, etc.)

Task 3. Simulate the particular tri-generation system representative of the OCSD plant
   a. Run the model with various operational parameters that will be used to verify the model with actual data

Task 4. Gather operational data from the site to verify the model
   a. Acquire operational parameters of the fuel cell system at OCSD
   b. Take gas samples along the process
   c. Compare actual data to the results of the model to determine model accuracy

Task 5. Develop dynamic models of two other potential hydrogen separation techniques
   a. Create models for a palladium membrane technique and an electrochemical hydrogen separator

Task 6. Modify and integrate the component models to represent second generation large scale tri-generation systems
   a. Scale up the previous fuel cell model by increasing the size of the stack
b. Incorporate the three hydrogen separation techniques including PSA, membrane, and EHS to compare HSU methods

c. Complete large scale system balance (thermal, electrical, flow rates, etc.)

**Task 7.** Run simulations with varied parameters to determine system performance

a. Run system configurations with all three HSUs

b. Vary fuel input including natural gas, ADG, and LFG
4 EXPERIMENT

As part of the model validation process, some experimentation was conducted from the fuel cell system at the Orange County Sanitation District. The purpose of these experiments is to determine the gas composition at several key points related to the water gas shift reactors in the system. These sample points include the anode off stream of the fuel which is also the inlet of the high temperature shift (HTS) reactor, the outlet of the HTS/inlet of the low temperature shift (LTS) reactor, and the outlet of the LTS. Running this analysis will be used as model verification but also provides insight into how effective the WGS reactors are at boosting the hydrogen composition in the flow stream.

4.1 Sampling

The samples are first taken at the fuel cell site from the sample ports along the system. The lines are first allowed to purge for at least five minutes to ensure that the sample line contains a representative sample that is free of contaminant gases that may have been present in the line. These sample ports can be seen below.
An apparatus containing Drierite is attached to the port and the sample is again allowed to purge through the Drierite before collecting the sample. The Drierite is used to remove any water in the form of liquid or vapor that may be present in the sample since water cannot be introduced into a gas chromatographer to analyze the gas. The Drierite apparatus can be seen below.

*Figure 2: Gas sampling ports at OCSD*
A 1 liter Flexfoil sample bag is then attached to the tubing after passing through the Drierite where the bag is filled and purged three times to once again ensure that the sample captured is as representative as possible. This multiple step process of purging the sample line, Drierite container, and sample bag are all necessary to rid all sampling components of previous gases (mostly air) that could have been contained inside previous to taking the sample. Once the bag has been purged three complete times, the bag is then filled and sealed. This same process is repeated for all three samples that are taken. One of the Flexfoil sample bags is shown below.
4.2 Gas Chromatography

Each sample bag is attached to the plastic tubing where the sample gas is introduced into the gas chromatographer sample loop. Ample amounts of gas are run through this sample loop while the excess escapes from an outlet port. The excess gas is passed through the line to purge the sample loop of any remnant gases that don’t represent the current sample. Once the analysis begins, the GC is calibrated to measure amounts of gases that include carbon monoxide, carbon dioxide, oxygen, nitrogen, hydrogen, and methane over an 11 minute process. The results from each GC
run show the percent composition of the constituent gases that are present in each sample. It is important to note that all samples are taken on a dry basis without water content since the GC is unable to handle water. Water is present throughout the WGS process so the water amount must be calculated back into the composition after the analysis and this calculation will be detailed in the model development and results sections. The external lab at Test America was used for a majority of the gas analysis. Figure 5 below shows a summary of the report for a few key points in the system.

**Detection Summary**

Client: University of California  
Project/Site: Tri-Gen  
TestAmerica Job ID: 340-6865-1

### Client Sample ID: HTS INLET

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>Qualifier</th>
<th>RL</th>
<th>MDL</th>
<th>Unit</th>
<th>Dil Fac</th>
<th>D</th>
<th>Method</th>
<th>Prep Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (TCD)</td>
<td>71</td>
<td>0.010</td>
<td></td>
<td></td>
<td>% v/v</td>
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<td>D1946</td>
<td>TotalRA</td>
<td></td>
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<tr>
<td>Carbon monoxide</td>
<td>7.8</td>
<td>0.0091</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>10</td>
<td>D1946</td>
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<td>Hydrogen</td>
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<td>0.020</td>
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<td>% v/v</td>
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</tr>
<tr>
<td>Methane (TCD)</td>
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<td>0.0040</td>
<td></td>
<td></td>
<td>% v/v</td>
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<td>D1946</td>
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<tr>
<td>Oxygen</td>
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### Client Sample ID: HTS OUTLET

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>Qualifier</th>
<th>RL</th>
<th>MDL</th>
<th>Unit</th>
<th>Dil Fac</th>
<th>D</th>
<th>Method</th>
<th>Prep Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (TCD)</td>
<td>73</td>
<td>0.010</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>1.3</td>
<td>0.0091</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>10</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>24</td>
<td>0.020</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Methane (TCD)</td>
<td>0.75</td>
<td>0.0040</td>
<td></td>
<td></td>
<td>% v/v</td>
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<td>D1946</td>
<td>TotalRA</td>
<td></td>
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### Client Sample ID: LTS OUTLET

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<th>Qualifier</th>
<th>RL</th>
<th>MDL</th>
<th>Unit</th>
<th>Dil Fac</th>
<th>D</th>
<th>Method</th>
<th>Prep Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (TCD)</td>
<td>73</td>
<td>0.010</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
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</tr>
<tr>
<td>Carbon monoxide</td>
<td>1.1</td>
<td>0.0091</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>10</td>
<td>D1946</td>
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<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>24</td>
<td>0.020</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Methane (TCD)</td>
<td>0.76</td>
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<td></td>
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<td>% v/v</td>
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<td>D1946</td>
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### Client Sample ID: HV-333-GC (feed ADG)

<table>
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<th>RL</th>
<th>MDL</th>
<th>Unit</th>
<th>Dil Fac</th>
<th>D</th>
<th>Method</th>
<th>Prep Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide (TCD)</td>
<td>54</td>
<td>0.010</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>1.0</td>
<td>0.0091</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>10</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.4</td>
<td>0.020</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Methane (TCD)</td>
<td>63</td>
<td>0.0040</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.35</td>
<td>0.20</td>
<td></td>
<td></td>
<td>% v/v</td>
<td>1</td>
<td>D1946</td>
<td>TotalRA</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 5: GC results from Test America Lab*
These values obtained would be used to confirm model performance and facilitate improvements to reaction kinetic models inside the fuel cell and for water gas shift reactors.

Analysis was also conducted on the system to ensure that there was no sulfur breakthrough from the cleanup skid that could be sent to the fuel cell. The same sampling process was used to obtain the gas samples and GC analysis was done using the SCAQMD method 307-91 with an Antek instrument. Samples were taken a number of times throughout project operation to verify gas cleanup performance which is seen in Figure 6.

![Figure 6: ADG cleanup performance](image-url)
Observe that outlet sulfur concentration remained below the limit for all cases and was measured as non-detect in multiple cases. This was all achieved without needing to replace the media in the capture beds.

4.3 Overall Plant Performance

The complete tri-generation fuel cell plant was monitored and controlled by FuelCell Energy using a modified version of the remote plant monitoring system. This allowed for complete remote operation of the plant with knowledge of performance characteristics, component trips or failures, and required maintenance. Ample data was collected throughout the 3 year operation of the plant to quantify the performance, make improvements to the system, and facilitate research on tri-generation systems. Collected data included: flow rates (fuel, air, water, exhaust, etc.), temperatures between system components, electricity production, parasitic loads, and hydrogen production. All information was recorded and compiled in report format for the parties involved each quarter during the 3 year agreement period. The plots below provide a summary of this operational data on a monthly basis for the previous year.
Figure 7: ADG and natural gas cumulative monthly usage
Figure 8: Gross and net power cumulative monthly production
This summary of project performance over the last year shows that many fluctuations can occur due to issues within the system and outstanding maintenance activity, but overall, the system is able to maintain steady production of power and hydrogen from both ADG and natural gas.

The project remained operation for a period of three years concluding in June 2014. The growth and consistent success of the project can be seen in the next set of figures for overall production, hydrogen fueling station use, and low emissions.
Figure 10: Accumulating three year production for OCSD

Figure 11: Number of fills and amount of hydrogen dispensed by quarter
Figure 12: Emissions comparison with other power generation technologies

<table>
<thead>
<tr>
<th></th>
<th>NO(_x) (lb/MWh)</th>
<th>SO(_x) (lb/MWh)</th>
<th>CO(_x) (lb/MWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average US Fossil Fuel Plant</td>
<td>4.200</td>
<td>9.21</td>
<td>2,017</td>
</tr>
<tr>
<td>Microturbine (60 kW)</td>
<td>0.490</td>
<td>0</td>
<td>1,862</td>
</tr>
<tr>
<td>Small Gas Turbine (250 kW)</td>
<td>0.467</td>
<td>0</td>
<td>1,244</td>
</tr>
<tr>
<td>DFC Fuel Cell 47% efficiency</td>
<td>0.016</td>
<td>0</td>
<td>967</td>
</tr>
<tr>
<td>DFC Fuel Cell – CHP 80% efficiency</td>
<td>0.016</td>
<td>0</td>
<td>545</td>
</tr>
</tbody>
</table>

Figure 13: Emissions based on limits established in California

Figure 10 shows steady operation over three years with the ability to run on ADG to produce power and hydrogen. The plot in Figure 11 shows drastic increase in fueling station usage beginning in the 3\(^{rd}\) quarter of 2013. This is due to fueling agreements signed with automakers.
such as Mercedes, Toyota, and Hyundai to begin fueling at OCSD when previously Honda was the only automaker with agreements to fuel at the station. These agreements led to much higher station traffic from one car every other day to nearly five cars each day. The station is still well under full capacity, but the increase in station utilization is very promising for hydrogen production and fuel cell vehicles in the area.

