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JOHN AND WILLIE LEONE FAMILY DEPARTMENT OF ENERGY AND MINERAL
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HYDROGEN PRODUCTION USING THE Cu-Cl THERMOCHEMICAL CYCLE IN A ZERO
EMISSIONS COAL-TO-LIQUIDS PLANT

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ABSTRACT

Coal-to-liquids has the potential to change the nation's energy economy due to its use of coal, a domestic resource. What is even more exciting is that coal-to-liquids has the potential to release zero emissions of CO_2. This possibility is attractive, especially with the reality of climate change and the ever-increasing pressure to produce environmentally friendly technologies, processes, and products in all sectors. This zero-emission coal-to-liquids concept was developed at Penn State. A start-up company, CoalStar, picked up this idea and is in the early planning stages of actually implementing such a plant.

A major concern for CoalStar is the production of hydrogen used for refining purposes in the plant. They are considering using an electrolyzer exclusively powered by clean electricity. Due to its required low electricity input as compared to other thermochemical cycles, the Cu-Cl thermochemical cycle has the potential to fill the need for electrolytically produced hydrogen in this coal-to-liquids plant. Much research is currently being performed on this cycle; this thesis examines a few parameters of the system and their effects on hydrogen production rate. These parameters are: the type of membrane used, the HCl concentration of the anolyte, and membrane degradation due to time. Furthermore, the actual feasibility of implementing such a cycle into CoalStar's hypothetical plant is examined.

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Chapter 1

Current Coal-to-Liquids Technology
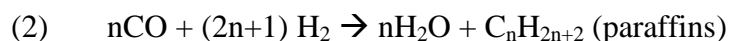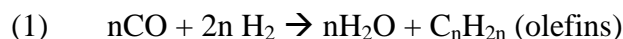
Importance of Coal-to-Liquids

In 2009, the United States consumed about 18.7 million barrels of oil per day (Clean Energy Jobs and Oil Company Accountability Act, 2010). Over fifty percent of this was imported and the transportation sector used about sixty percent (Ramage, 2009). Reliance on foreign oil makes the United States' energy security shaky at best, especially considering the political strife and unrest present in many of these countries. Also, the extraction and refining of petroleum contributes to the ever-growing problem of global warming. The burning of petroleum products comprises one-third of the total carbon dioxide emissions in the United States (Ramage, 2009). Furthermore, carbon-based fossil fuel resources make up about eighty percent of global primary energy (Hermann, 2005). The process of converting coal to a liquid fuel could be the answer lessening the nation's dependence on imported oil. A coal-to-liquids plant would use a domestic resource, coal, and turn it into a usable liquid fuel through much refining. Integrating this coal-to-liquids market into our energy infrastructure would not only create thousands of domestic jobs, but would also significantly lessen our dependence on foreign oil.

Direct vs. Indirect Liquefaction

The purpose of a coal-to-liquids process is to convert coal to usable, liquid fuel. Coal can be processed to fuel via either direct or indirect liquefaction. The process of direct coal liquefaction involves adding H_2 in the gas form to a slurry-like mixture of coal and coal-derived liquids in the presence of catalysts to yield synthetic crude oil. Significant amounts of hydrogen are needed to make the synthetic crude oil, as stated above, and to remove impurities in the form of H_2O, H_2S,

and NH_3. The hydrogen is either obtained through steam reforming of methane or coal gasification. This process is performed under high temperatures and pressures, around 400° C and 1500-3000 psi. Butane, propane, and partially upgraded gasoline- and diesel-like products result from the crude oil through distillation. However, these products need further refining at conventional refineries. Currently, direct coal liquefaction technology is not commercially available in the United States. The largest DCL process in the United States is a Process Development Unit at the Hydrocarbon Technology, Inc. R&D facility that uses 3 tons of coal per day (Williams, 2003).

The process of indirect liquefaction involves first gasifying coal to make syngas, or CO and H_2. This syngas is most commonly used in three processes, each process yielding different products. The first process is called Fischer-Tropsch, or F-T synthesis. Through the F-T synthesis, the syngas is converted to liquid fuels by way of a catalyst. The water-gas shift reaction, or CO + $H_2O \rightarrow H_2 + CO_2$, is used to adjust the H_2/CO ratio of the synthesis gas to the optimum value for the F-T reactions. The following two reactions summarize the basic reactions that can take place during F-T synthesis:

(1) $nCO + 2n\ H_2 \rightarrow nH_2O + C_nH_{2n}$ (olefins)

(2) $nCO + (2n+1)\ H_2 \rightarrow nH_2O + C_nH_{2n+2}$ (paraffins)

The specific yield of various products depends on the types of catalysts used and also on operating conditions, such as temperature, pressure, and residence time. The syngas produced from the initial coal gasification can also be used to make methanol through the following reactions:

(3) $CO + H_2O \rightarrow CO_2 + H_2$ (water gas shift)

(4) $CO + 2H_2 \rightarrow CH_3OH$ (methanol synthesis)
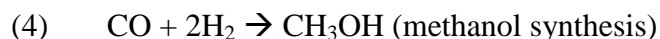
The MeOH can be further refined to produce gasoline through the Mobil process. Alternatively, the MeOH could be used as straight fuel. It can also be converted to dimethyl ether via MeOH dehydration, the third and final commonly used process. The methanol synthesized in reaction (4) above is converted to DME via the following reaction:

(5) $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$.
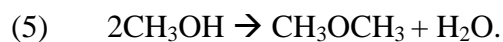
Presently, the NKK Corporation in Japan and Air Products and Chemicals are working towards a single-step process for industrial-scale DME production from coal-derived syngas by way of slurry-phase reactors (Williams, 2003).

The most well-known coal-to-liquids plant is the SASOL plant in South Africa. This plant utilizes indirect liquefaction and has produced more than 700 million barrels of synthetic fuels from coal since the early 1980s and 85% of the coal used in South Africa is used as a feedstock to make synthetic fuels or electricity. The downsides to these plants, however, are still keeping them from worldwide commercial success. If the CO_2 produced as a by-product of the water-gas shift reaction, as discussed above, is *not* sequestered, a coal-to-liquids plant will release approximately twice the amount of CO_2 emitted by conventional hydrocarbons (American Association for the Advancement of Science, 2009). The Sasol plant is the largest point source of CO_2 on the planet.

Both direct and indirect methods of coal-to-liquids processing produce CO_2 as an unwanted by-product. This CO_2 is formed due to the need for hydrogen, a critical component to any coal-to-liquids plant. There is a need for a coal-to-liquids process that is both efficient and produces little to no CO_2. Penn State has formulated such a process. A company called CoalStar is attempting to raise capital to build the first plant using this method. The plant would convert coal to liquid fuels through solvent extraction, rather than direct or indirect liquefaction. Also, this

unique coal-to-liquids process would yield close to zero CO_2 emissions due to its use of electrolysis for hydrogen production and an algae photobioreactor for CO_2 capture and conversion.

