CARBON NEUTRALIZATION OF A COAL-TO-LIQUIDS PLANT UTILIZING SOLID OXIDE ELECTROLYSIS FOR HYDROGEN PRODUCTION

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ABSTRACT

Coal to liquid (CTL) technology has the potential to help decrease America’s foreign energy demand for liquid transportation fuels. However, no large-scale refinery will be built in the United States without first proving itself to be carbon neutral in its operations. Due to coal’s relatively high sulfur content, hydroprocessing is a very important part of operations. H₂ is a vital part of many industrial applications. However, H₂ does not occur naturally and must be liberated from other compounds. The current method of H₂ production is steam reforming of methane, but that requires the extraction of methane through drilling operations and produces a large quantity of CO, which is subsequently converted to CO₂ via water gas shift. A growing environmental consciousness has led to a need for a low-emission substitute to steam reforming.

Solid oxide electrolysis offers a high-efficiency alternative that also has the capability to utilize captured CO₂ as a reactant. Due to the ceramic electrolyte in a solid oxide electrolytic cell (SOEC), it can be run at high temperatures; this allows for coelectrolysis of H₂O and CO₂. This study aims to test the cell efficiency and H₂ production as a function of temperature. The results from this study show that cell efficiency and H₂ production not only increase with temperature, but increase at a greater-than-linear rate. Future work will include an introduction of CO₂ to the feed stream to determine percent conversion of CO₂ to CO, which may be used in either a water gas shift reactor or be used to synthesize other fuels.
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Chapter 1

Introduction to Coal to Liquid Technology

Coal to liquid(s) (CTL) is the colloquial term in the energy industry that refers to any process that converts solid, often pulverized, coal into some sort of liquid hydrocarbon fuel. However, this process brings along with it the difficulty of converting a ~0.85 H:C ratio fuel to a ~1.9 H:C ratio fuel, which can only be achieved by carbon rejection, hydrogen addition, or a combination of the two (Bellman, 2007). However, carbon rejection often leads to waste, which does not promote overall process sustainability. Keeping in line with overall process sustainability, Chapter 3 will focus on a form of hydrogen production able to increase the H:C ratio to an appropriate level.

CTL has been used for over seventy years in nations spanning from the British Isles to the southern tip of Africa. CTL provides countries, in this case America, opportunity for enhanced energy independence. America currently obtains over 20% of its imported oil from middle-eastern countries, which are in a state of political unrest (U.S. Energy Information Administration, 2011). The United States’ energy future depends on its ability to begin distancing itself from foreign imports in order to provide a continuous supply of liquid transportation fuel at a stable price while providing jobs to people in the United States. Because CTL technology requires only materials that are domestic to America, the benefits to the domestic economy could potentially span multiple industries all over the United States; the industries affected include, but are not limited to: construction, concrete, refineries, agriculture,
transportation, and mining. However, coal to liquids is not something that America can just jump into without first looking to the past.

Overview of CTL Technology

CTL, or coal liquefaction, is both a traditional and an evolving technology. There are many different methods of deriving liquid middle distillate fuels from coal, but the two main technologies are direct and indirect coal liquefaction. Liquid middle distillate fuel is a generic term for any diesel or kerosene derived from any refining process. On the most basic level, direct liquefaction of coal uses solvents, pressure, heat, and catalysts to crack the coal to generate distillate liquids, whereas indirect liquefaction gasifies the coal to create synthesis gas, which is then converted to middle distillates through Fischer-Tropsch (F-T) synthesis (John Winslow, 2009). Before going further, it would be prudent to have a deeper understanding of both direct and indirect coal liquefaction to understand why neither are ideal and therefore not the subject of this study.

Direct coal liquefaction is actually the first form of coal liquefaction, being developed in 1913 by Friedrich Berguis. The idea that liquid transportation fuels could be derived from a seemingly limitless supply of coal helped Berguis win the Nobel Prize in chemistry for his work (Liu, 2005). Direct liquefaction was used during World War II in both Great Britain and Germany due to the dangers of trade associated with importing foreign oil, among other circumstances of war. The basic chemistry behind direct liquefaction, as previously stated, involves the reaction of a coal slurry with H₂ over catalysts under high pressure and temperature (425°C and 15-20 MPa) (Sun, 2008). The coal-derived solvent is used to ease refinery flow by providing a liquid
medium through which the coal can be transported and introduced to a pressure vessel. The solvent can dissolve molecular coal fragments, stripping loose aliphatic chains of ethers and sulfides that exist between the lattice body of the coal, in order to hinder chemical recombination and precipitation (D. Kang, 1977).

Due to the high temperatures and pressures, this process is very energy intensive and, in turn, costly to operate. The heat input needs to be great enough to thermally crack the dense aromatic hydrocarbons, which requires the combustion of either coal or natural gas. In addition, direct liquefaction requires vast quantities of hydrogen, which is often obtained by steam reforming of methane or gasification coupled with water-gas shift. Unfortunately, steam reforming, gasification, and water-gas shift all produce large quantities of carbon dioxide. When accounting for all of these refining operations, it becomes evident that the overall carbon footprint of the process is extremely large, which acts as a deterrent to investment given the current public environmental conscience. There aren’t any historical direct coal liquefaction refineries still in operation today. In terms of new facilities, there was one direct coal liquefaction plant recently built by Shenhua. One may question why a company would invest so much capital into a technology that seems have such a large drawback related to energy consumption, but diversifying the energy portfolio of a country in some instances may outweigh the costs of operating a more expensive fuel refining operation. Also, the primary fuel derived from direct coal liquefaction is much too “dirty” and requires further refining to meet many emissions standards (Alliance for Synthetic Fuels in Europe, 2011). The energy-intense nature and low-quality products of direct coal liquefaction are enough of a deterrent to prevent any further research for this project.
Unlike direct coal liquefaction, indirect coal liquefaction is still in large-scale commercial use today. Indirect coal liquefaction has been in commercial use for over 70 years and currently provides over 30% of South Africa’s liquid transportation fuel needs (Alliance for Synthetic Fuels in Europe, 2011). The basic process of indirect coal liquefaction is pulverization of coal, followed by gasification in the presence of steam. The steam and coal then react to form synthesis gas, CO\(_{(g)}\) and H\(_2(g)\), which are then pumped over an iron catalyst to synthesize fully hydrogenated alkanes. Important to note is that South Africa’s Sasol indirect coal liquefaction plant is the single largest point source of CO\(_2\) on Earth, emitting 73 million tons of CO\(_2\) per year (Sasol, 2010).