Figure 12 and Figure 13 reveal just how low the emissions are compared to other power generation technologies and to current California emissions standards. The fuel cell plant generates extremely low emissions considering it is operating on a carbon fuel (either natural gas or ADG). Of course operation on ADG classifies as renewable power generation since the fuel source is biogas and not a fossil fuel.

The cumulative performance of the plant has now been summarized but steady state operation is also important for quantifying performance. The next figures demonstrate steady state operation data under a few operating conditions.

Figure 14: Steady state snapshot of system at factory test
Table 1: Steady state operational data from OCSD

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>268 kW Gross AC</td>
<td>260 kW Gross AC</td>
<td>260 kW Gross AC</td>
<td></td>
</tr>
<tr>
<td>120 mA/cm2</td>
<td>120 mA/cm2</td>
<td>120 mA/cm2</td>
<td></td>
</tr>
<tr>
<td>7.5 lb/hr H2</td>
<td>7.6 lb/hr H2</td>
<td>10.7 lb/hr H2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel to Fuel Cell</th>
<th>34.4</th>
<th>58.9</th>
<th>59.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Flow Rate (scfm)</td>
<td>64.7</td>
<td>61.5</td>
<td>62.0</td>
</tr>
<tr>
<td>Fuel Energy Input (kW)</td>
<td>555</td>
<td>584</td>
<td>587</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electricity Export (kW)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave Cells Volts</td>
<td>0.816</td>
<td>0.781</td>
<td>0.777</td>
</tr>
<tr>
<td>Inverter Gross AC</td>
<td>268</td>
<td>259</td>
<td>259</td>
</tr>
<tr>
<td>DFC BOP Loads</td>
<td>19</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>H2 Recovery Loads</td>
<td>58</td>
<td>58</td>
<td>66</td>
</tr>
<tr>
<td>Electricity for Sup. Heat</td>
<td>0</td>
<td>0</td>
<td>41</td>
</tr>
<tr>
<td>ADG Clean Up</td>
<td>0</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Reported Net AC</td>
<td>188</td>
<td>155</td>
<td>106</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reported Net AC less ADG (22 kW), Sup. Heater, Trailer Power 3 kW</th>
<th>188</th>
<th>180</th>
<th>172</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>H2 Product Export</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate (lb/hr)</td>
<td>7.5</td>
<td>7.6</td>
<td>10.7</td>
</tr>
<tr>
<td>kW Equivalent</td>
<td>113</td>
<td>114</td>
<td>162</td>
</tr>
<tr>
<td>Elec + H2 Efficiency</td>
<td>54.3%</td>
<td>50.4%</td>
<td>53.2%</td>
</tr>
</tbody>
</table>

Figure 14 gives a screenshot of system operation under a steady state condition during factory testing. The major flows, power generation, hydrogen production, and parasitic loads are shown.

A comparison of natural gas and ADG operation of the operating plant is shown in Table 1. The overall efficiency is boosted by hydrogen production but it is important to notice how high the parasitic loads for hydrogen separation and compression are. This is one aspect that should be improved for future tri-generation systems and is a major topic of focus in this thesis.
5 MODEL DEVELOPMENT

5.1 Modeling Methodology

5.1.1 Matlab Simulink

The bulk of the modeling work was conducted using the Matlab Simulink package. Using Simulink along with standard Matlab source code allows for a wide range of modeling capabilities and flexibility that are desirable for complex system models. The general layout of a Simulink model provides a strong visual of what is actually being modeled by organizing system components into individual blocks that contain the necessary governing equations. Each block requires certain input and output parameters that are then connected to the other blocks present in the system that is being modeled. The equations are also constructed piece by piece rather than just simply containing the function on one line of code. This concept of block modeling will be explained more throughout this thesis.

Other advantages of Simulink modeling include the ability to use different forms of solvers such as fixed time step or variable time step. This will play an important role for controlling the dynamics of the system and temporally resolving a full system model with numerous components. The ability to use vectors and matrices for variables also provides the ability to spatially resolve each component of the system by breaking it up into several nodes. Rather than simply having input and output values for a particular heat exchanger for example, all variables including temperature, concentrations, flow rates, etc. are calculated at multiple points along the heat exchanger to show how fast or slow the temperature is actually changing. This can be applied to any system component to provide a deeper understanding of the phenomena this being captured by the model. These concepts are expounded upon in later sections.
5.1.2 Physical Modeling

The amount detail that must be captured during modeling depends upon the size, scope, and end goal of the model. Capturing less physical behavior leads to making more assumptions that create simplicity but can reduce accuracy. The main purpose of this work is focused on entire system operation and performance with consideration of certain components in the system so deeper levels of physical processes may not be necessary. However, each component of the model attempts to capture the governing physical details to generate greater accuracy and allow for deeper insight into the performance and design throughout the system. The list below displays the major physical and chemical phenomena modeled in the system:

- Energy balances – consideration of energy for all flows throughout the system
- Mass balances – accounts for all flows present in the system
- Heat transfer – convective heat transfer for flows through components and conductive heat transfer through plates and membranes in multiple directions
- Fluid dynamics – friction factor calculations for pressure losses and flow rates
- Chemical reaction kinetics – captures chemical and electrochemical reactions for kinetic behavior and extent of reaction
- Fuel cell losses – Nernst potential with activation, concentration, and ohmic losses for fuel cell operation

Capturing this physical behavior produces the useful results that portray the real system performance such as temperatures, species concentrations, flow rates, power input/output, hydrogen production, and system efficiency. A very detailed description of model development and governing equations is provided in the work of McLarty et al. [25] [26]. A short list of fuel
cell governing equations is provided below. The Nernst equation yields the highest achievable voltage of the molten carbonate fuel cell. The actual voltage achieved takes into account the activation, ohmic, and concentration losses defined below.

\[
E = E^0 + \frac{R_T}{2F} \ln \left( \frac{X_{H_2}O_{2.5/2}X_{CO_2,Cathode}^{1/2}}{X_{H_2}OX_{CO_2,Anode}^{1/2}} \right) \tag{5.1-1}
\]

\[
\eta_{act} = -\frac{R_T}{anF} \ln j_0 + \frac{R_T}{anF} \ln j \tag{5.1-2}
\]

\[
\eta_{Ohmic} = \frac{i}{A_{cell}} * ASR_{eff} = j * ASR_{eff} \tag{5.1-3}
\]

\[
\eta_{conc} = \left( 1 + \frac{1}{\alpha} \right) \frac{R_T}{2F} \ln \frac{j_L}{j_L - j} \tag{5.1-4}
\]

5.1.3 Dynamic Modeling

A steady state model is able to use the governing equations to predict what the steady state performance of a system would be without consideration of control schemes or any temporal resolution. This modeling approach takes advantage of the ability to model dynamics of the system until it is able to converge to steady state. Dynamic modeling is able to introduce control schemes for flow rates, blower powers, recirculation, etc. that mirrors how a real system must be operated. It also has the ability to capture the kinetic behavior of chemical reactions to determine the actual equilibrium states and extent of reaction. These factors play an important role to the overall design aspects of the system and its components because now the properties of materials, thicknesses of piping, sizes of heat exchangers, flow directions, temperature gradients, etc. all make a difference for creating a system model that actually resembles a real world system. Of course the model will converge to a steady state point to produce results, but the
means to get there is more intricate and requires careful design with control to achieve the correct end state.

5.1.4 Kinetic Modeling

The modeling approach taken realizes the difference between simply modeling the equilibrium states of reactions and modeling the kinetics with rates of reactions. If the equilibrium method was used, this assumes that all chemical reactions reach their equilibrium states based on the temperature that the reaction occurs at. This can be a fairly accurate assumption to make in some cases, but the reactions do not reach the full equilibrium state in real cases. Utilizing a kinetic model takes into account the rates of each reaction and the residence time of the gas inside the reactor based on reactor conditions, dimensions, and flow rates. This method of modeling reaction kinetics provides a more accurate physical representation of reaction chemistry which allows the model to predict the outlet species concentrations that more closely follow real system performance.

5.2 System Model

5.2.1 MCFC System

Previous modeling of the MCFC system followed a similar approach to model discussion in previous sections. The organization of the model follows a vector format to obtain spatial resolution while temporal resolution is obtained by the use of kinetic modeling, thermal gradients, and control systems to converge components to steady state. This method allows for a wide variety of capabilities to investigate the dynamics of a system and the performance and effect of system components. The initial system contained the fuel cell stack, anode off-gas oxidizer, fuel/air preheat heat exchangers, anode/cathode mixing, and blower control for the
incoming air stream. The configuration mirrors what a typical MCFC system would look like to produce power as the main product while using the heat internal to the system with recirculation, but additional complexity is needed to investigate a tri-generation system that also produces a pure hydrogen stream. The initial system schematic can be seen in Figure 15. This system layout was previously developed by McLarty et al. and the overall approach for the model follows the explanation of the modeling methodology section provided earlier in this thesis [25][26].