Chapter 2

CoalStar's Hypothetical Coal-to-Liquids Plant

Overview

A basic schematic of CoalStar's proposed coal-to-liquids plant can be seen below.
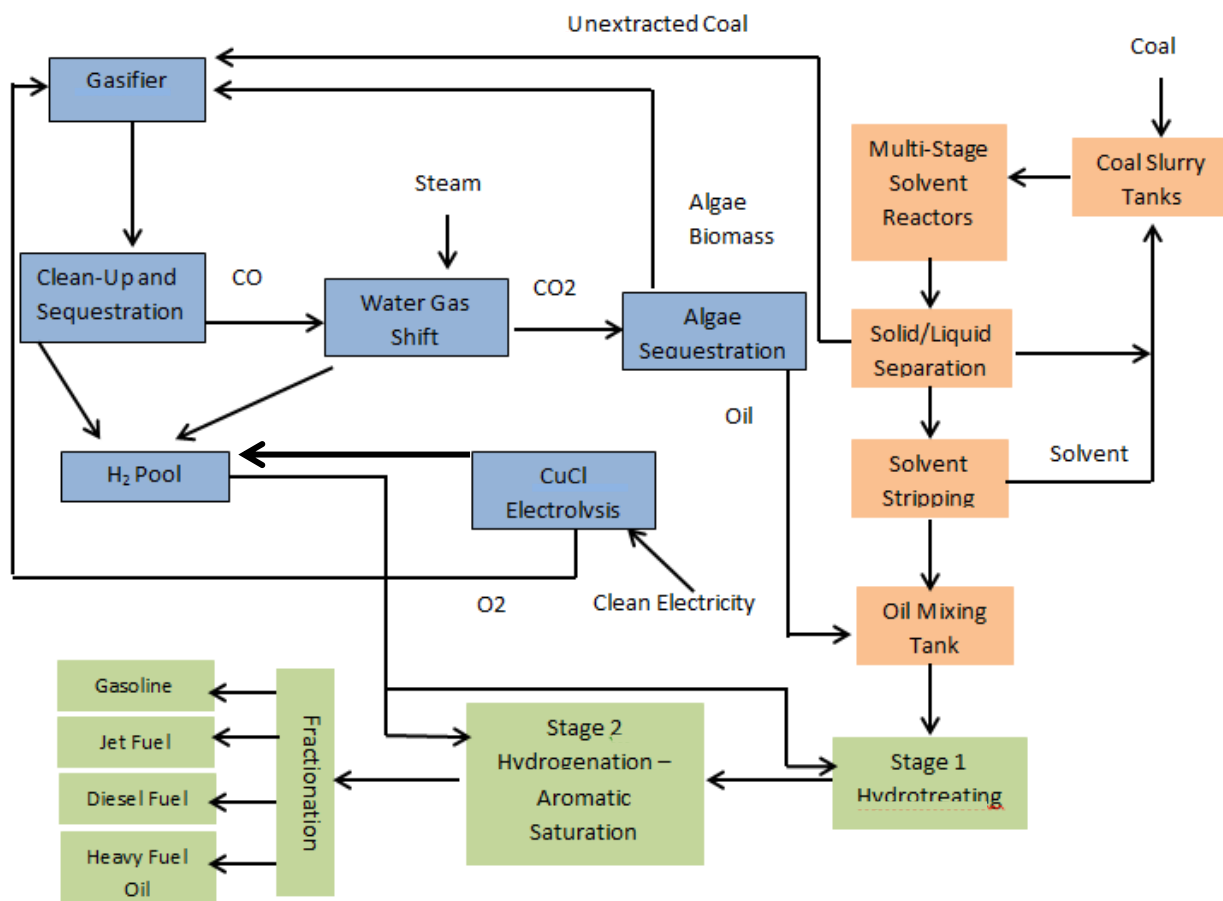
Figure 2-1: Schematic of CoalStar's Coal-to-Liquids Plant

CoalStar's hypothetical plant aims to be completely carbon neutral through the use of a few unique technologies. One of these is the algae photobioreactor unit which takes in the any produced CO_2. The algae in the photobioreactor use CO_2 and sunlight to grow. The algae can

then be pressed for their oils and the "used" algae can be sent to the gasifier as "biomass" to be co-fired with coal. Another unique feature of this design is the electrolyzer which will be powered by clean electricity. The purpose of this electrolyzer is to provide hydrogen to the rest of the plant for refining purposes.

Electricity Sources for Electrolyzer

The electricity source for this electrolyzer could be provided by a slew of sources such as: wind turbines, concentrated solar thermal power, or a hydroelectric station. The source of this electricity depends largely on the location of the plant. If the plant is near a river, perhaps a hydroelectric station is the best fit. A generalized price for constructing a hydroelectric plant is about $45.80 per kW. This value is based on the price of the Chief Joseph Dam in Washington (Hydrokinetic News, 2010). The frequency and velocity of the wind will determine if turbines would be most efficient. Alternatively, electricity produced from wind turbines could be purchased at $0.05/kWh. Concentrated solar thermal parabolic troughs largely depend on the intermittency and intensity of sunlight. Furthermore, this technology is extremely expensive to implement, costing about $1,800 per kW (Price, 1999). Perhaps a combination of multiple sources of energy could be the most effective solution.

Sub-processes of Plant

The overall CoalStar process can be divided into three sub-processes: solvent extraction, coal gasification, and refining. In *solvent extraction*, coal is broken down with petroleum derived light cycle oil solvent, which is a mixture of many two- and three- ring aromatic compounds and their alkylated derivatives; this slurry moves onto multi-stage solvent reactors and a solid/liquid separation unit. The liquid stream from this separation unit has a lot of solvent since the

extraction process is run with a large excess of solvent. Therefore, the solvent from this stream is stripped off by distillation or flashing so it can be recycled back to the reactors. The ideal operating conditions of extraction are 360^0C, a 10:1 solvent:coal ratio, and a 1 hour residence time. At this point, a portion, anywhere from forty to seventy percent, of the coal has turned into a crude oil type of substance; any "leftover" coal and ash is separated out and sent to the gasifier. The preferred method for this separation is pressure filtration. The coal extract is then sent to an oil mixing tank where it then moves onto two stages of hydrotreating in order to turn it into a usable fuel.