There is a large number of people who do not believe CO\(_2\) is a pollutant and therefore should not be of concern when attempting to achieve technical excellence; however, there exists an ever-growing population, including judges and politicians, who believe that CO\(_2\) is a pollutant and must be addressed in the preliminary plant designs. The EPA implemented a mandatory greenhouse gas rule reporting program under the Code of Federal Regulations that requires reporting at the end of the financial year in 2011; this rule is generally referred to as 40 CFR Part 98 (Environmental Protection Agency, 2011). This is pertinent to CO\(_2\) because in 2007, the Supreme Court decided in *Massachusetts v. Environmental Protection Agency* that “greenhouse gases fit well within the Clean Air Act’s capacious definition of an air pollutant,” and CO\(_2\) is undoubtedly a greenhouse gas (Massachusetts v. Environmental Protection Agency, 2007). The addition of CO\(_2\) to the already present CO and VOC regulation, found in 40 CFR Part 60, leads to the accountability of every carbon-containing emission from any combustion or gasification process.
Carbon neutrality

Carbon neutrality is a relatively new concept that essentially implies zero carbon waste; carbon waste implies any carbon-containing emission, such as CO$_2$ or CO, not just elemental carbon or any of its solid forms. All carbon waste streams must be converted into a byproduct stream, or the carbon waste that is not or cannot be avoided is offset by the planting of any carbon uptake vessel (e.g. trees, bushes, etc.). Due to the current environmental consciousness and political caution when dealing with any petroleum or chemical endeavor, no significant (sophisticated) refinery has been erected in the United States since 1977 in Garysville, Louisiana; there have been smaller simple refineries built since then, but the grand total of refineries built between 1977 (post Garysville refinery) and 2011 is only eleven, with only one operating over 26,000 bbl/day (U.S. Energy Information Administration, 2011). There is an almost unwritten rule in today’s political climate that implies no refinery will receive any sort of funding or sincere thought from the federal government unless it can prove that it is designed to be carbon neutral.

In order to obtain the title of a carbon neutral refinery, environmentally conscious engineering innovations will need to be employed both upstream and downstream operations. In terms of upstream, reduction in material used, higher process efficiency, and quality of energy used play major roles. In terms of downstream operations, often termed sequestration or cleanup, different capture and storage mechanisms will be necessary. Both of these will be explained in more detail in Chapter 2.
Chapter 2

CoalStar Green: CTL Plant Process Flow

Researchers at The Pennsylvania State University have developed a method to convert coal to liquid middle distillates without the need for thermal cracking or Fischer-Tropsch synthesis. A startup company, CoalStar, is seeking investment capital to build a pilot plant and eventually scale up to a 10,000 ton/day commercial plant. Most of the technical details regarding which specific catalyst are still being researched and optimized at this time, but some general operating conditions and constituents have been determined. The desired conditions of extraction are 360°C, 10:1 solvent:coal ratio, and one hour residence time. The unextracted coal and mineral matter are then separated out via some physical separation process (e.g. pressure filtration, gravity separation, flocculation, centrifugal separation, etc.). The solvent is then stripped from the liberated hydrocarbons via some physical or thermal separation process, leaving a 1:1 solvent:coal extract blend.

The plant will have a daily output of approximately ten thousand barrels of liquid fuel, with an estimated 80% comprised of middle distillates. Assuming that one barrel of oil requires three thousand standard cubic feet (scf) of H_2(g) leads to the conclusion that the plant requires thirty million scf of H_2(g) per day. This H_2(g) will be used in hydroprocessing – that is, the removal of sulfur – and the hydrogenation of unsaturated olefins and aromatics.

The first stage of hydrotreating is hydrodesulfurization, with a small degree of hydrodenitrogenation and ring saturation; this paper does not focus on the hydrodenitrogenation or ring saturation in this step as they are assumed to be negligible to the hydrodesulfurization.
The sulfur compounds extracted from the coal react with the hydrogen and forms hydrogen sulfide, which is something that needs to be dealt with and will be discussed later in Chapter 2. After the majority of the sulfur is removed, the hydrocarbons are then hydrotreated to saturate any aromatics present. The resultant saturated and desulfurized hydrocarbons are then sent to a fractional distillation column where they are separated based on their boiling points into gasoline, kerosene (a precursor to jet fuel), diesel, and fuel oil, with diesel being the desired and most abundant product. These products are then sold for profit and the process continues. This entire process is outlined in Figure 2-1.

Figure 2-1: CoalStar Green coal liquefaction backbone process flow

While this process is very innovative and provides insight into what future middle distillate refining processes may look like, it still leaves much to be desired. As stated in Chapter 1, no
major refineries have been built in the United States since 1977 because of the large capital investment and, more recently, the federal government’s de-facto ban on all new major refinery developments unless these prospective refineries can prove that they are carbon neutral. In order to do this, all inputs and outputs of the refinery operation must be accounted for; the major input being H₂ and major output being CO₂. There are a number of other inputs and outputs that need to be accounted for, and they will all be addressed in the subsequent subsections of Chapter 2.

It is important to note that this backbone process flow will and can perform the action that it is designed to: that is, convert coal to liquid middle distillate fuel. However, pressure from the federal government and a growing environmental awareness has forced refinery processes like the one pictured in Figure 2-1 to evolve and adopt environmentally prudent technologies and practices. The following units will help address these concerns and potentially aid in gaining both government support and financial backing for future refining operations.

**Unit 1: Claus**

In its simplest form, the Claus process is the act of removing elemental sulfur from hydrogen sulfide by reacting the hydrogen sulfide with sulfur dioxide (Spencer, 1989). First, a flue stream is run through methanol at -40°C, which separates acid gas from the rest of the flue; this is known in the refining industry as the Rectisol Process. The acid gas is then sent to the Claus Unit, where the conversion of hydrogen sulfide takes place.

**Equation 2-1:**

\[ 2H_2S(g) + SO_2(g) = \frac{3}{2}S_n(g) + 2H_2O(g) \]
Equation 2-1 has an enthalpy of -108 kJ/mol at 25°C, which implies an exothermic and spontaneous reaction, even at relatively low operating temperatures (Martin P. Elsner, 2003). The two products of this reaction are elemental sulfur and water vapor, neither of which are pollutants. In fact, the sulfur has a plethora of potential uses and, in turn, a large market of possible consumers. Sulfur is used the following manners: fabrication of gunpowder; vulcanization of rubber; applications in fungicide, fumigant, and the development of fertilizers; synthesis of sulfuric acid; and electrical insulation (Melmenstine, 2011).

Unfortunately, it is impossible to only look at the Claus process in its simplest form when attempting to design a refinery; there are many things that need be accounted for including mass flows and plant footprint. In a traditional Claus process, one third of the H₂Sₕ is converted to SO₂ₕ by reacting the hydrogen sulfide with excess oxygen (i.e., in the presence of air). The resultant hydrogen sulfide and sulfur dioxide are then reacted together in a high-temperature furnace, which achieves about 60-70% conversion efficiencies. The balance is then sent to a set of second-stage catalytic operations to enhance conversion and increase reaction rates; second stage conversions typically achieve 95-97% sulfur recovery, which generally does not meet the current 10 ppm environmental standards on H₂Sₕ emissions set forth by OSHA (M. P. Heisel, 2011; Occupational Safety & Health Administration, 2011).

Recent advancements have led to achieving between 98-99.98% sulfur recoveries via secondary tail-gas treating practices. The three main principles of Claus tail-gas treatment that sets it apart from the industry standard are the following: recycle processes that convert any residual sulfur species into either hydrogen sulfide or sulfur dioxide, with a recycle stream that directs these newly converted species to the beginning of the Claus process; cyclical catalytic sub dew point
that perpetuate the conversion of hydrogen sulfide and sulfur dioxide to elemental sulfur at temperatures below the dew point and shift the reaction equilibrium toward the formation of elemental sulfur; and selective oxidation of $\text{H}_2\text{S}(g)$ directly to $\text{S}(s)$ without the need for $\text{SO}_2(g)$ to be present (M. P. Heisel, 2011). This process is extremely desirable because it generates steam, which can be used for process heat or a myriad of other operations, with virtually zero $\text{CO}_2(g)$ emissions – barring any $\text{CO}_2(g)$ present in the feed stream.

