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## UNIVERSITY OF CALIFORNIA, SAN DIEGO

A Continuous Solar Thermochemical Hydrogen Production Plant Design

A Thesis submitted in partial satisfaction of the requirements

for the degree Master of Science

in

**Chemical Engineering** 

by

Wesley Wai Luc

Committee in charge:

Professor Jan Talbot, Chair Professor Richard Herz Professor Pao Chau

The Thesis of Wesley Wai Luc is approved and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2013

Dedicated to my friends and family

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#### ABSTRACT OF THE THESIS

#### A Continuous Solar Thermochemical Hydrogen Production Plant Design

by

Wesley Wai Luc Master of Science in Chemical Engineering University of California, San Diego, 2013 Professor Jan Talbot, Chair

The sulfur-ammonia thermochemical water-splitting cycle for hydrogen production driven by solar thermal energy is a promising technology for large-scale commercial production of hydrogen. Hydrogen is an attractive alternative to fossil fuels because it is environmentally friendly, transportable, and can be manufactured. The process utilizes the electrolytic oxidation of aqueous ammonium sulfite in the hydrogen producing half-cycle and the thermal decomposition of molten potassium pyrosulfate and gaseous sulfur trioxide in the oxygen producing half-cycle. The thermochemical cycle is an all-fluid cycle driven by solar thermal energy captured from a heliostat array focused on a receiver and required electricity is generated internally from waste heat. The only

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input into the process is water, and the only products are oxygen and hydrogen gas. A sulfur-ammonia thermochemical plant was designed and modeled with a chemical process simulator, Aspen Plus. The plant was designed to operate continuously by using a phase-change thermal-storage system with NaCl which provides large thermal capacity at 800 °C. The plant model generates  $\sim 1.7 \times 10^5$  kg of hydrogen per day, which is equivalent to  $\sim 268$  MW thermal equivalent on a lower heating value basis, with a US Department of Energy efficiency of 13%. Various parameters, such as reactor operating temperature, plant pressure, and salt concentration, were varied to study to their effects on plant efficiency and performance. Plant cost estimation was also performed to estimate the projected costs of hydrogen to determine the viability of the sulfur-ammonia thermochemical plant.

# **1. Introduction**

According to the Energy Information Administration of the Department of Energy of the United States, it was estimated that the total marketed energy consumption of the world was 447 quadrillion BTU in 2004 and is projected to reach 702 quadrillion BTU in 2030 [1]. Currently, about 80% of the world's energy is derived from the combustion of fossil fuels, which include oil, coal, and natural gas. The other 20% is dominated by biomass, mostly fuel wood used for cooking and heating [2]. Despite being the world's primary energy source, there are several disadvantages of combusting fossil fuels. These disadvantages include the production of unwanted by-products such as carbon dioxide and the depletion of nonrenewable energy sources. Because of these drawbacks and the increased growth of energy consumption, there is a pressing need for green and sustainable energy. Currently, there are many areas of study on sources of sustainable energy including hydroelectric, wind, geothermal, biomass, photovoltaic, and solar thermal, each having its own advantages and disadvantages [2]. The main interest of this study is solar thermal.

Unlike photovoltaic that uses semiconductor materials to transform solar energy directly into electricity, solar thermal uses heat from the sun to help drive a power or thermochemical plant. Solar thermal energy is harnessed by reflecting sunlight off mirrors and reflective lens to help capture and focus sunlight in order to heat a working fluid or a heat storage device. In order to reach temperatures up to 1000 °C, a solar field, made up of several hundreds or even thousands of mirrors, called heliostats, is placed around a centralized receiver in which sunlight is reflected and concentrated at one

1

centralized point. Air, steam, or a molten salt is heated and is used to drive a power plant or a thermochemical plant [3]. Solar fields are further discussed in Section 2.5.

Although there is an abundance of solar thermal energy, the problem is storing the energy as a useable form. One viable solution is harnessing that thermal energy and storing that energy in the form of hydrogen gas. Currently, there are hydrogen fuel cell technologies that use hydrogen gas to produce electricity by reacting hydrogen gas with oxygen gas to form water. Hydrogen fuel cells are an environmentally-friendly alternative to the combustion engine [4]. If hydrogen can be produced with low to zero carbon dioxide emissions, hydrogen as a fuel is an attractive option because it is environmentally friendly, transportable, and can be manufactured [5, 6]. Because of these advantages, the US Department of Energy (DOE) has set a goal of producing 10 quads (1 quad =  $10^{15}$  Btu) of hydrogen per year for transportation use from renewable sources in the years 2030 to 2050 [7]. Furthermore, the DOE has also set the goal of reducing the cost of hydrogen to \$3.00 per gge (gallon of gasoline equivalent) by 2017 [8].

Contemporary methods for producing hydrogen use fossil fuels, that ultimately nullify the environment advantages of hydrogen. Currently, 95% of hydrogen production in the US utilizes steam-methane reforming (SMR) technology. The remaining 5% consist of various method of producing hydrogen, such as gasification of coal and biomass, water-splitting electrolysis, and photolytic processes. The SMR process is a two-step process, that involves the endothermic reaction of methane with steam to produce hydrogen and carbon monoxide and an exothermic reaction of carbon monoxide with steam over a catalyst to produce hydrogen and carbon dioxide. The second reaction is commonly known as the water-gas shift reaction [9]. The reactions are as follow:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1.1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1.2}$$

Other fuels such as ethanol, propane, and gasoline can be used in stream reforming to produce hydrogen. Despite the high efficiency of SMR, carbon dioxide is released as natural gas is consumed. The challenge is finding an alternative and sustainable method of producing hydrogen.

One method for producing hydrogen is the one-step direct thermal decomposition of water, shown by the following reaction:

$$2H_2O \rightarrow 2H_2 + O_2 \tag{1.3}$$

This process involves heating the water until it decomposes into hydrogen and oxygen. The direct thermal decomposition of water is possible at elevated temperatures exceeding 2000 °C, because the Gibbs free energy of formation of water decreases as a function of temperature [10]. However, this process requires large amount of energy to thermally decompose water and expensive materials that can withstand the high temperature, making this process economically infeasible. Furthermore, the separation of hydrogen and oxygen needs to occur at high temperature. If these gases are not separated at high temperature, they have the tendency to recombine or form an explosive mixture at low to moderate temperatures [11].

One method for hydrogen production is a water-splitting thermochemical cycle (WSTC). There are over 800 published WSTCs, but only a few are economically or technically feasible [10, 12]. One common family of WSTC is the metal oxide cycle, which usually requires very high temperatures. One such cycle is the two-step Zn/ZnO thermochemical cycle [13]. This two-step process allows for the production of oxygen

and hydrogen at different steps which eliminates the need for a hydrogen and oxygen separation step. However, there are challenges associated with this cycle. The required temperature for the first step is still comparable to the required temperature for direct thermal decomposition of water. Furthermore, Zn and  $O_2$  have a tendency to recombine as they cool, resulting in low  $H_2$  yield or a need for a separation process [11]. A more indepth discussion of the metal oxide WSTC is found in Section 2.1.

To combat these issues, multi-step cycles have been explored. Similar to the twostep thermochemical cycles, hydrogen and oxygen are released at different stages. One well-studied family of multi-step WSTC is the sulfuric acid/metal sulfate cycle. One such cycle is the sulfur-iodine (S-I) cycle [13]. This cycle is a three-step cycle with a maximum temperature of 870 °C, making this cycle a competitor of the solid oxide cycles. The first step involves reacting  $H_2O$ ,  $I_2$ , and  $SO_2$  to produce  $H_2SO_4$  and HI. The products,  $H_2SO_4$  and HI, are separated and decomposed into two mixtures: one of  $H_2O$ ,  $SO_2$ , and  $O_2$  and the other of  $I_2$  and  $H_2$ , respectively [14]. Although this process operates at a lower temperature then metal oxide cycles, sulfur and iodine are highly reactive; thus, an energy intensive separation process is needed. Furthermore, this process uses corrosive chemicals, which is another disadvantage [11]. A more in-depth discussion of this multi-step WSTC is found in Section 2.1.

The current work focuses on a new solar-thermal cycle: a sulfur-ammonia (SA) cycle. The SA cycle is a modified version of the Westinghouse cycle which consists of five steps involving both thermochemical and electrochemical reactions. Similar to other thermochemical cycles, this process produces hydrogen and oxygen at different stages [15]. In order to avoid the issues mentioned for the previously discussed cycles, this

process operates continuously at low temperatures, uses no solids, and bypasses the need for costly gas separations. A more in-depth discussion of the SA cycle is found in Section 2.2.

The purpose of this research is to design a process flow sheet with Aspen Plus chemical process simulator that best simulates the SA cycle in a continuous solar thermal hydrogen production plant. Furthermore, plant operating parameters, such as reactor operating temperature, plant pressure, and salt concentration, were varied to determine their effects on overall plant efficiency and performance. Plant cost estimation was also performed to estimate the projected costs of hydrogen to determine the viability of the sulfur-ammonia thermochemical plant. Chapter 2 provides specific background information on thermochemical cycles, the SA cycle, Rankine cycle for power generation, phase-change thermal-storage systems, and solar fields. Chapter 3 describes how Aspen Plus was used and the tools used to create the process flow sheet. Chapter 4 lists the results of the base case simulation. Chapter 5 describes the results of various cases by changing operating parameters. Chapter 6 describes the economic analyses of the production plant and Chapter 7 states the conclusions and recommendations for future work.

The current Aspen Plus simulation of the sulfur-ammonia solar thermochemical hydrogen production plant is based on previous work done by Jessie Littlefield, a graduate student at University of California, San Diego [16], and the Florida Solar Energy Center (FSEC) [13, 15]. Jessie Littlefield as well as FSEC developed flow sheets that were used as starting points for the current work. The current work developed a new Aspen Plus model that uses more realistic parameters and incorporates thermodynamic properties obtained from the literature.

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# 2. Background

The current work is part of a Department of Energy (DOE) funded project that was started in 2007 with Science Applications International Corporation (SAIC) to develop an advanced thermochemical water splitting process powered by solar thermal energy for hydrogen production. The thermochemical cycle utilizes a sulfur-ammonia (SA) process that involves separate hydrogen and oxygen producing half-cycles. Figure 2.1 shows a schematic of the SA cycle. The process is an all-fluid cycle that uses a phasechange thermal-storage system with NaCl for continuous operation. Solar thermal energy is used to drive the overall process and required electricity is generated internally from waste heat. The SA process will be further discussed in Section 2.2.



Figure 2.1: Schematic of a Sulfur-Ammonia Thermochemical Cycle

#### **2.1 Thermochemical Cycles**

Thermochemical cycles consist of a series of chemical reactions at different temperatures in which thermal energy is transformed into chemical energy. One requirement for a water-splitting thermochemical cycle (WSTC) for hydrogen production is that the sum of enthalpies of reaction must equal or exceed the enthalpy of formation of water. Another requirement is that the minimum number of reactions is two [1]. There are hundreds of published WSTCs, but only a few are economically and technologically feasible [2,3]. Advantages over direct thermal decomposition of water include generally lower operating temperatures, separate hydrogen and oxygen evolving steps, and the absence of a high temperature gas separation step [4]. Disadvantages include lower process efficiency as the number of reaction steps increases and the possible requirement for intermediate separation stages. Furthermore, multi-step WSTC involves chemicals other than water; therefore, reagents must be completely regenerated and recycled within the system for a process to be entirely sustainable and renewable [4].

One major class of WSTC is the metal oxide cycle. The cycle consists of two steps: a high temperature endothermic oxidation step and an exothermic hydrolysis step [4]. The general reactions are as follow:

$$M_x O_y \rightarrow M_x O_{y-1} + \frac{1}{2} O_2 \tag{2.1}$$

$$M_x O_{y-1} + H_2 O \rightarrow H_2 + M_x O_y$$
(2.2)

where M represents a metal, such that it or its metal oxide can reduce water to generate hydrogen. Several metal oxide cycles are tabulated in Table 2.1

The two-step metal oxide cycle generates oxygen and hydrogen at different stages, thus, eliminating the need for a high temperature gas separation step. However,

the main drawback is the high temperatures needed. The maximum temperatures of several metal oxide cycles are listed in Table 2.1. The Mo/MoO<sub>2</sub> and W/WO<sub>3</sub> cycles operate at temperatures comparable to direct thermal decomposition of water, thus, making these cycles economically infeasible [5,6]. The MnO/Mn<sub>3</sub>O<sub>4</sub> cycle operates at lower temperatures, however due to thermodynamic constraints; the amount of hydrogen produced is insignificant. The Hg/HgO and Cd/CdO cycles operate at low temperatures, however these two cycles use heavy metals and are generally viewed as environmentally undesirable cycles [5]. The Zn/ZnO and  $FeO/Fe_3O_4$  cycles are two feasible and experimentally-confirmed cycles [7]. Chemicals involved in these cycles are inexpensive. However, the maximum temperatures of these cycles are still comparable to direct thermal decomposition of water. Furthermore, zinc and oxygen are highly reactive in the presence of each other, thus resulting in low hydrogen yield. Currently, research is being conducted to design better reactors and quenching apparatus for the Zn/ZnO cycle to increase solar-to-chemical conversion efficiency [7]. Furthermore, research is also being conducted to partially substitute iron in Fe<sub>3</sub>O<sub>4</sub> with other metals (Mn, Co, Mg, Ni, Zn, etc) to form mixed metal oxides which may lower the maximum temperate of the cycle [7].

	Cycles	Max. Temp.	Reference
Hg/HgO	HgO $\rightarrow$ Hg + $\frac{1}{2}O_2$	600 °C	[5]
	$Hg + H_2O \rightarrow HgO + H_2$		
Cd/CdO	$CdO \rightarrow Cd + \frac{1}{2}O_2$	1400 °C	[5]
	$Cd + H_2O \rightarrow CdO + H_2$		
MnO/Mn <sub>3</sub> O <sub>4</sub>	$2Mn_3O_4 \rightarrow 6MnO + O_2$	1537 °C	[6]
	$3MnO + H_2O \rightarrow Mn_3O_4 + H_2$		
Zn/ZnO	$ZnO \rightarrow Zn + \frac{1}{2}O_2$	2000 °C	[5]
	$Zn + H_2O \rightarrow ZnO + H_2$		
FeO/Fe <sub>3</sub> O <sub>4</sub>	$Fe_3O_4 \rightarrow 3FeO + \frac{1}{2}O_2$	2200 °C	[6]
	$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$		
Mo/MoO <sub>2</sub>	$MoO_2 \rightarrow Mo + O_2$	3713 °C	[5]
	$Mo + 2H_2O \rightarrow MoO_2 + 2H_2$		
W/WO <sub>3</sub>	$W + H_2O \rightarrow WO_3 + 3H_2$	3910 °C	[5]
	$WO_3 \rightarrow W + 3/2O_2$		

 Table 2.1: Metal-Oxide Cycles

The high temperature reactions of the metal oxide cycles requires higher material and maintenance costs; thus, low temperatures are more desirable [4]. Multi-step cycles that can operate at lower temperatures have been explored. Several multi-step cycles are tabulated in Table 2.2

	Cycles	Max. Temp.	Reference
Cu-Cl	$2Cu + 2HCl \rightarrow 2CuCl + H_2$	500 °C	[10]
	$2CuCl \rightarrow CuCl_2 + Cu$		
	$2CuCl + H_2O \rightarrow CuO \cdot CuCl_2 + 2HCl$		
Westinghouse	$2H_2O + SO_2 \rightarrow H_2 + H_2SO_4$	850 °C	[5]
	$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2$		
S-I	$2H_2O + SO_2 + xI_2 \rightarrow H_2SO4 + 2HI_x$	870 °C	[4]
	$2HI_x \rightarrow xI_2 + H_2$		
	$H_2SO_4 \rightarrow H_2O + SO_4 + \frac{1}{2}O_2$		
MnO/ Mn <sub>2</sub> O <sub>3</sub>	$Mn_2O_3 \rightarrow 2MnO + \frac{1}{2}O_2$	1650 °C	[11,12]
	$MnO + NaOH \rightarrow \frac{1}{2}H_2 + NaMnO_2$		
	$NaMnO_2 + \frac{1}{2}H_2 \rightarrow \frac{1}{2}Mn_2O_3 + NaOH$		

**Table 2.2: Low Temperature Cycles** 

The sulfur-iodine (S-I) cycle, developed by General Atomics in the 1970s, is a three-step cycle that operates at a maximum temperature of 870 °C. This cycle was

designed to utilize waste heat from a nuclear power plant. Although the lower operating temperature makes the S-I cycle a competitor of metal oxide cycles, an energy intensive separation process is needed due to the high reactivity of sulfur and iodine. Therefore, this research was discontinued in 2009 [4,8].

Another cycle that is currently being explored by several research organizations in both Canada and the United States is the copper-chloride (Cu-Cl) cycle. This process is a hybrid cycle that uses both thermochemical and electrochemical reactions. The cycle was also designed to utilize waste heat from a nuclear power plant. The maximum operating temperature is 500 °C [9]. Similar to the S-I cycle, the low operating temperature makes the Cu-Cl cycle a competitor of metal oxide cycles. Furthermore, this process is also more efficient than conventional water splitting electrolysis [10]. However, this process utilizes solid materials, as well as highly corrosive chemicals such as hydrochloric acid, that poses a reactor design challenge.

The MnO/  $Mn_2O_3$  cycle, currently being studied by University of Colorado and the Swiss Federal Research Institute, is a three-step cycle that operates at a maximum temperature of 1650 °C. The cycle was designed to use concentrated solar energy and the low operating temperature also makes this cycle a competitor to the two-step metal oxide cycles. Similar to the Cu-Cl cycle, this process utilizes solid materials that pose a reactor design challenge. Furthermore, the separation of NaOH from  $Mn_2O_3$  is energy intensive [11, 12].

Another alternative to the metal oxide cycle is the Westinghouse cycle that was first developed by Westinghouse Electric Corporation in 1973 [13]. This process is a twostep cycle that also uses both thermochemical and electrochemical reactions. The maximum operating temperature is 850  $^{\circ}$ C, also making this process a competitor of metal oxide cycles. This process uses inexpensive chemicals and no solid materials. However, this process is hampered by the low solubility of SO<sub>2</sub> in water and challenges presented by the acidity of the SO<sub>2</sub> in the electrolytic oxidation process [13].

#### 2.2 Development of the Sulfur-Ammonia Cycle

The sulfur-ammonia cycle, first developed by the Florida Solar Energy Center (FSEC), is a modified version of the Westinghouse cycle [13]. This cycle consist of hydrogen and oxygen producing half-cycles. The reactions are as follow:

$$SO_2(g) + 2NH_3(g) + H_2O(l) \rightarrow (NH_4)_2SO_3(aq)$$
 (2.3)

(25 °C, chemical absorption)

$$(NH_4)_2SO_3(aq) + H_2O(l) \rightarrow (NH_4)_2SO_4(aq) + H_2(g)$$
 (2.4)

(77 °C, photocatalyic)

$$(NH_4)_2SO_4 (aq) \rightarrow 2NH_3 (g) + H_2SO_4 (g)$$

$$(2.5)$$

(252 °C, thermochemical)

$$H_2SO_4(l) \rightarrow SO_2(g) + H_2O(g) + \frac{1}{2}O_2(g)$$
 (2.6)

(852 °C, thermochemical)

The oxygen producing half-cycle consists of the reactions in Eq. (2.5) and Eq. (2.6). Solar thermal energy is used to drive both reactions for the production of oxygen, ammonia, and sulfur dioxide gas via decomposition of ammonium sulfate and sulfuric acid. Oxygen is separated through its low solubility in water. The hydrogen producing half-cycle consists of the reactions in Eq. (2.3) and Eq. (2.4). In Eq. (2.3) ammonia and sulfur dioxide gases are chemically absorbed in water to produce ammonium sulfite. In Eq. (2.4) hydrogen is produced by a photocatalytic process in which  $SO_3^{2-}$  ions are oxidized to  $SO_4^{2-}$ . Hydrogen is then separated from the ammonium sulfate solution via a vapor-liquid separator. The photocatalytic reaction avoids the solubility and acidity challenges faced in the Westinghouse cycle.

The decomposition of sulfuric acid at high temperature requires expensive materials to withstand the highly corrosive nature of sulfuric acid. An alternative to the decomposition of sulfuric acid is the introduction of metal sulfates into the oxygen producing half-cycle. FSEC modified the cycle by replacing Eq. (2.5) and (2.6) with a zinc sulfate/zinc oxide oxygen producing half-cycle. The reactions are as follow:

$$(NH_4)_2SO_4(aq) + ZnO(s) \rightarrow 2NH_3(g) + ZnSO_4(s) + H_2O(g)$$
(2.7)

(500 °C, thermochemical)

$$ZnSO_4(s) \rightarrow SO_2(g) + ZnO(s) + O_2(g)$$
(2.8)

(1000 °C, thermochemical)

In Eq. (2.7), ammonium sulfate is reacted with zinc oxide to produce ammonia, zinc sulfate, and water. In Eq. (2.8), zinc sulfate is decomposed to produce sulfur dioxide, zinc oxide, and oxygen. Zinc oxide is recycled, while oxygen and sulfur dioxide are separated.

Similar to the Cu-Cl cycle, the main concern with the zinc sulfate/zinc oxide halfcycle is the handling and transportation of solids. The zinc sulfate/zinc oxide half-cycle was then further changed to an all-fluid system by replacing Eq. (2.7) and (2.8) with the following reactions:

$$(NH_4)_2SO_4(aq) + K_2SO_4(l) \rightarrow K_2S_2O_7(l) + 2NH_3(g) + H_2O(g)$$
 (2.9)

(400 °C, thermochemical)

$$K_2S_2O_7(l) \rightarrow K_2SO_4(l) + SO_3(g) \tag{2.10}$$

(790 °C, thermochemical)

$$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g) \tag{2.11}$$

(1000 °C, thermochemical)

In Eq. (2.9), ammonium sulfate is reacted with potassium sulfate to produced potassium pyrosulfate, ammonia, and water. Potassium pyrosulfate is then decomposed to potassium sulfate and sulfur trioxide, Eq. (2.10). Sulfur trioxide is then catalytically decomposed to produce sulfur dioxide and oxygen, Eq. (2.11). Experimental studies have been conducted by Mimi Wang, at University of California, San Diego, and have determined the conditions of temperature and composition needed for the decomposition of potassium pyrosulfate and the mixture of potassium sulfate and ammonium sulfate [14]. Moreover, the decomposition of sulfur trioxide has been well-studied and reactors have been designed and tested [15,16].