The second sub-process within the plant is *coal/biomass gasification.* The "leftover" coal and ash from solid/liquid separation in the s*olvent extraction* process is fed to a gasifier. It is combusted with oxygen that comes from an electrolyzer powered by clean electricity. Additionally, steam will be provided to the gasifier as well as algal biomass coming from the algae photobioreactor. The overall gasification reaction will be as follows:

$CH_x + H_2O \rightarrow (1 + 0.5x)H_2 + nCO$
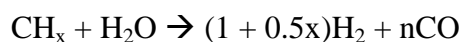
The raw syngas from the gasifier will be treated for removal of ammonia, particulate, H_2S, and any tars. The cleaned syngas will be sent to a water gas shift reactor, where it reacts with steam to produce CO_2 and H_2. After the shift unit, the CO_2 and H_2 are separated. The produced CO_2 will be fed to the algae photobioreactor. Algae photobioreactors need four components in order to work properly: water, algae, CO_2, and sunlight. The algae use CO_2, water, and sunlight to grow (Cultivation of Algae in Photobioreactor). About 50% of their weight is oil, and this oil can ultimately be "squeezed" out of the algae by way of a press (Walton, 2008). This oil can be

processed and refined into diesel fuel. The algae, after being pressed of its oils, can be sent to the gasifier to be co-fired with the incoming coal.

The third and final sub-process is *refining*. The refining portion of the plant will upgrade the coal extract produced in the solvent extraction portion of the process. The first step will be hydrotreating in order to remove H_2S. The second step will then be hydrogenation to saturate aromatic rings to make cycloalkanes. The third and final step is fractionation which will produce gasoline, jet fuel, diesel, and heavy fuel oil. The first two processes, hydrotreating and hydrogenation, require a great deal of hydrogen. One barrel of produced fuel requires roughly 3,000 SCF of H_2. With the 10,000 BPD targeted throughput, this equates to about 30,000,000 SCF of H_2 per day. The means of producing hydrogen and how much hydrogen can be produced is a major concern for CoalStar. In a typical coal-to-liquids plant, the majority of CO_2 stems from coal gasification in order to produce hydrogen. Therefore, CoalStar Green is looking to produce hydrogen by means of electrolysis. Not only should the electrolyzer use clean electricity, it also will be the primary source of hydrogen. A Cu-Cl electrolysis unit could meet this requirement and a study on this type of electrolysis is discussed in *Chapter 3*.

Chapter 3

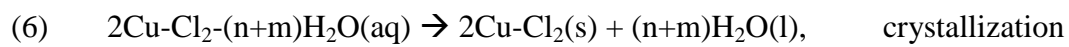## Cu-Cl Electrolysis for Hydrogen Production

Objectives

The purpose of this paper is to illustrate one possible method of electrolytically producing hydrogen using only green electricity. Rudimentary research was performed on Cu-Cl electrolysis for hydrogen production in the Cu-Cl thermochemical cycle at The Pennsylvania State University. Currently, ninety-six percent of hydrogen production in the United States is through the use of nonrenewable sources such as steam reforming of methane or coal gasification (Balashov, 2011). Due to its required low electricity input as compared to other thermochemical cycles, the Cu-Cl thermochemical cycle has the potential to fill the need for electrolytically produced hydrogen in this coal-to-liquids plant.

The system used for the study was the Electrochemical Technology Program's Cu-Cl electrolyzer at the EMS Energy Institute located in University Park, PA. This paper will focus on the performed research on the electrolysis step in the Cu-Cl thermochemical cycle. The three governing reactions of the overall thermochemical cycle are:

(1) $2Cu\text{-}Cl\text{-}nH_2O(aq) + 2HCl\text{-}mH_2O(aq) \rightarrow 2Cu\text{-}Cl_2\text{-}(n+m)H_2O(aq) + H_2(g)$,

$$\text{electrolysis } (25\text{-}80^oC)$$

(2) $2Cu\text{-}Cl_2(s) + H_2O(g) \rightarrow Cu\text{-}Cl_2\text{-}CuO(s) + 2HCl(g)$, hydrolysis $(310\text{-}375^oC)$

(3) $Cu\text{-}Cl_2\text{-}CuO(s) \rightarrow 2Cu\text{-}Cl(s) + (1/2)O_s(g)$, decomposition $(450\text{-}530^oC)$

Four other supporting reactions are required in the system:

(4) $H_2O(l) \rightarrow H_2O(g)$, evaporation

(5) $2Cu\text{-}Cl(s) + nH_2O(l) \rightarrow 2Cu\text{-}Cl\text{-}nH_2O(aq)$, dissolution

(6) $2Cu-Cl_2-(n+m)H_2O(aq) \rightarrow 2Cu-Cl_2(s) + (n+m)H_2O(l)$,   crystallization

(7) $2HCl(g) + mH_2O(l) \rightarrow 2HCl-mH_2O(aq)$,   dissolution

Thermochemical water decomposition via the Cu-Cl thermochemical cycle is a hot topic in the world of renewable hydrogen production. However, most of the research has not extended beyond theoretical calculations (G. Naterer, 2008). The scope of this Cu-Cl thermochemical cycle represents emerging experimental work in this field. The objective of this study is three-fold. The research performed was only concerned with reaction (1), the electrolysis reaction. First, the actual hydrogen production rate is compared against the theoretical production rate as determined by Faraday's Law. Second, the effect of the anolyte concentration on the rate of hydrogen production is studied. Third, this study looks into improving system durability with different membranes. The purpose of this study also extends beyond these three narrow objectives and seeks to determine the probability of using this cycle in CoalStar's CTL plant.

Overview of System

The system used was the Electrochemical Technology Program's Cu-Cl electrolyzer at the EMS Energy Institute located in University Park, PA. A very basic overview of the system and related reactions can be seen in *Figure 3-1*. This schematic represents the electrolysis step in the overall Cu-Cl thermochemical cycle.
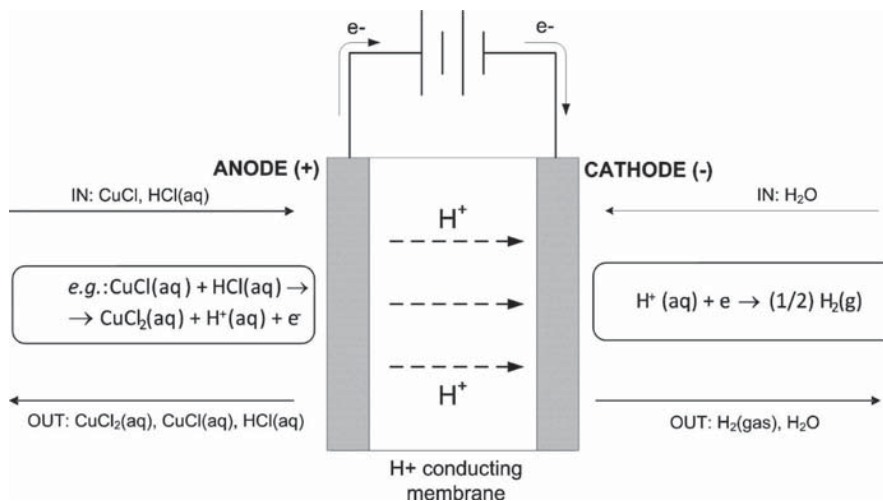
Figure 3-1: Overview of the System (G. Naterer, 2008)

Once the system is warmed up and running and there is a recordable current density, the production of hydrogen will begin. Production of hydrogen is caused by an external applied voltage from a DC power supply, as seen in *Figure A-2* in Appendix A. The hydrogen gas produced is passed through a tube leading to a tank that is partially filled with distilled water. This tank sits on a scale, as can be seen in *Figure A-1* in Appendix A. The reading on the scale can be periodically recorded to determine the rate of hydrogen production.