As stated earlier, there are three principles that separate traditional Claus operations from newer progressive operations. The first, recycle processes, are the most simplistic in that they recycle any unconverted $\text{H}_2\text{S}(g)$ back to the primary Claus units for another cycle. All sulfur-containing species in the Claus tail-gas are catalytically reduced to $\text{H}_2\text{S}(g)$, which is then captured and recycled back to the plant (M. P. Heisel, 2011). This process is shown in Figure 2-2.

![Figure 2-2: Claus unit recycle process flow](image)

Fortunately, this process does allow for a high degree of variation (M. P. Heisel, 2011). For example, the hydrogenation bed can be filled with a plethora of different hydrogenation catalysts, given a specific time, operating temperature, and desired conversion rate. For the CTL
plant in this study, a low temperature hydrogenation catalyst would be best because any excess heat can be extracted and harnessed for preheat to another unit in the plant – such as the solid oxide electrolyzer or gasifier, both of which will be discussed in the upcoming subsections. The H₂S wash shown in Figure 2-2 is a tertiary amine scrubber, used to absorb H₂S, while limiting other acid gas (e.g. CO₂) absorption. This recycle process has been shown to actually have a negative CO₂e footprint due to its generation of higher energy products that can be used in lieu of other CO₂(g) generating sources of energy (M. P. Heisel, 2011).

The second progressive Claus technique, cyclical sub dew point processes, continues the Claus reaction at lower temperatures, which favor formation of elemental sulfur while having a lower energy input (M. P. Heisel, 2011). Sulfur solidifies at temperatures around 120°C, which requires inlet temperatures of operation of 125-135°C (RH Perry, 1984; M. P. Heisel, 2011). As is common in many catalytic reactions, the catalyst will eventually become poisoned with solid sulfur. This requires the entire unit to be filled with an inert gas, which is heated to high temperatures in order to vaporize the elemental sulfur, which will then be recovered after it leaves the catalyst-containing unit.

The third progressive Claus process, direct oxidation, operated in air-deficient conditions, resulting in a very high H₂S(g) to SO₂(g) ratio. The H₂S(g) is then separated out and directly oxidized to generate H₂O(g) and S(s). As with the recycle process, this process actually generates more energy in the form of steam than it consumes, thus making it a carbon negative process by providing energy for other operations (M. P. Heisel, 2011).

All three of these progressive Claus techniques require five main inputs: electric power, hydrogen, fuel, high-pressure steam, and low-pressure steam. The electric power can be
provided by means discussed later in this chapter. The hydrogen can be provided by techniques demonstrated in Chapter 3. The fuel can be any sort of liquefied petroleum gas (LPG) produced in the distillation column during the last stage of the plant. The high-pressure and low-pressure steam can be generated by utilizing excess heat from other plant processes (e.g. gasification or Claus reaction).

The Claus process is essential for converting H$_2$S produced by hydrotreating coal-derived liquids, and progressive measures described above do so in an environmentally conscious manner by their use of catalysts and low-temperature operations. While sulfur removal is not the main goal of the plant, it is an important requirement that requires significant attention in order to be met in an efficient and safe manner.

**Unit 2: Solid Oxide Electrolyzer**

Due to coal’s low hydrogen-to-carbon ratio relative to petroleum, the conversion of coal to middle distillate transportation fuel requires the addition of large quantities of hydrogen and/or the removal of excess carbon (Lumpkin, 1988). Solid oxide electrolysis involves the endothermic splitting of H$_2$O$_{\text{(l)}}$ into H$_2(g)$ and O$_2(g)$ by virtue of heat and an applied cell voltage. Solid oxide electrolysis not only affords the opportunity to utilize waste heat as a fuel source for H$_2(g)$ production, but also opens up a gateway for CO$_2$ sequestration and utilization. Due to the large role that H$_2$ plays in this process, the entirety of Chapter 3 is dedicated to an in-depth look at solid oxide electrolysis for H$_2$ production.
Unit 3: Electricity Generation

Electrolyzers require a great deal of energy due to their operating voltage being greater than that of their open circuit voltage (CH Hamann, 1998). The electricity can be generated by a myriad of carbon-neutral sources, such as wind turbines, concentrated solar thermal troughs or heliostats, photovoltaic arrays, nuclear reactors, or hydroelectric generators. Each of these electricity sources is site-dependent, which is important for this project because the actual site has not yet been chosen. It is also important to note that owners or affiliates of the CTL plant need not generate the electricity; it can also be purchased from a carbon-neutral electricity provider.

Wind turbines may be used if there is available land for lease and the cost of installing the wind turbines does not exceed the cost of electricity for the turbine’s expected lifetime. Concentrated solar thermal troughs or heliostats would likely not work unless the plant was sited to be built in latitudes south of Pennsylvania because of the high temperatures (~1000°F) that the working fluid is designed to reach (Bengtson, 2010). Photovoltaic arrays will likely not work as a viable source of electricity generation due to the high costs, large land requirement, and relatively low efficiencies – between 12-20% for polycrystalline cells (Miguel A. Contreras, 1999). Nuclear reactors would not be built by the company, but power could easily be purchased from a nuclear energy provider, therefore making the carbon footprint of the plant’s electricity usage effectively zero; this may be the most economical choice for the plant with the current electricity price of nuclear-generated electricity at 1.87 cents per kWh (World Nuclear Association, 2011). If the plant is built near a free-flowing river in a state that allows the installation of a run-of-river...
hydroelectric plant and capital is available for construction and operation of one, it may provide low cost, carbon neutral electricity for as long as the river is running.

**Unit 4: Gasifier with Water Gas Shift Unit**

A gasifier with an adjoining water gas shift unit is one of the busiest units in the plant, with inlet and outlet streams coming from and going to over six different units. The gasifier takes in some organic feedstock and reacts it with oxygen and steam at high temperatures to convert the solid organic mass into carbon monoxide, carbon dioxide, and hydrogen gas. The desired products are carbon monoxide and hydrogen gas, commonly referred to as synthesis gas. The resultant synthesis gas can be used to synthesize many straight chain organic fuels, but the CTL plant is most interested in utilizing the $\text{H}_2(\text{g})$ for hydroprocessing.

The feedstock to the gasifier is comprised of crushed coal, unextracted coal from the solvent extraction step, and algae biomass, which will be discussed further in the following subsection. The C:H ratio is impossible to determine without knowing the exact blend of coal or strain of alga that will be used in the process. Work is currently being conducted on the optimal coal blend and algae strain, with Kentucky bituminous coal and *Chlorella vulgaris* alga residing as the current favorites. No hard data on the exact ratio of $\text{H}_2(\text{g})$ produced from coal to $\text{H}_2(\text{g})$ produced from algae biomass will be available until all the specific coal blend and alga strain is decided upon. Regardless of the blend, the reaction is essentially the same, as shown in Equation 2-2.

$$2\text{CH} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{CO}_2 + 2\text{H}_2$$

where the C:H ratio is of no real importance and is just used as a placeholder in the equation to demonstrate the chemical reaction. The resultant $\text{H}_2(\text{g})$ will then be sent to an $\text{H}_2(\text{g})$ pool to be
used for hydroprocessing needs in the plant. The CO$_2(g)$ will be fed to the algal photo bioreactor, which will be discussed in the next subsection. The CO$_{(g)}$ will be sent to the water gas shift unit with steam.