The photochemical reaction, Eq. (2.4), was also replaced with an electrolytic step in order to increase overall process efficiency and lower cost. The electrolytic half-cell reactions in basic media are as follow:

$$2(NH_4)^{+} + SO_3^{2^{-}} + 2OH^{-} \rightarrow 2(NH_4)^{+} + SO_4^{2^{-}} + H_2O + 2e^{-}$$
(2.12)  
(E<sup>o</sup> = -0.936 V, anode)  
$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$
(2.13)

 $(E^{o} = -0.828 \text{ V}, \text{ cathode})$ 

$$(NH_4)_2SO_3 (aq) + H_2O (l) \rightarrow (NH_4)_2SO_4 (aq) + H_2 (g)$$
 (2.14)  
(E<sup>o</sup> = 0.108 V, overall)

The SA cycle is an all fluid cycle and all intermediate chemicals are recycled. The only input into the process is water, and the only products are oxygen and hydrogen gas. The full SA cycle is depicted in Figure 2.1. A summary of all reactions is as follows: Oxygen Producing Half-Cycle:

$$(NH_4)_2SO_4(aq) + K_2SO_4(l) \rightarrow K_2S_2O_7(l) + 2NH_3(g) + H_2O(g)$$
 (2.9)

(400 °C, adiabatic mixing)

$$K_2S_2O_7(l) \rightarrow K_2SO_4(l) + SO_3(g)$$

$$(2.10)$$

(790 °C, thermochemical)

$$2SO_3(g) \rightarrow 2SO_2(g) + O_2(g) \tag{2.11}$$

(900-1200 °C, electrical heating)

Hydrogen Producing Half-Cycle:

$$SO_2(g) + 2NH_3(g) + H_2O(l) \rightarrow (NH_4)_2SO_3(aq)$$
 (2.3)

(25 °C, chemical absorption)

$$(NH_4)_2SO_3(aq) + H_2O(l) \rightarrow (NH_4)_2SO_4(aq) + H_2(g)$$
 (2.14)

(80-150 °C, electrolytic)

In order to operate the SA cycle continuously, a phase-change thermal-storage system with NaCl has been proposed which would supply heat to the mid-temperature reactor to drive the thermal decomposition of potassium pyrosulfate to produce potassium sulfate and sulfur trioxide, Eq. (2.10). Solar thermal energy required for the thermal-storage system is provided by solar concentrators which use mirrors and reflective lens to help capture and focus sunlight to produce temperature up to 800 °C. The mid-temperature reactor operates at 790 °C to ensure that heat is transported from the phase-change thermal-storage system to the mid-temperature reactor. The thermal-storage system is discussed in Section 2.4. Sulfur trioxide is separated from the molten potassium pyrosulfate/potassium sulfate salt mixture by a vapor-liquid separator. The molten salt stream is then used to heat the low temperature reactor in which ammonium sulfate is reacted with potassium sulfate to produced potassium pyrosulfate, ammonia, and water at  $400^{\circ}$ C, Eq. (2.9). Potassium pyrosulfate is recycled to the mid-temperature reactor while ammonia and water are transported to the chemical absorber. The catalytic decomposition of sulfur trioxide, Eq. (2.11), occurs in the high temperature reactor, operating between 900 to 1200 °C. In order to eliminate reradiation losses and reduce capital cost, electric heating is used to drive the high temperature reactor. Sulfur dioxide is mixed with ammonia and then chemically absorbed in water in the chemical absorber to produce ammonium sulfite, Eq. (2.3). Ammonium sulfite is then transported to the electrolyzer where hydrogen and ammonium sulfate is then produced, Eq. (2.14). Hydrogen is then separated while ammonium sulfate is recycled to the low temperature reactor. Electricity needed for the electrolyzer and electrical heating is generated internally from waste heat. The Rankine power recovery system is discussed in Section 2.3.

#### 2.3 Power Recovery System, Rankine Cycle

The oxygen producing half-cycle operates at high temperatures; therefore, waste heat is present in the process. This excess energy can be utilized in a steam power plant to produce electricity needed for the electrolytic reactor and the heating of the high temperature reactor. A steam power plant is a large scale heat engine in which the working fluid flows through a boiler, turbine, condenser, and a pump in a steady-state cyclic process. Energy is transferred through a physical boundary from the heat source to the working fluid. A simple steam power plant is illustrated in Figure 4. Heat is transferred to the working fluid in the boiler while heat is released by the working fluid in the condenser. Work is produced by the turbine and work is used by the pump [17].



Figure 2.2: Diagram of a Simple Rankine Cycle

The Carnot-engine cycle is the most efficient thermodynamic heat engine that operates reversibly. The Carnot-engine cycle consists of two isothermal steps connected by two adiabatic steps which is illustrated on a temperature-entropy (T-S) diagram shown in Figure 2.2 [17], where:


Figure 2.3: Temperature (T) – Entropy (S) Diagram of a Carnot Cycle Step 1  $\rightarrow$  2, Saturated liquid is isothermally heated in the boiler to produce saturated vapor

Step 2  $\rightarrow$  3, Saturated vapor is isentropically expanded in the turbine to produce a mixture of saturated liquid and vapor

Step 3  $\rightarrow$  4, Mixture of saturated liquid and vapor is partially isothermally condensed in the condenser

Step 4  $\rightarrow$  5, Partially-condensed mixture is isentropically compressed to produce saturated liquid

Although the Carnot-engine cycle is the most efficient heat engine, there are some impracticalities associated with this process. Turbines that take in saturate steam, steps 2  $\rightarrow$  3, produce high liquid content which causes erosion problems. Furthermore, it is difficult to design a pump to take in a mixture of liquid and vapor and produce a saturated liquid, steps 4  $\rightarrow$  1. The Rankine cycle, sometimes referred as the practical Carnot cycle, is an alternative that can overcome these impracticalities. There are two major differences between the Rankine and Carnot cycle. Unlike the Carnot cycle, heating in step 1  $\rightarrow$  2 is

carried well beyond vaporization to produce superheated vapor. Also, cooling in step 3  $\rightarrow$  4 is carried to complete condensation to produce saturated liquid [17]. The Rankine cycle is illustrated on a T-S diagram shown in Figure 2.3, where:



Figure 2.4: Temperature (T) – Entropy (S) Diagram of a Rankine Cycle

Step 1  $\rightarrow$  2, Subcooled liquid is heated in a constant pressure boiler to produce a superheated vapor

Step 2  $\rightarrow$  3, Superheated vapor is isentropically expanded in a turbine to the pressure of the condenser to produce a wet vapor

Step 3  $\rightarrow$  4, Wet vapor is isobarically and isothermally condensed in a condenser to produce saturated liquid.

Step 4  $\rightarrow$  5, Saturated liquid is isentropically compressed in a pump to the pressure of the boiler to produce subcooled liquid

# 2.4 NaCl Phase-Change Thermal-Storage System

One disadvantage of solar thermal energy is that this energy is only available during the day. A solution to this problem is a phase-change thermal-storage system that collects surplus heat during sunshine hours for later use during nighttime operation [18]. This would allow the SA cycle to operate continuously.

A phase-change thermal storage system is based on heat absorption (or release) as a storage material undergoes a phase change from solid to liquid or liquid to gas (or viceversa). Typical storage materials include inorganic salts because of their high energy storage density and the ability to discharge heat at a constant temperature corresponding to the phase transition temperature of the material [19].

A schematic of a phase-change thermal-storage system with NaCl as the storage material is shown in Figure 2.5. Molten NaCl is stored at the bottom of the container, while liquid sodium floats on top of the NaCl. Two heat exchangers are part of the storage unit: one to heat the salt stream coming from SA cycle and one to melt the solidified NaCl. NaCl with a melting point of 800 °C is an attractive storage material in terms of low cost and high specific latent heat, 481 kJ/kg [19].



Figure 2.5: Schematic of a Phase-Change Thermal-Storage System with NaCl [20]

During daytime and nighttime operations, molten NaCl undergoes a phase change and solidifies at a constant temperature of 800 °C as energy is exchanged via the vaporization of liquid sodium. The vaporization and condensation of sodium over the molten salt is used as an intermediate highly conductive fluid to transfer heat from the storage material to the heat exchanger. Vapor flows upward, to a heat exchanger, where condensation occurs on the surface. Due to gravity, the liquefied sodium in the form of small droplets is passively returned to the storage region. This avoids directly embedding the heat exchanger into the storage material where direct solidification of the molten salt will occur and thus, increasing heat transfer resistance. Furthermore, the high vapor pressure and low solubility of sodium in NaCl makes sodium as an attractive heat transfer fluid. During daytime, liquid sodium is transported to and from the solar receiver where it is heated by solar thermal energy. Solidified NaCl is then re-melted by the heated sodium via a heat exchanger. The amount of sodium and NaCl can be adjusted so that surplus thermal energy can be stored as latent heat for nighttime operation. Studies on phasechange thermal-storage system with NaCl have been conducted by others on a lab-scale level [19].

#### **2.5 Solar Thermal Energy and Solar Fields**

The SA process is driven by solar thermal energy. In order to reach temperatures up to 800 °C, the required temperature to melt NaCl, a solar field, consisting of hundreds of heliostats, is used to concentrate sunlight to heat liquid sodium being transported from the NaCl phase-change thermal-storage system to the receiver tower. The phase-change thermal-storage system is used in order to operate the SA thermochemical plant continuously. A diagram of the solar field, the receiver tower, the NaCl phase-change thermal-storage system, and the SA thermochemical plant is shown in Figure 2.6.



Figure 2.6: Schematic of the Solar Field and the SA Thermochemical Plant [21]

Sizing of the solar field was conducted by using the National Renewable Energy Laboratory (NREL) Solar Advisor Model (SAM) and was accomplish by Roger Davenport of SAIC. Based on conditions at Barstow, California, a heliostat field of 231,600 m<sup>2</sup> with a tower height of 150 m is needed to deliver 50 MW<sub>th</sub> at 800 °C to the thermochemical plant [21]. A basis of 50 MW<sub>th</sub> was used for cost analysis of the SA production plant and is discussed in Chapter 6. The peak power was estimated to be 150 MW<sub>th</sub>. Figure 2.7 shows an example of a solar field with a solar receiver centralized in the middle of the field. Figure 2.7 is an image of Solar 2, which was a solar thermal plant built by the Department of Energy in 1995 in the Mohave Desert in California. Solar 2 consisted of 1926 heliostats, occupying a total area of 82,750 m<sup>2</sup>.



Figure 2.7: Solar Two, Mojave Desert, California [22]

Solar thermal is not a new technology and is currently being developed to generate electricity. Currently, a 2,600,000 m<sup>2</sup> solar thermal power plant called Ivanpah Solar Electric Generating System is being constructed by BrightSource Energy in the Mojave Desert, California and is reported to be 90% completed. This plant consists of 173,500 heliostat units with a concentrating tower of 459 ft in height and is projected to have a maximum power production of 392 MW [23]. The phase-change solar-thermal system as well as the SA thermochemical plant can be sized to match the power delivered by the solar field.

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# 3. Process Modeling of the Sulfur-Ammonia Cycle

# **3.1 Aspen Plus Process Simulation Software**

Simulation of the sulfur ammonia cycle was conducted with Aspen Plus chemical process simulation software. Aspen Plus V7.2 (24.0.4819) was the version used in this simulation. Aspen Plus is a graphical user interface that simulates chemical processes by predicting the behavior of chemical reactions using standard engineering principles, such as mass and energy balances, rate correlations, and phase and chemical equilibrium. By choosing the appropriate thermodynamic model, Aspen Plus uses mathematical models to predict the overall performance of chemical processes [1]. Aspen Plus can help design better plants, reduce plant design time, and increase profitability in existing plants by improving on current processes. Furthermore, Aspen Plus can be used to interactively change plant operating conditions and flow sheet configurations to predict new designs. Aspen Plus was used to simulate the steady-state SA cycle to determine the feasibility and the efficiency of the process and to incorporate laboratory data into the flow sheet. Figure 3.1 shows the full Aspen Plus process flow sheet of the sulfur-ammonia solar thermochemical hydrogen production plant. The process flow sheet consists of the oxygen producing half-cycle, the hydrogen producing half-cycle, and the Rankine power recovery system. Figure 3.2 illustrates a simplified plant schematic. The individual halfcycles and the Rankine power recovery system are discussed in Section 3.3, 3.4, and 3.5, respectively.









#### **3.2 Aspen Plus Model Chemistry**

The sulfur ammonia cycle consist of an oxygen and hydrogen producing halfcycles, each with their own set of reactions as discussed in Chapter 2. The process has electrolyte solutions, molten salts, and liquid as well as gas phases. Besides the stated reactions in Chapter 2, there are also complex interactions between by-products throughout the process. In order to properly design a process flow sheet that realistically simulates the SA cycle as a continuous solar thermal production plant, the appropriate thermodynamic model must be chosen, the correct general chemistry must be present, and thermodynamic data on salt mixtures obtained from literature must be incorporated.

## 3.2.1 Thermodynamic Model, ENTRL-SR

In an electrolyte solution, there is a larger degree of interactions between species compared to a non-electrolyte solution. Besides physical and inter-molecular interactions, ionic reactions and molecule-ion and ion-ion interactions occur. In the SA cycle, there are electrolytes present in the process, due to the dissociation of ammonium salts in water. The thermodynamic model chosen to govern the equilibrium relations within the reactors was the Electrolyte Non-Random Two-Liquid method (ENTRL-SR). The ENTRL-SR model is based on the Symmetric Electrolyte NRTL property model that is the most versatile electrolyte property model in Aspen Plus. The Symmetric Electrolyte NRTL property model is based on two fundamentals assumptions: the like-ion repulsion assumption and the local electroneutrality assumption [2]. The ENTRL-SR model calculates the activity coefficients, Gibbs free energy, enthalpy, and entropy based on a symmetric reference state for ionic components of pure fused salts. The symmetric option for the reference state for activity coefficients of ionic components must be specified when using this model in order to ensure consistency for the simulation. It is not possible to combine symmetric and nonsymmetric reference states for ions in the same simulation.

Furthermore, the ENTRL-SR model uses the Redlich-Kwong equation of state for the vapor phase as well as the Henry's law for solubility of supercritical gases. The ENTRL-SR model also uses the Symmetric Electrolyte NRTL model for handling of zwitterions.

#### **3.2.2 General Chemistry**

Reactions throughout the process flow sheet are subject to thermodynamic and equilibrium constraints, and thus, unreacted species are present. Besides the stated reactions in Chapter 2, side reactions as well as complex interactions between byproducts were incorporated into the process flow sheet. A summary of the primary reactions associated with their specific reactors as well as side reactions are as follow: Low temperature reactor:

$$(NH_4)_2SO_4 (aq) + K_2SO_4 (l) \leftrightarrow K_2S_2O_7 (l) + 2NH_3 (g) + H_2O (g)$$
(2.9)

$$(\mathrm{NH}_4)_2\mathrm{SO}_3(\mathrm{aq}) \leftarrow \mathbf{\mathcal{S}O}_2(\mathrm{g}) + \mathrm{H}_2\mathrm{O}(\mathrm{g}) + 2\,\mathrm{NH}_3(\mathrm{g}) \tag{3.1}$$

Mid-temperature reactor:

$$K_2S_2O_7(l) \leftrightarrow K_2SO_4(l) + SO_3(g)$$
(2.10)

High temperature reactor:

$$2SO_3(g) \leftrightarrow 2SO_2(g) + O_2(g) \tag{2.11}$$

Chemical absorber:

$$SO_2(g) + 2NH_3(g) + H_2O(l) \leftrightarrow (NH_4)_2SO_3(aq)$$
 (2.3)

$$SO_3(g) + 2NH_3(g) + H_2O(l) \leftrightarrow (NH_4)_2SO_4(aq)$$
(3.2)

Electrolyzer:

$$(NH_4)_2SO_3(aq) + H_2O(l) \rightarrow (NH_4)_2SO_4(aq) + H_2(g)$$
 (2.14)

$$O_2(aq) + 2(NH_4)_2 SO_3(aq) \rightarrow (NH_4)_2 SO_4(aq)$$
(3.3)

$$NH_3(aq) + H_2SO_4(aq) \rightarrow NH_4)_2SO_4(aq)$$
(3.4)

Other side reactions:

$$H_2SO_4(aq) \leftrightarrow SO_3(aq) + H_2O(l)$$
(3.5)

Furthermore, there are also electrolyte reactions throughout the process, due to

the dissociation of salts in water, and were also incorporated into the flow sheet.

Electrolyte reactions are summarized in Table 3.1.

Reaction	Туре	Stoichiometry	Equation
1	Equilibrium	$H_2O + HSO_3^- \leftrightarrow H_3O^+ + SO_3^{2-}$	(3.6)
2	Equilibrium	$2 H_2O + SO_2 \leftrightarrow H_3O^+ + HSO_3^-$	(3.7)
3	Equilibrium	$H_2O + H_2SO_4 \leftrightarrow H_3O^+ + HSO_4^-$	(3.8)
4	Equilibrium	$H_2O + HSO_4^- \leftrightarrow H_3O^+ + SO_4^{2-}$	(3.9)
5	Equilibrium	$H_2O + NH_3 \leftrightarrow OH^- + NH_4^+$	(3.10)
6	Equilibrium	$2 \text{ H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+$	(3.11)
AM2SO3	Dissociation	$AM_2SO_3 \rightarrow SO_3^{2-} + 2 NH_4^+$	(3.12)
AM2SO4	Dissociation	$AM_2SO_4 \rightarrow SO_4^{2-} + 2 NH_4^+$	(3.13)

**Table 3.1: Electrolyte Reactions** 

# **3.2.3 Thermodynamics of Molten Salts**

The oxygen producing half-cycle involves high temperature molten potassium sulfate and potassium pyrosulfate salts; however, Aspen Plus did not have thermodynamic data for molten potassium pyrosulfate. To design a realistic flow sheet of this process, thermodynamic properties for potassium pyrosulfate was obtained from literature and was input manually. Table 3.2 shows the thermodynamic properties of potassium pyrosulfate that were used [3].

 Table 3.2: Thermodynamic Properties of Potassium Pyrosulfate [3]

Component	Temperature	∆H <sup>0</sup> 298.15 K	$\Delta S^{o}_{298.15 \text{ K}}$	C <sub>p</sub> [
	range [K]	[J/mol]	[J/mol/K]	J/mol/K]
$K_2S_2O_7$	298.15 <b>→</b> 3000	$-2.0 \times 10^{6}$	285.9	260.0

Phase equilibrium data of the  $K_2SO_4 + K_2S_2O_7$  system was also incorporated into the simulation to model the decomposition of potassium pyrosulfate, Eq. (2.10), in the mid-temperature reactor. The phase diagram of this system was obtained from literature and is shown in Figure 3.3 [3]. The vapor-liquid equilibrium line, in the region between approximately 850 K and 1050 K and a composition of 0% to 30%  $K_2SO_4$  at a pressure of 0.1 MPa, was mathematically modeled and incorporated into a design specification to simulate the equilibrium between the molten potassium salts and gaseous sulfur trioxide. The mathematical model and design specification blocks are discussed in Section 3.6.1.



# 3.3 The Oxygen Producing Half-Cycle Aspen Plus Process Flow Sheet

Figure 3.4 shows the Aspen Plus process flow sheet of the oxygen producing half-cycle which involves the production of ammonia, sulfur dioxide and oxygen gases. The oxygen producing half-cycle consists of the low temperature, mid-temperature, and high temperature reactors. The oxygen producing half-cycle reactions as well as side reactions are stated in Section 3.2.2.



Figure 3.4: Aspen Plus Flow Sheet of the Oxygen Producing Half-Cycle

# 3.3.1 Oxygen Producing Half-Cycle Simulation Blocks

The Gibbs reactor simulation block was used to simulate the low temperature reactor where ammonium sulfate was reacted with potassium pyrosulfate to produce gaseous water and ammonia. A Gibbs reactor simulation block was used where reaction kinetics are not known. Details of simulation blocks are discussed in

Appendix A. The Gibbs reactor was also used to simulate the high temperature reactor where sulfur trioxide decomposed to produce sulfur dioxide and oxygen. The low temperature and high temperature reactors were labeled LOWTEMRXR and HITEMRXR, respectively, and are shown in Figure 3.4. The stoichiometric reactor simulation block was used to simulate the mid-temperature reactor where potassium pyrosulfate decomposed to produce potassium sulfate and sulfur trioxide. The stoichiometric reactor simulation block was used because equilibrium data between liquid  $K_2S_2O_7$  and  $K_2SO_4$  and gaseous  $SO_3$  were known [3]. The mid-temperature reactor was labeled MIDTEMRXR. A separator simulation block was used to simulate the sulfur trioxide vapor-liquid separator and was labeled SEP-MID. MHeatX simulation blocks were used to simulate the heat exchange between stream SO2-O2-1 with streams SO3, K2S2O7, and SULFATE1 and were labeled HX1, HX2, and HX3, respectively. A heater simulation block was used to simulate the condensing of stream NH3-HOT, the low temperature reactor vapor product stream, as well as the heat exchange with the working fluid in the Rankine power recovery system. The heater block was labeled HX4H. The process flow sheet of the Rankine power recovery system is discussed in Section 3.5. Furthermore, a duplication simulation block, labeled NH3-DUP, was used to copy stream NH3-HOT and create an identical stream, stream NH3DEW. The heater block, labeled HXDEW, was used to determine the dew point temperature of stream NH3-HOT. The NH3-DUP and HXDEW simulation blocks are not part of the thermochemical plant, but were used to extract thermodynamic properties for design specification and optimization blocks.