Figure 15: Initial fuel cell system model

The expanded system schematic shown in Figure 16 below displays the full model created to simulate a tri-generation system. Many components are needed to create such a system including additional heat exchangers, high and low temperature water gas shift reactors, evaporator, condenser, and the hydrogen separation unit. Adding the additional components described in the next sections elevate the system model to a high temperature fuel cell system that can tri-generate power, heat, and hydrogen to investigate and optimize the performance of this novel system.
5.2.2. Hydrogen Production Components

The majority of the added components are needed for the anode off-gas stream before the oxidizer to perform the hydrogen separation steps. The water gas shift reactors are required first to reduce the amount of carbon monoxide while increasing the amount of hydrogen. Since this is done in two steps at separate temperatures, two heat exchangers are needed. The first heat exchanger cools the anode stream from the fuel cell to about 350 °C before entering the HTS reactor and the second heat exchanger cools the stream from the HTS reactor to about 200 °C to enter the LTS reactor. This process has successfully reduced the CO composition while boosting the hydrogen composition by a few percent. Further details on shift reactors and WGS kinetics will be provided in later sections.
Removal of water is the next step of the system before the HSU and oxidizer. A condenser is added to the system using air as the cold fluid to remove most of the water present in the stream. This step is important to the overall system because the recirculation of this water back into the anode with the fuel is needed to achieve the steam to carbon ratio required for the internal reformation inside the fuel cell. The amount of water created is also large enough to sustain the steam to carbon ratio and allow for water neutral operation so no external source of water is needed to run the system.

The liquid water produced at the condenser must first be sent through an evaporator before mixing with the fuel and preheating to the appropriate temperature. An evaporator block is added to the system to take this liquid water stream and utilize the remaining heat from the cathode off-gas to generate a steam flow with some initial preheating. This steam flow must now be mixed with the ambient temperature flow of fuel to produce the desired steam to carbon ratio inside the anode of the fuel cell. Using an energy balance, the temperature of the fuel and steam mixture is maintained above 100 °C to ensure that no water condenses out before the mixture is sent to the fuel preheater. The amount of steam generated by this recirculation of water is sufficient without any additional input of water into the system.

The other post condenser stream, now containing mostly hydrogen and carbon dioxide, has now gone through WSG and water removal before entering the HSU where the pure hydrogen stream is obtained. The real system at OCSD uses PSA to separate the hydrogen but this system model will investigate the feasibility of electrochemical and membrane separation techniques as a system design comparison. The HSU models will be explained in greater detail in later sections. All separation techniques require an input of either heat or power to generate a pure hydrogen stream that will cause a decrease in system efficiency. Each technology will create a pure stream
of hydrogen while sending the remaining gas constituents to the oxidizer. The small quantities remaining of CO and hydrogen are then oxidized to CO$_2$ and water which is recirculated to mix and heat the incoming air before entering the cathode.

5.3 Reformation and Water Gas Shift Correlations

Solid Oxide Fuel cell internal reformation reactions have been experimented and modeled in the literature. Previous work in the literature is comprised of small scale experiments for a variety of applications accompanied by modeling work and correlations that are created from the experimental results. The modeling approach for this process attempts to find the balance of the steam methane reformation and water gas shift reaction shown below since they are the prominent reactions during reformation. Other chemical reactions can take place but are either very unlikely to occur or occur at a much slower rate which allows a model to maintain accuracy when neglecting them. Governing equations for modeling remain similar throughout the literature by following the Arrhenius equation and determining the activation energy and pre-exponential constant experimentally.

\[
CH_4 + H_2O \leftrightarrow 3H_2 + CO 
\]

\[
H_2O + CO \leftrightarrow H_2 + CO_2 
\]

\[
k_i = A_i \cdot \exp\left(-\frac{E}{RT}\right) 
\]

The experiments and corresponding correlations produced by Xu and Froment focused on the steam methane reformation process used to produce hydrogen for industry. The reformation
reaction along with methanation and water gas shift were the primary reactions investigated. These experiments focused on the use of nickel-alumina catalyst beds while considering many reaction mechanisms and thermodynamics of the process. The modeling approach would be simplified when certain reactions were deemed negligible. The three remaining mechanisms include SMR, WGS, and a combination of the reactions given by reaction below. The rate equations for each of the reactions are also provided below [27].

\[ CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \] (5-4)

\[ r_1 = \frac{k_1}{p_{H_2}^{2.5}} \left( \frac{p_{CH_4} p_{H_2O} - p_{CO} p_{H_2}^3}{K_1} \right) \] (5-5)

\[ r_2 = \frac{k_2}{p_{H_2}} \left( \frac{p_{CO} p_{H_2O} - p_{CO_2} p_{H_2}^2}{K_2} \right) \] (5-6)

\[ r_3 = \frac{k_3}{p_{H_2}^{3.5}} \left( \frac{p_{CH_4} p_{H_2O}^2 - p_{CO_2} p_{H_2}^5}{K_2} \right) \] (5-7)

Reaction kinetics have also been specifically investigated with regard to the anode compartment of a solid oxide fuel cell. A small scale experiment was developed to simulate the internal reformation of methane to hydrogen inside the anode rather than using an external reformer. This work produced a correlation to model steam methane reaction kinetics for internal reforming high temperature fuel cells shown in the rate expression below [28].

\[ r_r = p_{CH_4} \cdot 4274 \left( 1 - \frac{p_{CO} p_{H_2}^2}{p_{CH_4} p_{H_2O}^2 K_p} \right) \cdot \exp \left( - \frac{8.2 \times 10^4}{RT} \right) \] (5-8)
The work of Paradis compiled knowledge from published work on this topic in an effort to create a more accurate and robust kinetic model of the internal reformation process of a solid oxide fuel cell. A water gas shift equilibrium rate equation from Haberman and Young correlated well with experimental results in the literature and meshed well within the model of internal reformation that was generated. This WGS correlation was produced during 3-D modeling simulations for a planar solid oxide fuel cell [29]. SMR reaction kinetics were modeled using three separate correlations developed in previous literature including Achenbach, Drescher, and Leinfelder to develop a combined modeling approach that used SMR with WGS kinetics for an internal reforming fuel cell. All SMR correlations include a surface area to volume ratio to account for the size of the reactions space [30]. This more recent work by Paradis successfully combined previous work and knowledge that improves modeling capabilities for reformation reactions to be used in a number of applications.

\[
\tau_s = k_s \cdot p_{CO} \left( 1 - \frac{P_{CO_2}P_{H_2}}{K_e,s \cdot P_{CO}P_{H_2O}} \right) \quad (5-9)
\]

\[
K_{e,s} = \exp\left( \frac{4276}{T} - 3.1961 \right) \quad (5-10)
\]

\[
k_s = 0.0171 \exp\left( -\frac{103191}{RT} \right) \quad (5-11)
\]

\[
r_{r,Ach} = p_{CH_4} \cdot 4274 \cdot \exp\left( -\frac{8.2 \times 10^4}{RT_s} \right)AV \quad (5-12)
\]

\[
r_{r,Dre} = \left( \frac{288.52 \cdot p_{CH_4}P_{H_2O} \cdot \exp\left[ -\frac{11,000}{RT_s} \right]}{1 + 16 \cdot p_{CH_4} + 0.143 \cdot p_{H_2O} \cdot \exp\left[ -\frac{39,000}{RT_s} \right]} \right)AV \quad (5-13)
\]

\[
r_{r,Lei} = 30.8 \times 10^{10} \cdot p_{CH_4}P_{H_2O} \cdot \exp\left( -\frac{205,000}{RT_s} \right)AV \quad (5-14)
\]
Seo et al conducted a study that involved a more closely related application for modeling SMR and WGS. The basis of this work is to model an SMR plant that then uses a high temperature and low temperature shift reactors to boost the hydrogen composition before the hydrogen is separated [31]. The use of two stage shift reactors is the process that is also used at the tri-generation plant at OCSD. The correlation that Seo developed for WGS closely matches experimental data in the literature and could be utilized accurately in a system model. Other correlations described above show the best promise for kinetic modeling internal to the fuel cell stack.

\[ r_{wgs} = k_{wgs} \cdot p_{CO}p_{H_2} \left( 1 - \frac{p_{CO_2}p_{H_2}}{K_{eq} \cdot p_{CO}p_{H_2}O} \right) \]  
\[ k_{wgs} = 1.85 \times 10^{-5} \exp \left( 12.88 - \frac{1855.5}{T} \right) \]  

The purpose of modeling water gas shift kinetics is to investigate the performance of both high temperature and low temperature water gas shift reactors when coupled with a high temperature fuel cell system. The specific application applies to a tri-generating fuel cell system that contains shift reactors at the anode out stream to boost the hydrogen concentration before purifying to a hydrogen stream that is used to fuel hydrogen fuel cell vehicles. Previous modeling work has been conducted which modeled Xu Froment, Achenbach, and Paradis correlations in Matlab Simulink to be used for internal reformation kinetics of a fuel cell model. The Seo correlation was more recently developed for the purpose of a high temperature shift reactor coupled with an auto thermal reformer in a high temperature Proton Exchange Membrane (PEM) fuel cell system. The current work involves comparing the results of these models for simulating internal reformation kinetics and when used as a water gas shift reactor model to determine the most
accurate and robust model for each application. From there, the model will be incorporated into a fuel cell system model that could include the fuel cell stack, hydrogen separation processes, and absorption chilling to investigate the performance and feasibility of different fuel cell systems.

A similar modeling approach was taken for creating each model for the four correlations. A mass balance and heat exchange were included with the reaction kinetics unique to each correlation to allow for a more complete model that includes the effects on the entire fuel cell system. Since these are kinetic models, the residence time of the particular gas species in the reactor plays a very important role in determining how long the reactions are able to take place. This time is varied by changing the size of the reactor and the flow rate of the incoming stream. Each model is also given spatial resolution by creating a nodal model that essentially splits the reactor into separate pieces along the reactor. Now instead of merely having inlet and outlet parameters, intermediate steps of the reactions can be seen as the gases flow through the reactor. This phenomenon is created in the models by repeating the same Simulink blocks connected in series where the outlet of the first flows into the second node and so on. This development of the model follows the same methodology as McLarty [25]. The Xu Froment and Achenbach models were already created in this form but the Paradis model had to be improved from a signal nodal model without heat exchange to a five nodal model that included the heat exchange. Further development of these models simplified the physical size of each model by using a vector approach rather than copying blocks to simulate individual nodes. Now only one block that uses vector calculations can be used to run any number of nodes by simply specifying the number of rows and columns desired to obtain spatial resolution. The Seo model was created to follow this
form to allow for comparison between the models to determine the best correlation for kinetics inside the fuel cell stack and the water gas shift reactors.