The anodic inputs are Cu-Cl (s) dissolved in an HCl aqueous solution. The cathodic input is pure water. When a voltage is applied across the cell, Cu(I), which is present in the Cu-Cl (aq) solution, is oxidized to Cu(II), as it is present in $Cu-Cl_2$ on the right side of the reaction. This increase in oxidation state indicates a release of an electron. The HCl in aqueous solution produces protons and chlorine anions; these protons permeate through the membrane where they are electrochemically reduced to hydrogen gas by the electrons that travel around the circuit from the anode.

One of the drawbacks of the electrolyzer system is that the Cu(I) and Cu(II) complexes present on the anode side can sometimes permeate through the membrane, especially when it starts to degrade, where they will be reduced to copper on the cathode side. A schematic of this process is seen in *Figure 3-2*.
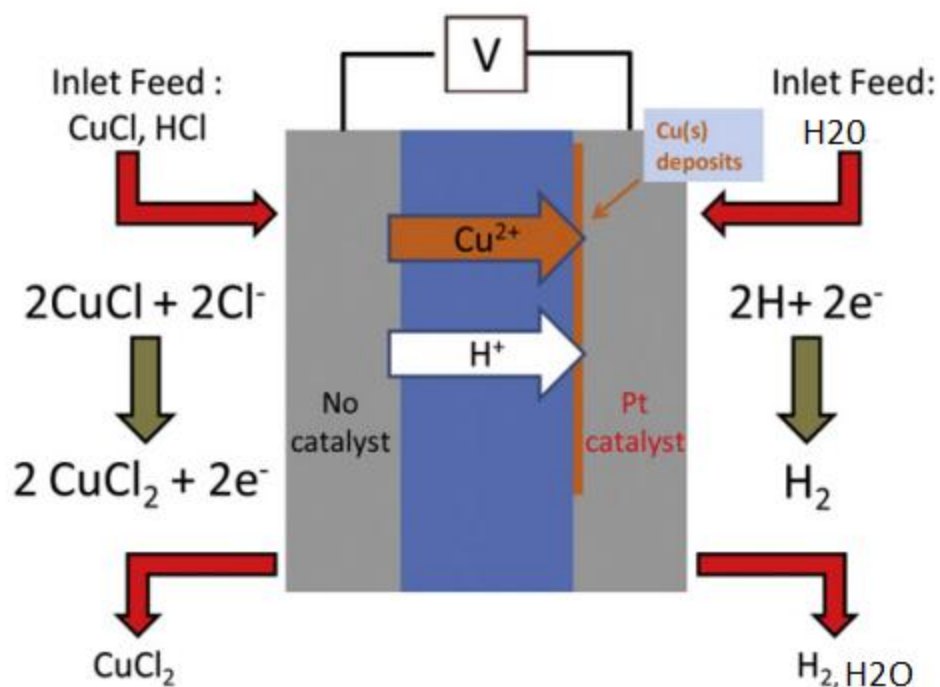
Figure 3-2: Copper complexes (G. Naterer, 2008)

This copper build up tends to harm the membranes and decrease the activity of the Pt catalyst and, consequently, reduces the hydrogen production rate, as will be discussed more in *Results* (Naterer G. S., 2010).

Methodology

Before collecting any data, the system was prepared. The temperature of the system for experimental purposes was kept at 80° C after warming up for about 3 hours. The cell was built with a 5 cm^2 proton exchange membrane. Nafion-based HYDRion membrane electrode

assemblies (MEAs) from Ion Power Inc. were used in the cell. Two carbon paper diffusion layers were placed on each side of the working membrane. These membranes ensured good electrical contact with the two graphite bipolar plates. These plates had serpentine channels for solution supply and removal of the products of the electrolysis reaction. With the cell in place, the system was evacuated with a vacuum pump and then purged with distilled water. This helped to remove any air left in the diffusion layers and to give a better access of the reagents to the electrodes (Balashov, 2011).

In order to test varying the concentration of the anolyte, the membrane type was held constant. The anolyte concentration was held constant to test the two different membranes. The first step to running a test at one of the HCl concentrations was performing a polarization curve. The voltage was changed on the power supply, and, after allowing stabilization for about 30 seconds, the resulting current was recorded. The starting voltage was 0.1 V and was stepped up to 0.985V and then stepped back down to 0.1 V. This polarization curve was run to check that the system was working properly and that it correctly responded to changes in the applied voltage. After the polarization curve was completed, hydrogen production was measured. The system was set to the lowest voltage on the polarization curve, or 0.1 V. The resulting current was recorded. The highest rates were seen at the highest voltage of 0.985 V. The produced hydrogen was siphoned to a tub of water sitting on a scale, as can be seen in *Figure A-1* in Appendix A. To read the mass of hydrogen produced, the scale was zeroed; the resulting readings on the scale were indicative of the incoming hydrogen gas. The mass of the total hydrogen produced was recorded after 6 minutes. This was repeated for each voltage and corresponding current density at each concentration, 3.3 M HCl and 10 M HCl. At the 3.3 M HCl concentration, this process was performed at different system run times as well. Run times of 0, 4, and 12 hours were tested.