Design specification and optimization blocks are discussed in Sections 3.6.1 and 3.6.2.

### 3.3.2 Oxygen Producing Half-Cycle Material and Energy Streams

Four sets of material streams were color coded and are shown in Figure 3.4. The neon green colored streams modeled the transport of aqueous ammonium salts, ammonium sulfite and ammonium sulfate, and were labeled SULFATE1, SULFATER, and SULFATE. The magenta colored streams modeled the transport of molten potassium salts, potassium sulfate and potassium pyrosulfate, and were labeled K2S2O7, K2S2O7-2, K2SO4SO3, K2SO4-R, and K2SO4. The gold colored streams modeled the transport of sulfur trioxide gas and gaseous mixtures of sulfur trioxide, sulfur dioxide, and oxygen and were labeled SO3, SO3-1, SO2-O2-1, SO2-O2-2, SO2-O2-3, and SO2-O2-4. The dark red colored streams modeled the transport of gaseous mixtures containing ammonia and were labeled NH3-HOT, NH3HOT1, and NH3 COLD. Furthermore, stream NH3DEW and NH3DEW1 were used to extract thermodynamic properties of stream NH3-HOT and are not physically part of the plant.

Recycle streams in the oxygen producing half-cycle were simulated with tear streams. Tear streams remove a recycle stream by manually guessing parameters of the initial stream and allowing Aspen Plus to progress through the simulation. Eventually the final stream is compared to the initial stream. In order for tear streams to properly simulate a recycle stream, tear streams needed to be identical or nearly identical. Design specification blocks were used to aid in the convergence of tear streams. Tear streams were labeled K2SO4, K2SO4-R, SULFATE, and SULFATER. Streams K2SO4 and K2SO4-R were used to simulate the recycling of potassium salts while streams SULFATE and SULFATER were used to simulate the recycling of ammonium salts.

The energy stream labeled Q1B modeled the transport of energy released from the condensing of the stream NH3-HOT. The energy stream labeled Q1DEW was used to determine the amount of energy released when stream NH3-HOT condensed to its dew point.

#### **3.3.3 Process Flow Sheet Description of the Oxygen Producing Half-Cycle**

In the oxygen producing half-cycle, aqueous ammonium salts, transported in stream SULFATE from the hydrogen producing half-cycle, and molten potassium salts, transported in stream K2SO4, entered the low temperature reactor where aqueous ammonium sulfate reacted with molten potassium sulfate to produce molten potassium pyrosulfate and gaseous ammonia and water vapor, Eq. (2.9). The gaseous mixture of ammonia and water were then transported in stream NH3-HOT to the HX4H heater block where the vapor stream was condensed before transported to the hydrogen producing half-cycle. Simultaneously, the molten potassium salts was transported in stream K2S2O7 to the HX2 heat exchanger and then to the mid-temperature reactor where molten potassium pyrosulfate decomposed to produce molten potassium sulfate and sulfur trioxide gas, Eq. (2.10). Sulfur trioxide gas was then separate from the molten potassium salts in the sulfur trioxide vapor-liquid separator, labeled SEP-MID, while the remaining potassium salts were recycled to the

low temperature reactor. Sulfur trioxide gas was transported in stream SO3 to the HX1 heat exchanger and then to the high temperature reactor, where sulfur trioxide decomposed to produce a gaseous mixture of sulfur trioxide, sulfur dioxide and oxygen, Eq. (2.11). The gaseous mixture was then transported in stream SO2-O2-1 through the HX1, HX2, and HX3 heat exchangers and then eventually to the hydrogen producing half-cycle. Parameters and results of each simulation block as well as heat integration are discussed in Chapter 4.

# 3.4 The Hydrogen Producing Half-Cycle Aspen Plus Process Flow Sheet

Figure 3.5 shows the Aspen Plus process flow sheet of the hydrogen producing half-cycle which involves the production of ammonium sulfate and hydrogen gas and the separation of oxygen gas. The hydrogen producing half-cycle consists of the chemical absorber and the electrolyzer. The hydrogen producing halfcycle reactions as well as side reactions are stated in Section 3.2.2.



Figure 3.5: Aspen Plus Flow Sheet of the Hydrogen Producing Half-Cycle

# 3.4.1 Hydrogen Producing Half-Cycle Simulation Blocks

A Gibbs reactor simulation block was used to simulate the chemical absorber where ammonia and sulfur dioxide were chemically absorbed in water to produce ammonium sulfite. The chemical absorber was labeled ABSORBER and is shown in Figure 3.5. Furthermore, the Gibbs reactor simulation block was used to simulate the reaction of water with sulfur trioxide and sulfur dioxide to produce sulfuric acid and was labeled GSOX. The stoichiometric reactor simulation block was used to simulate the electrolyzer where ammonium sulfite and water were electrochemically reacted to produce ammonium sulfate and hydrogen gas. The stoichiometric reactor simulation was also used to simulate side reactions that may occur with dissolved oxygen, ammonia, and sulfuric acid. The electrolyzer was labeled ELECTROL. A separator simulation block was used to simulate the hydrogen vapor-liquid separator and was labeled H2-SEP. A flash simulation block was used to simulate the oxygen vaporliquid separator and was labeled O2-SEP. Furthermore, a Radfrac simulation block was used to simulate the oxygen scrubber and was labeled O2WASH. A heater simulation block was used to model the cooling of stream MIXED, the chemical absorber product stream, as well as the heat exchange with the working fluid in the Rankine power recovery system. The heater block was labeled HX5. A pump simulation block was used to simulate the pressure change of the feed water and was labeled H2OPUP. A compressor simulation block was used to simulate the compression of hydrogen gas and was labeled H2COMP. One mixer and two splitter simulation blocks were used to simulate the mixing and splitting of materials streams and were labeled MIXER, H2OFDSP, and SO2SP, respectively.

### 3.4.2 Hydrogen Producing Half-Cycle Material and Energy Streams

Seven sets of material streams were color coded and are shown in Figure 3.5. The neon colored stream modeled the transport of aqueous ammonium salts and was labeled SULFATE1. The dark red colored stream modeled the transport of gaseous mixtures containing ammonia and was labeled NH3-COLD. The gold colored streams modeled the transport of aqueous sulfuric acid and gaseous mixtures of sulfur trioxide, sulfur dioxide, and oxygen, and were labeled SO2-O2-4, SO2-O2-5, SOX-1, and SOX-2. The dark green colored streams modeled the transport of oxygen containing mixtures and were labeled MIXED, MIXED1, O2-SEP, and O2. The black colored streams modeled the transport of the ammonium sulfite containing mixtures and were labeled SFITPRD, SFITDPRD2, and ELECPROD. The red colored streams modeled the transport of hydrogen gas and were labeled H2-2 and H2. The blue colored streams modeled the transport of water and were labeled H2OFEED, H2OFEED2, H2OFEED1, H2ORECYC, and H2OGS.

The energy stream labeled Q2B modeled the transport of energy released from the cooling of the stream MIXED. The energy stream labeled HEATIN modeled the required electrical energy needed to operate the electrolyzer. The required electrical energy was calculated with the ELECPOWR calculator block and is discussed in Section 3.6.3. The energy stream labeled HEATOUT modeled the transport of excess energy generated from the electrolyzer.

#### 3.4.3 Process Flow Sheet Description of the Hydrogen Producing Half-Cycle

In the hydrogen producing half-cycle, gaseous ammonia and water vapor were transported in stream NH3-COLD from the oxygen producing half-cycle to the chemical absorber. A gaseous mixture of sulfur trioxide, sulfur dioxide, and oxygen was transported in stream SO2-O2-4 from the oxygen producing half-cycle. A small fraction of the gaseous mixture was diverted to be used in the oxygen scrubber and the remaining mixture was transported to the chemical absorber, where condensed ammonia and sulfur dioxide was chemically absorbed in water to produce ammonium sulfite, Eq. (2.3). The chemical absorber vapor-liquid product mixture was transported in stream MIXED and then cooled in the HX5 heater block. Oxygen gas

was then separated from the ammonium sulfite containing liquid mixture in the oxygen vapor-liquid separator. The oxygen was then further purified by scrubbing the gaseous mixture with sulfuric acid and liquid water to separate out traces of water vapor from the oxygen gas. Simultaneously, the ammonium sulfite containing liquid mixture was transported in stream SFITPRD and then mixed with liquid water before entering into the electrolyzer, where hydrogen gas and aqueous ammonium sulfate was produced electrochemically, Eq. (2.14). Hydrogen gas was then separated in the hydrogen vapor-liquid separator, labeled H2-SEP, and then compressed to 25 bars. Simultaneously, the electrolyzer liquid product mixture, containing aqueous ammonium salts, was then transported in stream SULFATE1 and recycled to the oxygen producing half-cycle. Parameters and results of each simulation block are discussed in Chapter 4.

#### **3.5 The Rankine Power Recovery Aspen Plus Process Flow Sheet**

The Rankine power recovery system consists of two Rankine power cycles, labeled Rankine 1 and Rankine 2. Figure 3.6 shows the Aspen Plus process flow sheet of Rankine 1 and Figure 3.7 shows the Aspen Plus process flow sheet of Rankine 2. Rankine 1 was designed to use excess heat generated from the condensing of stream NH3-HOT, the low temperature vapor product stream, and the cooling of stream MIXED, the chemical absorber product stream, to generate electrical energy. Rankine 2 was design to use excess heat generated from Joule heating and heat of reaction in the electrolyzer to generate electrical energy. Joule heating is discussed in Section 3.6.2.



Figure 3.6: Aspen Plus Flow Sheet of Rankine 1



Figure 3.7: Aspen Plus Flow Sheet of Rankine 2

#### **3.5.1 Rankine Power Recovery Simulation Blocks**

Heater simulation blocks were used to simulate the recuperator where heat was exchange between stream 6, the outlet turbine stream, and stream 2, the outlet pump stream. The heater blocks were labeled RECUPSR and RECUPSIN and are shown in Figure 3.6. A heater block was also use to simulate the preheater where excess heat extracted from the cooling of stream MIXED was used to heat liquid ammonia, the working fluid. The Rankine 1 vaporizer, where liquid ammonia was vaporized by heat extracted from the condensing of stream NH3-HOT, was simulated with two heater blocks, labeled HX4C1 and HX4C2. Furthermore, the Rankine 2 vaporizer, where liquid ammonia was vaporized by heat extracted from excess heat generated in the electrolyzer, was also simulated with a heater block, labeled HXELECTR. Also, heater simulation blocks were used to model the condensing of the working fluid in both cycles and were labeled C-101 and C-102. Two pump simulation blocks were used to model the pressure change of the working fluid and were labeled P-101 and P-102. The compressor simulation block was specified to operate as an isentropic turbine and was used to simulate both turbines in the Rankine power recovery system. The turbines were labeled T-101 and T-102. Furthermore, a duplication simulation block, labeled DUP3, was used to copy stream 22 and create an identical stream, stream 22-DUP2. The heater block, labeled HXDUP3, was used to determine the dew point temperature of stream 22. The DUP3 and HXDUP3 blocks are not part of the thermochemical plant, but were used to extract thermodynamic properties for design specification and optimization blocks.

# **3.5.2 Rankine Power Recovery Material and Energy Streams**

Two sets of material streams were color-coded blue and are shown in Figures 3.6 and 3.7. Streams 1, 2, 3, 4, 4-1, 5, 6, 7 and 8 modeled the transport of ammonia in Rankine 1 while streams 11, 22, 22-DUP1, 33, 44, and 55 modeled the transport of ammonia in Rankine 2. Streams 22-DUP2 and 22-DUP3 were used to extract thermodynamic properties of stream 22 and are not physically part of the plant.

Similar to the oxygen producing half-cycle, tear streams were used to simulate recycle streams. Stream 1 and 8 are tear streams that simulate the recycle process of Rankine 1 while streams 11 and 55 are tear streams that simulate the recycle process of Rankine 2.

The energy stream labeled Q2A, modeled the transport of energy extracted from the cooling of the stream MIXED. The energy streams labeled Q1A and Q1AA modeled the transport of energy extracted from the condensing of stream NH3-HOT. The energy stream labeled QREC modeled the energy transfer within the recuperator. The energy stream labeled Q3A, modeled the transport of energy extracted from the electrolyzer.

#### 3.5.3 Process Flow Sheet Description of the Rankine Power Recovery System

In Rankine 1, liquid ammonia was pumped to high pressure in pump P-101 and then heated in the recuperator. Liquid ammonia was then further heated in the preheater and then fully vaporized in the vaporizer. Ammonia vapor at high pressure was then transported to turbine T-101 where ammonia was partially condensed and work was generated. The working fluid was then cooled in the recuperator and then condensed into liquid where it was then recycled to the pump. Parameters and results of each simulation block are discussed in Chapter 4.

In Rankine 2, liquid ammonia was pumped to high pressure in pump P-102 and then fully vaporized in the vaporizer. Ammonia vapor at high pressure was then transported to turbine T-102 where ammonia was partially condensed and work was generated. The working fluid was then condensed into liquid and then recycled to the pump.

# **3.6 Tools in Aspen Plus**

Besides simulation blocks, Aspen Plus has numerous tools including design specification, optimization, and calculator blocks to appropriately model chemical plants. Aspen Plus also has a sensitivity analysis tool. Design specification, optimization, and calculator blocks were used to determine operating parameters and to calculate the overall process efficiency. Sensitivity analyses were used to plot temperature profiles of heat exchangers and to verify if the determined operating parameters were feasible.

A summary of all the design specification, optimization, and calculator blocks as well as parameters that are associated with each individual block are tabulated in Table 3.3. Individual design specification, optimization, and calculator blocks are further discussed in Section 3.6.1, 3.6.2, and 3.6.3.

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DIOCKS					
Name of Block	Type of Block	Parameters that the block determines			
SO3CONV	Design specification	Conversion of mid-temperature reactor			
DS-1	Design specification	Temperature of mid-temperature reactor			
DS-2	Design specification	Total molar flow rate of stream K2SO4			
DS-3	Design specification	Water feed rate of stream H2OFEED			
DS-4	Design specification	Conversion of electrolyzer			
DS-5	Design specification	Temperature of stream SULFATE			
DS-6	Design specification	Split fraction of H2OFDSP splitter block			
PDS-1	Design specification	Discharge pressure of turbine T-101			
PDS-2	Design specification	Heat duty of HX4C1 heater block			
PDS-3	Design specification	Heat duty of HX4C2 heater block			
PDS-4	Design specification	Discharge pressure of turbine T-102			
MAXWORK1	Optimization	Discharge pressure of pump P-101			
		Total molar flow rate of stream 1			
MAXWORK2	Optimization	Discharge pressure of pump P-102			
		Total molar flow rate of stream 11			
		Heat duty of HXELECTR heater block			
ELECPOWER	Calculator	Electrical power needed for electrolyzer			
PLANTEFF	Calculator	Overall plant efficiency			

 Table 3.3: Summary of Design Specification, Calculator, and Optimization

 Blocks

# **3.6.1 Design Specification Blocks**

Design specification block allows for the control of certain flow sheet parameters based on defined constraints. Aspen Plus uses an iterative method to determine parameters based on these constraints. In Aspen Plus, design specifications are set up by defining a FORTRAN expression and variables that will be manipulated. Furthermore, design specification acts as a controller in which varying one parameter can alter another parameter in order to meet design criteria. A total of 11 design specification blocks were used throughout the simulation and were defined as SO3CONV, DS-1, DS-2, DS-3, DS-4, DS-5, DS-6, PDS-1, PDS-2, PDS-3, and PDS-4. The SO3CONV design specification block was used to determine the conversion within the mid-temperature reactor using phase equilibrium data obtained from literature. Four variables were defined: F4 as the molar flow rate (kmol/sec) of potassium sulfate, F7 as the molar flow rate (kmol/sec) of potassium pyrosulfate, T as the temperature (°C), and P as the pressure (bar) of stream K2SO4SO3, the mid-temperature product stream. The design criterion of this block was defined by the following FORTRAN expression:

$$\{10^{\left[-9.94+22.6\left(\frac{T\left[\circ C\right]+273.15}{1000}\right)-13.53\left(\frac{T\left[\circ C\right]+273.15}{1000}\right)^{0.838}\right]}\}\times\left\{\frac{F7}{P\left[bar\right]\times F4}\right\}=1$$
(3.14)

This expression was derived by Dr. Lloyd Brown and Jessie Littlefield [4] from the  $K_2SO_4 + K_2S_2O_7$  phase diagram shown in Figure 3.3. The equilibrium at the upper vapor-liquid interface is defined by:

$$K_{eq}[bar] = \frac{P[bar]X_{K2SO4}}{1 - X_{K2SO4}} = \frac{P[bar]F4}{F7}$$
(3.15)

The curve in the phase diagram was mathematically model to fit the data points. Because Eq. (3.15) and the equilibrium values from the paper should be equal, the target value of Eq. (3.14) was set to 1. The tolerance was set to 0.0001. The lower and upper boundaries of the mid-temperature reactor conversion were set to 0.001 and 0.999, respectively. The SO3CONV design specification varied the conversion at a given temperature and pressure from the lower to the upper boundary to determine the exact conversion that satisfied the equilibrium relationship.

The DS-1 design specification block was used to determine the temperature of the mid-temperature reactor such that stream KSO4SO3, the mid-temperature reactor product stream, and stream K2SO4, the low temperature reactor reactant stream, have the same composition of potassium sulfate and potassium pyrosulfate. Three variables were defined: F as the mole fraction of potassium sulfate in stream K2SO4, and F4 and F7 as the molar flow rate (kmol/sec) of potassium sulfate and potassium pyrosulfate, respectively in stream K2SO4SO3. The design criterion of this block was defined by the following FORTRAN expression:

$$F^{*}(F4+F7)/F4 = 1 \tag{3.16}$$

This forced the composition of tear streams K2SO4 and K2SO4-R to be identical. The tolerance was set to 0.0001. The lower and upper boundaries of the manipulated variable were set to 500 and 870 °C, respectively. The DS-1 design specification varied the mid-temperature reactor temperature from the lower to upper boundaries to determine the specific temperature that satisfied the design criterion.

The DS-2 design specification block was used to determine the total molar flow rate of the stream K2SO4 such that the operating temperature of the low temperature reactor was 400 °C. One variable was defined: TNH3 as the temperature (°C) of stream NH3-HOT, the low temperature reactor vapor product stream. The design criterion of the block was defined by the following FORTRAN expression:

$$\Gamma NH3 = 400$$
 (3.17)

In order for the low temperature reactor to run adiabatic, without direct solar thermal energy input, there must be enough specific heat from the molten potassium salt stream transported from the mid-temperature reactor in order to heat and drive the low temperature reactor at 400 °C. The tolerance was set to 0.01. The lower and upper boundaries of the manipulated variable were set to 1 and 300 kmol/sec, respectively. The DS-2 design specification varied the total molar flow rate from the lower to

upper boundaries to determine the specific flow rate of stream K2SO4 that satisfied the design criterion.

The DS-3 design specification block was used to determine the water feed flow rate into the process such that water flow rate in tear streams SULFATE and SULFATER were equal. Furthermore, this determined the required make-up feed water due to water losses from the electrolytic reduction of water to produce hydrogen in the electrolyzer. Two variables were defined: WA as the water molar flow rate (kmol/sec) in stream SULFATE and WB as the water molar flow rate (kmol/sec) in stream SULFATER. The design criterion of this block was defined by the following FORTRAN expression:

$$WA/WB = 1 \tag{3.18}$$

This forced the water flow rate of these two tear streams to be equal. The tolerance was set to 0.0001. The lower and upper boundaries of the manipulated variable were set to 0.1 and 10 kmol/sec, respectively. The DS-3 design specification varied the flow rate of stream H2OFEED from the lower to upper boundary in order to determine the specific flow rate that satisfied the design criterion.

The DS-4 design specification block was used to determine the conversion of the electrolytic reaction, Eq. (2.14), such that composition of ammonium sulfite and ammonium sulfate in tear streams SULFATE AND SULFATER were equal. Four variables were defined: SFATE and SFITE as the molar flow rate (kmol/sec) of ammonium sulfate and ammonium sulfite in stream SULFATE, respectively and SPHATE and SPHITE as the molar flow rate (kmol/sec) of ammonium sulfate and ammonium sulfite in stream SULFATER, respectively. The design criterion of this block was defined by the following FORTRAN expression:

$$(SPHATE * SFITE)/(SFATE * SPHITE) = 1$$
 (3.19)

This forced the composition of the two tear streams to be equal. The tolerance was set to 0.0001. The lower and upper boundaries of the manipulated variable were set to 0.0001 and 0.9999, respectively. The DS-4 design specification varied conversion in the electrolyzer from the lower to upper boundary to determine the exact conversion that satisfied the design criterion.

The DS-5 design specification was used to determine the temperature of stream SULFATE such that the temperature of tear streams SULFATE and SULFATER were equal. Two variables were defined: TSULFAT as the temperature (°C) of stream SULFATE and TSULFATR as the temperature (°C) of stream SULFATER. The design criterion of this block was defined by the following FORTRAN expression:

$$TSULFATR/TSULFAT = 1$$
(3.20)

This forced the temperature of the two tear streams to be equal. The tolerance was set to 0.0001. The lower and upper boundaries of the manipulated variable were set to 120 and 380 °C, respectively. The DS-5 design specification varied the temperature of stream SULFATE from the lower to upper boundary to determine the exact temperature that satisfied the design criterion.

The DS-6 design specification block was used to determine the split fraction in the H2OFDSP splitter block such that molar flow rate of the water feed stream (H2OGS) to the sulfuric acid wash reactor was 0.1 kmol/sec. One variable was defined: H2OGS as the molar flow rate (kmol/sec) of water in stream H2OGS. The design criterion of this block was defined by the following FORTRAN expression:

$$H2OGS = 0.1$$
 (3.21)

The tolerance was set to 0.0001. The lower and upper boundaries of the manipulated variable were set to 0.00001 and 1, respectively. The DS-6 design specification varied the split fraction from the lower to upper boundary to determine the exact split fraction that satisfied the design criterion.