The water gas shift unit holds four compounds in equilibrium, as shown in Equation 3-8 and explained in detail in the “CO$_2$ electrolysis” subsection of Chapter 3. In short, the equilibrium is driven by an equal amount of moles of reactants and products in the reactor, comprising of carbon monoxide and water on one side, and carbon dioxide and hydrogen on the other. The removal of any amount of any reagent will cause a shift in species from the more populated side to the less populated side. This phenomenon, termed Le Chatelier’s Principle, will aid in the production of H$_2(g)$ by the addition of CO$_{(g)}$ from the gasifier and the extraction of CO$_2(g)$ for use in the algal photobioreactor (YT Kim, 2009; ED Park, 2009).

**Unit 5: Algal Photobioreactor**

Algal photobioreactors are a natural way of CO$_2(g)$ utilization that produces valuable byproducts in the form of algal biomass and oils. The two most common types of photobioreactors are tubular and open pond reactors (Christina Gonzalez-Fernandez, 2010). There are advantages and drawbacks to both reactor types, with the former being best in cooler climates and the latter being best in warmer climates. Algae require CO$_2(g)$, sunlight, and nitrogen in order to grow in a photobioreactor, all of which can be controlled by the operator. Due to the uncertainty in algae strain, parameter optimization (i.e., CO$_2(g)$ feed rate, N$_2(g)$ feed rate, solar irradiance) has not been studied. Nitrogen can be taken out of the air and converted to nitrates in an aerobic reactor. It has been shown that nitrogen is the limiting nutrient in many algae-growing operations, and tubular
reactors have a higher nitrogen uptake rate than do open pond reactors because the former are enclosed, almost forcing the nitrogen into the algae (Christina Gonzalez-Fernandez, 2010). The open pond reactors also showed and decreased rate of $\text{CO}_2(\text{g})$, actually resulting in fugitive emissions. As a result of these findings, a tubular photobioreactor is recommended for any algae operations in the CTL plant.

Fully-grown algae can be either physically pressed or reacted with hexane to strip out the resultant oils (Oilgae, 2011). The resultant oil is run through the fractional distillation column and blended with the coal-derived middle distillates. The resultant biomass is sent to the gasifier as an organic feedstock for $\text{H}_2(\text{g})$ production. In accordance with the American Power Act, any $\text{CO}_2(\text{g})$ produced in this process is not counted toward the CTL plant’s overall carbon footprint because any biomass-derived emissions are counted as carbon-neutral due to their life cycle emissions (Greene, 2010). This leads to the algal photobioreactor not only being a $\text{CO}_2(\text{g})$ sink, but a carbon-neutral energy and $\text{H}_2(\text{g})$ source for other plant operations, potentially offsetting high-emissions coal gasification. This waste stream utilization and byproduct generation is the goal of environmentally conscious engineering and the future of efficient plant design.

**Overall Process Flow**

The combination of the previous auxiliary units with the CoalStar Green backbone leads to the overall process flow in the plant. There are some inputs that are missing (e.g. nitrate feedstock to algal photobioreactor, heat into gasifier, heat into fractionation column, etc.), but the main components are represented in Figure 2-3.
The main idea behind the overall process flow is to minimize waste streams while converting all waste streams into sellable commodities. The most obvious case of this is the conversion of \( \text{H}_2\text{S} \) into elemental sulfur, which turns a volatile health hazard into a profitable byproduct (Ober, 1997). There are other, less obvious waste streams that are helping generate profit, such as the utilization of algal biomass and algal oil for gasification and middle distillate fractionation, respectively. The algal biomass could easily be discarded, but the utilization of it as a gasification feedstock limits not only the amount of coal that needs to be purchased, but also
reduces the overall carbon footprint of the plant. The oil from the algae, if the algae are of an appropriate strain, would be a perfect blending agent for the coal-derived middle distillates separated out in the fractional distillation column.

All of the auxiliary units and their benefits have been discussed in detail in the preceding subsections of this thesis. The overall process flow shown in Figure 2-3 should serve as a visual aid in helping internalize the concepts expanded upon above. However, the auxiliary units shown in the figure above are not the only units that may, or even should, be used. There are alternative auxiliary units that may serve as either compliments or substitutes to any of primary auxiliary units expanded upon above, given specific operating conditions and evolving plant goals. These alternative auxiliary units and in what capacity they are being used can be found on Massachusetts Institute of Technology’s Carbon Capture and Sequestration Technologies website at sequestration.mit.edu. This list is not comprehensive, as the field is ever growing and new laboratory techniques are being devised, but it is a good look at practical projects and their performance.
Chapter 3

High Temperature H$_2$O Electrolysis in a SOEC

Introduction

Hydrogen production is an area of growing research due to America’s reemerging environmental conscious. Hydrogen is not only an important reactant in aromatic saturation and sulfur removal, but a desirable fuel because it is both an effective energy carrier as well as a clean-burning fuel with minimal environmental impact. However, H$_2$ does not occur naturally, so it must be generated from other sources (B Alexander, 2010). Electrolytic hydrogen production depends on system temperature, feed stream flow rates, applied overpotential, and applied current, among other parameters (CH Hamann, 1998; Labarbera, 2009). Hence, many of these parameters need be held constant in order to obtain a definitive relationship between a single variable and its relation to hydrogen production. The current method for H$_2$ generation is steam reforming of methane, but this method relies on the drilling and extraction of a fossil fuel, which is far from ideal. It is also important to note that the H$_2$ produced in steam reforming contains trace levels of CO, which makes the fuel unsuitable for use in an H$_2$-powered fuel cell (Molburg 2004).

Solid oxide electrolysis splits water into hydrogen and oxygen via a series of reactions and transports (CH Hamann, 1998; P Stuart, 2008; Z Zhan, 2010). This is not unlike traditional proton exchange membrane (PEM) electrolytic cells in the sense that a solid oxide electrolytic cell (SOEC) draws a current from an external source while applying an overpotential (CH Hamann, 1998). However, SOEC holds a significant advantage over
traditional electrolyzers; the electrode in an SOEC is a ceramic yttria-stabilized zirconia (YSZ) that is able to withstand extremely hot temperatures. This ceramic electrode allows the cell to operate at temperatures from 600 °C up to greater than 1200 °C; these high temperatures minimize kinetic losses and increase the overall efficiency of the process when compared to a traditional electrolyzer (CH Hamann, 1998). It has been shown that variances in temperature, current density, and humidity do not adversely affect the cell; the only aspect that negatively affects the durability of a cell is the impurities present in the inlet gas stream (A Brisse, 2008; SD Ebbesen, Exceptional Durability of Solid Oxide Cells, 2010).