5.4 Water Content

The experimental results from the gas sampling of the OCSD fuel cell system provided a method to verify the models compared to a real application, however, the results are reported on a dry basis without water content when in reality there is a high percentage of water in the gas streams. The absolute value of water content was not determined experimentally but a model was developed in Engineering Equation Solver (EES) to calculate the water content of the three samples related to the water gas shift reactors.

The overall modeling approach was to input the GC results from the gas samples in the order that they occur in the system. In this case, that meant the anode off stream, HTS out stream, and finally the LTS out stream. Modeling in this way allows for only one assumption of original water content in the anode out stream while the water content in the following two samples are calculated from that assumption. Regardless of the assumed water composition, the actual behavior of the shift reactors based on the GC data will still reflect performance trends that can be compared to the models when they are run with the same input water content. Previous modeling work with the fuel cell itself showed that the composition of the anode off stream contained about 45% water vapor so this value was used as the starting assumption in the EES model.

The known composition from the GC analysis shows gas species that include: Carbon Dioxide, Carbon Monoxide, Hydrogen, Methane, Oxygen, and Nitrogen. After assuming a water composition, the composition must be re-balanced to include the water content and normalized to
100% to account for the experimental error with the GC process. Since the three samples of the system all occur in series, the outlet of one sample is the inlet composition to the shift reactor which allows the composition to be calculated by using a simple atom balance from the inlet to the outlet of the two shift reactors. This process of atom balance and normalization of the composition yields new composition values based on the experimental results that now contain the water content. The calculated anode off stream composition could then be used as the input to equilibrium calculations and developed WGSR models where all of the outputs could be compared to the data that is now on a wet basis. This comparison of equilibrium calculation, experimental data, and model results from the three correlations was the primary method in which the ideal model was chosen and verified.

5.5 NASA Chemical Equilibrium with Applications

Rather than developing a chemical equilibrium model to determine WGS equilibrium compositions, the NASA chemical equilibrium with applications (CEA) software was used to generate equilibrium state curves. Using CEA allowed for quick equilibrium modeling for different input compositions that could easily be varied across a range of temperatures. One option was also utilized to either allow or disallow the formation of methane since this was one issue in question regarding how WGS reactors behave and how certain models attempt to model a WGSR. The obvious difference with an equilibrium model compared to the kinetic models or the actual system is that the residence time is allowed to go to infinity in order to reach the absolute state of equilibrium at every temperature. Actually achieving these equilibrium states would require extremely large reactors coupled with slow flow rates through the reactors which aren’t practical. Using equilibrium modeling provided another step of model verification that
could determine what the correct trends should be with a gas stream undergoing the water gas shift reaction.

5.6 Electrochemical Hydrogen Separation

A component model for hydrogen separation using an electrochemical cell was created to capture the physical performance of hydrogen separation and compression. A steady state model was first generated in EES to conduct parametric studies before duplicating the model in Simulink as a component in the full system model. Since EHS is very similar to running a Proton Exchange Membrane fuel cell in the reverse direction, similar factors will apply including the reversible voltage. The reversible voltage and total voltage calculated is the over potential that must be applied to obtain hydrogen separation, yet the actual operating voltage will be higher. The over voltage is what must be applied to the cell and contributes to the power draw of the EHS. At high flow rates, determining the actual voltage considers the ohmic losses for transporting the hydrogen but activation and concentration losses can be neglected [19].

\[
E = E_{rev} + I\Omega \tag{5-17}
\]

\[
E_{rev} = \frac{RT}{nF} \cdot \ln \left( \frac{P_{out}}{P_{in}} \right) \tag{5-18}
\]

\[
\Omega = \frac{L}{\sigma S} \tag{5-19}
\]

The partial pressures used to calculate the reversible voltage correspond to the hydrogen partial pressures. Calculation of ohmic losses requires the thickness, surface area, and conductivity of the membrane. The thickness of a Nafion 117 membrane found in PEM fuel cells is 0.018 cm
Determining the power required and the resulting hydrogen flow rate can be done by the following equations [19].

\[ P = IE \quad (5-20) \]
\[ \text{flow}_{H_2} = B I \quad (5-21) \]

Where B is a dimensional constant determined by experiment. Obviously hydrogen purity and hydrogen recovery are key performance factors for hydrogen separation, and hydrogen back diffusion can be an issue especially at higher outlet pressures. Back diffusion flow of hydrogen is calculated with knowledge about the solubility, diffusivity, and [33].

\[ \text{flow}_{H_2,\text{back}} = \frac{p_{H_2} \cdot S \cdot \delta P}{L} \quad (5-22) \]
\[ p_{H_2} = D_{H_2} \cdot S_{H_2} \quad (5-23) \]
\[ D_{H_2} = 0.0041 \cdot \exp \left( -\frac{2602}{T} \right) \quad (5-24) \]

The main gas constituent entering the cell that can decrease the purity of the outlet hydrogen is carbon dioxide. It doesn’t participate in the electrochemistry to be transported across the cell, but it does have the ability to diffuse across the membrane in small amounts. Although most of the carbon dioxide doesn’t diffuse, about 1% of inlet concentration is able to cross the membrane and dilute the hydrogen stream [20]. However, this transport is mitigated when the outlet pressure increases because the difference of carbon dioxide partial pressure decreases thus limiting the diffusion potential. Even with this diffusion phenomenon, the hydrogen purity achieved is above 99%. 

\[ 46 \]
With performance and accuracy of the EHS model verified by completed studies from the EES model, a component block was created in Simulink that would replace the previous simple version of hydrogen separation. The addition of this EHS component was the major final step in creating a full fuel cell tri-generation model.
6 RESULTS

6.1 Fuel Cell Kinetics

Following the Fuel Cell Energy stack design, the fuel cell stack contains cells that only reform the fuel by SMR before this reformed gas mixture is sent to cells that perform the electrochemistry. The model captures this behavior by utilizing separate calculation blocks for the reformer plates and the anode plates of the stack. Improvement to the reaction kinetics inside the fuel cell from the original model was necessary since the anode outlet species concentrations contained very unexpectedly low carbon monoxide. To investigate this, the kinetic expressions developed by Achenbach and Paradis for SMR coupled with the work by Haberman & Young for WGS are inserted into both the anode and reformer blocks of the model to determine which combination obtains the most accurate results. The data acquired from OCSD by gas sampling will be used to verify the results.

The models were first run using only the fuel cell stack without any of the system components to determine which correlations would require more fine tuning during full system modeling. Table 2 below displays the anode outlet compositions with multiple combinations for the anode block and reformer block. The Achenbach correlation corresponds to a model that uses the SMR reaction without the Haberman & Young expression for WGS. The Paradis expression contains this WGS and includes three separate expressions for SMR including Achenbach (Ach), Drescher (Dre), and Leinfelder (Lei).
Using Achenbach without Haberman & Young WGS kinetics results in very low CO concentrations as seen in previous modeling work yet this addition of improved WGS kinetics displays much better results regardless of which SMR expression is captured. There were also issues with how robust the model was while only considering Achenbach because it would not converge to a result for all temperatures. These two factors provided reason to not consider this expression on its own for modeling purposes. It is also seen that Leinfelder kinetics show no difference to Achenbach kinetics for SMR so Leinfelder will not be considered in the system model. The combinations using Paradis with Achenbach and Drescher kinetics yield the best results and both will be considered in system modeling to determine the most accurate expression for the application.
6.2 Water Gas Shift Reactor Kinetics

Capturing accurate water gas shift chemistry is important when modeling a tri-generation system because the shift reactors in the system boost the hydrogen percentage before pure hydrogen is separated from the gas stream. It was unclear on which kinetic correlation would most accurately model the behavior of a shift reactor so many were considered initially. Brief analysis using Xu & Froment kinetics showed that the model was not robust enough to perform at the temperature ranges necessary for water gas shift so this model would not be considered during future work.

6.2.1 Equilibrium

The first stage of model comparison utilized equilibrium modeling that could be verified using NASA CEA which determines the equilibrium state of a gas mixture at specified temperatures. This curve was generated using a specified anode outlet composition using OCSD data as the input gas species to the model since the composition is close to what enters the high temperature water gas shift reactor in the system. This composition in Table 3 below will also be used as the input species for the Simulink models. Analysis with only this input to a high temperature shift reactor will be used for equilibrium modeling, but more work with high and low temperature reactors will be necessary as more detailed models are created.

*Table 3: Inlet composition for high temperature shift correlation comparisons*

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCSD data .45 water</td>
<td>0.003</td>
<td>0.042</td>
<td>0.419</td>
<td>0.100</td>
<td>0.450</td>
</tr>
</tbody>
</table>
With the inlet species and pressure set to atmospheric, the CEA model generates two curves for a temperature range of 400-1800K that displays the equilibrium composition of the five major gas species. The purpose of generating two separate curves pertains to capturing the real behavior of a WGSR. The catalysts in the reactors attempt to favor water gas shift chemistry but not the process of methanation since the goal of the reactor is convert carbon monoxide to hydrogen. The methanation reaction itself is the reverse of SMR which produces methane rather than hydrogen. The first curve generated shown in Figure 17 produces the equilibrium curve while allowing the methanation reaction in the calculations. The second curve in Figure 18 does not allow for methanation to occur at all.