The PDS-1 design specification block was used to determine the discharge pressure of turbine T-101 in the Rankine power recovery system in order to complete the cyclic process of the power plant. Two variables were defined: T1 as the temperature (°C) of stream 1 and T8 as the temperature (°C) of stream 8. The design criterion of this block was defined by the following FORTRAN expression:

$$T1 - T8 = 0$$
 (3.22)

This forced the temperature of tear streams 1 and 8 to be equal, thus closing the cyclic process. The tolerance was set to 0.001. The lower and upper boundaries were set to 0.01 and 20 bar, respectively. The PDS-1 design specification varied the discharge pressure of T-101 from the lower to upper boundary to determine the exact pressure that satisfied the design criterion.

The PDS-2 and PDS-3 design specification blocks were used to determine the amount of heat extracted from stream NH3-HOT, the low temperature reactor vapor product stream, to the Rankine power recovery system. Stream NH3-HOT must be condensed before entering the chemical absorber; thus, a phase change will occur when stream NH3-HOT cools from the vapor phase to the liquid phase. Information

was needed on the dew point of the stream NH3-HOT as well as the amount of heat that was extracted when the stream reached its dew point. In order to extract information, the total extracted energy, Q1B, from the cooling of stream NH3-HOT was divided into two heat streams, Q1A and Q1AA, both going into two separate heater blocks, HX4C1 and HX4C2, respectively. Furthermore, by using two heater blocks, thermodynamic properties of stream 4-1 were incorporated into an optimization constraint to ensure that there was no temperature crossover with the working fluid of the power plant and stream NH3-HOT. Optimization blocks and constraints are discussed in Section 3.6.2.

In the PDS-2 design specification block, three variables were defined: Q1A (MW) as the heat stream leaving the HX4C1 heater block, Q1B (MW) as the heat stream leaving the HX4H heater block, and Q1DEW (MW) as the heat stream leaving the HX4DEW heater block. The design criterion of the PDS-2 block was defined by the following FORTRAN expression:

$$Q1A/(Q1B-1DEW) = -1$$
 (3.23)

The tolerance was set to 0.001. The lower and upper boundaries were set to 400 and 2000 MW, respectively. The PDS-2 block varied the heat duty of the HXC1 heater block from the lower to upper boundary to determine the exact heat duty that satisfied the design criterion. Based on the design specification, Q1A was the amount of energy extract from stream NH3-HOT when the stream condensed from the dew point to the liquid phase.

In the PDS-3 design specification block, two variables were defined: Q1AA (MW) as the heat stream leaving the HX4C2 heater block and Q1DEW (MW) as the
heat stream leaving the HX4DEW heater block. The design criterion of the PDS-3 block was defined by the following FORTRAN expression:

$$Q1AA/Q1DEW = -1 \tag{3.24}$$

The tolerance was set to 0.0001. The lower and upper boundaries were set to 50 and 500 MW, respectively. The PDS-3 block varied the heat duty of the HXC2 heater block from the lower to upper boundary to determine the exact heat duty that satisfied the design criterion. Based on the design specification, Q1AA was the amount of energy extracted from stream NH3-HOT when the stream condensed from its vapor phase to its dew point.

The PDS-4 design specification block was used to determine the discharge pressure of the turbine T-102 in the Rankine power recovery system in order to complete the cyclic process of the power plant. Two variables were defined: T as the temperature (°C) of stream 11 and TR as the temperature (°C) of stream 55. The design criterion of this block was defined by the following FORTRAN expression:

$$\mathbf{T} - \mathbf{T}\mathbf{R} = \mathbf{0} \tag{3.25}$$

This forced the temperature of tear streams 11 and 55 to be equal, thus closing the cyclic process. The tolerance was set to 0.001. The lower and upper boundaries were set to 0.01 and 20 bar, respectively. The PDS-4 design specification varied the discharge pressure of T-102 from the lower to upper boundary to determine the exact pressure that satisfied the design criterion.

# **3.6.2 Optimization Blocks**

Optimization block allows for the maximizing and minimizing of userspecified objective functions by manipulating specified parameters based on design constraints. In Aspen Plus, optimization block is set up by specifying either maximizing or minimizing of a user-defined FORTRAN expression, variables that will be manipulated, and design constraints. Unlike design specification blocks, optimization blocks allow for inequality constraints as well as equality constraints. Optimization blocks were used to maximize total obtainable work from the Rankine power recovery system while avoiding temperature crossovers in the heat exchangers.

The Rankine power recovery system consists of two Rankine power plants, labeled Rankine 1 and Rankine 2, as shown in Figures 3.6 and 3.7. The MAXWORK1optimization block was used to maximize the total output work of Rankine 1 by determining the discharge pressure of pump P-101 and the flow rate of the working fluid while avoiding temperature crossovers in the heat exchangers. Nine variables were defined: TOTW1 as the total work output (W) of Rankine 1, T4 as the temperature (°C) of stream 4, TNH3COLD as the temperature (°C) of stream NH3-COLD, T41 as the temperature (°C) of stream 4-1, TNH3DEW1as the temperature (°C) of stream NH3DEW1, T5 as the temperature (°C) of stream 5, and TMIXED as the temperature (°C) of stream MIXED, T6 as the temperature (°C) of stream 6, TMIXED1 as the temperature (°C) of stream MIXED1. The objective function was set to maximize the following FORTAN expression:

The negative sign was used to correct for the direction of work flow. Four constraints were defined and are as the follow:

$$T4 \le TNH3COLD - 10 \tag{3.27}$$

$$T41 \le TNH3DEW - 10 \tag{3.28}$$

$$T5 \le TMIXED - 10 \tag{3.29}$$

$$T6 \le TMIXED1 - 10 \tag{3.30}$$

Aspen Plus can only detect temperature crossovers at the inlet and outlet streams of heat exchangers and cannot detect phase change temperature crossovers during the vaporizing or condensing of streams. Eq. (3.28) ensured that at the dew point of stream NH3-HOT, there was no temperature crossover with the working fluid as the stream condensed. Setting these four design constraints ensured that there was a  $\Delta T_{min}$  of 10 degrees in the heat exchangers, thus avoiding temperature crossovers. The lower and upper boundaries of pump P-101 were set to 80 and 160 bar, respectively, and the lower and upper boundaries of the flow rate for stream 1 were set to 35 and 100 kmol/sec, respectively.

The MAXWORK2 optimization block was used to maximize the total output of work of Rankine 2 by determining the discharge pressure of pump P-102, the flow rate of the working fluid, and the heat duty of the HXELECTR heater block while avoiding temperature crossovers. Seven variables were defined: TOTW2 as the total work output (W) of Rankine 2, Q3 as the heat stream (MW) leaving the HXELECTR heater block, ELECT as the required energy (MW) needed for the electrolyzer, NETHEAT as the net duty (MW) of the electrolyzer, T33 as the temperature (°C) of stream 33, T as the temperature (°C) of stream ELECPROD, and TDEW as the temperature (°C) of stream 22-DUP3. The objective function was set to maximize the following FORTRAN expression:

$$-1*TOTW2$$
 (3.31)

The negative sign was used to correct for the direction of work flow. Three constraints were defined as the follow:

$$-1*Q3 \le (ELECT*0.865) - (NETHEAT + ELECT)$$
 (3.32)  
T33 < T - 10 (3.33)

$$T33 \ge TDEW + 2 \tag{3.34}$$

Eq. (3.32) was used to determine the amount of heat extracted from excess heat generated by the electrochemical process in the electrolyzer. Excess heat was generated from heat of reaction and also from the applied cell voltage known as Joule heating. Heat generated from Joule heating was determined by the following equation:

$$Q_{\text{HEAT}} = i(E_{\text{CELL}} - E_{\text{eq}}) \tag{3.35}$$

where Q is heat, i is current,  $E_{CELL}$  is the potential of the electrolyzer, and  $E_{eq}$  is the thermodynamic potential of the overall electrolytic reaction shown in Eq. (2.14) [5]. Even though the thermodynamic potential of the overall electrolytic reaction is small, 0.108 V, a cell potential of 0.8 V is needed to overcome the kinetics of the reaction. Excess heat was extracted and used to generate electricity in Rankine 2 and were incorporated into Eq. (3.32). Moreover, Eq. (3.33) and Eq. (3.34) ensured that the working fluid was at least superheated by 2 degrees and heated to a temperature that did not cause a temperature crossover. The lower and upper boundaries of pump P-102 were set to 1 and 300 bar, respectively. The lower and upper boundaries of the

flow rate for stream 11 were set to 1 and 50 kmol/sec, respectively. The lower and upper boundaries of the HXELECTR heater block were set to 50 and 300 MW, respectively.

# **3.6.3 Calculator Blocks**

The calculator block is a user model that is capable of performing calculations and manipulations of defined variables. In Aspen Plus, the calculator block is set up by defining a FORTRAN code in a form of an equation to calculate a user-defined value. In order to accomplish this, variables associated with the code must be defined. Furthermore, the calculated value can be exported and used in the flow sheet or it can be displayed as a stand-alone value for reference. Calculator blocks were used to calculate the heat duty required for the electrolyzer and the overall process efficiency.

The ELECPOWR calculator block was used to calculate the required electrical power needed for the electrolyzer. The required power for the electrolyzer was calculated based on the FORTRAN code that was written on the basis of electrochemical relations and derivations. These derivations are shown Appendix B. The value of 0.8 V for the potential difference between the electrodes in the electrolyzer was provided by Electrosynthesis Company Inc. The power requirement was exported directly to the electrolyzer via the heat stream HEATIN. Excess heat from the electrolyzer was rejected by the heat stream HEATOUT. The required power for the electrolyzer was calculated by the following FORTRAN expression:

ELECPOWR = (2 \* 1000 \* F \* FH2 \* E)/1000000(3.36)

where ELECPOWR is the electrical energy (MW) needed to operate the electrolyzer, F is the Faraday's constant of 96,485 C/mol, FH2 is the molar flow rate (kmol/sec) of hydrogen produced, and E is the cell's potential (V). A snapshot of the complete FORTRAN code is shown in Appendix B.

The PLANTEFF calculator block was used to calculate the overall process efficiency. The FORTRAN code was written based on the DOE's working definition on efficiency which is defined as the following:

$$\eta = -\Delta H^{o}_{f[H2O(g)]} / (Q + E/\eta_e)$$
(3.37)

where  $\Delta H^{o}_{f[H2O(g)]}$  is the enthalpy of formation of water vapor in ideal gas state also known as lower heating value, Q is the total heat input to the cycle, E is the total electrical input into the process, and  $\eta_{e}$  is the efficiency by which imported electricity is produced. Efficiency is further discussed in Section 4.9.2.

The PLANTEFF block exported two variables: LHV and ETA. LHV is calculated by the follow expression:

LHV =  $(119.96 \text{ MJ/kg of } H_2)(1X10^6 \text{ J/MJ})(2.016 \text{ kg/kmol})(FH2)$  (3.38)

where LHV is the lower heating value (W) and FH2 is the molar flow rate (kmol/sec) of hydrogen produced. An If-Then-Else statement was incorporated into the FORTRAN expression. If the total generated power from the Rankine power system exceeded the total required power to operate the plant which includes electrical power to operate the electrolyzer, run the pumps and compressors, and electrically heat the high temperature reactor, then the efficiency was calculated by the following FORTRAN expression: where ETA is efficiency, LHV is the low heating value (W), and MIDTEMQ is the require energy (W) to operate the mid-temperature reactor. Extra electricity produced was not accounted for in the efficiency equation. If the required power exceeded the total generated power from the Rankine power system, electricity must be imported into the process. The efficiency was calculated by the following FORTRAN expression:

$$ETA = LHV/((ECSWORK + HITEMQ)/\eta_e + MITEMQ)$$
(3.40)

where ETA is efficiency, LHV is the low heating value (W), MIDTEMQ is the require energy (W) to operate the mid-temperature reactor, ECSWORK is the remaining energy (W) after the required power to operate the electrolyzer and pumps and compressors have been subtracted from the total generated power, HITEMQ is the require energy (W) to operate the high temperature reactor, and  $\eta_e$  is the efficiency at which imported electrical is produced. A snapshot of the complete FORTRAN code is shown in Appendix B.

# **3.6.4 Sensitivity Analyses**

Sensitivity analysis is a tool for determining process changes with varying operating and design variables. In Aspen Plus, a sensitivity analysis is set up by specifying lower and upper boundaries of a manipulated variable and dependent variables. Furthermore, a sensitivity analysis can be used to verify if solution to a design specification lies within the range of manipulated variable and design constrains. It can also be used to perform a process optimization. Sensitivity analyses were done to verify operation parameters, determined by the MAXWORK1optimization block, to ensure that there were no temperature crossovers in the heat exchanger.

The SENSNH3 sensitivity analysis was used to determine the temperature profile as the low temperature reactor vapor product stream condensed from the vapor phase to the liquid phase. A separate flow sheet was constructed to perform the sensitivity analysis and is shown in Figure 3.8. Determined operating conditions and composition of material streams were imported into the SENSNH3 sensitivity analysis. The temperature (°C) as a function of duty (MW) of the HX4H heater block was determined.

The SENSVAP sensitivity analysis was used to determine the temperature profile of the working fluid as the working fluid was heated from the liquid phase to the vapor phase. Similar to the SENSNH3 sensitivity analysis, operation conditions determined by the MAXWORK1 optimization block were imported into the SENSVAP sensitivity analysis. The temperature (°C) as a function of duty (MW) of the HX4C heater block was also determined.

The two temperature profiles generated were plotted together to verify that there were no temperature crossovers in the heat exchanger. Temperature profiles were also plotted for other heat exchangers in the Rankine power recovery system.

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Figure 3.8: Sensitivity Analysis Flow Sheet

# References

- [1] Aspen Plus Steady State Simulation User Guide Vol. 2, Aspen Technology Inc., Houston, TX. accessed on 22 April 2013.
- [2] Aspen Physical Property System, Physical Property Methods and Models 11.1, Aspen Technology In., Cambridge, MA. accessed on 22 April 2013.
- [3] Lindberg, D., Backman, R., Chartrand, P., "Thermodynamic Evaluation and Optimization of the (Na<sub>2</sub>SO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>S<sub>2</sub>O7 + K<sub>2</sub>S<sub>2</sub>O7) System," *Journal of Chemical Thermodynamics*, v.38, **2006**, p. 1568-1583
- [4] Littlefield, J., "Solar Thermochemical Hydrogen Production Plant Design," M.S. Thesis, University of California, San Diego, CA (2012)
- [5] Pletcher, D., Walsh, F., "Electrochemical Engineering," *Industrial Electrochemistry*, 2<sup>th</sup> ed. Blackie Academic & Professional: UK, **1990**, p. 60-64

# 4. Base Case Results

A continuous SA thermochemical plant was simulated in Aspen Plus and the flow sheet is shown in Figure 3.1. The NaCl phase-change thermal-storage system and the solar field were not modeled in Aspen Plus and are not shown in the flow sheet. The main focus was to design a flow sheet to simulate the SA thermochemical plant, such that the plant can incorporate a NaCl phase-change thermal-storage system for continuous operation. Furthermore, a Rankine power recovery system was also integrated into the process, such that all required electricity needed to operate the entire SA thermochemical plant was generated internally from waste heat. This would eliminate the need to import electricity, thus making the plant self-sustaining. A base case was first designed and simulated. Then operating parameters were varied to study their effects on overall process efficiency and performance. Case studies in which specific variables were studied are discussed in Chapter 5.

Various tools such as design specification, duplication, and optimization blocks were used to simulate the process, as well as optimizing the total power produced from the Rankine power recovery system. Sensitivity analyses were done to determine if there were temperature crossovers in heat exchangers by plotting temperature profiles.

#### 4.1 Energy and Mass Balances of a Continuous SA Thermochemical Plant

Energy and mass balances for a continuous SA thermochemical plant are shown in Table 4.1. Table 4.1 summarizes the flow of energy and materials in and out of the thermochemical plant. These results were derived from the base case scenario in which the operating plant pressure was 9 bar. This pressure was chosen as the base case because previous simulations done by Jessie Littlefield [1] and FSEC [2] were at this pressure. The concentration of ammonium sulfate in the electrolyzer product stream was specified to be 3.0 M because Electrosynthesis Company Inc. was conducting research on the electrolyzer at this concentration [3]. The low temperature reactor was specified to operate at 400 °C because experimental studies conducted by Mimi Wang showed that the production of ammonia gas occurred approximately at that temperature [4]. The mid-temperature reactor was specified to operate at 790  $^{\circ}$ C to ensure that heat will flow from the phase-change thermal-storage system, operating at 800 °C, to the reactor. The high temperature reactor was specified to operate at 956 <sup>o</sup>C such that was enough energy generated by the Rankine power recovery system to run the entire thermochemical plant. The electrolyzer was specified to operate at 140 <sup>o</sup>C because Electrosynthesis Company Inc. was also operating a lab-scale electrolyzer at that temperature [3]. The chemical absorber was specified to operate adiabatically and the operating temperature was determined by Aspen Plus. Key parameters are summarized in Table 4.2. Operating parameters are further discussed with their associated simulation blocks. The simulated thermochemical plant has the capacity to produce and deliver hydrogen at 25 bar at a production rate of  $\sim 1.7 \text{ X } 10^5 \text{ kg/day}$ . This is equivalent to ~268 MW of energy, based on the lower heating value of hydrogen. The efficiency of the overall process was calculated to be 13%. This value was based on DOE's working definition of efficiency and is defined by Eq. (3.27). Lower heating value and process efficiency are discussed in Section 4.9.2. The overall plant design can be linearly scaled up or down by matching the thermal

energy needed to operate the mid-temperature reactor to the thermal energy captured by the solar field.

Energy Balance [MW]		Mass Balance [kg/sec]	
Energy In		Mass In	
Low Temp. Reactor Solar Thermal Input	0	Feed Water	22
Mid Temp. Reactor Solar Thermal Input	2025	Potassium Salt Stream (Manual Tear)	6787
High Temp. Reactor Solar Thermal Input	110	Ammonium Salt Stream (Manual Tear)	693
Electrolyzer Power Requirement	172	Rankine 1 Working Fluid (Manual Tear)	1247
H2 Compressor	6	Rankine 2 Working Fluid (Manual Tear)	207
H2O Pump	0	Total:	8956
H2O Feed	-351		
Rankine 1 Pump	22	Mass Out	
Rankine 2 Pump	4	Hydrogen Product	2
Sulfur Trioxide Separator	2	Oxygen Product	20
Potassium Salt Stream (Manual Tear)	-32825	Potassium Salt Stream (Manual Tear)	6787
Ammonium Salt Stream (Manual Tear)	-9272	Ammonium Salt Stream (Manual Tear)	693
Rankine 1 Working Fluid (Manual Tear)	-4781	Rankine 1 Working Fluid (Manual Tear)	1247
Rankine 2 Working Fluid (Manual Tear)	-794	Rankine 2 Working Fluid (Manual Tear)	207
Total:	-45682	Total:	8956
Energy Out		Difference [%]	0
Turbine 1	285		
Turbine 2	30	Performance Summary	
H2 Separator	25	Overall Efficiency [% }	13%
Condenser 1	1453		
Condenser 2	191		
Electrolyzer Heat Loss	23		
Н2	10		
02	-25		
Potassium Salt Stream (Manual Tear)	-32825		
Ammonium Salt Stream (Manual Tear)	-9272		
Rankine 1 Working Fluid (Manual Tear)	-4782		
Rankine 2 Working Fluid (Manual Tear)	-794		
Total:	-45683		
Difference [%]	0.002		

 Table 4.1: Energy and Mass Balances of Base Case

Key Operating Plant Parameters for Base Case	
Plant Pressure (bar)	9
Concentration of $(NH_4)_2SO_4$ in electrolyzer product stream (M)	3.0
Temperature of low temperature reactor (°C)	400
Temperature of mid-temperature reactor (°C)	790
Temperature of high temperature reactor (°C)	956
Temperature of electrolyzer (°C)	140
Temperature of chemical absorber (°C)	161

 Table 4.2: Plant Parameters for Base Case

Enthalpies were based on an elemental reference state where the enthalpy is zero for the elements in their standard state at 25 °C. This standard state was used by Aspen Plus so that reaction enthalpies were computed automatically from reaction stoichiometry. The total energy in and out of the system differed by 0.002%, -45,682 and -45,683 MW, respectively. The difference was caused by convergence error from iterative simulations done by the Aspen Plus software to achieve a final result. The total material in and out of the system did not differ. Furthermore, not only were the total energy and material streams in and out of the system were nearly identical, the tear streams were also nearly identical in energy as well as mass. The energy of the Rankine 1 tear streams differed by 0.02 %. It was concluded that the recycle streams were properly simulated with tear streams. These identical tear streams were achieved by the DS-1, DS-3, DS-4, DS-5, PDS-1, and PDS-4 design specification blocks. Results of these design specification blocks are shown in Section 4.8. Compositions of tear streams are shown in Appendix D. The heat duties, tabulated in Table 1, are further discussed with their associated simulation blocks.

#### 4.2 Thermochemical Reactors, Chemical Absorber, and Electrolyzer

The low, mid, and high temperature reactors either uses heat directly from the NaCl phase-change thermal-storage unit, from the specific heat of molten salts, or from electrical heating to drive their respective reactions. The low and high temperature reactors as well as the chemical absorber were modeled using a Gibbs reactor. However, the mid-temperature reactor and electrolyzer were modeled using stoichiometric reactors.

Table 4.3 lists the operating parameters of the low temperature reactor as well as the outlet vapor fraction. Note that values generated by Aspen Plus software are reported; the large number of significant figures does not reflect the actual accuracy of the results. The operating pressure was specified to be 9 bar. Experimental studies conducted by Mimi Wang showed that 400 °C was a reasonable temperature to drive the reaction of ammonium sulfate with potassium sulfate to produce molten potassium pyrosulfate and gaseous ammonia and water vapor, Eq. (2.9) [4]. The DS-2 design specification was used to determine the flow rate of stream K2SO4 such that the reactor operated adiabatically at 400 °C. Results of the DS-2 design specification block are shown in Section 4.8. Based on this configuration, the low temperature reactor did not need to be directly linked to the phase-change thermal-storage unit because there was enough specific heat from the molten potassium salt mixture, transported from the mid-temperature reactor, to heat the low temperature reactor up to  $400 \,^{\circ}$ C. This simplified the overall solar configuration of the plant because only the mid-temperature reactor is heated by the phase-change thermal-storage unit and the rest of the plant is powered by the recycling of heat.