The aim of this study is to examine the temperature dependence of H₂ production in a SOEC. The current hypothesis proposes that an increase in system operating temperature will directly correlate to an increased rate in hydrogen production. Theoretically, the cell should generate hydrogen at a faster rate when the cell is operating at a higher temperature due to the decrease in kinetic losses and a decrease in ionic resistivity of the YSZ membrane. There are three main losses in electrochemical processes: mass transport, ionic transport, and kinetics (CH Hamann, 1998). Changing the temperature of a system should not significantly change the mass transport but it should affect ionic transport and kinetic efficiencies. A higher temperature means that a system has a higher internal kinetic energy (RH Perry, 1984). If a system has a higher internal kinetic energy, the odds of chemical reactions taking place increases in accordance with the Arrhenius equation, illustrated in Equation 3-1.

\[
\text{Equation 3-1: } k = Ae^{-\frac{E_a}{RT}}
\]
where \( k \) is the rate constant, \( A \) is the pre-exponential factor for a specific reaction, \( E_a \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the temperature (RH Perry, 1984). From this equation, it is clear that an increase in temperature increases the magnitude of the rate constant, resulting in a faster rate of hydrogen generation. If the hypothesis is correct in assuming that kinetics will be negligible in terms of electrochemical efficiency losses, the rate-limiting step lies in either mass transport, ionic transport, or a combination of the two. Mass transport is dictated by how quickly a substance (e.g., water) can adsorb and desorb from the electron double layer (EDL) interface. Ionic transport is dictated by how quickly ions can be transported through the cell itself (CH Hamann, 1998). Equations 3-2 and 3-3 illustrate the electrochemical reactions that take place in the system.

Equation 3-2: \[ 2O_o + H_2O \rightarrow 2OH_o + \frac{1}{2} O_2 + 2e^- \] (anode)

Equation 3-3: \[ 2OH_o + 2e^- \rightarrow H_2 + 2O_o \] (cathode)

These reactions help govern mass transport and ionic transport. The extent to which each reaction is carried out is governed by the forward rate constant expressed in Equation 1, which will prohibit the system from achieving 100% efficiency. The above reactions are written in Kroger Vink notation to illustrate the electron-hole pairs that are forming and/or resolving. The flow of compounds relative to various areas of the system can be seen in Figure 3-3.

This project is a section of a larger coal-to-liquids (CTL) plant project. The overall goal is to design a zero-emission CTL plant that converts coal into middle distillate fuel. These plants use a solvent to strip hydrocarbon chains and aromatics out of crushed coal, which need to be extensively hydrotreated and hydrogenated. In order to clean the hydrocarbons
into a usable middle distillate, 30,000,000 ft$^3$ of hydrogen will be used every day. In addition to investigating the temperature dependence of H$_2$ production in a SOEC, the success of these tests will help determine if any further research into SOEC H$_2$ production is a worthwhile task.

**Methodology**

Prior to any testing, the cell needs to be prepared. The prepared cell has a YSZ base electrolyte with a Ni-YSZ cathode and a lanthanum strontium manganite (LSM) anode. The YSZ electrolyte is used because it allows the transport of oxygen anions while withstanding extreme temperatures. The Ni is used in the cathode because the metal allows for the conduction of current and the electrochemical reduction of H$_2$O vapor to H$_2$ gas and oxygen anions. The LSM is used because it can conduct oxygen anions and electrons as well as oxidize the oxygen anions to O$_2$ gas. NextCell Fuel Cell Materials produced this cell. In order to allow for current to flow through the cell, a gold lead was cut and placed on the cathode. The gold lead was connected to the cathode via silver paste. Gold leads and silver paste were used for their relatively similar and low resistivity. The resultant cell was placed on an alumina block and slid into an oven at 100 °C in order to dry the silver paste.

Next, an alumina support tube was fastened to a ring stand. An alumina paste was used to attach the prepared cell to the support tube, cathode down. It is important to ensure a good fit, but one must leave room for growth because YSZ and alumina do not have the same coefficients of thermal expansion (RH Perry, 1984). A gold lead was placed on the anode and connected via silver paste. The end of the support tube with the attached cell was
placed into a furnace at 100 °C for thirty minutes to remove volatiles. The dried column was taken out of the furnace and a final portion of cement was applied. The column was left to dry at room temperature for two hours. The column was placed in a furnace at 93 °C to cure the alumina paste. After the two hours had expired, the furnace temperature was increased to 260 °C for two hours. The column was removed from the furnace and allowed to cool. After cooling, the gold leads were attached to silver wires; gold wires would be better because there would be no resistivity differences between the leads and the wires, but there were fiscal constraints. The silver wires were attached to the potentiostat. The assembled system was first heated up under H₂. This is required to reduce the cathode from NiO to Ni. Once the system was up to temperature, the open circuit potential (OCP) was measured. A voltage sweep was then performed to ensure that the cell was assembled correctly. Also, the voltage sweeps were carried out at an intentionally slow speed to obtain the steady state current voltage relationship.

After the cell was determined to be acceptable and the voltage sweep looked correct, the feedstream was switched over to an inert N₂ feed. Once the system was purged of H₂, the H₂O injection began. The N₂ flow rate was 47 cm³/sec and the H₂O flow rate was 6 microliters/sec. The H₂O flow rate is not continuous; the technology used is a mechanized pump acting on periodic pulses of force to force water into the system. Even though the pump was not continuous, it had a relatively high frequency, so error should be minimal. An overpotential of about 0.98 V was then applied to the cell above the measured open circuit potential of 1.0237 V to turn the solid oxide galvanic cell into a solid oxide electrolytic cell. Voltage sweeps were then performed at temperatures of 700 °C, 800 °C, and 900 °C.
**System Overview**

The system described in the methodology section can be broken up into separate parts. On the macroscopic scale, there is a ceramic tube, a YSZ-based cell, gold leads, silver paste, silver wires, a furnace, a pump, inlet and outlet tubes, a potentiostat, and a thermocouple. These components can be broken up into two groups:

<table>
<thead>
<tr>
<th>Auxiliary Materials:</th>
<th>Cell Materials:</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Furnace</td>
<td>• Gold Lead</td>
</tr>
<tr>
<td>• Thermocouple</td>
<td>• Silver Wire</td>
</tr>
<tr>
<td>• Pump</td>
<td>• Silver Paste</td>
</tr>
<tr>
<td>• Piping</td>
<td>• YSZ Electrolyte Base</td>
</tr>
<tr>
<td>• Potentiostat</td>
<td>• NiO Cathode</td>
</tr>
<tr>
<td>• Ceramic Tube</td>
<td>• LSM Anode</td>
</tr>
</tbody>
</table>