![Figure 17: Equilibrium compositions at various temperatures while allowing methanation](image)

Figure 17: Equilibrium compositions at various temperatures while allowing methanation
Figure 18: Equilibrium compositions at various temperatures while not allowing methanation

These are the baseline cases used to compare the similar outputs that are generated from the models in question. The three models under consideration are Achenbach, Paradis, and Seo. Using the model as an equilibrium reactor requires greatly increasing the size of the reactor to essentially increase the residence time of the gases to react to the final state of equilibrium. The reactors don’t behave like this in real applications, but investigating model performance at equilibrium conditions is a method to determine which rate expressions provide better accuracy for modeling WGS chemistry. The curves generated by the three models are seen in the Figure 19, Figure 20, and Figure 21 below.
Figure 19: Equilibrium conditions using Achenbach kinetics

Figure 20: Equilibrium conditions using Paradis kinetics
The Seo model contains a noteworthy difference from the other two because it doesn’t contain a SMR reaction and therefore cannot allow methanation while the other two models capture both WGS and SMR reaction chemistry. This is apparent when comparing the curves since the Seo curve closely follows the equilibrium curve that doesn’t allow methanation. The Achenbach curve allows for the most methanation while Paradis seems to follow a similar form of Seo but with a different behavior at lower temperatures.

The temperature range is very important to consider for the application of a WGSR since the high and low temperature reactors are maintained between 400-650K for the best performance. Notice that the Achenbach curve has no data point for 500K because the model doesn’t function from about 450-550K and in some cases it won’t converge anywhere below 550K. The Achenbach expression is not viable for this purpose due to the lack of performance at the necessary temperature range and will not be considered in system modeling.
6.2.2 System

Fully integrating the WGSR model into a working system model was the final step to determine the most viable correlation. Both Seo and Paradis still showed promise up to this point so an attempt was made to integrate each model into the system model. However, the system never successfully converged when using Paradis as the WGSR while Seo was able to generate results which can be found in the next section for initial system modeling. The Seo correlation was developed based on an experiment with water gas shift reactors so it makes sense that it would converge and be more accurate at lower temperatures than other correlations such as Paradis or Achenbach.

6.3 Electrochemical Hydrogen Separation

These results correspond to the parametric performance evaluation of the steady-state EHS model created in EES. This component model used input temperature, concentrations, and flow rate from system models shown in Table 4, to determine EHS performance characteristics including voltage, current density, power, hydrogen production, hydrogen recovery, and outlet pressure.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
<th>Flow(mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.003</td>
<td>0.004</td>
<td>0.700</td>
<td>0.239</td>
<td>0.053</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The plots shown in this section are run at constant total surface area of 50 m², total current of 250000 A, and outlet pressure of 102 kPa unless the parameter is the focus of each specific study. If there are 200 cells in the EHS stack, a current of 1250 amps per cell is obtained at the
specified voltage and a reasonable current density of 500 A/cm$^2$. The values for current plotted in this section correspond to total current for the total active surface area where each cell operates at the voltage shown. This method allows for a better visual of the total EHS performance. Also remember that the voltage plotted is the over voltage required for hydrogen separation which contributes to the power draw of the unit, but is not representative of the actual operating voltage. This stems from operating the cell in reverse fuel cell mode. Figure 22 displays the V-I curve and power curve while Figure 23 and Figure 24 display V-I curves from the literature.

*Figure 22: V-I curve and power curve of EHS*
Figure 23: V-I curve from Thomassen et al.
Notice that the trend is the opposite of a PEM fuel cell because the ohmic losses result in a higher voltage as current increases, which requires higher power input for separation. It is also important to realize the huge effect that ohmic losses have that is directly related to current. A similar linear trend is observed between the model and the literature while specific values differ due to stack size and operational characteristics. The correlation of hydrogen production and required power is shown in Figure 25. Greater hydrogen production requires more power input as expected. Figure 26 shows the effect that surface area has on current density and power draw under constant current operation.
Figure 25: Performance correlation of hydrogen produced to power required of EHS
Without increasing current, the current density and power required expectedly decrease as the size of the separation unit is increased. Size of the unit certainly will play a significant role in the performance of hydrogen separation. The effect of outlet pressure on voltage and hydrogen recovery is shown in Figure 27 and the back diffusion effect from the literature is shown in Figure 28.
**Figure 27:** Effect of simultaneous hydrogen compression/separation on EHS performance

**Figure 28:** Back diffusion of hydrogen from Rholand et al.
The combination of hydrogen purification and compression is a major interest with electrochemical separation since it has the potential to greatly reduce compressor loads of the full system. Increasing pressure does require an increase in voltage, yet even small changes in voltage cause a drastic increase in outlet pressure. Because of hydrogen back diffusion, hydrogen recovery decreases as the outlet pressure increases. The increasing effect of back diffusion as outlet pressure increases from the literature follows the trend that model displays as a decrease in hydrogen recovery. Theoretically, EHS can be used to fully pressurize the hydrogen produced to proper storage pressure, but further research is needed on the robustness of the unit when operating under such pressures.

6.4 Tri-Gen System

6.4.1 Initial System

The system model used for analysis hasn’t reached the final version yet, but it does contain almost all of the necessary components. The HSU is still a simplified model that assumes 85% of the hydrogen is removed at 100% purity. All other components are present in their physical form but there is no ability to calculate system efficiency numbers because there is a lack of calculation for power needs of the HSU and the condenser. This version of the system model is used to verify new component models such as WGSR, evaporator, condenser, fuel mixing, and additional heat exchangers as they all work together in a complete model. Table 5 displays temperature, species concentrations, and flow rates of nearly all flows present into and out of each component for a particular simulation with parameters similar to the OCSD plant. Note that the flow out and flow in labels correspond to the same flow that leaves one component and enters into the next. Fuel cell stack performance is also seen in Table 6.
Table 5: Flow characterization of system components in the improved system model for tri-generation

<table>
<thead>
<tr>
<th>Flows out</th>
<th>Flows in</th>
<th>Temp (K)</th>
<th>CH4</th>
<th>CO</th>
<th>CO2</th>
<th>H2</th>
<th>H2O</th>
<th>N2</th>
<th>O2</th>
<th>Flow (kmol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Input</td>
<td>Fuel Mix</td>
<td>300</td>
<td>0.630</td>
<td>0</td>
<td>0.370</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0014</td>
</tr>
<tr>
<td>Fuel Mix</td>
<td>Fuel Heater (cold)</td>
<td>381</td>
<td>0.249</td>
<td>0</td>
<td>0.146</td>
<td>0</td>
<td>0.605</td>
<td>0</td>
<td>0</td>
<td>0.0035</td>
</tr>
<tr>
<td>Air Heater (hot)</td>
<td>Fuel Heater (hot)</td>
<td>721</td>
<td>0</td>
<td>0</td>
<td>0.061</td>
<td>0</td>
<td>0.022</td>
<td>0.768</td>
<td>0.149</td>
<td>0.0223</td>
</tr>
<tr>
<td>Fuel Heater (hot)</td>
<td>Evaporator (hot)</td>
<td>645</td>
<td>0</td>
<td>0</td>
<td>0.061</td>
<td>0</td>
<td>0.022</td>
<td>0.768</td>
<td>0.149</td>
<td>0.0223</td>
</tr>
<tr>
<td>Fuel Heater (cold)</td>
<td>Anode</td>
<td>713</td>
<td>0.249</td>
<td>0</td>
<td>0.146</td>
<td>0</td>
<td>0.605</td>
<td>0</td>
<td>0</td>
<td>0.0035</td>
</tr>
<tr>
<td>Air Input</td>
<td>Air Heater (cold)</td>
<td>296</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.790</td>
<td>0.210 0.0217</td>
</tr>
<tr>
<td>Cathode to HX</td>
<td>Air Heater (hot)</td>
<td>879</td>
<td>0</td>
<td>0</td>
<td>0.061</td>
<td>0</td>
<td>0.022</td>
<td>0.768</td>
<td>0.149</td>
<td>0.0223</td>
</tr>
<tr>
<td>Cathode to Oxidizer</td>
<td>Oxidizer</td>
<td>879</td>
<td>0</td>
<td>0</td>
<td>0.061</td>
<td>0</td>
<td>0.022</td>
<td>0.768</td>
<td>0.149</td>
<td>0.0295</td>
</tr>
<tr>
<td>Air Heater (cold out)</td>
<td>Cathode Mix in</td>
<td>479</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.750</td>
<td>0.210 0.0217</td>
</tr>
<tr>
<td>Cathode Mix</td>
<td>Cathode</td>
<td>758</td>
<td>0</td>
<td>0.0003</td>
<td>0.058</td>
<td>0</td>
<td>0.020</td>
<td>0.721</td>
<td>0.160</td>
<td>0.0551</td>
</tr>
<tr>
<td>Cathode</td>
<td>Flow Split</td>
<td>879</td>
<td>0</td>
<td>0</td>
<td>0.061</td>
<td>0</td>
<td>0.022</td>
<td>0.768</td>
<td>0.149</td>
<td>0.0518</td>
</tr>
<tr>
<td>Anode</td>
<td>HTS HX (hot)</td>
<td>838</td>
<td>0.002</td>
<td>0.0441</td>
<td>0.437</td>
<td>0.121</td>
<td>0.395</td>
<td>0</td>
<td>0</td>
<td>0.0075</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>Cathode Mix</td>
<td>913</td>
<td>0</td>
<td>0.0005</td>
<td>0.162</td>
<td>0</td>
<td>0.033</td>
<td>0.677</td>
<td>0.128</td>
<td>0.0334</td>
</tr>
<tr>
<td>LTS HX (cold)</td>
<td>HTS HX (cold)</td>
<td>577</td>
<td>0.003</td>
<td>0.0047</td>
<td>0.883</td>
<td>0.045</td>
<td>0.068</td>
<td>0</td>
<td>0</td>
<td>0.0041</td>
</tr>
<tr>
<td>HTS HX (cold)</td>
<td>Oxidizer</td>
<td>802</td>
<td>0.003</td>
<td>0.0047</td>
<td>0.883</td>
<td>0.045</td>
<td>0.068</td>
<td>0</td>
<td>0</td>
<td>0.0041</td>
</tr>
<tr>
<td>HTS HX (hot)</td>
<td>HTS</td>
<td>626</td>
<td>0.002</td>
<td>0.0441</td>
<td>0.437</td>
<td>0.121</td>
<td>0.395</td>
<td>0</td>
<td>0</td>
<td>0.0075</td>
</tr>
<tr>
<td>HTS</td>
<td>LTS HX (hot)</td>
<td>640</td>
<td>0.002</td>
<td>0.0122</td>
<td>0.469</td>
<td>0.153</td>
<td>0.363</td>
<td>0</td>
<td>0</td>
<td>0.0075</td>
</tr>
<tr>
<td>HSU</td>
<td>LTS HX (cold)</td>
<td>298</td>
<td>0.003</td>
<td>0.0047</td>
<td>0.883</td>
<td>0.045</td>
<td>0.068</td>
<td>0</td>
<td>0</td>
<td>0.0041</td>
</tr>
<tr>
<td>LTS HX (hot)</td>
<td>LTS</td>
<td>469</td>
<td>0.002</td>
<td>0.0122</td>
<td>0.469</td>
<td>0.153</td>
<td>0.363</td>
<td>0</td>
<td>0</td>
<td>0.0075</td>
</tr>
<tr>
<td>LTS</td>
<td>Condenser (hot)</td>
<td>478</td>
<td>0.002</td>
<td>0.0026</td>
<td>0.479</td>
<td>0.163</td>
<td>0.354</td>
<td>0</td>
<td>0</td>
<td>0.0075</td>
</tr>
<tr>
<td>Condenser (hot)</td>
<td>HSU</td>
<td>298</td>
<td>0.003</td>
<td>0.0037</td>
<td>0.701</td>
<td>0.239</td>
<td>0.054</td>
<td>0</td>
<td>0</td>
<td>0.0051</td>
</tr>
<tr>
<td>Condenser (H2O)</td>
<td>Evaporator (cold)</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.0024</td>
</tr>
<tr>
<td>HSU</td>
<td>H2 produced</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.0010</td>
</tr>
<tr>
<td>Evaporator (hot)</td>
<td>Exhaust</td>
<td>491</td>
<td>0</td>
<td>0</td>
<td>0.061</td>
<td>0</td>
<td>0.022</td>
<td>0.768</td>
<td>0.149</td>
<td>0.0223</td>
</tr>
<tr>
<td>Evaporator (cold)</td>
<td>Fuel Mix</td>
<td>440</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.0021</td>
</tr>
<tr>
<td>Evaporator (cold)</td>
<td>H2O excess</td>
<td>440</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Table 6: Fuel cell stack performance during tri-generation system model run