<b>RGibbs Results</b>	
Outlet Temperature [°C]	400.001892
Outlet Pressure [bar]	9
Heat Duty [MW]	0
Net Heat Duty [MW]	0
Vapor Fraction	0.53871536

 Table 4.3: Summary of the Low Temperature Reactor Results

Table 4.4 shows the mass and energy balances of the low temperature reactor. The column labeled "generated" shows the production of gaseous ammonia and sulfur dioxide at a total rate of 3.17 kmol/sec. The default error tolerance for Aspen Plus was preset to  $10^{-4}$  and as long as the relative difference was less than the specified tolerance within a certain maximum number of iterations, the mass balance is deemed to have converged.

 Table 4.4: Mass and Energy Balances of the Low Temperature Reactor

Total	In	Out	Generated	Relative Difference
Mole Flow [kmol/sec]	56.078242	59.249842	3.1716	2.3985e-16
Mass Flow [kg/sec]	7480.0614	7480.0614	0	1.2755e-13
Enthalpy [MW]	-42097.397	-42097.397	0	-7.091e-11

Table 4.5 shows the phase fractions, total flow rates, and compositions for the low temperature reactor product streams. The vapor and liquid phase fractions of the low temperature reactor were 0.54 and 0.46, respectively. The total flow rates for streams NH3-HOT, the low temperature reactor vapor product stream, and K2S2O7, the low temperature reactor liquid product stream, were 31.9 and 27.3 kmol/sec, respectively. The mole fractions of water vapor, ammonia, and sulfur dioxide gases for stream NH3-HOT were 0.90, 0.10, and 2.4 X  $10^{-3}$ , respectively. The mole

fractions of molten potassium sulfate and potassium pyrosulfate for stream K2S2O7 were 0.02 and 0.98, respectively.

Iteactor .				
Phase	Vapor	Liquid		
Phase Fraction	0.53871536	0.46128464		
Outlet Stream	NH3-HOT	K2S2O7		
Total Flow [kmol/sec]	31.9188	27.331042		
Component	Mole Fraction	Mole Fraction		
H2O	0.90063536	0		
NH3	0.09694600	0		
SO2	0.00241863	0		
K2SO4	0	0.02121500		
K2S2O7	0	0.978785		

 Table 4.5: Phase Composition of Outlet Streams of the Low Temperature Reactor

Table 4.6 lists the operating parameters of the mid-temperature reactor as well as the outlet vapor fraction. The outlet temperature and pressure of the midtemperature reactor were 792 °C and 9 bar, respectively. A total heat duty of 2025 MW was needed to decompose potassium pyrosulfate to produce potassium sulfate and sulfur trioxide gas. The heat duty is also tabulated in Table 4.1. The outlet vapor fraction of the mid-temperature reactor was determined to be 0.05. The NaCl phasechange thermal-storage system is used to heat the mid-temperature reactor and to drive the thermal decomposition of potassium pyrosulfate to produce potassium sulfate and sulfur trioxide, Eq. (2.10). The SO3CONV and DS-1 design specification blocks were used to determine the conversion and the temperature of the midtemperature reactor at a given pressure and stream composition such that the reactor followed thermodynamic data obtained from literature [5]. Results of the two design specifications are shown in Section 4.8. With a total flow rate of 27.3 kmol/sec at 9 bar for stream K2SO4 and mole fractions of 0.075 and 0.925 for potassium sulfate and potassium pyrosulfate, respectively, an outlet temperature of ~790 °C was achieved. The phase-change thermal-storage unit was designed to operate at 800 °C. A  $\Delta T_{min}$  of 10 degrees was used to ensure that heat will flow from the phase-change thermal-storage system to the mid-temperature reactor. The integration of the phasechange thermal-storage system will allow for the SA thermochemical plant to operate continuously.

 Table 4.6: Summary of the Mid-Temperature Reactor Results

RStoich Results	
Outlet Temperature [°C]	791.619984
Outlet Pressure [bar]	9
Heat Duty [MW]	2025.10097
Net Heat Duty [MW]	2025.10097
Vapor Fraction	0.0495898

Table 4.7 shows the mass and energy balances of the mid-temperature reactor. The column labeled "generated" indicates sulfur trioxide generation. Sulfur trioxide was generated at a rate of 1.47 kmol/sec.

Total	In	Out	Generated	<b>Relative Difference</b>
Mole Flow	27.331042	28.8011628	1.47012079	0
[kmol/sec]				
Mass Flow	6904.52738	6904.52738	0	0
[kg/sec]				
Enthalpy [MW]	-35357.899	2025067640	0	-1.0000175

 Table 4.7: Mass and Energy Balances of the Mid-Temperature Reactor

Table 4.8 shows the vapor-liquid (VL) equilibrium results for the midtemperature reactor. In Table 4.8, column labeled "F" shows the mole fractions of each component in stream K2SO4SO3, the mid-temperature reactor product stream. The column labeled "X" is the equilibrium liquid mole fraction and the column labeled "Y" is the equilibrium vapor mole fraction in the product stream. The column labeled "K" is the vapor-liquid-equilibrium constant (K = Y/X) of the product stream. Most of the vapor phase consisted of sulfur trioxide gas with a mole fraction of 1, while most of the liquid phase consisted of potassium pyrosulfate with a mole fraction of 0.92.

Component	F	X	Y	Κ
SO3	0.0510438	0.00152986	1	653.652916
K2SO4	0.07117590	0.07488967	1.3522e-81	1.8056e-80
K2S2O7	0.87778029	0.92358046	1.5826e-80	1.7136e-80

Table 4.8: VL Equilibrium Results for the Mid-Temperature Reactor

Table 4.9 shows the operating parameters of the high temperature reactor as well as the outlet vapor fraction. The high temperature reactor was specified to operate at 956 °C and 9 bar. A total heat duty of 110 MW was needed to decompose sulfur trioxide to produce sulfur dioxide and oxygen and is also tabulated in Table 4.1. Furthermore, the outlet vapor fraction of the high temperature reactor was determined to be 1.00. Electrical heating was used to drive the decomposition of sulfur trioxide, Eq. (2.11). At an operating temperature of 956 °C with a plant pressure of 9 bar, there was enough energy generated by the Rankine power recovery system to operate the electrolyzer, run the pumps and compressors, and electrically heat the high temperature reactor. Power generation and requirements are discussed in Section 4.6.3.

RGibbs Results	
Outlet Temperature [°C]	955.785
Outlet Pressure [bar]	9
Heat Duty [MW]	110.29808
Net Heat Duty [MW]	110.29808
Vapor Fraction	1

 Table 4.9: Summary of the High Temperature Reactor Results

Table 4.10 shows the mass and energy balances of the high temperature reactor. The column labeled "generated" shows the oxygen generation from the high temperature reactor. Oxygen was produced at a rate of 0.56 kmol/sec via the decomposition of sulfur trioxide.

Total	In	Out	Generated	Relative Difference
Mole Flow	1.47012079	2.03176141	0.56164062	0
[kmol/sec]				
Mass Flow	117.704045	117.704045		-2.173e-15
[kg/sec]				
Enthalpy [MW]	-488.68165	110297702		-1.0000044

 Table 4.10: Mass and Energy Balances of the High Temperature Reactor

Table 4.11 shows the phase compositions of stream SO2-O2-1, the high temperature reactor product stream. The total material flow rate of stream SO2-O2-1 was determined to be 2.03 kmol/sec with mole fractions of 0.28, 0.55, and 0.17 for oxygen, sulfur dioxide and sulfur trioxide, respectively.

Phase	Vapor
Phase Fraction	1
Outlet Stream	SO2-O2-1
Total Flow [kmol/sec]	2.03176141
Component	Mole Fraction
02	0.2764304
SO2	0.5528608
SO3	0.1707088

 
 Table 4.11: Phase Composition of Outlet Streams of the High Temperature Reactor

Table 4.12 lists the operating parameters of the chemical absorber as well as the outlet vapor fraction. The chemical absorber was specified to operate adiabatically at 9 bars. An outlet temperature of 161 °C was achieved. No energy input was required; thus the Gibbs free energy was the main driving force for the chemical absorption of sulfur dioxide and ammonia in water, Eq. (2.3). The outlet vapor fraction of the chemical absorber was determined to be 0.05.

 Table 4.12: Summary of the Chemical Absorber Results

<b>RGibbs Results</b>	
Outlet Temperature [°C]	160.8
Outlet Pressure [bar]	9
Heat Duty [MW]	0
Net Heat Duty [MW]	0
Vapor Fraction	0.05098458

Table 4.13 shows the mass and energy balances of the chemical absorber. The column labeled "generated" indicates the chemical absorption of ammonia, sulfur dioxide, and sulfur trioxide in water. Ammonia, sulfur dioxide and sulfur trioxide were absorbed at a total rate of 4.64 kmol/sec.

Total	In	Out	Generated	Relative Difference
Mole Flow [kmol/sec]	33.9485296	29.3109777	-4.637552	0
Mass Flow [kg/sec]	693.120365	693.120365		2.9524e-14
Enthalpy [MW]	-8797.0423	-8797.046		4.1613e-7

Table 4.13: Mass and Energy Balances of the Chemical Absorber

Table 4.14 shows the phase fractions, total flow rates, and compositions of stream MIXED, the chemical absorber product stream. The vapor and liquid fractions were 0.05 and 0.95, respectively. The mole fractions of the vapor component in stream MIXED were 0.37, 0.62, and  $1.8 \times 10^{-3}$  for oxygen, water, and ammonia, respectively. The mole fractions of the liquid component in stream MIXED were 0.94, 0.04, and 0.01 for water, ammonium sulfite, and ammonium sulfate, respectively.

respectively.

Table 4.14. VE Equilibrium Results for the Chemical Absorber					
Phase	Vapor	Liquid			
Phase Fraction	0.05098458	0.94901541			
Outlet Stream	MIXED	MIXED			
Total Flow [kmol/sec]	1.4944081	27.8165696			
Component	Mole Fraction	<b>Mole Fraction</b>			
02	0.37400517	7.7736e-5			
H2O	0.62418899	0.94434924			
NH3	0.00180584	1.3088e-17			
AMHSO3	0	0			
AM2SO3	0	0.04311667			
AM2SO4	0	0.01245634			
SO2	0	0			
SO3	0	0			

Table 4.14: VL Equilibrium Results for the Chemical Absorber

Table 4.15 shows the operating parameters of the electrolyzer as well as the outlet vapor fraction. The electrolyzer was specified to operate at 140  $^{\circ}$ C and 9 bar which was given by Electrosynthesis Company Inc [3]. The outlet vapor fraction of

the Electrolyzer was determined to be 0.06. Stream SULFATE, the electrolyzer product stream, was specified to have a concentration of 3.0 M ammonium sulfate because Electrosynthesis Company Inc. was conducting electrolyzer research at that concentration. Furthermore, the molar ratio of ammonium sulfite to total salt was also specified at be 0.05. This represented a 95% conversion of ammonium sulfite to ammonium sulfate in the electrolyzer.

RStoich Results	
Outlet Temperature [°C]	140
Outlet Pressure [bar]	9
Heat Duty [MW]	-68.07935
Net Heat Duty [MW]	-239.97985
Vapor Fraction	0.05820450

 Table 4.15: Summary of the Electrolyzer Results

In order to maintain the electrolyzer at 140 °C, excess energy of 68 MW was generated from heat of reaction and is represented by the row labeled "Heat Duty". Because there was an input heat stream, stream HEATIN, on the electrolyzer, the Heat Duty and the Net Heat Duty values were different. The Net Heat Duty is sum of the Heat Duty and the total required energy, calculated by the ELECPOWR calculator block, to operate the electrolyzer. Results of the ELECPOWR calculator block are shown in Section 4.9.1. The required power to run the electrolyzer was determined to be 172 MW and was exported to the electrolyzer block via the heat stream HEATIN. The Net Heat Duty of the electrolyzer is -240 MW.

However, a fraction, 0.865, of the calculated required power to run the electrolyzer as well as 68 MW of excess energy was used in the Rankine power recovery system to transform excess heat generated by Joule heating and heat of reaction into electrical energy. This resulted in an energy loss of 23 MW and is

tabulated in Table 4.1. Joule heating is discussed in Section 3.6.2.

Table 4.16 shows the mass and energy balances of the electrolyzer. The column labeled "generated" shows the reaction of dissolved oxygen, ammonia, and sulfuric acid at a total rate of 0.01 kmol/sec. Table 4.17 shows the VL equilibrium results for the electrolyzer.

Total	In	Out	Generated	Relative Difference
Mole Flow [kmol/sec]	29.8681033	29.8610856	-0.0070177	1.1895e-16
Mass Flow [kg/sec]	695.489386	695.489386		-1.635e-16
Enthalpy [MW]	-9200.5947	-9028.692		-0.0186836

 Table 4.16: Mass and Energy Balances of the Electrolyzer

 Table 4.17: VL Equilibrium Results for the Electrolyzer

Component	F	Χ	Y	K
H2O	0.91089274	0.94413053	0.37307862	0.39515577
H2SO4	4.0522e-6	4.3026e-6	3.3179e-17	7.7113e-12
AM2SO3	0.00258531	0.00274508	2.107e-96	7.038e-106
AM2SO4	0.04922793	0.05227030	2.8103e-96	4.929e-107
H2	0.03728996	0.00084977	0.62692138	737.749083

# 4.3 Separators and Scrubber

Separators and a gas scrubber were used to separate intermediate gas components from liquid components as well as to separate hydrogen and oxygen gases. The Sep block was used to simulate the sulfur trioxide vapor-liquid separator and the hydrogen vapor-liquid separator. The Flash block was used to simulate the oxygen vapor-liquid separator, and the RadFrac block was used to simulate the oxygen scrubber. Table 4.18 shows the heat duty and the split fractions of the sulfur trioxide vapor-liquid separator. Sulfur trioxide was specified to be completely separated from the molten potassium salt mixture. Furthermore, a heat duty of 2 MW was needed to separate sulfur trioxide from the molten salt mixture and is also tabulated in Table 4.1. Table 4.19 shows the mass and energy balances. A total material flow rate of 28.80 kmol/sec was transported in and out of the separator. Sulfur trioxide gas was separated from the molten potassium salt mixture and transported to the high temperature reactor.

Heat Duty [MW]	2.09981128		
Component ID	K2SO4-R	SO3	
H2O	0	0	
H2	0	0	
02	0	0	
NH3	0	0	
SO2	0	0	
SO3	0	1	
H2SO4	0	0	
K2SO4	1	0	
K2S2O7	1	0	
AM2SO4	0	0	
AM2SO3	0	0	
AMHSO3	0	0	
H2SO3	0	0	

 Table 4.18: Summary of Sulfur Trioxide Vapor-Liquid Separator Results

Table 4.19: Mass and Energy	Balances of Sulfu	ır Trioxide	Vapor-Liquid
	Separator		

Total	In	Out	<b>Relative Difference</b>
Mole Flow [kmol/sec]	28.8011628	28.8011628	0
Mass Flow [kg/sec]	6904.52738	6904.52738	1.3172e-16
Enthalpy [MW]	-33332.798	-33330.698	-6.3e-05

Table 4.20 shows the heat duty and the split fractions of the hydrogen vapor-

liquid separator. Hydrogen was specified to be completely separated from the

electrolyzer liquid product components. Furthermore, a total heat loss of 25 MW was determined when separating hydrogen gas and is also tabulated in Table 4.1. Table 4.21 shows the mass and energy balances. A total material flow rate of 29.86 kmol/sec was transported in and out of the separator.

Heat Duty [MW]	-24.940222	
<b>Component ID</b>	H2-2	SULFATE1
H2O	0	1
H2	1	0
02	0	0
NH3	0	0
SO2	0	0
SO3	0	0
H2SO4	0	1
K2SO4	0	0
K2S2O7	0	0
AM2SO4	0	1
AM2SO3	0	1
AMHSO3	0	0
H2SO3	0	1

 Table 4.20: Summary of Hydrogen Vapor-Liquid Separator Results

Tab	le 4	.21:	Mass	and	Energy	<b>Balances</b>	of the	Hydroge	en Var	or-Lia	uid Se	parator
	-				- 0/							

Total	In	Out	<b>Relative Difference</b>
Mole Flow [kmol/sec]	29.8610856	29.8610856	0
Mass Flow [kg/sec]	695.489386	695.489386	0
Enthalpy [MW]	-9268.674	-9293.6143	0.00268358

Table 4.22 shows the operating parameters of the oxygen vapor-liquid

separator as well as the outlet vapor fraction. Table 4.23 shows the mass and energy balances. The separator was specified to operate adiabatically and the outlet temperature was determined to be 142 °C. Furthermore, the outlet vapor fraction of the separator was determined to be 0.03. A total material flow rate of 29.31 kmol/sec was transported in and out of the separator. Table 4.24 shows the vapor-liquid

equilibrium results of the separator. The mole fraction of oxygen in the vapor phase was 0.62 while the mole fraction of oxygen in the liquid phase was  $1.4 \times 10^{-4}$ , indicating that most of the oxygen was separated from the liquid phase.

Table 4.22: Summary of the Oxygen Vapor-Liquid Separator

Flash Results	
Outlet Temperature [°C]	142.002876
Outlet Pressure [bar]	9
Heat Duty [MW]	0
Net Heat Duty [MW]	0
Vapor Fraction	0.03081855

 Table 4.23: Mass and Energy Balances of the Oxygen Vapor-Liquid Separator

Total	In	Out	<b>Relative Difference</b>
Mole Flow [kmol/sec]	29.3109777	29.3109777	-2.424e-16
Mass Flow [kg/sec]	693.120365	693.120365	0
Enthalpy [MW]	-8874.9806	-8874.9703	-1.169e-06

Component	F	X	Y	K
H2O	0.928026	0.94543531	0.38053833	0.40249689
O2	0.01914228	0.00014799	0.61647418	4164.8313
NH3	0. 9.207e-05	0. 2.9573e-17	0.00298749	1.0102e+14
AM2SO3	0.04091838	0.04221953	1.1432e-95	2.7071e-94
AM2SO4	0.01182126	0.01219715	1.7056e-95	1.398e-93

 Table 4.24: VL Equilibrium Results for the Oxygen Vapor-Liquid Separator

Table 4.25 shows the split fraction results for the oxygen scrubber. Table 4.26 shows the mass and energy balances. The scrubber was specified to operate adiabatically at 9 bar. A total material flow rate of 2.13 kmol/sec was transported in and out of the scrubber. The mole fraction of oxygen in stream O2, the vapor product stream, is 1.00 while the mole fraction of oxygen in steam H2ORECYC, the liquid product stream, is  $2.1 \times 10^{-4}$ , also indicating that most of the oxygen was separated from the liquid component.

Component ID	02	H2ORECYC
H2O	0.07146577	0.92853423
02	0.99979319	0.00020680
NH3	0.00015981	0.99984018
H2SO4	0	1
H2SO3	0	1

 Table 4.25: Split Fraction Results for the Oxygen Scrubber

Table 4.26: Mass and Energy Balances of the Oxygen Scrubber

Total	In	Out	<b>Relative Difference</b>
Mole Flow [kmol/sec]	2.12928304	2.12928304	0
Mass Flow [kg/sec]	46.261745	46.261745	7.2282e-12
Enthalpy [MW]	-431.18412	-431.18411	-1.516e-08

# 4.4 H2O Feed Pump and H2 Compressor

A pump was used to pump feed water from 1 bar to 9 bar. The pump simulation block was used to simulate the pressure change of the feed water. Table 4.27 shows the results of the feed water pump. The net work to operate the pump was determined to be  $2.6 \times 10^{-2}$  MW and is also tabulated in Table 4.1. Figure 4.28 shows the mass and energy balances. A total feed water flow rate of 1.22 kmol/sec was pumped.

H2OPUP Results	
Water Flow Rate [kmol/sec]	1.22596104
Inlet Temperature [°C]	25
Outlet Temperature [°C]	25.2825673
Inlet Pressure [bar]	1
Outlet Pressure [bar]	9
Inlet Vapor Fraction	0
Outlet Vapor Fraction	0
Net Work [MW]	0.02607920

 Table 4.27: Summary of the H2OPUP Results

Total	In	Out	<b>Relative Difference</b>
Mole Flow [kmol/sec]	1.22596104	1. 1.22596104	1.8112e-16
Mass Flow [kg/sec]	22.0860315	22.0860315	1.6086e-16
Enthalpy [MW]	-350.63395	-350.63395	-5.877e-09

Table 4.28: Mass and Energy Balances of the Feed Water Pump

A compressor was used to compress hydrogen gas from 9 bar to 25 bar. The

compressor simulation block was used to simulate the compression of hydrogen gas.

Table 4.29 shows results of the hydrogen compressor. The net work required to

operate the compressor was determined to be 6 MW and is also tabulated in Table

4.1. Figure 4.30 shows the mass and energy balances. A total hydrogen flow rate of

1.11 kmol/sec was transported through the compressor.

H2COMP Results	
Hydrogen Flow Rate [kmol/sec]	1.11351885
Inlet Temperature [°C]	140
Outlet Temperature [°C]	335.417177
Inlet Pressure [bar]	9
Outlet Pressure [bar]	25.145
Inlet Vapor Fraction	1
Outlet Vapor Fraction	1
Net Work [MW]	6

 Table 4.29: Summary of the H2COMP Results

	Table 4.30: Mass	and Energy	Balances of	the Hvdrogen	Compressor
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Total	In	Out	<b>Relative Difference</b>
Mole Flow [kmol/sec]	1.11351885	1.11351885	0
Mass Flow [kg/sec]	2.24472038	2.24472038	7.2282e-12
Enthalpy [MW]	3.68509656	3.68509593	1.6869e-07

### **4.5 Heat Integration**

The SA thermochemical plant operates at different temperatures at various parts of the plant; therefore excess heat is produced throughout the process. Heat integration was done such that useable heat from material streams were exchanged with material streams that required heating or where it was useful to increase the temperature prior to entering a reactor. Furthermore, heat integration was also crucial for extracting waste heat to be used in the Rankine power recovery system in which thermal energy was transformed into electrical energy.