The auxiliary materials listed above can be any brand/type, and it will not have an effect on the outcome of the tests. However, the cell materials need to be of a specific chemical composition to achieve the desired results. As long as an auxiliary material (e.g., tube) serves its desired purpose (e.g., carrying the working fluids with no leak), the system will perform perfectly well. If a cell material (e.g., silver wire) is changed (e.g., to copper wire) the amount of current getting to the electrode will change due to intrinsic material properties (e.g., conductivity). Visual depictions of auxiliary materials and cell materials are shown below in Figures 3-1 and 3-2, respectively.
A further analysis of the auxiliary system components and their purposes is pivotal to a complete understanding of the system. The furnace is a heat source that can either operate via resistor coils or some fuel (e.g., methane). The furnace is essential in the startup operation of a solid oxide system because there is a certain activation energy required for the progression of the chemical reactions that will be occurring inside the system. Conversely, once the cell is operational, the overpotential applied multiplied by the current passed will be lost as waste heat within the SOEC and at high current densities can be greater than the heat of reaction in electrolysis. This project tests the sensitivity of efficiency as a function of temperature, so the furnace is integral. The thermocouple measures the temperature of the system due to the furnace. A type-K thermocouple is used to obtain accurate measurements at high temperatures. The pump is required to feed H₂O into the system. Since H₂O is the substance that is being electrolyzed to liberate H₂, which is the desired product, the pump is an extremely important
apparatus. However, the pump used was not ideal because it operated on a timed mechanical impulse, which does not provide a continuous flow of water. Even though this is not ideal, the impulse frequency was high enough that the results yielded were clean and major trends were easily identified. The piping used in the system was a flexible polymer. The piping is used to provide a casing for any inlet and outlet streams (e.g., H$_2$O in, H$_2$ out), which is essential in maintaining a pure and controlled fluid flow. Essentially any tubing can be used as long as it will not leach or bleed into its inner fluid stream. The potentiostat applies a specific voltage across the cell; this voltage is also known as overpotential, or voltage excess of open circuit potential (OCP). This device is what determines the mode of operation in the cell: galvanic or electrolytic. The potentiostat in this system applied excess voltage, so the cell operates in the electrolytic region, converting electric energy to chemical energy. The final auxiliary component is the ceramic tube. The ceramic tube is the base that the cell sets on. The only properties that the tube needs are a low thermal conductivity and high stability at high temperatures; most ceramic materials can accomplish this, but the ceramic tube used in this project was alumina.

Additionally, a further analysis and explanation of cell properties are essential to the understanding of the system. The gold leads that are seen on top of the cell, seen in Figure 3-2, are important because they directly bring current to the cell. It is important to note that the leads are gold because, as previously stated, different materials have different intrinsic properties; the property of interest in the lead is conductivity. Not only does the conductivity need to be very high in order to realize as few losses as possible, the conductivity of the lead needs to be very similar to the conductivity of the wire to ensure a uniform charge distribution.
Silver wires were used in conjunction with the gold leads because both silver and gold have very similar and low resistivity values. Copper has a lower resistivity than both, but it forms oxides, which decreases the lifetime of the wire. The silver paste was chosen to connect the gold lead to the cell for the same reason that the silver wire was chosen. The paste itself will dry and only silver and a ceramic will be left to hold the gold lead in place on the cell. The YSZ electrolyte base is chosen for two reasons: a high thermal tolerance and its ability to conduct oxygen anions while obstructing flow of protons. Without the YSZ base, the cell would not separate O2 and H2, effectively rendering the process completely ineffectual. Placed upon the YSZ base is a NiO cathode, which will be reduced to pure Ni under the presence of H2 and heat. The Ni acts as a current conductor to deliver electricity from the power supply to the H2O, where it is converted into chemical energy through electrolysis. The other material placed upon the YSZ base is the LSM anode. The LSM has the unique characteristics of being able to conduct both oxygen anions as well as electricity. The cell itself is depicted below in Figure 3-3. The process flow begins with the dotted arrow in the top right, and ends with the solid outlet arrows in the top right and bottom center. The electron flow is being forced by an externally applied overpotential.
To generate a significant rise in current through an electrolysis cell, the potential difference between the anode and the cathode must exceed a certain value, referred to as the decomposition potential (CH Hamann, 1998). In order for the electrolysis cell utilized in this system to perform efficient electrolysis of water, all of the aforementioned materials and processes need to work together seamlessly.

**Results and Discussion**

The system was run once at 700 °C, twice at 800 °C, and twice at 900 °C. The inconsistent number of runs at differing temperatures was due to data consistency/quality and time constraints. There were a few anomalies in the results, but most were due to mechanical or environmental characteristics of the testing system. For example, all small spikes in production can be contributed to the impulse-based injection of water. Another error relates to frequency measurements discussed later in conjunction with the Nyquist plot; there is a natural
frequency of the room that causes the impedance to be critically damped and gives a faulty impedance value; this value was removed from the graph to provide a truer depiction of the system’s impedance. As seen in Figure 5, the run at 700 °C was much more consistent with fewer outliers than any of the runs at 800 °C and 900 °C.

![Figure 3-4: H₂ Production as a function of current at various temperatures, hydrogen production rates are proportional to current, see Equation 3-6](image)

The OCP of the system was measured to be 1.023 V, which can be approximated as 1 on the y-axis of the above figure. At a full polarization curve, like the one seen in Figure 3-4, all energy under the OCP does work in the system and converts H₂O to H₂ and ½ O₂. However, all of the area underneath the curve above the OCP represents energy lost as heat in the system. This means that a smaller slope on a polarization curve provides a higher overall system efficiency.
The main message to take away from Figure 3-4 is that higher temperatures achieve system voltages closer to OCP.

The efficiency of an electrochemical system is often calculated by determining how far above the open circuit potential an electrolytic cell is operating; this excess potential is referred to as overpotential (CH Hamann, 1998). The calculation was carried out by choosing an arbitrary current and calculating relative efficiency of different runs based off the observed potential differences. In an electrolytic cell, all power above the OCP is lost to heat while all the power at the OCP and below does work. The closer to the OCP a cell operates, the greater the efficiency. Equation 3-4 shows how voltage efficiency is calculated, given $V_{oc}$ (OCP) and $V$ (system voltage).

Equation 3-4: $$\varepsilon_v = \frac{V_{oc}}{V}$$

Using Equation 4 above, system efficiency was calculated at 700 °C, 800 °C, and 900 °C using the data in Figure 3-5. The resultant efficiencies are displayed in Figure 3-5. It is clear that as temperature increases, process efficiency also increases. In order to properly optimize a system, the specific losses and how temperature affects them need to be addressed.
A good measure of resistance and losses is area-specific resistance (ASR) (Doctor, 2004). The impedance due to the ionic transfer of the actual cell is first normalized as an intrinsic property by dividing it by the thickness and area of the cell. The reciprocal of the resultant resistivity is then taken to determine the conductivity of the cell. The conductivity was then multiplied by the thickness of the cell to obtain the cell’s ASR, as seen in Equation 3-5.

Equation 3-5: \[ \text{ASR} = \text{Conductivity} \times \text{Area} \]

The ASR for the cell used in this project was calculated to be 0.5208 cm\(^2\)-Ω. The ASR is an important characteristic of a cell because it can help determine specific losses, which leads to a better understanding of the overall system (Doctor, 2004). By multiplying the ASR by current at a specific point, the voltage loss due to ohmic resistances may be determined. For example, the voltage loss due to ohmic resistances at 0.51 amps is 0.2656 V*nm. The voltage loss due
to ohmic resistance is shown in Figure 5 as the difference between the system voltage at a specific current and the OCP. However, this is not the only loss mechanism. In fact, voltage loss due to ohmic resistances is only a portion of a larger type of loss: ion transfer.