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Ut</td>
<td>0.630</td>
</tr>
<tr>
<td>O2 Ut</td>
<td>0.126</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>300</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>0.701</td>
</tr>
<tr>
<td>Current (A)</td>
<td>1502</td>
</tr>
</tbody>
</table>

63
This table fully characterizes flows throughout the system and displays the complexity of each component having an effect on other components in all stages of the system. For this reason, the robustness of the model as a whole needed to be investigated to determine if the model could be run for a range of parameters without requiring constant tinkering with initial conditions and other values. This study will focus on the performance of recently added components including the WGSR, condenser, and evaporator to also confirm that they behave as expected.

The three parameters shown in this study will include fuel utilization, flow direction in the fuel cell stack, input fuel type, and system size. The base case for these parameters occurs at 0.65 fuel utilization, cross flow direction, biogas input fuel with 63% methane, 300 kW stack size, and a 3x3 nodal array. Unvaried parameters in each study will be held at these values to allow for the most direct comparison. The base case results for the primary flows through added components are shown in the Table 7 below.

Table 7: Hydrogen separation component performance base case

<table>
<thead>
<tr>
<th></th>
<th>Temp (K)</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
<th>Flow (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS In</td>
<td>626</td>
<td>0.002</td>
<td>0.044</td>
<td>0.437</td>
<td>0.121</td>
<td>0.395</td>
<td>7.5</td>
</tr>
<tr>
<td>HTS Out</td>
<td>640</td>
<td>0.002</td>
<td>0.012</td>
<td>0.469</td>
<td>0.153</td>
<td>0.363</td>
<td>7.5</td>
</tr>
<tr>
<td>LTS In</td>
<td>469</td>
<td>0.002</td>
<td>0.012</td>
<td>0.469</td>
<td>0.153</td>
<td>0.363</td>
<td>7.5</td>
</tr>
<tr>
<td>LTS Out/Condenser In</td>
<td>478</td>
<td>0.002</td>
<td>0.003</td>
<td>0.479</td>
<td>0.163</td>
<td>0.354</td>
<td>7.5</td>
</tr>
<tr>
<td>Condenser Out</td>
<td>298</td>
<td>0.003</td>
<td>0.004</td>
<td>0.701</td>
<td>0.239</td>
<td>0.054</td>
<td>5.1</td>
</tr>
<tr>
<td>Evaporator In</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>Evaporator Out</td>
<td>440</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.1</td>
</tr>
</tbody>
</table>
This data displays about what is expected for these components of the system. The temperatures are in a valid range while the flow rates demonstrate the condensing and evaporating of water accurately. The behavior of the HTS and LTS is captured in the species concentration data which shows trends that lower carbon monoxide and water while increasing hydrogen and carbon dioxide. This occurs at a faster rate through the HTS and at a lower rate yet more complete state in the LTS. Although only a few flows are demonstrated for the figures of this study, the full set of results follows the same reasonable accuracy that is captured by the selected flows. Using this base case set of results, the robustness of the model will be analyzed by observing the trends seen when varying parameters. Table 8 shows how increasing the fuel utilization to 0.85 affects the system.

Table 8: Effect of fuel utilization on HSU component performance

<table>
<thead>
<tr>
<th>Component</th>
<th>Temp (K)</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
<th>Flow (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS In</td>
<td>621</td>
<td>0.003</td>
<td>0.019</td>
<td>0.506</td>
<td>0.047</td>
<td>0.426</td>
<td>6.7</td>
</tr>
<tr>
<td>HTS Out</td>
<td>627</td>
<td>0.003</td>
<td>0.004</td>
<td>0.521</td>
<td>0.062</td>
<td>0.411</td>
<td>6.7</td>
</tr>
<tr>
<td>LTS In</td>
<td>458</td>
<td>0.003</td>
<td>0.004</td>
<td>0.521</td>
<td>0.062</td>
<td>0.411</td>
<td>6.7</td>
</tr>
<tr>
<td>LTS Out/Condenser In</td>
<td>461</td>
<td>0.003</td>
<td>0.001</td>
<td>0.524</td>
<td>0.065</td>
<td>0.408</td>
<td>6.7</td>
</tr>
<tr>
<td>Condenser Out</td>
<td>298</td>
<td>0.004</td>
<td>0.001</td>
<td>0.833</td>
<td>0.103</td>
<td>0.058</td>
<td>4.2</td>
</tr>
<tr>
<td>Evaporator In</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>Evaporator Out</td>
<td>417</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The most important difference here is the drastic reduction in hydrogen present after the fuel cell since most of it now reacts to generate electricity in the stack. Lower flow rates are also present
throughout the system. Table 9 and Table 10 represent counter flow, and co-flow directions in the stack.

Table 9: Effect of fuel cell counter-flow direction on HSU component performance

<table>
<thead>
<tr>
<th></th>
<th>Temp (K)</th>
<th>CH(_4)</th>
<th>CO</th>
<th>CO(_2)</th>
<th>H(_2)</th>
<th>H(_2)O</th>
<th>Flow (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS In</td>
<td>626</td>
<td>0.0002</td>
<td>0.044</td>
<td>0.438</td>
<td>0.128</td>
<td>0.390</td>
<td>7.4</td>
</tr>
<tr>
<td>HTS Out</td>
<td>639</td>
<td>0.0002</td>
<td>0.013</td>
<td>0.469</td>
<td>0.159</td>
<td>0.359</td>
<td>7.4</td>
</tr>
<tr>
<td>LTS In</td>
<td>468</td>
<td>0.0002</td>
<td>0.013</td>
<td>0.469</td>
<td>0.159</td>
<td>0.359</td>
<td>7.4</td>
</tr>
<tr>
<td>LTS Out/Condenser In</td>
<td>476</td>
<td>0.0002</td>
<td>0.03</td>
<td>0.479</td>
<td>0.169</td>
<td>0.349</td>
<td>7.4</td>
</tr>
<tr>
<td>Condenser Out</td>
<td>298</td>
<td>0.0003</td>
<td>0.004</td>
<td>0.696</td>
<td>0.246</td>
<td>0.053</td>
<td>5.1</td>
</tr>
<tr>
<td>Evaporator In</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>Evaporator Out</td>
<td>450</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 10: Effect of fuel cell co-flow direction on HSU component performance

<table>
<thead>
<tr>
<th></th>
<th>Temp (K)</th>
<th>CH(_4)</th>
<th>CO</th>
<th>CO(_2)</th>
<th>H(_2)</th>
<th>H(_2)O</th>
<th>Flow (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS In</td>
<td>628</td>
<td>0.001</td>
<td>0.051</td>
<td>0.431</td>
<td>0.119</td>
<td>0.399</td>
<td>7.6</td>
</tr>
<tr>
<td>HTS Out</td>
<td>644</td>
<td>0.001</td>
<td>0.013</td>
<td>0.468</td>
<td>0.156</td>
<td>0.361</td>
<td>7.6</td>
</tr>
<tr>
<td>LTS In</td>
<td>471</td>
<td>0.001</td>
<td>0.013</td>
<td>0.468</td>
<td>0.156</td>
<td>0.361</td>
<td>7.6</td>
</tr>
<tr>
<td>LTS Out/Condenser In</td>
<td>480</td>
<td>0.001</td>
<td>0.003</td>
<td>0.479</td>
<td>0.167</td>
<td>0.351</td>
<td>7.6</td>
</tr>
<tr>
<td>Condenser Out</td>
<td>298</td>
<td>0.001</td>
<td>0.004</td>
<td>0.698</td>
<td>0.243</td>
<td>0.054</td>
<td>5.2</td>
</tr>
<tr>
<td>Evaporator In</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>Evaporator Out</td>
<td>416</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.2</td>
</tr>
</tbody>
</table>
The flow direction doesn’t appear to have a major impact on overall system performance since the three results are very similar for cross flow, counter flow, and co-flow. The flow direction will however have an effect on the temperature distribution in the fuel cell stack, but that is not investigated in depth for this study. Table 11 shows the results when fueled with natural gas rather than a biogas mixture.