The outlet temperature of the high temperature reactor was specified to be 956 <sup>o</sup>C. Therefore, stream SO2-O2-1, the high temperature reactor outlet product stream, contained useful heat that could be extracted to heat other material streams in order to reduced overall energy consumption of the process. The hot vapor product stream was used to heat up stream SO3, the reactant stream entering the high temperature reactor, stream K2S2O7, the reactant stream entering the mid-temperature reactor, and stream SULFATE1 the electrolyzer product stream entering the low temperature reactor. MHeatX simulator bocks were used simulate the heat exchange between stream SO2-O2-1 and the stated material streams. These blocks were labeled HX1, HX2, and HX3 and are shown in Figure 3.1.

In the HX1 heat exchanger, stream, SO2-O2-1 was cooled from 956  $^{\circ}$ C to 801  $^{\circ}$ C while stream SO3 was heated from 792  $^{\circ}$ C to 940  $^{\circ}$ C. Stream SO2-O2-1 was furthered cooled in the HX2 heat exchanger to 410  $^{\circ}$ C while stream K2S2O7 was heated from 400  $^{\circ}$ C to 406  $^{\circ}$ C. Stream SO2-O2-1 was finally cooled to 150  $^{\circ}$ C in the HX3 heat exchanger while stream SULFATE1 was heated from 140  $^{\circ}$ C to 148  $^{\circ}$ C.

Table 4.31, 4.32, and 4.33 show results of the HX1, HX2, and HX3 heat exchangers,

respectively. A  $\Delta T_{min}$  of 10 degrees was specified in order to avoid temperature

crossovers in the heat exchangers.

Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]
HOT	SO2-O2-1	SO2-O2-2	955.785	801	-16.879526
COLD	SO3	SO3-1	791.619984	939.74623	16.8795478

Table 4.31: Energy Balance of the HX1 Heat Exchanger

 Table 4.32: Energy Balance of the HX2 Heat Exchanger

Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]
HOT	SO2-O2-2	SO2-O2-3	801	410	-41.072587
COLD	K2S2O7	K2S2O7-2	400.001892	405.685378	41.0726396

 Table 4.33: Energy Balance of the HX3 Heat Exchanger

Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]
HOT	SO2-O2-3	SO2-O2-4	410	150	-24.816395
COLD	SULFATE	SULFATE	140	147.863499	24.8163946
	1	R			

Stream NH3-HOT, the low temperature reactor vapor product stream, needed to be condensed before entering the chemical absorber such that sulfur dioxide and ammonia can be chemical absorbed by water. Furthermore, heat must be extracted from stream MIXED, the chemical absorber product stream, such that the electrolyzer could run isothermally at 140 °C. Heats extracted from these two streams were used in a Rankine power recovery system to generate electricity needed for the thermochemical plant. Heater blocks were used to simulate the heat extraction of

streams NH3-HOT and MIXED and were labeled HX4H and HX5H, respectively. Results of the Rankine power recovery system are discussed in Section 4.6.

# 4.6 The Rankine Power Recovery System

In the SA thermochemical plant, electricity is needed to drive the electrolytic reactor, to run the compressors and pumps, and to electrically heat the high temperature reactor. In order to reduce the amount of electricity imported into the process, a Rankine power recovery system was designed such that it converted waste heat generated by the thermochemical plant into electrical energy. This electrical energy was then used to power the electrical components of the process. The Rankine power recovery system consisted of two Rankine cycles. One cycle was designed to use waste heat from the condensing of stream NH3-HOT and the cooling of stream MIXED and was labeled Rankine 1. The other cycle was designed to use waste heat produced from the electrolyzer and was labeled Rankine 2. Two cycles, instead of one, were design such that all energy could be efficiently used without having temperature crossovers. Moreover, ammonia was used as the working fluids for both cycles. Ammonia was chosen because of its lower boiling point compared to water; thus more energy could be generated from the power recovery system. Furthermore, ammonia is cheap, has been used in industrial organic Rankine cycles, and is already present in the SA cycle [6].

# 4.6.1 Rankine 1

Rankine 1 produced a total power of ~283 MW. This is the energy produced from turbine T-101 minus the energy needed to operate pump P-101.

The pump block was used to simulate the pump component of the Rankine cycle. Table 4.34 shows a summary of the results of P-101. The initial temperature of the ammonia stream was set to 40 °C. The inlet pressure of 16 bar and the outlet pressure of 104 bar were determined by the PDS-1 design specification block and the MAXWORK1 optimization block. Results of the design specification block are shown in Section 4.8. The flow rate of 73 kmol/sec was also determined by the MAXWORK1 optimization block. A total of 22 MW of energy was needed to operate the pump and is also tabulated in Table 4.1.

P-101 Results	
Ammonia Flow Rate [kmol/sec]	73.2267926
Inlet Temperature [°C]	40
Outlet Temperature [°C]	43.2773489
Inlet Pressure [bar]	16.24905
Outlet Pressure [bar]	103.611707
Inlet Vapor Fraction	0
Outlet Vapor Fraction	0
Net Work [MW]	22

 Table 4.34: Summary of Pump P-101 Results

Heat extracted from the cooling of stream MIXED, the chemical absorber product stream, was used to preheat the working fluid before entering the vaporizer. The preheater was simulated with the HX5H and PREHEAT heater blocks. Table 4.35 shows a summary of the results of the HX5H and PREHEAT heater blocks. Stream MIXED was cooled from 161 °C to 142 °C while stream 3 was heated from 60 °C to 72 °C. The preheater operated at constant pressure at 104 bar for the cold stream and 9 bar for the hot stream.

Tuble 4.55. Summary of HAGH and TALIHLATT Heater Divers Results					
Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]
НОТ	MIXED	MIXED1	160.781412	142	-77.934645
COLD	3	4	59.8022158	71.9391308	77.934645

Table 4.35: Summary of HX5H and PREHEAT Heater Blocks Results

Heat extracted from the condensing of stream NH3-HOT, the low temperature reactor vapor product stream, was used to vaporize the working fluid. The vaporizer was simulated with the HX5H, HX4C1, and HX4C2 heater blocks. Table 4.36 shows a summary of the results of the HX4H, HX4C1, and HX4C2 heater blocks. The vaporizer operated at a constant pressure of 104 bar for the cold stream and 9 bar for the hot stream. Stream NH3-HOT was cooled from 140 °C to 90 °C while stream 4 was heated from 72 °C to 230 °C. Heat duties of the HX4C1 and HX4C2 heater blocks were determined by the PDS-2 and PDS-3 design specification blocks. Results of both design specification blocks are shown in Section 4.8. Because there was a phase change that occurred as stream NH3-HOT condensed from the vapor phase to the liquid phase, sensitivity analyses were done in order to generate temperature profiles of the hot and cold streams. This was done to determine if there were phase change temperature crossovers that Aspen Plus could not detect as well as to verify if parameters, determined by the MAXWORK1 optimization block, did not violate design constraints. Results of sensitivity analyses are shown in Section 4.7.

Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]
HOT	NH3-	NH3-	400	90	-1637.9256
	HOT1	COLD			
COLD	4	5	71.9391308	229.628977	1637.9256

Table 4.36: Summary of HX4H, HX4C1, and HX4C2 Heater Blocks Results

The compressor block was used to simulate the electrical generation component of the Rankine cycle. Table 4.37 shows a summary of the results of turbine T-101. Turbine T-101 was specified to operate isentropically. Furthermore, net output power was assumed to have 100% electrical power recovery. The discharge pressure of 16 bar was determined by PDS-1 design specification block. The net output power was 285 MW and is also tabulated in Table 4.1.

T-101 Results	
Ammonia Flow Rate [kmol/sec]	73.2267926
Inlet Temperature [°C]	229.628977
Outlet Temperature [°C]	87.1953499
Inlet Pressure [bar]	103.611707
Outlet Pressure [bar]	16.2484488
Inlet Vapor Fraction	1
Outlet Vapor Fraction	1
Net Work [MW]	-285

 Table 4.37: Summary of Turbine T-101 Results

A recuperator was incorporated into the power recovery design in order to reuse heat in the Rankine cycle. The recuperator was simulated with the RECUPSR and RECUPSIN heater blocks. Table 4.38 shows a summary of the results of the RECUPSR and RECUPSIN heater blocks. Stream 7, the outlet turbine stream, was used to heat stream 2 before entering the condenser. Stream 7 was cooled from 87 °C
to 53  $^{\circ}$ C while stream 2 was heated from 43  $^{\circ}$ C to 60  $^{\circ}$ C. The recuperator operated at a constant pressure of 16 bar for both hot and cold streams.

Tuble floor Summary of RECOTSK and RECOTSK (floater blocks) Results						
Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]	
HOT	7	8	87.1953499	53	-101.95334	
COLD	2	3	43.2773489	59.8022158	101.95334	

Table 4.38: Summary of RECUPSR and RECUPSIN Heater Blocks Results

A heater block was used to simulate the condenser component of the Rankine cycle. Table 4.39 shows a summary of the results of condenser C-101. The outlet temperature was determined by using a specification of 2 degrees of subcooling to ensure that the vapor stream was fully condensed before being recycled to the pump. The heat duty of the condenser was -1453 MW and is also tabulated in Table 4.1.

C-101 Results			
Ammonia Flow Rate [kmol/sec]	73.2267926		
Inlet Temperature [°C]	53		
Outlet Temperature [°C]	39.9995939		
Inlet Pressure [bar]	16.2484488		
Outlet Pressure [bar]	16.2484488		
Inlet Vapor Fraction	1		
Outlet Vapor Fraction	0		
Net Heat Duty [MW]	-1453		

 Table 4.39: Summary of Condenser C-101 Results

## 4.6.2 Rankine 2

Rankine 2 produced a total power of ~26 MW. This is energy produced from

turbine T-102 minus the energy needed to operate the pump P-102. Unlike Rankine 1,

a recuperator was determined not to be beneficial on the overall performance of

Rankine 2; thus it was not incorporated into the design.

Similar to Rankine 1, the Pump block was also used to simulate the pump component of the Rankine cycle. Table 4.40 shows a summary of the results of P-102. The initial temperature of the ammonia stream was set to 40 °C. The inlet pressure of 16 bar and the outlet pressure of 104 bar were determined by the PDS-4 design specification block and the MAXWORK2 optimization block. Results of the design specification block are shown in Section 4.8. The flow rate of 12.16 kmol/sec was also determined by the MAXWORK2 optimization block. A total of 4 MW of energy was needed to operate the pump and is also tabulated in Table 4.1.

P-102 Results	
Ammonia Flow Rate [kmol/sec]	12.1599641
Inlet Temperature [°C]	40
Outlet Temperature [°C]	43.2989111
Inlet Pressure [bar]	16.24887
Outlet Pressure [bar]	104.170638
Inlet Vapor Fraction	0
Outlet Vapor Fraction	0
Net Work [MW]	4

 Table 4.40: Summary of Pump P-102 Results

Excess heat generated, by the electrolyzer due to Joule heating as well as heat of reaction, was extracted to vaporize the working fluid in order to maintain the electrolyzer at a constant temperature of 140 °C. This process was simulated with the HXELECTR heater block. Table 4.41 shows a summary of the results of the HXELECTR heater block. The electrolyzer, the hot stream, operated at a constant pressure of 9 bar while stream 22-DUP1, the cold stream, operated at a constant pressure of 104 bar. Stream 22-DUP1 was heated from 43 °C to 130 °C. The heat duty of the HXELECTR heater block was determined by the MAXWORK 2 optimization block. This optimization block determined the amount of heat extracted due to excess energy generated by Joule heating as well as heat of reaction and is discussed in Section 3.6.2.

Stream Type	In Stream	Outlet Stream	Inlet Temp. [°C]	Outlet Temp. [°C]	Heat Flow [MW]
HOT	SFITPRD2	ELECPROD	141.6273	140	-
					239.979854
COLD	22-DUP1	33	43.2989111	130.009244	239.979854

 Table 4.41: Summary of ELECTROL and HXELECTR Heater Blocks Results

Similar to Rankine 1, the compressor block was also used to simulate the electrical generation component of the Rankine cycle. Table 4.42 shows a summary of the results of turbine T-102. The turbine T-102 was specified to operate isentropically. Furthermore, net output power was assumed to have 100% electrical power recovery. The discharge pressure of 16 bar was determined by PDS-4 design specification block. The net output power was 30 MW and is also tabulated in Table 4.1.

 Table 4.42: Summary of Turbine T-102 Results

T-102 Results	
Ammonia Flow Rate [kmol/sec]	12.1599641
Inlet Temperature [°C]	130.003399
Outlet Temperature [°C]	42.0005575
Inlet Pressure [bar]	104.170638
Outlet Pressure [bar]	16.2488743
Inlet Vapor Fraction	1
Outlet Vapor Fraction	0.80738221
Net Work [MW]	-30

A heater block was also used to simulate the condenser component of the Rankine cycle. Table 4.43 shows a summary of the results of condenser C-102. The outlet temperature was determined by setting a specification of 2 degrees of subcooling to ensure that the vapor stream was fully condensed before being recycled to the pump. The heat duty of the condenser was -191 MW and is also tabulated in Table 4.1.

C-102 Results	
Ammonia Flow Rate [kmol/sec]	12.1599641
Inlet Temperature [°C]	42.0005575
Outlet Temperature [°C]	40.0005575
Inlet Pressure [bar]	16.2488743
Outlet Pressure [bar]	16.2488743
Inlet Vapor Fraction	0.80738221
Outlet Vapor Fraction	0
Net Heat Duty [MW]	-191

 Table 4.43: Summary of Condenser C-102 Results

#### 4.6.3 Power Generation and Power Requirement

In order operate the thermochemical plant without importing electricity, the power generated by the Rankine power recovery system must be equal or greater than the power required to run the plant. This required energy includes electricity needed to operate the electrolyzer, run the pumps and compressors, and electrically heat the high temperature reactor. The Rankine power recovery system produced a total of 289 MW of energy. A total of 172 MW of energy was needed to drive the electrolytic reactor. This required energy was determined by the ELECPOWR calculator block. Results of the ELECPOWR calculator block are shown in Section 4.9.1. Furthermore, a total of 6 MW of energy was needed to run pumps and compressors, resulting in an excess energy of 1 MW. This eliminated the need to import electricity, thus creating a more self-sustaining thermochemical plant. Table 4.44 shows a summary of the required power needed to operate the plant and total power produced by the Rankine power recovery system.

Total Power Produced from Rankine Power Recovery System [MW]	289
Power Needed for the Electrolyzer [MW]	172
Power Needed for the High Temperature Reactor [MW]	110
Power Needed for Pumps and Compressors [MW]	6
Excess Power [MW]	1

Table 4.44: Summary of Produced/Required Power

#### 4.7 Sensitive Analyses, Temperature Profiles

The SENSNH3 and SENSVAP sensitivity analyses were used to plot temperature profiles of the condensation process of stream NH3-HOT and the vaporization process of stream 4 in order to verify that parameters determined by the MAXWORK1 optimization block did not cause temperature crossovers in the Rankine 1 vaporizer. Section 3.6.4 describes the setups for the SENSNH3 and SENSVAP sensitivity analyses. Figure 4.1 shows the temperature profiles of the two streams. Stream NH3-HOT was condensed from the vapor phase at 400 °C to its dew point at ~176 °C and then further condensed through its saturated vapor-liquid mixture at a relatively constant temperature and then to a final temperature of 90 °C. Meanwhile, stream 4 was heated from the liquid phase at 72 °C through its saturated vapor-liquid mixture and then superheated to a final temperature of 230 °C. A  $\Delta T_{min}$ of 10 degrees was specified at the dew point of stream NH3-HOT by Eq. (3.20) in the MAXWORK1 optimization block. Other temperature profiles were plotted using the same procedure as in the SENSNH3 and SENSVAP sensitivity analyses.



Figure 4.1: Temperature Profiles of Rankine 1 Vaporizer

Figure 4.2 shows the temperature profiles of the cooling of stream MIXED and the heating of stream 3 in the Rankine 1 preheater. Stream MIXED was cooled from 161  $^{\circ}$ C to 142  $^{\circ}$ C while stream 3 was heated from 60  $^{\circ}$ C to 72  $^{\circ}$ C.



**Figure 4.2: Temperature Profiles of Rankine 1 Preheater** 

Figure 4.3 shows the temperature profiles of the cooling of stream 7 and the heating of stream 2 in the Rankine 1 recuperator. A  $\Delta T_{min}$  of 10 degrees was specified at the outlet temperature of stream 7 and inlet temperature of stream 2. Stream 7 was cooled from 87 °C to 53 °C while stream 2 was heated from 43 °C to 60 °C.



**Figure 4.3: Temperature Profiles of Rankine 1 Recuperator** 

Figure 4.4 shows the temperature profiles of the electrolyzer and the heating of stream 22-DUP1 in the Rankine 2 vaporizer. The electrolyzer operated isothermally at 140 °C. A  $\Delta T_{min}$  of 10 degrees was specified at the outlet temperature of stream 22-DUP1 and inlet temperature of the electrolyzer by Eq. (3.24) in the MAXWORK2 optimization block. Furthermore, stream 22-DUP1 was also specified to be at least superheated by 2 degrees. Stream 22-DUP1 was heated from 43 °C to 130 °C while the electrolyzer operated isothermally at 140 °C.



Figure 4.4: Temperature Profiles of Rankine 2 Vaporizer

### **4.8 Design Specification Results**

A total of 11 design specification blocks were used in the simulation. Table 3.3 shows a summary of design specification blocks and parameters that each block determined. Section 3.6.1 describes each individual design specification setup. The SO3CONV design specification block determined the conversion of the mid-temperature reactor, while the DS-2 design specification block determined the flow rate of stream K2SO4. The PDS-2 and PDS-3 design specification blocks determined the heat duties of the HXC1 and HXC2 heater blocks which were used to simulate the vaporizer in Rankine 1. The DS-1, DS-3, DS-4, DS-5, PDS-1, and PDS-4 design specification blocks were used to simulate recycle streams by varying parameters stated in Table 3.3 such that tear streams were identical in composition, flow rates, temperature, and pressure.

The SO3CONV design specification block varied the conversion of potassium pyrosulfate according to equilibrium thermodynamics from a phase diagram to account for pressure effects on the mid-temperature reactor [5]. Table 4.45 shows the results of SO3CONV. The initial value of the conversion of potassium pyrosulfate was determined by Aspen Plus, but then overwritten with the final value due to equilibrium data supplied by the design specification block. The initial and final values of F4, the molar flow rate of  $K_2SO_4$ , correspond to different conversion of  $K_2S_2O_7$ . The final conversion was determined to be 0.055. In some cases, the initial and final values were equal.

Variable	Initial value	Final value	Units
MANIPULATED	0.055001	0.054955	
Т	791.62	791.62	С
Р	9	9	BAR
F4	2.051181	2.049949	KMOL/SEC
F7	25.27986	25.28109	KMOL/SEC

 Table 4.45: Results of the SO3CONV Design Specification Block

The DS-1 design specification block varied the temperature of the midtemperature reactor such that stream KSO4SO3, the mid-temperature reactor product stream, and stream K2SO4, the low temperature reactor reactant stream, as to have the same composition of potassium sulfate and potassium pyrosulfate. Table 4.46 shows results of the DS-1 design specification block. The final temperature was determined to be 790  $^{\circ}$ C.

81				
Variable	Initial value	Final value	Units	
MANIPULATED	791.62	791.62	С	
F	0.075	0.075		
F4	2.049949	2.049949	KMOL/SEC	
F7	25.28109	25.28109	KMOL/SEC	

 Table 4.46: Results of the DS-1 Design Specification Block

The DS-2 design specification block varied the flow rate of stream K2SO4 such stream NH3-HOT, the low temperature reactor vapor product stream, was 400 <sup>o</sup>C. This allowed the low temperature reactor to operate adiabatically. Table 4.47 shows results of the DS-2 design specification block. The final flow rate was determined to be 27.4 kmol/sec.

Variable **Initial value Final value** Units MANIPULATED 27.30468 27.33104 KMOL/SEC 399.6874 TNH3 400.0019 С

Table 4.47: Results of the DS-2 Design Specification Block

The DS-3 design specification block varied the water feed flow rate such that streams SULFATE and SULFATER have the equal water flow rate. Due to the electrolytic reduction of water to produce hydrogen, the water feed flow rate was determined to compensate for the water loss. Table 4.48 shows results of the DS-3 design specification block. The final water flow rate was determined to be 1.23 kmol/sec.

Table 4.48: Results of the DS-3 Design Specification Block

Variable	Initial value	Final value	Units
MANIPULATED	1.225961	1.225961	KMOL/SEC
WA	27.2	27.2	KMOL/SEC
WB	27.20025	27.20025	KMOL/SEC

The DS-4 design specification block varied the conversion of the electrolyzer such that streams SULFATE and SULFATER have same composition of ammonium sulfite and ammonium sulfate. Table 4.49 shows results of the DS-4 design specification block. The final conversion of the electrolyzer was determined to be 0.94.

Variable	Initial value	Final value	Units		
MANIPULATED	0.935165	0.935165			
SFATE	1.47	1.47	KMOL/SEC		
SFITE	0.0772	0.0772	KMOL/SEC		
SPHATE	1.47	1.47	KMOL/SEC		
SPHITE	0.0772	0.0772	KMOL/SEC		

Table 4.49: Results of the DS-4 Design Specification Block

The DS-5 design specification block varied the temperature of stream SULFATE such that the temperature of streams SULFATE and SULFATER were equal. Table 4.50 shows results of the DS-5 design specification block. The final temperature was determined to be 148  $^{\circ}$ C.