Results and Discussion

Comparison of Actual vs. Theoretical Hydrogen Production Rate

Before comparing the hydrogen production rates between the two anolyte solution concentrations, the actual amount of hydrogen produced was compared to the theoretical amount of hydrogen produced at *each* concentration. The graphs below show the actual hydrogen production rate as a function of current density versus the theoretical hydrogen production rate for both 3.3 M and the 10 M HCl condition using the Nafion membrane. Nafion is a sulfonated tetrafluorethylene copolymer (Son, 2009) made by DuPont (Ye, 2010). *Figure 3-3* displays the 3.3 M HCl data and the 10.0 M HCl data are shown in *Figure 3-4*.
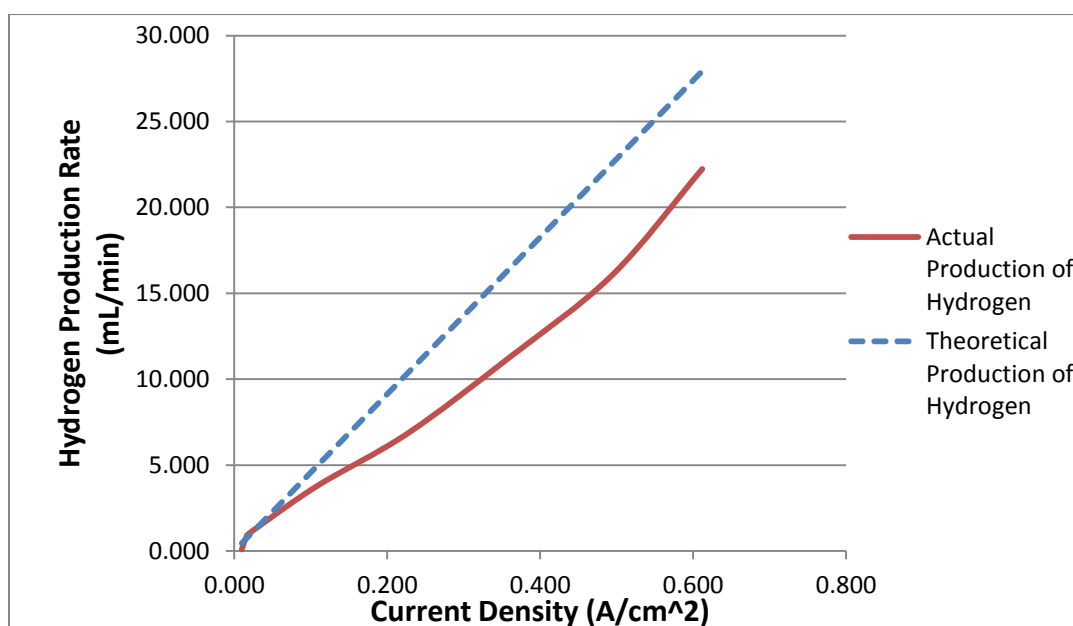
Figure 3- 3: 3 M HCl Theoretical vs. Actual
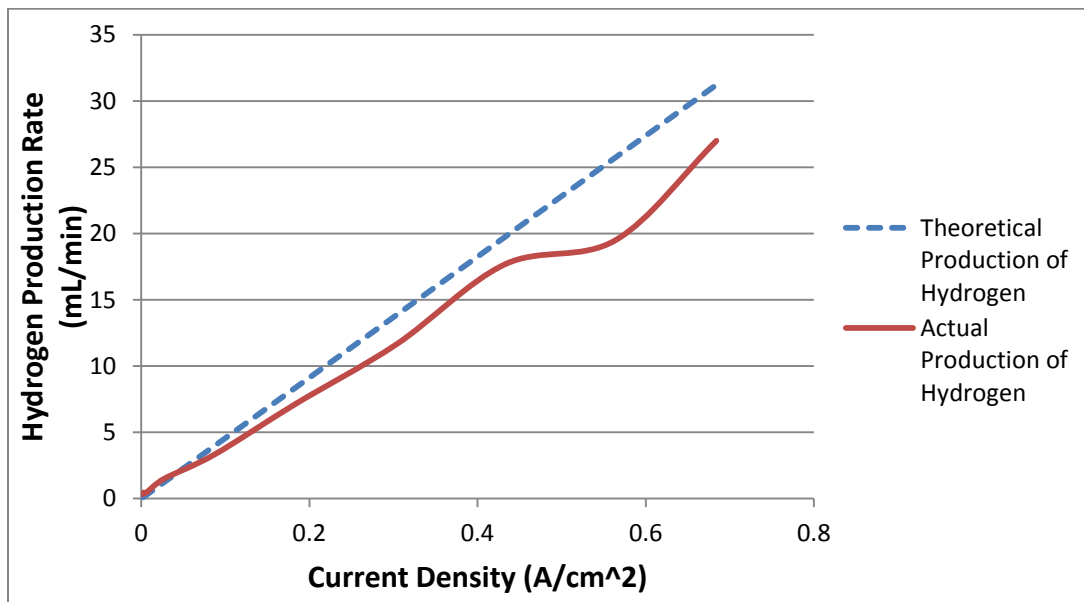
Figure 3-4: 10.0 M HCl Theoretical vs. Actual

The actual production rate of hydrogen was simply taken from the recorded data. The power supply was set to a specific voltage and the current was recorded in amps. At this specific current, the system was allowed to run for a total of 6 minutes. At this time, the mass displayed on the scale was recorded. This was performed for each voltage up until a voltage of 0.985 V. The current densities seen on the graph were obtained by simply dividing each current value by the area of the electrode, 5 cm^2.

The theoretical production rate of hydrogen was obtained by using Faraday's law of electrolysis and the ideal gas law. Faraday's law is as follows:

$$m = \left(\frac{Q}{f}\right) * \left(\frac{M}{z}\right)$$

The total charge passed is denoted as 'Q,' the molar mass of hydrogen gas is 'M,' the valency number of ions of the substance is 'z,' the Faraday constant, or 96,485 C/mol, is 'f,' and the mass of the substance produced at the electrode in grams is denoted by 'm.' Since charge is current multiplied by time, the above equation can be solved for each current at which the hydrogen production rate was measured to get how much hydrogen should ideally be produced (Hamann, 2007). This value was then converted to moles of H_2. This mole value was then converted to a volume by using the ideal gas equation:

$$PV = nRT$$

The pressure is atmospheric pressure, the temperature is $80^{\circ}C$ converted to kelvin, R is the universal gas constant, and n, or the number of moles, was obtained by using Faraday's law. Therefore, each the theoretical volume of H_2 produced at each current was solved for and then divided by 6 minutes to obtain a rate.

At a single concentration, the deviation from ideal is greater at a greater current density. At a single current density, the deviation seems to be greater at the lower concentration.

The deviation from theoretical production is due to system inefficiencies and degradation of the membrane. The inefficiencies of the system can be attributed to four types of losses in an electrochemical system: mass transfer losses, electron transfer losses, kinetics losses and permeation losses. Mass transfer losses take into account diffusion of the reacted species from the electrode surface region to the bulk solution. Electron transfer losses include inefficiencies in transferring electrons in the reactions taking place at the electrode surface. Kinetics losses refer to the adsorption or desorption of the reacted chemical complexes from the electrode

(NASA Hydrogen Research, 2011). Permeation losses refer to the permeation of copper complexes through the membrane, as was discussed in *Overview of System* (Balashov, 2011).