*Table 11: Effect of natural gas fuel input on HSU component performance*

<table>
<thead>
<tr>
<th></th>
<th>Temp (K)</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
<th>Flow (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS In</td>
<td>623</td>
<td>0.006</td>
<td>0.045</td>
<td>0.440</td>
<td>0.129</td>
<td>0.381</td>
<td>6.5</td>
</tr>
<tr>
<td>HTS Out</td>
<td>637</td>
<td>0.006</td>
<td>0.013</td>
<td>0.472</td>
<td>0.160</td>
<td>0.349</td>
<td>6.5</td>
</tr>
<tr>
<td>LTS In</td>
<td>460</td>
<td>0.006</td>
<td>0.013</td>
<td>0.472</td>
<td>0.160</td>
<td>0.349</td>
<td>6.5</td>
</tr>
<tr>
<td>LTS Out/Condenser In</td>
<td>469</td>
<td>0.006</td>
<td>0.003</td>
<td>0.483</td>
<td>0.171</td>
<td>0.338</td>
<td>6.5</td>
</tr>
<tr>
<td>Condenser Out</td>
<td>298</td>
<td>0.009</td>
<td>0.004</td>
<td>0.691</td>
<td>0.244</td>
<td>0.053</td>
<td>4.5</td>
</tr>
<tr>
<td>Evaporator In</td>
<td>298</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.0</td>
</tr>
<tr>
<td>Evaporator Out</td>
<td>610</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Performance is once very similar to the base case with biogas fuel, but the flow rates are slightly decreased because less initial fuel is needed when there is no carbon dioxide present in the fuel stream. The outlet evaporator temperature is also higher compared to the base system. The final parameter investigated in this study is the size of the system. Table 12 below displays results for a 1.2 MW fuel cell.
Table 12: Effect of a larger scale system on HSU component performance

<table>
<thead>
<tr>
<th></th>
<th>Temp (K)</th>
<th>CH₄</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>H₂O</th>
<th>Flow (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS In</td>
<td>652</td>
<td>0.002</td>
<td>0.043</td>
<td>0.438</td>
<td>0.122</td>
<td>0.395</td>
<td>29.9</td>
</tr>
<tr>
<td>HTS Out</td>
<td>664</td>
<td>0.002</td>
<td>0.019</td>
<td>0.462</td>
<td>0.146</td>
<td>0.371</td>
<td>29.9</td>
</tr>
<tr>
<td>LTS In</td>
<td>561</td>
<td>0.002</td>
<td>0.019</td>
<td>0.462</td>
<td>0.146</td>
<td>0.371</td>
<td>29.9</td>
</tr>
<tr>
<td>LTS Out/Condenser In</td>
<td>567</td>
<td>0.002</td>
<td>0.010</td>
<td>0.472</td>
<td>0.155</td>
<td>0.361</td>
<td>29.9</td>
</tr>
<tr>
<td>Condenser Out</td>
<td>301</td>
<td>0.003</td>
<td>0.014</td>
<td>0.691</td>
<td>0.227</td>
<td>0.064</td>
<td>20.4</td>
</tr>
<tr>
<td>Evaporator In</td>
<td>301</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>9.5</td>
</tr>
<tr>
<td>Evaporator Out</td>
<td>373</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>8.5</td>
</tr>
</tbody>
</table>

The temperatures and species concentrations remain very similar to the 300 kW system but there is obviously a large increase in the flow rates to achieve the specified power output from a larger stack. This system configuration obtains valid solutions up to 7 MW before the model runs into convergence issues.

At this stage of the system modeling process, all components are behaving as expected and the results generated thus far closely follow the performance of a tri-generation system. This version now captures the condensation and evaporation of water that is recirculated back to the anode along with fully integrated water gas shift reactors and heat exchangers. The final state of the system model will contain a physical model of electrochemical hydrogen separation and the ability to calculate expected system efficiency values.
6.4.2 Fully Integrated System with EHS

The final results section of this thesis focuses on the performance characteristics of the EHS unit under different operating conditions of the entire tri-generation system. The previous section investigated the operation of pre-hydrogen separation components within the system, but now all additional model blocks required for tri-generation have been integrated together to form a model that mirrors the diagram shown in Figure 16 from the model development section. Varied parameters will include overall system size, fuel utilization of the fuel cell, and active area of the EHS unit. The major outputs include hydrogen flow produced, required EHS voltage, and required EHS power draw. All analysis will be done for two hydrogen outlet pressures at essentially zero compression, and compression up to 35 MPa which is the necessary storage pressure.

The standard state of these plots represents a 1400 kW fuel cell running at 65% fuel utilization and an EHS active area of 300 m². Remember that this is the total active area of the unit which consists of many cells stacked together to achieve the necessary surface area. Also note that EHS over voltage is always below 0.19 V and EHS current density never exceeds 850 mA/cm² while producing a hydrogen steam around 99% purity. Figure 29 and Figure 30 display the EHS voltage and power required for separation with varied EHS stack sizes of a 1400 kW system.
Figure 29: EHS voltage and power draw for different EHS stack sizes without hydrogen compression
Figure 30: EHS voltage and power draw for different EHS stack sizes with hydrogen compression to 35 MPa

These plots show that for similar hydrogen production, the voltage and power draw of the EHS unit can be decreased by increasing the EHS size but the benefit is reduced once you get above 300 m$^2$ for this particular system size. The additional power required to compress the hydrogen to 35 MPa also varies depending on the size of the EHS unit. The largest unit requires nearly 3 times the power for compression while the middle and smallest units require about 2 and 1.5 times the power respectively. Once again, the ideal size is the 300 m$^2$ to get the most compression for the amount of input power without needing an excessively large unit. Figure 31
and Figure 32 show the effect that fuel utilization of the fuel cell stack has on hydrogen production for a constant EHS size.

Figure 31: Hydrogen production and EHS power draw without compression for varying fuel utilizations
Figure 32: Hydrogen production and EHS power draw with compression to 35 MPa for varying fuel utilizations

Hydrogen production is drastically reduced when operating at higher fuel utilizations due to the smaller concentration of hydrogen in the anode off gas. However, the hydrogen production per unit of EHS power is slightly higher at the higher fuel utilizations. Production performance is displayed in the next two figures for increasing system size.
Figure 33: Hydrogen production and EHS power draw without compression for varying system sizes
A few different trends can be seen with these plots. One major finding relates to hydrogen production when scaling the system to multi megawatt sizes. Doubling the system size increases hydrogen production substantially but by less than double the amount. However, the power draw per hydrogen flow produced does decrease as system size is increased. This entails that increasing system size may not increase hydrogen production by the same magnitude, (i.e. double system size doesn’t result in double hydrogen production) yet the effectiveness of the hydrogen separation slightly increases at larger systems. Another observation relating to pressurization of hydrogen shows that more than double the amount of power is required to pressurize the hydrogen to 35 MPa for all system sizes.
To gain a better perspective of EHS performance in a tri-generation system, a comparison was made between operating system at OCSD and the system model developed with EHS integrated. The system model isn’t a mirror image of the system at OCSD but running the model under similar operating conditions yields very similar results. Table 13 provides a comparison between the model which uses EHS and system at OCSD that uses PSA for separation. The PSA by itself provides very little compression so the power draw in table corresponds to both the PSA load and the compressor load to obtain pressurized hydrogen.