There are three main losses in an electrochemical system: mass transfer, ion transfer, and kinetics (CH Hamann, 1998; AJ Bard, 2001). An important characteristic of solid oxide systems is the extreme temperatures at which they are run (often greater than 800 °C). The escalated operating temperature of solid oxide systems greatly decreases the amount of kinetic losses the system suffers.

In the case of the system used in this experiment, the H₂O had to transfer through the inert N₂(g) media to reach the electrode surface region. The transfer from the bulk to the surface caused the system to incur losses due to friction and motion, among other things (CH Hamann, 1998). Once the H₂O made its way to the surface, it was required to adsorb onto the Ni cathode in order to be electrolyzed into H₂ and O⁻². For many chemical reactions, particularly at high overpotentials, the rate-limiting step is often the adsorption and desorption of the material to and from the electrode. Diffusion coefficients in aqueous solution show much lower temperature dependence than standard chemical reaction, increasing only at a rate of 2-3% per kelvin. In short, electrochemical reactions in the adsorption/desorption region show little temperature sensitivity (CH Hamann, 1998). However, it has been shown that electron transfer increases greatly with an increase in temperature (Y Zeng, 1992; G Venturoli, 1993).

Electrochemical losses can also be represented by a Nyquist plot, which is generated by performing electrochemical impedance spectroscopy. The system is tested by varying frequency at a constant temperature. The corresponding values of impedance, both real and the
negative imaginary, are then plotted against each other to determine what percentage of the total cell resistance each individual resistance makes up. The Nyquist plot generated for the data generated in this experiment can be seen below in Figure 3-6.

![Nyquist plot at 900 °C](image)

**Figure 3-6:** Nyquist plot at 900 °C

The first point on the Nyquist plot represents the ionic resistance/impedance of the cell; the actual resistance measured is real impedance. This means that the ionic resistance of the cell itself is about 0.28 Ω. The next region, which is represented by the distance between the first dot and the local minimum between the two semicircles, represents the electron transfer loss. The loss contribution from electron transfer is relatively small due to its temperature dependence. The loss due to electron transfer was measured to be about 0.095 Ω, which is the system’s kinetic loss. The final resistance is due to mass transport. These mass transport losses relate to adsorption/desorption and movement of the compounds through the bulk. The corresponding resistance was measured to be about 0.20 Ω. When all of the resistances are
summed up, it is found that ionic resistances account for 48.7% of losses, electron transfer resistance accounts for 16.5% of losses, and mass transport resistance accounts for 34.8% of losses. These relative contributions can be seen in Figure 3-7.

![Pie Chart: Resistive Loss Contributions](image)

**Figure 3-7: Resistive Loss Contributions**

An important note about the Nyquist plot is that losses occur at different frequencies. Impedance is the measure of resistance present in a cell under alternating current, which will inherently have an operating frequency. As the frequency of the cell approaches zero, the current begins to behave like direct current, as opposed to alternating current. At an infinite frequency, the only resistance realized in the cell is the inner ionic transfer resistances. Electron transport and mass transport losses don’t occur at extremely high frequencies due to the extremely short residence times. As the frequencies decrease, the residence time in a specific applied field due to the current increases, which allows for electron transport, which will inherently have losses (CH Hamann, 1998). The sum of all impedances is commonly
referred to as the internal resistance of the cell; that value multiplied by the square of the current is lost as waste heat within the SOEC (Labarbera, 2009).

All energy not lost is converted to work. The work done by the system is converted directly to chemical energy in the form of H\textsubscript{2} through the splitting of a water molecule. The theoretical amount of H\textsubscript{2} produced in the system at any given time is given by Faraday’s Laws of Electrolysis. These laws can be distilled into Equation 3-6.

Equation 3-6: \[ m = \frac{QM}{Fz} \]

where m is the mass of H\textsubscript{2} liberated, Q is charge (assumed to be the current operated at for one second), M is molar mass of H\textsubscript{2}, F is Faraday’s constant, and z is the valency number of ions (which is two). The mass of the hydrogen generated over a potential sweep of 1 V was calculated using Equation 6 and is shown in Figure 3-8.

**Figure 3-8:** H\textsubscript{2} Production as a function of voltage at various temperatures
As seen in Figure 3-8, theoretical H\textsubscript{2} production increases with system temperature. There are a few outlying points in a few of the plots, but those are due to the impulse-forced injection of water rather than a continuous flow. The variances between the runs are likely due internal system error, but the trends between the two runs at each temperature remains constant. The general trend of the increase in H\textsubscript{2} produced with increasing voltage follows a polynomial distribution, which implies that an increased overpotential will generate H\textsubscript{2} in a nonlinear fashion. A parametric study of heat lost at higher voltages against the rate of H\textsubscript{2} production should be performed to determine what the optimal range of temperature and voltage are in terms of H\textsubscript{2} production if SOEC should ever become a commercial vessel for H\textsubscript{2}.

\textit{CO\textsubscript{2} Electrolysis}

H\textsubscript{2} is used for many applications in industry; two of which are hydrogenating and hydrotreating liquid fuels during petroleum refining. However, many petroleum processes are very energy-intensive and have large quantities of CO\textsubscript{2} emissions. One possible outlet for CO\textsubscript{2} sequestration and use is coelectrolysis of H\textsubscript{2}O with CO\textsubscript{2}. It has been shown that SOEC can be used to reduce both H\textsubscript{2}O and CO\textsubscript{2} to synthesis gas and oxygen, as shown in Equation 3-7 (S Jensen, 2007; G Tao, 2004; SD Ebbesen, Electrolysis of carbon dioxide in Solid Oxide Electrolytic Cells, 2009).
Coelectrolysis of H$_2$O and CO$_2$ is an appealing option because it produces compounds that have multiple applications. H$_2$ can be used for hydroprocessing while CO can be placed in a WGS unit to generate H$_2$ via Le Chatelier’s Principle; the WGS reaction is shown in Equation 3-8 (Q Fu, 2003; YT Kim, 2009; ED Park, 2009).

Equation 3-7: \[ H_2O(g) + CO_2(g) \rightarrow H_2(g) + CO(g) + O_2(g) \]

Equation 3-8: \[ H_2O(g) + CO(g) \leftrightarrow H_2(g) + CO_2(g) \]

O$_2$ can be fed to a gasifier, generating more CO, which could be fed to the WGS reactor to generate more H$_2$. These are all viable options if the ultimate goal of the processes was to produce H$_2$. However, there are many other options given the products generated. The mixture of H$_2$ and CO is also known as synthesis gas because they can be converted into any straight-chain hydrocarbon fuel (Q Zhang, 2004). The chemical process of synthesis gas formation via SOEC can be seen in Figure 3-9. More specifically, it shows the flow of oxygen anions across the YSZ electrolyte, causing the formation of synthesis gas at the upper contact.
(cathode). The above system seems similar based on the molecular flow, but it will likely see different loss contributions from ionic, electron transfer, and mass transfer resistances.

From a thermodynamic point of view, it is prudent to operate endothermic reactions, such as CO₂ electrolysis, at high temperatures because a great deal of the energy required from the reaction can be obtained in the form of high-temperature waste heat from other processes, such as a gasifier; it is also possible to use a water-jacketed gasifier, which would use preheated steam from the gasifier as the feed for the SOEC. Electrolysis in SOECs is performed between 750 and 1000 °C, and can therefore be operated with a lower electricity consumption compared to lower temperature electrolysis operations (SD Ebbesen, Electrolysis of carbon dioxide in Solid Oxide Electrolytic Cells, 2009). It is also important to note that higher temperatures produce more favorable reaction kinetics, as shown in Figure 3-5.