Variable	Initial value	Final value	Units
MANIPULATED	191	147.8697	С
TSULFATR	147.8631	147.8635	С
TSULFAT	191	147.8697	С

 Table 4.50: Results of the DS-5 Design Specification Block

The DS-6 design specification block varied the split fraction in the H2OFDSP Splitter block such that the molar flow rate of stream H2OGS was 0.1 kmol/sec. Table 4.51 shows results of the DS-6 design specification block. The final split fraction was determined to be 0.08.

Variable	Initial value	Final value	Units			
MANIPULATED	0.081949	0.081949				
H2OGS	0.100466	0.100466	KMOL/SEC			

Table 4.51: Results of the DS-6 Design Specification Block

The PDS-1 design specification block varied the discharge pressure of turbine T-101 such that the temperature of streams 1 and 8 were equal. Table 4.52 shows results of the PDS-1 design specification block. The final discharge pressure was determined to be 16 bar.

Variable **Initial value Final value** Units MANIPULATED 16.24845 16.24845 BAR T1 40 40 С **T8** 39.99959 39.99959 С

Table 4.52: Results of the PDS-1 Design Specification Block

The PDS-2 design specification block varied the heat duty of HX4C1 heater block such that the heat stream Q1A was the amount of energy extracted from stream NH3-HOT when the stream condensed from its dew point to the liquid phase. Table 4.53 shows results of the PDS-2 design specification block. The final heat duty of HXC1 heater block was determined to be 1370 MW.

1 ubic 4651 ites	Tuble neet Results of the 1 Do 2 Design Specification Diver							
Variable	Initial value	Final value	Units					
MANIPULATED	1370.139	1370.139	MW					
Q1A	-1370.14	-1370.14	MW					
Q1B	1637.926	1637.926	MW					
Q1DEW	267.7865	267.7865	MW					

Table 4.53: Results of the PDS-2 Design Specification Block

The PDS-3 design specification block varied the heat duty of HX4C2 heater block such that the heat stream Q1AA was the amount of energy extracted from stream NH3-HOT when the stream condensed from the vapor phase to its dew point. Table 4.54 shows results of the PDS-3 design specification block. The final heat duty of HXC2 heater block was determined to be 268 MW.

Variable	Initial value	Final value	Units			
MANIPULATED	267.7865	267.7865	MW			
Q1AA	-267.787	-267.787	MW			
Q1DEW	267.7865	267.7865	MW			

Table 4.54: Results of the PDS-3 Design Specification Block

Similar to the PDS-1 block, the PDS-4 design specification block varied the discharge pressure of turbine T-102 such that the temperature of streams 11 and 55 were equal. Table 4.55 shows results of the PDS-4 design specification block. The final discharge pressure was determined to be 16 bar.

Table 4.55: Results of the PDS-4 Design Specification Block

Variable	Initial value	Final value	Units
MANIPULATED	16.24887	16.24887	BAR
Т	40	40	С
TR	40.00056	40.00056	С

#### 4.9 Calculator Block Results, ELECPOWR and PLANTEFF

The ELECPOWR and PLANTEFF calculator blocks were used to calculate the power requirement of the electrolyzer based on the amount of hydrogen produced and the overall efficiency of the process, respectively. Section 3.6.3 describes the setup of ELECPOWR and PLANTEFF calculator blocks

#### **4.9.1 Electrolyzer Power Requirement**

The ELECPOWR calculator block imported the molar flow rate (kmol/sec) of hydrogen produced to calculate the electrical power requirement of the electrolyzer based on a cell voltage of 0.8 V. Table 4.56 shows the results of the ELECPOWR calculator block.

Variable	Value read	Value written	Units
FH2	1.113519		KMOL/SEC
ELECPOWR	171.9005	171.9006	MW

 Table 4.56: Results of the ELECPOWR Calculator Block

Based on the amount of hydrogen produced, the electrolyzer required 172 MW of electrical power to produce 1.11 kmol/sec of hydrogen gas. This is equivalent to 2.24 kg/sec of hydrogen gas. This value was exported as an input heat stream to the electrolyzer to simulate the power input to the reactor and is tabulated in Table 4.1

#### 4.9.2 Efficiency

The PLANTEFF calculator block imported several parameter values from the flow sheet to calculate the overall process efficiency based on the amount of hydrogen produced. The definition of these efficiency values are discussed in Section 3.6.3. The overall process efficiency was determined to be 13%. Table 4.57 shows the results of the PLANTEFF calculator block.

Variable	Value read	Value written	Units
ELECPOWR	171.9005		MW
TOTW1	-262651522		WATT
FH2	1.11351885		KMOL/SEC
ETA		0.13297741	UNITLESS
WORKTOT	6413500.63		WATT
LHV			WATT
TOTW2	-25961400		WATT
HITEMQ	-110.29808	110298080	WATT
MIDTEMQ	-2025.101	2025100970	WATT
GENWORK		288612922	WATT
ECSWORK		-110298912	WATT
REQWORK		288612090	WATT

HEATIN is the calculated power (W) requirement of the electrolyzer.

 Table 4.57: Results of the PLANTEFF Calculator Block

TOTW1 is the total power (W) generated from Rankine 1 while TOTW2 is the total power (W) generated from Rankine 2. FH2 is the molar flow rate (kmol/sec) of hydrogen produced from the process. WORKTOT is the total work (W) required to operate all pumps and compressors. HITEMQ is the required heat duty (W) to operate the high temperature reactor while MIDTEMQ is the required heat duty (W) to operate the mid-temperature reactor. GENWORK is the total power (W) generated from Rankine 1 and 2. REQWORK is the total power (W) to run the electrolyzer, high temperature reactor, and all the pumps and compressors while ECSWORK is the excess work (W) after the required power needed to run the electrolyzer and pumps and compressors have been subtracted from the total generated power. LHV is the lower heating value (W) and ETA is efficiency.

The efficiency of the process was based on DOE's working definition of efficiency. The efficiency is calculated by the following equation:

$$\eta = -\Delta H^{o}_{f[H2O(g)]}/(Q + E/\eta_e)$$
(3.27)

where  $\Delta H^{o}_{f[H2O(g)]}$  is the enthalpy of formation of water vapor in ideal gas state, Q is the total heat input to the cycle, E is the total electrical input into the process, and  $\eta_{e}$ is the efficiency by which imported electricity is produced. The negative sign represents the dissociation of water vapor into hydrogen and oxygen.

The numerator of Eq. (3.27) is also known as the lower heating value of hydrogen. Based off the DOE website, a conversion factor of 119.96 MJ/kg H<sub>2</sub> was used to calculate the process efficiency [7]. The LHV was determined to be 268 MW.

The total heat input, Q, into the process is solely the heat required to operate the mid-temperature reactor. The low temperature reactor operates adiabatically while the high temperature reactor uses electrical heating. The total electrical input, E, is the required energy to operate the electrolyzer, run the pumps and compressors, and electrically heat the high temperature reactor. Because there was enough power generated by the Rankine power recovery system to operate all the electrical components of the thermochemical plant, no imported electricity was needed. The efficiency formula was simplified and is as follow:

$$\eta = LHV/MIDTEMQ$$
 Eq. (4.1)

where LHV is the lower heating value and MIDTEMQ is the heat input into the midtemperature reactor. The heat required to operate the mid-temperature reactor was 2025 MW.

### References

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## 5. Case Studies

A base case for a continuous solar thermochemical plant was modeled and results of the Aspen Plus simulation were described in Chapter 4. The continuous solar thermochemical plant is a complex process with many inter-related variables that can affect the overall plant performance and efficiency. Previous work, done by Jesse Littlefield and FSEC, did not explore the effects of varying operating parameters on overall plant performance. Independent variables such as operating temperature of the high temperature reactor, plant pressure, and salt concentration of the electrolyzer were varied to determine their effects on the overall plant efficiency.

#### 5.1 High Temperature Reactor Study

The operating temperature of the high temperature reactor was varied to determine the effects on overall plant efficiency and performance. The reactor temperature was varied from 900 °C to 1200 °C at a given ammonium sulfate salt concentration of 3 M and plant pressure of 9 bar. The water feed flow rate of 1 kmol/sec was set for the overall process. The maximum temperature was 1200 °C so that silicon carbide can be used as the material for the industrial electrical heater. Figure 5.1 shows that as the operating temperature of the high temperature reactor increased from 900 °C to 1200 °C, the efficiency also increased from ~11% to ~15%. The decomposition of sulfur trioxide to produce sulfur dioxide and oxygen gas is favored at high temperatures by Eq. (2.11); therefore as the reactor temperature increased, more sulfur dioxide was produced. With an increase in sulfur dioxide production, more ammonium sulfite is produced, Eq. (2.3), and ultimately more

hydrogen is generated, Eq. (2.14). Therefore, the overall efficiency of the thermochemical plant is increased.



Figure 5.1: Effects of high temperature reactor operating temperature on efficiency at a plant pressure of 9 bars and ammonium sulfate concentration of 3 M

Despite the increased in efficiency, imported electrical energy is needed when the operating temperature of the high temperature reactor is greater than ~ 956 °C. This operating temperature was used in the base case scenario and is discussed in Chapter 4. At temperatures less than ~ 956 °C, the power generated by the Rankine power recovery system exceeded the required power needed to operate the thermochemical plant, as shown in Figure 5.2. However, at temperatures greater than ~956 °C, there was not enough power generated to operate the plant without importing electricity. The total power generated and the total required power are illustrated in Figure 5.2. Furthermore, the efficiency by which imported electricity is produced was specified to be 50%. Power requirement stayed relatively constant at ~230 MW and is the total electrical energy needed to operate the electrolyzer, to run the pumps and compressors, and to electrically heat the high temperature reactor.



Power generation and power requirements are discussed in Section 4.6.3.

Figure 5.2: Effects of high temperature reactor operating temperature on plant performance at a plant pressure of 9 bars and ammonium sulfate concentration of 3 M

Figure 5.2 shows that as the reactor temperature decreased, power generation increased. As the reactor temperature decreased from 1200 °C to 900 °C, there was a decreased in sulfur trioxide decomposition, and thus, two variables were affected: the outlet temperature of the chemical absorber and the amount of water being recycled in the process. At lower temperatures, since less decomposed, more sulfur trioxide was transported to the chemical absorber compared to higher temperatures. Two reactions occurred in chemical absorber: the chemical absorption of ammonia and sulfur dioxide in water and the chemical absorption of ammonia and sulfur trioxide in water. The following reactions as well as their heat of reactions at standard state are as follow:

$$SO_2 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_3 \quad \Delta H^o_{rxn} = -226 \text{ kJ/mol}$$
 (2.3)

$$SO_3 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_4 \quad \Delta H^o_{rxn} = -401 \text{ kJ/mol}$$
(3.2)

As more sulfur trioxide was chemically absorbed in water, the outlet temperature of the chemical absorber achieved a higher temperature due to higher heat of reaction. Therefore, more heat was extracted from the cooling of stream MIXED as the reactor temperature decreased.

Table 5.1 shows that the amount of heat extracted from condensing of stream NH3-HOT stays constant at 1637 MW as the reactor temperature was varied. This is because composition of stream NH3-HOT was specified to be constant by indirectly specifying stream SULFATE. Furthermore, the recycle water flow rate was also specified to be constant. However, the water feed flow rate into the overall process increased as the reactor temperature increased. As stated before, the decomposition of sulfur trioxide is favored at high temperatures; therefore as the reactor temperature increased more sulfur dioxide was produced, Eq. (2.11). This meant more ammonium sulfite was produced, Eq. (2.3), and ultimately more hydrogen was generated by the electrolytic reduction of water, Eq. (2.14). In order to compensate for water loss and also to maintain the concentration of ammonium sulfate at 3 M, the water feed rate increased as the reactor temperature increased. The water feed flow rate was determined by the DS-3 design specification block and is discussed in Section 3.6.1. With a base case of constant water feed rate of 1kmol/sec, more water was recycled throughout the process at lower reactor temperatures compared to higher reactor temperatures. With more recycled water, more water vapor was present in stream NH3-HOT. Due to the high heat capacity of water, more heat was extracted from the

condensing of stream NH3-HOT at lower reactor temperatures and is shown in Table

5.2.

i emperatures							
Temp. of high temperature reactor [C]	900	950	1000	1050	1100	1150	1200
Water feed rate into the process [kmol/sec]	1.10	1.21	1.31	1.38	1.43	1.47	1.5
Energy extracted from stream NH3-HOT [MW]	1637	1637	1637	1637	1637	1637	1637
Energy extracted from stream MIXED [MW]	115	81	55	36	21	10	2
Energy extracted from ELECTROL [MW]	190	214	233	247	258	265	271

 Table 5.1: Summary of Heat Extracted for Various High Temperature Reactor

 Temperatures

 Table 5.2: Summary of Heat Extracted for Various High Temperature Reactor

 Temperatures for a Water Feed Rate of 1 kmol/sec

Temp. of high temperature reactor [C]	900	950	1000	1050	1100	1150	1200
Energy extracted from stream NH3-HOT [MW]	1495	1349	1250	1189	1144	1113	1093
Energy extracted from stream MIXED [MW]	105	67	42	26	15	7	2
Energy extracted from ELECTROL [MW]	174	176	178	180	180	180	181

The energy extracted from the excess heat generated by the electrolyzer stayed relatively constant, but increased slightly due to heat of reaction as shown in Table 5.2. The electrical energy produced by Rankine 2 was not as affected by varying the operating temperature of the high temperature reactor.

Based on the high temperature reactor study, as the operating temperature of the high temperature reactor decreased, more heat was extracted and more electrical energy was produced by the Rankine power recovery system. From DOE's working definition of efficiency, excess energy generated from the Rankine power recovery system is not accounted for. Therefore, in order to operate the thermochemical plant without importing and producing excess electrical energy, the operating temperature of the high temperature reactor where the two lines cross in Figure 5.3, is preferred.

#### 5.2 Pressure Study Combined with High Temperature Reactor Study

The plant pressure as well as the high temperature reactor operating temperature was varied to determine the effects on overall plant efficiency and performance. The plant pressure was varied from 7 bar to 13 bar and at each plant pressure, the reactor temperature was varied from 900 °C to 1200 °C. Figures 5.3 and 5.4 illustrate the effects of plant pressure and reactor temperature on plant efficiency. Results were compared by using a basis of a water feed flow rate of 1 kmol/sec. Furthermore efficiency by which imported electricity is produced was specified to be 30% and 50% for Figures 5.3 and 5.4, respectively.

Figures 5.3 and 5.4 show that, at given plant pressures, as reactor temperature increased, efficiency increased. This is discussed in Section 5.1. Efficiency was greater at low pressure when the high temperature reactor was operating at low temperatures. For the case with 30% generation efficiency for imported electricity, at a reactor temperature of 900 °C, the efficiency at 7 bar was ~12.5%, while the efficiency at 13 bar was ~11%. At low pressures, the decomposition of sulfur trioxide is favored according to Le Chatelier's principle and thus more hydrogen is produced. However, as the reactor temperature increased, efficiency was greater at higher plant pressures because less imported electricity was needed. At a reactor temperature of 1200 °C, the efficiency at 7 bar was ~15%. This



is illustrated in Figure 5.3. Similar trends are shown in Figure 5.4 for the case with 50% generation efficiency for imported electricity.

Figure 5.3: Effects of plant pressure and high temperature reactor operating temperature on plant efficiency with a 30% generation efficiency for imported electricity for an ammonium sulfate concentration of 3 M



Figure 5.4: Effects of plant pressure and high temperature reactor operating temperature on plant efficiency with a 50% generation efficiency for imported electricity for an ammonium sulfate concentration of 3 M

Figure 5.5 shows that as plant pressure increased from 7 to 9 bar, the total required power increased from ~210 to ~260 MW. At higher plant pressures, less water was lost in stream O2, the oxygen stream leaving the oxygen scrubber, and thus, more water was transported to the electrolyzer. With more water present in the electrolyzer, more energy was needed to electrochemically reduce water to produce hydrogen gas. Furthermore, at higher pressures, more energy was also needed for the high temperature reactor to decompose sulfur trioxide.

Figure 5.5 also shows that, at a given reactor temperature, as plant pressure increased, power generated by the Rankine power recovery system also increased. At high plant pressure, stream NH3-HOT condensed at a higher temperature; therefore the working fluid of Rankine 1 was vaporized to a higher temperature without causing temperature crossovers. With the working fluid superheated to a higher



temperature, Rankine 1 produced more power from turbine T-101, and thus, the Rankine power recovery system generated more electrical energy.

Figure 5.5: Effects of plant pressure and high temperature reactor operating temperature on plant performance at an ammonium sulfate concentration of 3 M

Furthermore, Figure 5.5 illustrates that at lower plant pressures, more imported electrical energy is needed to operate the thermochemical plant as the reactor temperature increased compared to higher plant pressures. The intersection of the total power generated line and total required power line occurred at lower reactor temperatures for lower pressures. The difference between the required power and the total power generated at 7 bars at a reactor temperature of 1200 °C was greater than the difference between the required power and the total power generated at 13 bars at the same reactor temperature. This corresponded to more imported electricity needed to operate the plant at 7 bars. Imported electricity was specified to have an efficiency associated with it, either 30% or 50%. This corresponded to electrical losses due to

electrical transportation through the power grid. At higher pressures, less imported electricity was needed to operate the thermochemical plant; therefore the efficiency was greater at higher reactor temperatures.

Based on the pressure study, in order to increase the efficiency of the thermochemical plant without importing electricity, high pressure and high reactor temperature are favored. High pressure would allow the Rankine power recovery system to produce more electrical energy. With more electrical energy generated, the high temperature reactor can operate at higher temperatures without importing electricity, and thus, increase hydrogen production. Currently, the operating pressure of the electrolyzer determines the operating pressure of the thermochemical plant. Electrosynthesis Company Inc. has designed an electrolyzer with the capability of reaching ~10 bar [1]. If an electrolyzer could be designed to operate at high pressures, the plant efficiency would increase.

#### 5.3 Salt Concentration Study

The concentration of ammonium sulfate in stream SULFATE, the electrolyzer product stream entering the low temperature reactor, was varied to determine the effects on overall plant efficiency. The salt concentration of the electrolyzer product stream was varied, opposed to varying the salt concentration of the electrolyzer reactant stream, because stream SULFATE determined the maximum salt concentration of ammonium sulfate throughout the process. Furthermore, based on the flow sheet design, stream SULFATE was an independent variable stream. By specifying stream SULFATE at a given plant pressure and high temperature reactor operating temperature, Aspen Plus determined results of other plant components based on stream SULFATE through design constraints, design specification and optimization blocks. Figure 5.6 shows plant efficiency as a function of varying concentration of ammonium sulfate at a given high temperature reactor operating temperature and plant pressure. Results were based on a water feed flow rate of 1 kmol/sec. The efficiency by which imported electricity is produced was specified to be 50%.

The concentration of ammonium sulfate was increased from 2 M to 6 M. Based on solubility studies done by Electrosynthesis Company Inc. a concentration of 6 M of ammonium sulfate at 80 °C was achieved. Solubility data were not available for greater temperatures; therefore concentration was not increased above 6 M even though the outlet temperature of the electrolyzer was specified to be 140 °C. Figure 5.6 shows that as the concentration of ammonium sulfate increased from 2 to 6 M, the efficiency increased from ~10% to ~17%. As more ammonium sulfate entered the low temperature reactor, more ammonia vapor was produced, Eq. (2.9). This meant more ammonium sulfite was produced in the chemical absorber, Eq. (2.30), and ultimately more hydrogen gas was generated in the electrolyzer, Eq. (2.14). This increased the overall efficiency of the thermochemical plant.



Figure 5.6: Effects of ammonium sulfate concentration on efficiency at a plant pressure of 9 bars and at a high temperature reactor operating temperature of ~956 °C

Figure 5.7 shows the effect of ammonium concentration on the power generation and power requirement. As the concentration of ammonium sulfate increased, less water was recycled throughout the process. The required power to operate the plant stayed relatively constant at ~240 MW. A slight increase was present due to a decrease in water loss at higher concentrations of ammonium sulfate. However, as concentration increased, power generation decreased. At concentrations greater than 3.0 M, imported electrical energy was needed to operate the plant. However, at concentrations less than 3.0 M, the Rankine power recovery system generated enough electrical energy to operate the plant without importing electricity. Similar to the high temperature study, as the concentration increased, less water was recycled, and thus, less water was present in stream NH3-HOT. At higher concentrations, less energy was extracted from the condensing of stream NH3-HOT;

therefore the Rankine power recovery system produced less electrical energy as concentration increased.



Figure 5.7: Effects of ammonium sulfate concentration on plant performance at a plant pressure of 9 bars and at a high temperature reactor operating temperature of ~956 °C

Currently, Electrosynthesis Company Inc, the electrolyzer designer in this project, is running the electrolyzer with an inlet concentration of 2 M ammonium sulfite [1]. This corresponds to an electrolyzer outlet concentration of ~2 M ammonium sulfate. The concentration of ammonium sulfate is slightly greater than the inlet concentration of ammonium sulfite because of the electrolytic reduction of water to form hydrogen. Based on the concentration study case, if the electrolyzer can be designed to operate with high outlet concentration of ammonium sulfate, this would increase overall plant efficiency. Furthermore, solubility data should be explored beyond a temperature of 100  $^{\circ}$ C.

## References

[1] Taylor, R., "Solar High-Temperature Water Splitting Cycle with Quantum Boost" DOE Hydrogen Program Annual Merit Review, May 16, 2013.

# 6. Cost Analysis

In order to determine the viability of the sulfur-ammonia thermochemical plant, plant cost estimation was performed to determine projected costs of hydrogen based on the current process flow diagram with the following plant parameters summarized in Table 6.1. Costing was performed using the H2A Version 3 procedure [1] and the equation-based Guthrie method [2].