Table 13: Comparing hydrogen production performance between the OCSD system and tri-generation model

<table>
<thead>
<tr>
<th></th>
<th>Outlet Pressure (MPa)</th>
<th>EHS Power Required (kW)</th>
<th>Hydrogen Produced (kg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHS Model</td>
<td>35</td>
<td>36</td>
<td>152</td>
</tr>
<tr>
<td>OCSD Data</td>
<td>35</td>
<td>52</td>
<td>127</td>
</tr>
<tr>
<td>EHS Model</td>
<td>0.102</td>
<td>16</td>
<td>151</td>
</tr>
</tbody>
</table>

The use of EHS technology rather than PSA has significant theoretical advantage for both hydrogen production and HSU power draw when the system size is only 300 kW. However, PSA and EHS technology don’t scale in the same way, meaning that this advantage may be diminished for larger systems.
Table 14: Percentage of energy input allocated to power produced, hydrogen produced, and hydrogen production loads

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>OCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power Produced</strong></td>
<td>48%</td>
<td>51.7%</td>
</tr>
<tr>
<td><strong>Hydrogen Produced</strong></td>
<td>8.8%</td>
<td>9.8%</td>
</tr>
<tr>
<td><strong>Hydrogen Separation and Compression Load</strong></td>
<td>7.3%</td>
<td>10.9%</td>
</tr>
</tbody>
</table>

Table 15: Efficiency values for electrical, hydrogen, and overall performance with hydrogen production parasitic load

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>OCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrical Efficiency</strong></td>
<td>40.5%</td>
<td>36.6%</td>
</tr>
<tr>
<td><strong>Hydrogen Efficiency</strong></td>
<td>14.8%</td>
<td>15.4%</td>
</tr>
<tr>
<td><strong>Overall Efficiency</strong></td>
<td>49.3%</td>
<td>46.4%</td>
</tr>
</tbody>
</table>

Table 16: Efficiency values for electrical, hydrogen, and overall performance without hydrogen production parasitic load

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>OCSD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrical Efficiency</strong></td>
<td>47.6%</td>
<td>47.5%</td>
</tr>
<tr>
<td><strong>Hydrogen Efficiency</strong></td>
<td>16.9%</td>
<td>18.6%</td>
</tr>
<tr>
<td><strong>Overall Efficiency</strong></td>
<td>56.6%</td>
<td>57.2%</td>
</tr>
</tbody>
</table>

Recall that the OCSD plant uses PSA technology for hydrogen separation while the model utilizes EHS technology. Efficiency calculations are based from previous research [5] on tri-
generation overall efficiency along with separate hydrogen and electrical efficiencies. Table 14 shows the breakdown of products and the hydrogen separation with compression load as a percentage of the input energy from fuel. The power production calculation doesn’t consider any parasitic loads. Notice that the hydrogen separation and compression load is very high compared to the amount of hydrogen produced, especially for PSA. Table 15 displays efficiency values for pure electrical, hydrogen, and combined overall efficiency. The electrical efficiency now takes into account the fuel cell system parasitic loads and the hydrogen production parasitic loads. The higher parasitic load of PSA is responsible for the lower overall efficiency compared to the EHS case in the model. Table 16 now neglects the hydrogen production parasitic load to show the full effect that it has on system efficiency. The large increase in electrical and combined efficiency displays that this load greatly decreases system performance. Without this load, efficiency values are very similar and yield good operation. This analysis demonstrates that hydrogen separation and compression technology should be researched further in order to greatly improve the performance of tri-generation systems.
7 SUMMARY, CONCLUSIONS, & RECOMMENDATIONS

7.1 Summary

A brief summary and meaning of the findings in the results section will be addressed and cover the main topics including fuel cell and water gas shift kinetics, electrochemical hydrogen separation, and overall tri-generation system performance. General comments on the OCSD project and modeling experience will also be covered in the conclusion of this thesis.

Initial modeling efforts entailed improving the accuracy of fuel cell stack kinetics. With the original model outputting nearly zero concentration of carbon monoxide, an investigation of other kinetic correlations in the literature was conducted and a model comparison was done. A similar process was taken to model a two stage hydrogen booster that captures water gas shift kinetics at a high and low temperature. Rather than simply assuming equilibrium, this model could account for the size of each reactor and the extent of reaction for each temperature.

Experiments for electrochemical hydrogen separation in the literature are all based on small scale units, yet the system modeled in this thesis is on the order of megawatts. Using governing equations and experimental correlations from multiple sources, the performance of an EHS unit was simulated using similar operational limits as the experiments in terms of voltage and current density. However, greatly increasing the number of cells increases the overall active area of the unit and the total current that flows through the cells. Some experiments in the literature investigated simultaneous compression of the unit but none of them increased the pressure to 35 MPa. Modeling this magnitude of pressure increase is for theoretical purposes to characterize the potential performance of a tri-generation system assuming that the EHS could handle high pressure operation.
The major additional components necessary for hydrogen separation had been developed, but a number of system blocks were still needed to complete a full system model. This required the addition of two heat exchangers, condenser, evaporator, and fuel/steam mixing blocks with recirculating flows. The initial system of the results section confirmed accurate performance of temperatures, flow rates, and species concentrations through all new system components when coupled with a simplified hydrogen separation unit. All new component blocks had to be sized appropriately to obtain desired flow characteristics through all sections of the system model. After this system integration work, the physical EHS model was inserted to capture a full physical model of a tri-generation system using electrochemical hydrogen separation.

The results obtained from the tri-generation system model provide a new perspective on the technology by revealing performance characteristics under a number of different design and operating parameters. This analysis doesn’t attempt to optimize the system for any particular case, but instead tries to capture a wide range of possibilities which could be utilized for many applications.

### 7.2 Conclusions

A list of major conclusions is shown below, followed by a brief explanation:

- The work of Paradis yielded the most accurate kinetics for the fuel cell stack model. Analysis showed that the more recent work of Paradis to include Achenbach kinetics coupled with Haberman and Young kinetics yielded more accurate species concentrations of the anode off gas with the main point being that the carbon monoxide concentration was around 4-5% rather than near zero. The determined concentrations were now at expected values and closely matched data from OCSD. This was a crucial first step to modeling a complete tri-generation
system since the carbon monoxide concentration has a major effect on the hydrogen booster components that take advantage of the water gas shift reaction.

- The Seo et al. correlation modeled water gas shift reactor behavior most accurately.

By comparing correlations from the literature, the work of Seo et al. was determined to yield the most accurate performance of water gas shift reactors based on comparisons to equilibrium software and OCSD data.

- Parametric analysis of the EHS model presented useful operation trends on the technology.

The component model developed for EHS generated reasonable values and trends of important performance characteristics including V-I curve, power curve, hydrogen production, hydrogen purity, and hydrogen recovery. These trends provide valuable insight to the technology and show great promise in combining hydrogen separation and compression using an electrochemical device.

- EHS can be more effective and predictable than PSA separation technology especially at sub megawatt scales.

The major takeaway from EHS integration in a tri-generation system is that many design parameters of the unit can have a big impact on performance, but resulting behavior is very predictable. Changing the area, voltage, desired pressure, etc. of the EHS unit has predictable performance that isn’t drastically varied based on system size. PSA technology shows a different trend since the performance improves at the largest scales. From a practical point of view, there are other issues that must be considered for EHS technology. The first corresponds
to designing a unit that can handle pressures up to 35 MPa. From a theoretical standpoint this is feasible and lower pressure tests have been conducted in the literature, however, constructing an electrochemical unit that can operate under such high pressures will be a challenge.

Consideration must also be made especially for larger units that would require large amounts of platinum. The unit could be very comparable in price to a PEM fuel cell stack which can be very costly especially at larger stack sizes. Taking everything into account, EHS can still be a viable option that can boost hydrogen production and reduce system parasitic loads while simultaneously compressing the gas closer to desired pressures. This may be done most effectively at smaller scales but can still be viable for multi megawatt plants.

- The combination of hydrogen separation and compression using EHS could greatly reduce system complexity and parasitic loads.

By using EHS for both separation and compression, the use of multiple compression stages required for PSA followed by separate compression of the gas is no longer needed. PSA also requires more controls to determine opening and closing multiple valves during a multiple stage process of compressing and decompressing the mixture of gases. Reducing compression loads and the need for complex control schemes makes an EHS system a better alternative for simpler system design and reduction of parasitic loads.

- Hydrogen separation and compression loads are a very large parasitic that reduces the effectiveness of tri-generation.

Efficiency calculations reveal a very interesting characteristic of tri-generation systems due to the large parasitic load of separating and compressing the hydrogen. Operating a high temperature fuel cell plant for power and heat is relatively simple compared to the components
needed to create a pure hydrogen stream. These loads contribute to about 10% of the inlet energy to produce about 10% of that energy in a hydrogen product. A reduction in this load would greatly boost overall efficiency of a tri-generation plant.

- Even without heat recovery, tri-generation efficiency can still reach nearly 60%.

Overall efficiency of about 50% is achieved with all parasitic loads taken into account with a boost of about 10% coming from the generation of a hydrogen product. This efficiency reaches close to 60% without the large parasitic load for hydrogen production and compression. Once again, it puts the magnitude of this load in perspective as a focus for future research efforts.

7.3 Recommendations

The successful implementation and operation of the tri-generation plant at OCSD was the inspiration for this work in an effort to further understand and improve the technology. As a demonstration project, the plant wasn’t fully optimized for the best performance, yet it still provided a great resource to understand the benefits and challenges of the technology. The project is nearing the end of its first term but expansion and improvement is needed to progress tri-generation. Many new additions can be made to display the full potential including better thermal management, including heat recovery, using EHS on a slipstream, or even fully designing a larger system at 1.4 or 2.8 MW. Simply continuing operation at the current state allows for renewable production of hydrogen for an increasing fleet of fuel cell vehicles and promotes further outreach of the project. A strong push should be made to continue such a project to facilitate more research and development of such a promising technology in the energy field.
Generating a fully integrated system model of multiple dynamic components can be a very difficult task just like a complex real system. Simply changing the size of one component can have a major effect on the performance of the entire system. The goal of this thesis was to keep system operation as consistent as possible in order to capture the relative changes in performance to just the EHS unit based on changes to unit operation and some varied system parameters. As mentioned before, the results shown do not reflect a fully optimized model of a tri-generation system because so much work could be dedicated to this topic. There is still plenty of work that can be done to improve the model, but a solid framework has been created to encourage more work on tri-generation. Possible areas of investigation include a variety of points such as: detailed system component design, modeling other hydrogen separation technologies, using an SOFC stack rather than MCFC, creating detailed system efficiency calculations, investigating potential for carbon capture, and system optimization for different applications. This is just a short list of potential future projects that could benefit the progress of tri-generation technology.
REFERENCES