 Comparison of 3.3 M and 10 M HCl Anolyte Solutions – Nafion Membrane

The actual production rates of the two concentrations were also compared against each other rather than solely against the theoretical production rate. The graphical representation can be seen in *Figure 3-5*.
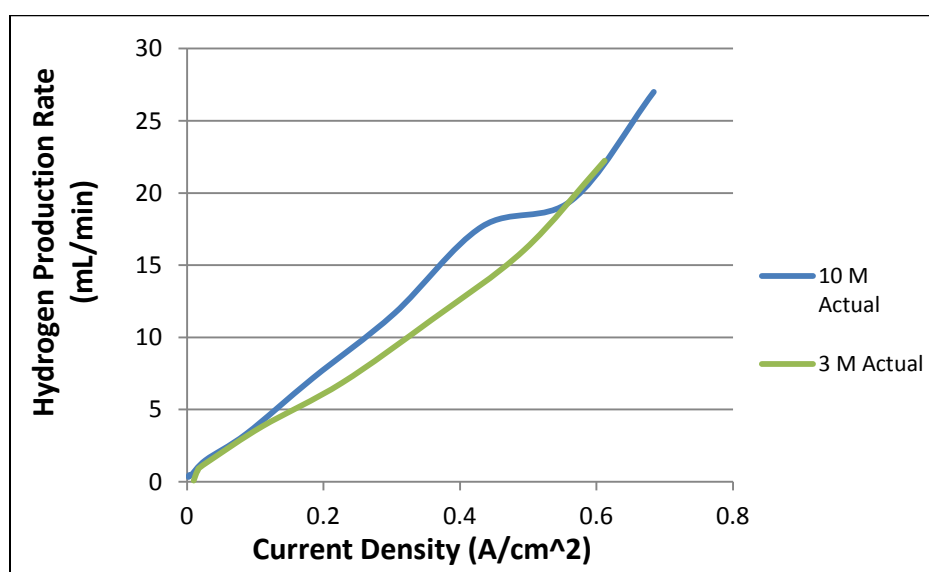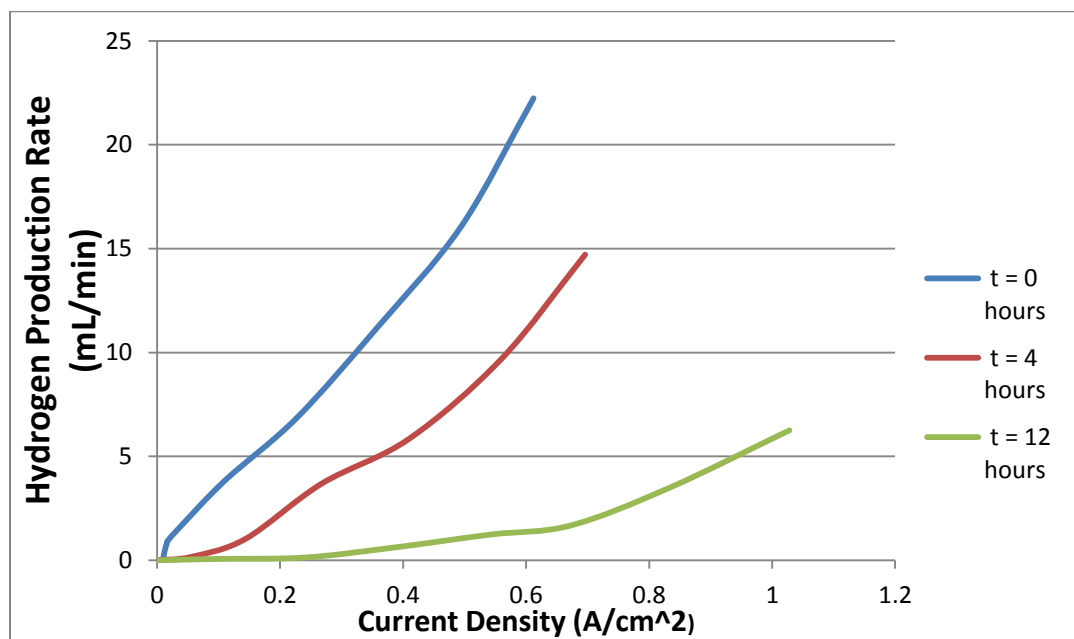

Figure 3- 5: Hydrogen Production Rate of 10.0 M HCl vs. 3.3 M HCl

This graph shows the hydrogen production rate as a function of current density for both the 10 M and 3.3 M HCl concentration using the Nafion membrane. A higher concentration provides faster electrode reaction kinetics so, even at low current densities, hydrogen is produced at a high rate. A higher HCl concentration in the anolyte yields a higher hydrogen production rate. A greater concentration of protons exist in the 10.0 M HCl solution than in the 3.3 M HCl solution. A greater concentration of protons results in a higher conductivity of the membrane because the presence of positive copper complexes limits the mobility of the protons through the membrane

due to the copper complexes' extremely low mobilities. Based on a recent study done by the Electrochemical Technical Program at the Energy Institute, the conductivity of Nafion 115 in a 2.13 mol/kg HCl solution was found to be 90 mS/cm and 15 mS/cm in a 2.13 mol/kg HCl + 0.2 mol/kg (Balashov, 2011). Furthermore, because the concentration of the copper complexes' in the anolyte decreases as the HCl concentration increases, less copper deposition on the Pt catalyst occurs at higher HCl concentrations (Naterer, 2010).

Hydrogen Production Rate over Time – Nafion Membrane

An area of heavy research in regard to the system is the performance of the proton exchange membrane. As the system runs over time, the membrane degrades. *Figure 3-6* shows the decreasing hydrogen production rate over time using a Nafion membrane and a 3.3 M HCl solution.

Figure 3-6: Decrease in Hydrogen Production Rate Over Time

There are two reasons for the observed decrease in hydrogen production rate over time. The first is the degradation of the Nafion membrane. "The stability and integrity of the proton exchange membranes is one of the most crucial factors affect the lifetime of the fuel cells since the PEMs function as both as electrolyte and as a separator of the reactant gases (Tang, 2007)." Research has shown that the degradation of overall cell performance is in part due to the decay of the membrane. It was shown that formation of hydrogen peroxide in the cathodic reaction region can directly degrade the membrane (Tang, 2007). Another reason the membrane degrades, especially in this specific system, is the formation of metallic copper through the following reaction:

$Cu-Cl(s) + e^- \rightarrow Cu(s) + Cl^-$
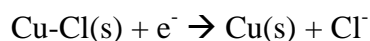
This formation of metallic copper is due to the permeation of copper complexes through the membrane. As the membrane degrades the anolyte diffuses through the membrane and the potential difference of the cell decreases. The potential of the anode is simply the difference between the redox potentials of Cu(I) and Cu(II) (Hamann, 2007). The potential of the cathode is the difference between a proton and H_2. Therefore, as the anolyte diffuses through the membrane and copper diffuses to the cathode side, the two potentials of the electrodes will slowly approach the same value, thus reducing the "driving force" for hydrogen production. These results suggest that the degradation of the membranes in hydrogen producing, electrochemical systems is still a major deterrent in their efficiency and overall performance.