The dissociation of H₂O is an endothermic reaction that has an enthalpy of reaction equal to 286 kJ/mol, which is not much different from the enthalpy of reaction for the dissociation of CO₂, which is equal to 283 kJ/mol (Christopher Graves, 2011). This implies a great deal of energy required to break these strong bonds, and most energy has with it a monetary cost, greenhouse gas cost, or both. However, other high-temperature operations being used in the refinery could be used to provide some of the energy required at little to no added monetary or greenhouse gas cost. Low current density operation of a coelectrolysis cell powered by a constant feed of electricity and heat has been proven to be both economical and durable in the long term (Christopher Graves, 2011). Another option may be to electrolyze CO₂ apart from H₂O, but it has been shown that the ASR of a CO₂ SOEC was actually higher than that of a coelectrolysis cell containing the same amount of CO₂ (Pattaraporn Kim-Lohsoontorn, 2011).
Also, the production of H\textsubscript{2} is a major concern of this plant, so coelectrolysis makes sense not only on a thermodynamic level, but also on a practical level.

The potential to perform coelectrolysis of CO\textsubscript{2} and H\textsubscript{2}O is a real and practical option. Studies have shown that the Ni-YSZ cermet electrode is catalytically active for both CO\textsubscript{2} and CO, which means that commercially available solid oxide fuel cells may be purchased and run with the coelectrolysis feed with no required retrofits or adjustments (Z Zhan, 2010). The most common commercially available solid oxide fuel cell is a planar stack comprised of Ni-YSZ cermet electrodes, which can be run in an electrolytic mode by simply applying an overpotential. These commercially available cells are also completely capable of performing coelectrolysis of CO\textsubscript{2} and H\textsubscript{2}O.

**Conclusions and Suggestions for Future Work**

Temperature has a direct and positive influence on H\textsubscript{2} production in a SOEC. Cells operating at higher temperatures also realize greater voltage efficiencies. Kinetic losses through electron transport are greatly reduced as cell temperature increases. Given the choice, a higher operating temperature in a SOEC will produce more desirable results due to both increased efficiency and H\textsubscript{2} production. Not enough work has been performed in this project to confidently state whether or not SOEC is a viable option for large-scale H\textsubscript{2} electrolysis. SOEC still remains an attractive option for low emission H\textsubscript{2} production, but future work will have to be performed. Future work should include: impedance spectroscopy performed at various temperatures to visually demonstrate the temperature dependence of different loss mechanisms; parametric study of the effects and tradeoffs of using a higher overpotential to
achieve greater H₂ production at the cost of efficiency; and coelectrolysis of H₂O and CO₂ in a SOEC. Coelectrolysis in a SOEC should be a highlight of future work due to the possibility of carbon taxes in the future, which would decrease the overall cost of the system. Also, the government has begun refusing building permission and loans to companies who cannot prove that their refinery designs are minimizing their potential carbon footprint, which helps improve the economic viability of SOEC coelectrolysis. It is important to note that a large scale planar SOEC must be used in order to simulate the type of flow rate that an industrial electrolyzer would likely experience.
Chapter 4

Summary and Closing Comments

The addition of auxiliary units to achieve overall process carbon neutrality is a very real possibility. The biggest hindrance is the lack of economic viability of current CCS technology. Once the overall process flow has been decided upon, each molecule of CO$_2$ can be accounted for in a material balance of the plant. A major consideration in determining which auxiliary units to employ lies within the ability for these auxiliary units to either generate revenue or cut down on operating costs in another area of the plant.

While the aforementioned auxiliary unit additions and process flow optimization are a step in the right direction, there is still a great deal of work that needs to be done. Laboratory-scale research of algae CO$_2$ uptake rates, reagent conversion, quantity of resultant slag from cofiring algal biomass with coal, as well as a host of other facets should be studied to further understand any complimentary or competing effects that may occur. Oftentimes individual processes or actions work perfectly fine in solitude, while having unforeseen and undesired consequences when integrated into a larger process scheme.

Another aspect of designing a carbon-neutral CTL plant is the governmental regulation and subsidization of specific control and process technologies. The regulatory environment not only influences, but also often dictates what type of technology is economically feasible; a prime example of this being Solar Renewable Energy Credits (SRECs). If SRECs are heavily funded and are being traded at a high price (e.g. $600 per MWh), the power supply for the SOEC could possibly consist of entirely photovoltaic panels. On the other hand, if the SRECs
are operating at a very low price (e.g. $100 per MWh), the power supply for the SOEC may be required to consist of at least 50% wind power.

The SOEC research, while basic, was important and conclusive. It is evident that a higher operating temperature and voltage not only produces H₂ at a faster rate, but does so at a higher efficiency. Solid oxide electrolysis is a viable option for H₂ production because of its high efficiency and ease of availability. SOEC can also handle a cofeed of H₂O and CO₂ with no noticeable drop in cell performance, which bodes well for future research. If an industrial scale SOEC can handle a sizeable stream of CO₂, the overall plant footprint would decrease tremendously because the other CO₂ sequestration options are very land intensive.

The business of energy, from extraction to use, changes with the seasons. This requires engineers, managers, and investors alike to remain flexible and vigilant. There may very well exist auxiliary technologies that were not mentioned in Chapter 2 that would fit perfectly into this process flow given a specific regulatory climate or recent breakthrough in a certain aspect of the technology’s operation. This thesis is not meant to be an exhaustive list of all the possibilities, nor is it meant to be a strict set of guidelines by which to determine and design carbon neutral process flow; this thesis is meant to help introduce the concept of carbon neutrality and how it may be applied and implemented in a real world issue.
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WORK, RESEARCH, & RELATED EXPERIENCE
Southwestern Energy Houston, Texas

- Identified areas in need of improvement and developed environmental metrics to help quantifiably identify and rectify lagging areas of business operations (e.g. power profile and associated emissions, JJJJ regulatory statutes applied to compressor stations, life cycle assessment of water usage, etc.).
- Drafted corporate sustainability statement and generated a business plan for further utilization of methane as a transportation fuel via Fischer-Tropsch Synthesis.

Senior Capstone Engineering Design University Park, Pennsylvania
Energy Engineer January 2010 – Present

- Engineered and constructed an electromagnetically enhanced hydrocyclone.
- Received highest honor at The Learning Factory’s Senior Engineering Capstone Design Fair, taking home first place in Best Engineering Design category, presented by Lockheed Martin.

The Pennsylvania State University University Park, Pennsylvania
Teaching Assistant January 2009 – Present

- Graded homework associated with the course EGEE 102: Energy Conservation and Environmental Protection.
- Answered questions posed by students regarding concerns related to assignment completion and clarification of subjects such as insulation (R value), energy usage, energy conversion, and associated emission profiles.

College of EMS: AESEDA St. Ann, Jamaica
Energy Engineer January 2009 – Present

- Aided in designing and building a library and school for mentally and physically handicapped children in Jamaica under the pretense of economic, environmental, agricultural, and energy sustainability.