Comparison of GTI and Nafion Membranes at 10 M HCl

Current density is a result of electrons moving across the cell via a circuit, as seen in *Figure 1*. Since these electrons reduce the protons to H_2 gas, the magnitude of a current density is directly

proportional to the hydrogen production rate; the higher the current density, the higher the

hydrogen production rate. *Figure 3-7* shows the current density as a function of voltage for both

the Nafion and GTI membranes at 10 M HCl.
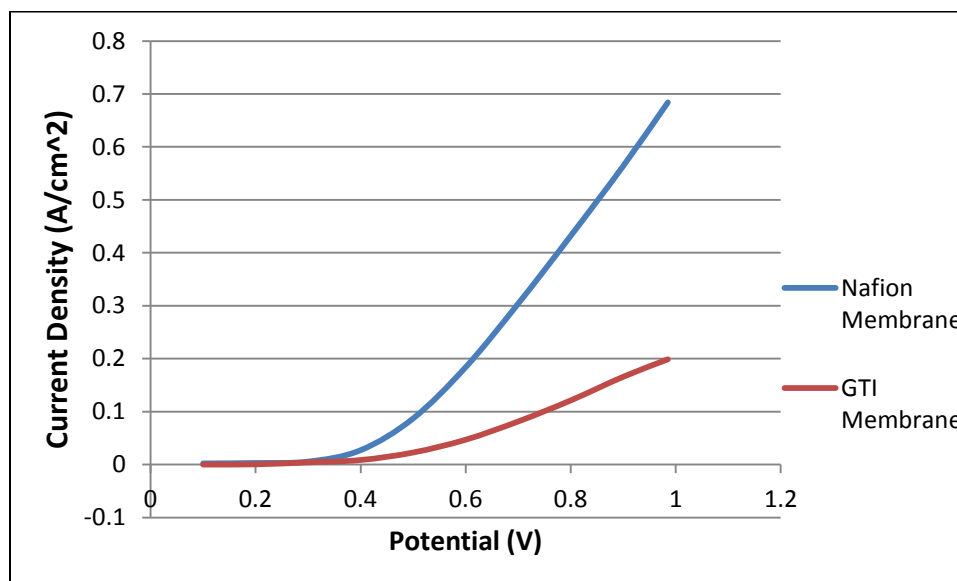
Figure 3-7: Current Density of Nafion vs. GTI Membranes

The Gas Technology Institute (GTI) claims its membrane to be less permeable to copper

complexes (Balashov, 2011). In an electrochemical cell, the "driving force" is the electromotive

force, also known as the cell potential. This cell potential is the difference between the potentials

of both electrodes (Hamann, 2007). If copper begins to permeate through the membrane,

"mixing" of the anodic and cathodic solutions occurs and, therefore, the electromotive force is

gradually diminished, thus reducing the overall performance of the cell. Also, the copper

complexes can deposit on the cathode as pure copper and will not only degrade the membrane,

but will also reduce the activity of the Pt (Naterer, 2008). However, the collected date showed

greater current densities for the Nafion membrane, probably due to its extremely high

conductivity. The conductivity of Nafion 115, which was used in the experiments, was found to

be 90 and 15 mS/cm in 2.13 mol/kg HCl(aq) and 2.13 mol/kg HCl(aq) + 0.2 mol/kg Cu-Cl(aq)

solutions, respectively (Balashov, 2011). The U.S. Department of Energy currently has a goal of

0.1 S/cm for the conductivity of any proton conducting membrane (Hickner, 2004). Nafion has

conductivity well above this standard. From the results, it is clear that the Nafion membrane is

preferred due to more stable hydrogen production rates when compared to the GTI membrane.

Chapter 4

Feasibility of Implementing the Cu-Cl Thermochemical Cycle

Many improvements need to be made to the overall system in order to be integrated into CoalStar's CTL plant. However, due to the amount of time between the initial planning stages and the final building of a tangible plant, this is a possibility. As stated earlier, this cycle requires a very low electricity input. In fact, the experimental decomposition potential for this cycle, or 0.98V, is more than three times lower than the potential needed for water electrolysis (Balashov, 2011). This means that this system would require less electricity input in order to produce the same amount of hydrogen when compared to water electrolysis and, therefore, is more efficient as well. This cycle is considered a "moderate temperature range" cycle as it can be run within a temperature range of $400 - 600^oC$. This temperature range makes using waste heat, from sources such as solar thermal cells or nuclear power plants, an attractive option (Balashov, 2011). Certain solar thermal cells, such as parabolic dish systems, can produce temperatures above 1000° C (UNEP Division of Technology, Industry and Economics).

Expected Hydrogen Output from Electrolyzer

 Figure 4-1 shows how the hydrogen production rate varies with power (watts), which is the voltage (volts) multiplied by current (amps). In the coal-to-liquids plant, the electrolyzer will receive its power from a "green" source, such as concentrated solar thermal parabolic troughs. A anolyte concentration of 10 M HCl is shown.
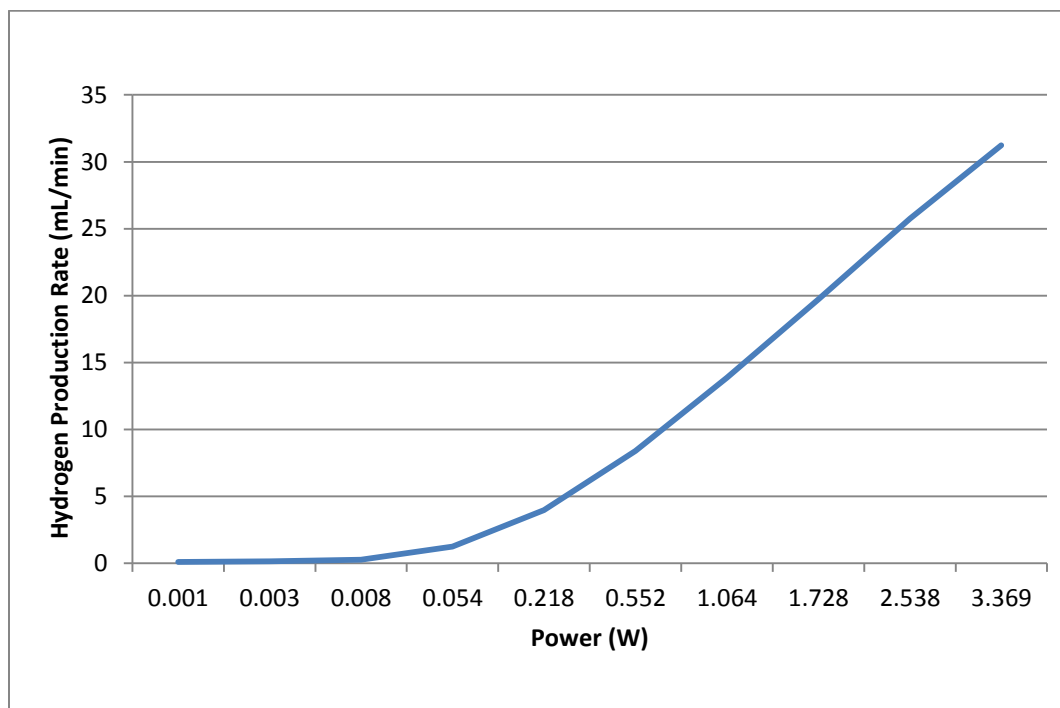
Figure 4-1: Hydrogen Production Rate vs. Power Output of Electrolyzer

A trade-off exists between the amount of hydrogen produced and the power needed to produce this hydrogen. The more power supplied to the unit, the greater the hydrogen production rate. However, more electricity will be needed as well, which could be a concern to the plant. As mentioned in *Chapter 2*, this plant requires roughly 30,000,000 SCF of H2 per day in order to meet their 10,000 BPD throughput target.

At the highest power output, one unit of the type used in the laboratory would produce about 91.5 SCF of hydrogen per day. The resultant hydrogen may seem a small amount but, in fact, is more than would result from water electrolysis. A typical water electrolyzer running at 300 mA produces about 5 mL/hr/cm^2 of hydrogen (Dopp, 2007). The Cu-Cl electrolyzer used in the EMS Energy Institute laboratory produced about 230 mL/hr/cm^2 of hydrogen when run at approximately 340 mA. Also, the above graph is representative of a system having a maximum

supplied power of about 3.4 W. The actual system will be powered by a source producing a much larger wattage. Once the thermochemical cycle becomes more developed and the various "kinks" worked out, the plant could employ much larger electrolyzer units than the one used in the lab. The hydrogen production rates displayed in the graph are per the 5 cm^2 membrane area. An electrolyzer having a larger surface area would therefore be capable of producing more hydrogen per day. This produced hydrogen would be sent to the hydrogen pool where it would be combined with the hydrogen coming from the water-gas shift unit and the clean-up and separation unit.

Conclusion

Cu-Cl electrolysis for hydrogen production in the Cu-Cl thermochemical cycle offers a promising new method for producing hydrogen using sustainable practices. However, many improvements need to be made before this technology can be permanently integrated into the hydrogen production sector. First, the proton exchange membranes need to be fabricated to allow less permeation of copper complexes and need to be more resistant to degradation in order to maintain an efficient process. This entails ensuring as little degradation as possible. Currently, the hydrogen production rate reaches zero after about 36 hours; this is certainly not acceptable for use in an industrial setting. Further work also includes optimizing certain parameters of the electrolysis reaction such as temperature, concentration of the electrolytes, and flow rates to achieve the best possible efficiency. As seen from the results, a high concentration of HCl in the anolyte combined with a copper resistant membrane would drastically increase the rate of hydrogen production. Also, improving reagent transport to the electrode and removal of the products from the reaction sites will improve the kinetics of the cycle and the overall

efficiency. An ever increasing interest in this field and extensive laboratory research will make this goal much more attainable.

The Cu-Cl thermochemical cycle offers much promise for CoalStar and the hypothetical zero emissions coal-to-liquids plant. Granted, the system is very much in an experimental stage but, upon further improvement, could be a great fit in the plant schematic. The purpose of this thesis was to provide an introduction and discussion of coal-to-liquids and explore the possibility of using the Cu-Cl thermochemical cycle to enable the potential carbon neutrality of CoalStar's plant. In a global context, the potential success of this carbon neutral coal-to-liquids plant would perhaps serve as a champion of sorts for the implementation of other carbon "friendly" technologies across industry.
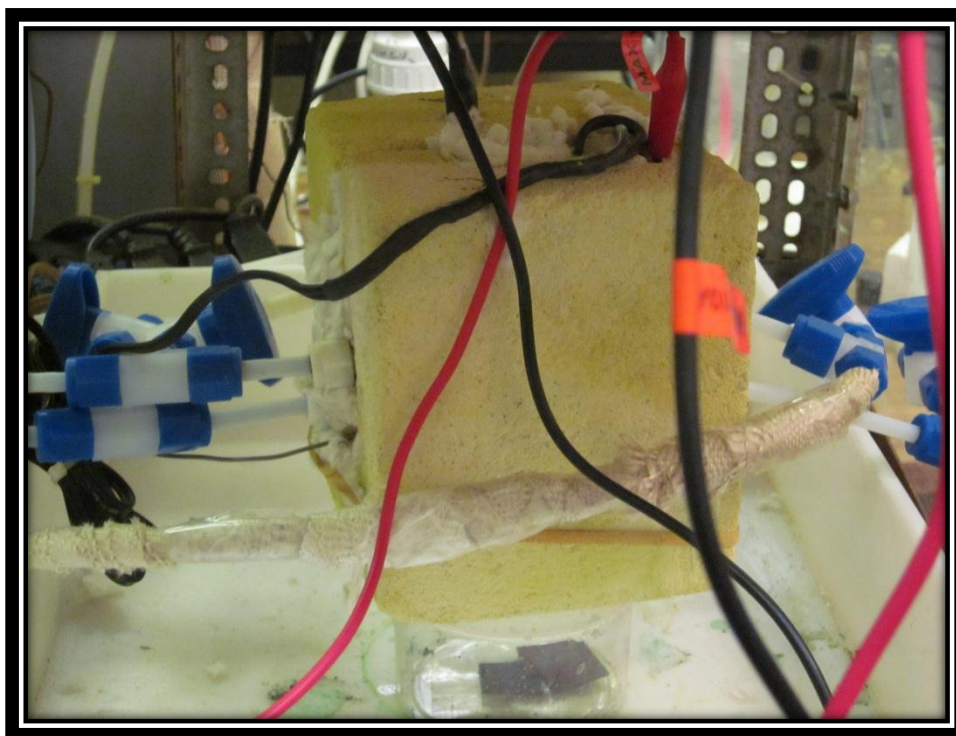
Appendix A

Components of System

Figure A-8: The water tub was placed on top scale. Any H_2 produced was sent to this tub.

Figure A- 9: The power source was used to of a control the voltage.

Figure A-10: The cell had leads connected to the power supply and anode

and cathode tubes.

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Process Engineering Intern
  · Optimized a pump to determine the effectiveness of using a working fluid with a low
  specific gravity.
  · Used Visual Flow 5.3 to build various piping systems located throughout the refinery.
  · Took temperature surveys on 25 heat exchangers in response to an overheated guard
  basin. Formulated a memo with recommendations from an engineering viewpoint.
Engineering Capstone Design, University Park, PA………………….…….January – May 2011
Energy Engineer
  · Worked with 5 other students, from various engineering majors, to design a small Tesla
  turbine to meet Boeing's requirement of a mechanical energy storage system that could
  store off-grid electricity without the use of batteries.
  · The group members formulated a 50+ page report detailing the design specifications,
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Electrochemical Technologies Program, University Park, PA…….…….....January – May 2011
Research Assistant
  · Assisted research on electrolysis for hydrogen production using the Cu-Cl
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Business Operations Intern
  · Used the Generation Knowledge Service database to develop 150+ graphs for a
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  · Interviewed employees throughout the company in order to develop a Self-Assessment
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