Key Operating Plant Parameters for Base Case	
Plant Pressure (bar)	9
Concentration of $(NH_4)_2SO_4$ in electrolyzer product stream (M)	6.0
Temperature of low temperature reactor (°C)	400
Temperature of mid-temperature reactor (°C)	790
Temperature of high temperature reactor (°C)	1000
Temperature of electrolzyer (°C)	140
Temperature of chemical absorber (°C)	180

Table 6 1. Diant Danamatana fan Cast Analysia

In order to compare the costs of various methods of hydrogen production, the Department of Energy Hydrogen Analysis team, consisting of researchers, scientists, and industry experts, has developed the H2A Version 3 model to provide a standard protocol to cost hydrogen production. The H2A uses a standard discounted cash flow rate of return methodology and it determines the minimum selling price to achieve a net present value of zero. H2A also includes a specified after-tax internal rate of return on investments. More information of H2A is found on the DOE's website [1]. The H2A was used to determine the capital cost of the solar field and the cost of operating and maintaining the plant.

The capital cost of the thermochemical plant was estimated with an equationbased Guthrie method [2]. Equipment cost is presented in a form of a high order polynomial expression and is expressed as the following:

$$C_{p} = \exp\{A_{0} + A_{1}[\ln(S)] + A_{2}[\ln(S)]^{2} + ...\}$$
(6.1)

where  $C_p$  is the purchase cost excluding the delivery cost to the plant, S is the sizing factor, and  $A_n$ 's are the constants derived from literature and previous costing graphs. A material factor for stainless steel and a pressure factor were also incorporated into the costing equation [2]. Costing equations are shown in Appendix C.

Cost estimation was performed on the bases of 50 MW<sub>th</sub> of energy received from the solar field. Sizing of the solar field was accomplished by Roger Davenport of SAIC and is discussed in Section 2.5. Furthermore, the process flow sheet was linearly scaled down to match the solar field and the simplified schematic of the thermochemical plant, illustrated in Figure 3.2, was used as a guide to estimate the cost of hydrogen. Table 6.2 summarizes the H2A cost results from Roger Davenport of SAIC. The cost of the solar field was determined to be ~\$55 million, while the cost of the thermochemical plant was determined to be ~17 million. Table 6.3 summarizes the equipment costing of the thermochemical plant. The scaled down plant was estimated to produce an average of 5000 kg of hydrogen per day. In order to produce 100,000 kg/day, 20 plants are required which would cost \$1,440 million. The 2015 projected cost of hydrogen is \$11.89/ kg of hydrogen and the 2020 project cost was \$7.67/kg of hydrogen [3].

Average Hydrogen Plant Production	5000 kg/day
Solar Plant Module Cost (with storage)	\$55 million
Thermochemical Plant Cost (including Electrolytic reactor)	\$17 million
2015 Hydrogen Production Cost:	
Capital	9.77
Fixed O&M	2.07
Other	0.05
Total:	\$11.89/kg Hydrogen
2020 Estimate	\$7.67/kg Hydrogen

Table 6.2: H2A Cost Results based on 50 MW<sub>th</sub> Modular Plant Design [3]

Currently, the most expensive component of the entire hydrogen production plant is the solar field, representing 76% of the total plant cost and is shown in Figure 6.1. The electrolyzer is the second most expensive component, representing 38% of thermochemical plant cost, excluding the cost of the solar field. Costing of the electrolyzer was based on the electrolytic performance of the reactor. Figure 6.2 illustrates the cost distribution of the thermochemical plant. One method of reducing the cost of hydrogen production is to decrease the cost of the electrolyzer by improving the electrolytic performance of the reactor. This can be accomplished by developing new catalysts and electrode and membrane materials to reduce the cell's overall potential, thus ultimately lowering the cost. This research is currently being conducted by Electrosynthesis Company Inc. and UC San Diego. Furthermore, if the electrolyzer could be run at a lower voltage, less electricity is needed to run the electrolyzer and more energy can be used to electrically heat the high temperature reactor. DOE has a set goal of reducing the cost of hydrogen to \$3.00/ kg by 2017; therefore the current projected cost of hydrogen production must be lowered in order to be competitive with the price of gasoline.



Figure 6.1: Cost Distribution of the Entire Hydrogen Production Plant



Figure 6.2: Equipment Cost Distribution of the Thermochemical Plant

Block Name	Equipment	Costs (Mil \$)
ABSORBER	Packed Bed Column w/ 2in Ceramic Berl Saddles	0.91
ELECTROL	Vertical Vessel with Membrane w/o cost of electricity	6.49
HX1	Floating Head Heat Exchanger	0.12
HX2	Floating Head Heat Exchanger	0.08
HX3	Floating Head Heat Exchanger	0.08
HXRECUPH/C	Floating Head Heat Exchanger	0.55
HX4H/4C1/4C2	Floating Head Heat Exchanger	0.45
HX5H/PREHEAT	Floating Head Heat Exchanger	0.14
HXELECTR	Floating Head Heat Exchanger	0.14
C101	Floating Head Heat Exchanger	0.31
C102	Floating Head Heat Exchanger	0.15
LOTEMRXR	Packed Bed Column w/ 2in Ceramic Berl Saddles	0.79
MIDTMRXR	Packed Bed Column w/ 2in Ceramic Berl Saddles	1.16
HITEMRXR	Floating Head Heat Exchanger w/o catalyst	0.50
H2OPUMP	Centrifugal Pump	0.01
P101	Centrifugal Pump	0.21
P102	Centrifugal Pump	0.10
O2-SEP	Vertical Vessel	0.08
O2WASH	Vertical Vessel w/ 4 Sieve trays	0.02
NaCl Storage	Vertical Vessel	1.65
T101	Gas Expander Power-Recovery Turbine	1.96
T102	Gas Expander Power-Recovery Turbine	0.43
H2COMP	Centrifugal Compressor	0.52
	Total	16.86

 Table 6.3: Equipment Cost Estimation for the Thermochemical Plant
# References

- [1] "DOE H2A Production Analysis." *DOE Hydrogen and Fuel Cells Program*, Web. 22 April 2013. <a href="http://www.hydrogen.energy.gov/h2a\_production.html">http://www.hydrogen.energy.gov/h2a\_production.html</a>
- [2] Seider, W., Seader, J.D., Lewin, D., Widagdo, S., "Purchase Costs of the Most Widely Used Process Equipment," Product and Process Design Principles, 3<sup>rd</sup> ed. John Wiley & Sons, Inc.:NJ, 2009, p. 558-596
- [3] Taylor, R., "Solar High-Temperature Water Splitting Cycle with Quantum Boost" DOE Hydrogen Program Annual Merit Review, May 16, 2013

# 7. Conclusions and Future Work

The objective of this study was design a process flow sheet with Aspen Plus chemical process simulator that simulate the sulfur-ammonia thermochemical cycle in a continuous solar thermal production plant in order to determine the overall viability of the process. This included convergence of the material and energy flows throughout the process, input of thermodynamic properties of salts and phase equilibrium data obtained from literature for more realistic reactor design, heat integration, design of a power recovery system, and efficiency calculation for a preliminary flow sheet. A base case was first designed and then operating parameters such as reactor temperature, plant pressure, and salt concentration were varied to determine their effects on overall plant efficiency and performance. Furthermore, a cost analysis was performed to determine the projected costs of hydrogen based on the process flow sheet.

Table 4.2 showed convergence of the energy and mass balance with a difference of 0.02% and none, respectively. Furthermore, tear streams were also nearly identical in energy and mass; therefore recycled streams were properly modeled with tear streams. These percent differences are very low. The process flow sheet is illustrated in Figure 3.1 and it incorporated thermodynamic properties and phase diagram data for the  $K_2S_2O_7/K_2SO_4$  system [1]. Design specification blocks were used to integrate the phase diagram into the mid-temperature reactor model. Moreover, design specification blocks were used to throughout the process flow sheet to model recycle streams by creating identical tear streams. For continuous operation, the flow sheet was designed such that a phase-change thermal-storage system with

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NaCl can be integrated with the thermochemical plant. The mid-temperature reactor was specified to operate at ~790 °C by changing the potassium sulfate and potassium pyrosulfate salt concentration to ensure that heat flowed from thermal-storage system to the thermochemical plant. Furthermore, the low temperature reactor was specified to operate adiabatically at 400 °C; thus simplifying the overall solar configuration of the plant. A design specification block was used to determine the flow rate of the recycled potassium salt stream such that there was enough specific heat to drive the low temperature reactor at 400 °C. The high temperature reactor was designed to use electrical heating in order to eliminate reradiation losses and to reduce capital cost of the solar field. The base case design had the capacity to generate ~1.7 X  $10^5$  kg of hydrogen/day which is equivalent to ~268 MW of energy, based on the lower heating value of hydrogen. In this study, an overall efficiency of 13% was achieved.

Heat integration and a Rankine power recovery system were designed in order to reuse useful energy throughout the system as well as to generate electricity to run the electrical components of the thermochemical plant. Optimization blocks were used to maximize power generation without causing temperature crossovers in heat exchangers. The Rankine power recovery system generated 289 MW of energy, producing enough energy to drive the electrolytic reactor, run the pumps and compressors, and to electrically heat the high temperature reactor. Sensitivity analyses were done in order verify if parameters determined by the optimization blocks did not violate design constraints by plotting temperature profiles of heat exchangers. A calculator block was designed in order to determine the overall efficiency of the plant based on DOE's working definition of efficiency. The calculator block was designed such that efficiency was calculated whenever the simulation was conducted and convergence was achieved.

Operating parameters of the continuous plant such as the operating temperature of the high temperature reactor, plant pressure, and salt concentration, were varied to determine their effect on plant efficiency and performance. Results show that as the operating temperature of the high temperature increased to  $1200 \,^{\circ}$ C, plant efficiency increased to  $\sim 15\%$ . However, less power could be generated by the Rankine power recovery system; thus imported electricity was needed at high reactor temperatures. On the contrary, as plant pressure increased, the Rankine power recovery system was able to generate more power because the working fluid was vaporized to a higher temperature without causing a temperature crossover. Furthermore, results show as ammonium sulfate concentration increased to 6 M, efficiency also increased to  $\sim 17\%$ . However, less heat could be extracted from the cooling of the low temperature reactor vapor product stream because less water was recycled throughout the process, and thus, less energy was generated from the power recovery system. A tradeoff between achieving higher efficiency or importing electricity is shown.

Cost estimation was completed to determine the projected costs of hydrogen. Costing was performed based on 50  $MW_{th}$  of solar energy obtained from the solar field. The process flow sheet was linearly scaled down to match the size of the solar field. The projected cost of hydrogen was estimated to be \$11.89/kg of hydrogen and \$7.67/kg of hydrogen for year 2015 and 2020, respectively [2]. In order to reach DOE's goal of reducing the cost of hydrogen to \$3/kg and to be competitive with the current cost of gasoline, the capital cost of the plant must be reduced.

Future works include studying the effects of reactor temperature and pressure at high ammonium sulfate concentrations. Reactor design and laboratory testing should be conducted to measure reaction kinetics and mass transfer rates in the low temperature reactor, mid-temperature reactor, and chemical absorber. Furthermore, catalytic research must be continued to reduce the over potential of the electrolyzer; thus ultimately reducing the cost of hydrogen production.

The flow sheet produced represents a preliminary design and with more research, it can aid in designing a scaled up hydrogen production plant.

# References

- [1] Lindberg, D., Backman, R., Chartrand, P., "Thermodynamic Evaluation and Optimization of the (Na2SO4 + K2SO4 + Na2S2O7 + K2S2O7) System," *Journal of Chemical Thermodynamics*, v.38, **2006**, p. 1568-1583
- [2] Taylor, R., "Solar High-Temperature Water Splitting Cycle with Quantum Boost" DOE Hydrogen Program Annual Merit Review, May 16, 2013

# Appendices

#### **A. Simulation Block Descriptions**

The following are descriptions of simulation blocks used in the Aspen Plus process flow sheet [1].

#### A.1 The Gibbs Reactor (RGibbs) Block

The RGibbs simulation block uses Gibbs free energy minimization with phase splitting to perform chemical and phase equilibrium calculations. RGibbs does not require reaction stoichiometry specification and can calculate the chemical equilibria between any number of conventional solid components and fluid phases. In Aspen Plus, RGibbs is set up by specifying possible products, phases of outlet streams for equilibrium calculations, inert components, and reactor operating conditions such as pressure and temperature. RGibbs reactors were used to simulate the low and high temperature reactors, as well as the chemical absorber.

#### A.2 The Stoichiometric Reactor (RStoich) Block

The RStoich simulation block models a reactor with specified reaction stoichiometry. Furthermore, extent of reaction and conversion can also be specified. In Aspen Plus, RStoich is set up by specifying reaction stoichiometry, order of reactions if multiple reactions are present, extent of reactions, and reactor operating conditions such as pressure and temperature. RStoich was used to simulate the mid-temperature reactor and the electrolyzer.

#### A.3 The Separator (Sep) Block

The Sep simulation block models component separations by combining inlet streams and separating components into two or more streams based on specified split fractions. In Aspen Plus, the Sep block is set up by entering split specification, flash specifications, and/or convergence parameters for the inlet and outlet streams. The Sep block was used to simulate the hydrogen vapor-liquid separator and the sulfur trioxide vapor-liquid separator.

#### A.4 The Flash Block

The flash simulation block models component separation by performing rigorous two (vapor-liquid) or three phase (vapor-liquid-liquid) equilibrium calculations. In Aspen Plus, the flash block is set up by entering the flash specifications, convergence parameters, and/or entrainment specifications. The flash block was used to simulate the oxygen vapor-liquid separator.

#### A.5 The Column Block (RadFrac)

The RadFrac simulation block models vapor-liquid, or vapor-liquid-liquid ordinary distillation, absorption, stripping, azeotropic distillations, and/or reactive distillation processes by doing rigorous fractionation calculations. In Aspen Plus, RadFrac is set up by specifying calculation type, number of stages, condenser type, reboiler type, any number of feeds, any number of side draws, and operating conditions such as pressure and temperature. The RadFrac block was used to simulate the oxygen scrubber.

#### A.6 The Pump Block

The pump simulation block models the pressure change of a single liquid input material stream and calculates the power requirement. In Aspen Plus, the pump block is set up by specifying the discharge pressure. Furthermore, vapor-liquid or vapor-liquidliquid calculations can also be specified to check phases in the outlet stream. The pump block was used to simulate both pumps in the Rankine power recovery system as well as the water feed pump.

#### A.7 The Compressor Block (Compr)

The Compr simulation block models the pressure change of a compressor or a turbine and calculates the power requirement. Compr block can handle both single and multiple phases. In Aspen Plus, the Compr block is set up by specifying the block as either an isentropic compressor or an isentropic turbine and the discharge pressure. The Compr block was used to simulate the hydrogen compressor as well as the turbines in the Rankine power recovery system.

#### A.8 Mixer and Splitter (FSplit) Blocks

Mixer and splitter simulation block models the mixing and splitting of material streams. Mixer and splitter blocks can also handle mixing and splitting of heat or work streams, however they cannot mix streams of different types such as material with heat or heat with work. In Aspen Plus, the mixer block does not require any specifications. On the contrary, split specifications are needed for splitter blocks. Mixer and splitter blocks were used to simulate various mixing and splitting of streams throughout the process flow sheet.

#### A.9 Heat Exchanger Blocks, Heater and MHeatX

The heater block models and performs simple energy balance calculations to determine thermal and phase conditions of material streams. In Aspen Plus, the heater block is set up by specifying flash specifications such as degrees of temperature change, outlet temperature, degrees of superheating or sub-cooling, vapor fraction, pressure, and/or heat duty. The heater block requires only one input material stream. Heater blocks were primarily used to simulate the extraction of waste heat from the SA cycle to be used in the Rankine power recovery system. heater blocks were also used to extract thermodynamic properties from material streams to be used in design specification and optimization blocks.

Similar to the heater block, the MHeatX block models and performs energy balance calculations to determine thermal and phase conditions of material streams. However, unlike the heater block, the MHeatX block can handle multiple material streams. In Aspen Plus, the MHeatX block is set up by specifying cold and hot streams, outlet stream temperature of either the hot, cold, or both streams, degrees of temperature change, temperature approach, degrees of superheating or sub-cooling, vapor fraction, pressure, and/or heat duty. The MHeatX blocks were used for heat integration, primarily simulating the heat exchange between materials streams within the SA cycle.

# A.10 Duplication Blocks

The duplication block copies and creates identical streams. In Aspen Plus, duplication blocks do not need any specification. Duplication blocks were used with heater blocks to determined dew point temperature at a given pressure of certain material streams.

#### **B.** Snapshots of FORTRAN Codes

Figure B.1 is a snapshot of the FORTRAN code written for the ELECPOWR calculator block. The ELECPOWR calculator block calculated the required power to operate the electrolyzer based on how much hydrogen gas was produced.



Figure B.1: Snapshot of the Aspen Plus Fortran Code for the ELECPOWR Calculator Block

To determine the power requirement of the electrolyzer, electrochemical relations were used to find power in terms of the amount of hydrogen produced and the voltage used in the electrolyzer. The following is the derivation of this relation. Power (W) = 2 \* F (Faraday's constant)\* FH2 (mol/sec of hydrogen) \* E (V) (B.1)

where F is 96,385 C/mol, FH2 is the flow rate of hydrogen produced, E is the cell's

voltage, and 2 is the number of electrons needed to form hydrogen. The number of

electrons is derived from the following equation:

$$2H^+ + 2e^- \rightarrow H_2 \tag{B.2}$$

Figure B.2 is a snapshot of the FORTRAN code written for the PLANTEFF calculator block. The PLANTEFF calculator block calculated the plant efficiency based on DOE's working definition of efficiency.



Figure B.2: Snapshot of the Aspen Plus Fortran Code for the PLANTEFF Calculator Block

HEATIN is the calculated power (W) requirement of the electrolyzer. TOTW1 is the total power (W) generated from Rankine 1 while TOTW2 is the total power (W) generated from Rankine 2. FH2 is the molar flow rate (kmol/sec) of hydrogen produced from the process. WORKTOT is the total work (W) required to operate all pumps and compressors. HITEMQ is the required heat duty (W) to operate the high temperature reactor while MIDTEMQ is the required heat duty (W) to operate the mid-temperature reactor. GENWORK is the total power (W) generated from Rankine 1 and 2. REQWORK is the total power (W) to run the electrolyzer, high temperature reactor, and all the pumps and compressors while ECSWORK is the excess work (W) after the required power needed to run the electrolyzer and pumps and compressors have been subtracted from the total generated power. LHV is the lower heating value (W) and ETA is efficiency.

## **C. Equation-Based Guthrie Costing Equations**

The following are costing equations used to estimate the cost of the thermochemical plant [2].

#### C.1 Centrifugal Pump

The costing equation for a centrifugal pump is as follows:

$$C_{p} = F_{M}C_{B} \tag{C.1}$$

where  $C_B$  is the base cost, and  $F_M$  is the material factor.  $F_M$  is 2 for stainless steel and  $C_B$  is calculated as follows:

$$C_{\rm B} = \exp[9.7171 - 0.6019\ln(S) + 0.0519[\ln(S)]^2]$$
(C.2)

where S is the costing factor. S is calculated as follows:

$$S = Q(H)^{0.5}$$
 (C.3)

where Q is the flow rate (gals/min) and H is the pump head (ft).

## C.2 Electrical Motor for Pump

The costing equation for an electrical motor for the pump is as follows:

$$C_p = F_T C_B \tag{C.4}$$

where  $F_T$  is the motor-type factor and was assumed to be 1 and  $C_B$  is the base cost.  $C_B$  is calculated as follows:

$$C_{\rm B} = \exp[5.8259 - 0.1314\ln(P_{\rm c}) + 0.053255[\ln(P_{\rm c})]^2]$$
(C.5)

where  $P_c$  is the motor power consumption (W).  $P_c$  is calculated as follows:

$$P_c = QHp/(33,000n_pn_m)$$
 (C.6)

where Q is the flow rate (gal/min), H is the pump head (ft), p is liquid density (lb/gal), and  $n_p$  and  $n_m$  is efficiency associated with the pump. Efficiency associated with the pump is calculated as follow:

$$n_p = -0.316 + 0.24015 \ln Q - 0.0119 (\ln Q)^2$$
 (C.7)

$$n_{\rm m} = 0.80 + 0.0319 \ln P_{\rm b} - 0.00182 (\ln P_{\rm b})^2$$
 (C.8)

where  $P_b$  is the pump break horsepower (hp).

#### C.3 Turbine

The costing equation for a turbine is as follows:

$$C_p = F_M C_B \tag{C.9}$$

where  $C_B$  is the base cost, and  $F_M$  is the material factor.  $F_M$  is 2 for stainless steel and  $C_B$  is calculated as follows:

$$C_{\rm B} = 530 P^{0.81} \tag{C.10}$$

where P is the power extracted (hp).

## C.4 Centrifugal Compressor

The costing equation for a centrifugal compressor is as follows:

$$C_{p} = F_{D}F_{M}C_{B} \tag{C.11}$$

where  $C_B$  is the base cost,  $F_M$  is the material factor, and  $F_D$  is the motor type factor.  $F_M$  is 2.5 for stainless steel and  $F_D$  is 1 for an electrical motor.  $C_B$  is calculated as follows:

$$C_{\rm B} = \exp[7.5800 + 0.80\ln P_{\rm C}] \tag{C.12}$$

where Pc is the required power (hp).

### **C.5 Floating Head Heat Exchanger**

The costing equation for a floating head heat exchanger is as follows:

$$C_p = F_p F_m F_L C_B \tag{C.13}$$

where  $F_p$  is the pressure factor,  $F_m$  is the material factor,  $F_L$  is the tube length factor, and  $C_B$  is the base cost.  $C_B$  is calculated as follow:

$$C_{\rm B} = \exp[11.9052 - 0.8709\ln(A) + 0.09005[\ln(A)]^2]$$
(C.14)

where A is the heat transfer surface area ( $ft^2$ ). The material factor is calculated as follow:

$$F_{\rm m} = a + (A/100)^{\rm b} \tag{C.15}$$

where "a" is 2.70 and "b" is 0.07 for stainless steel. The pressure factor is calculated as follow:

$$F_{p} = 0.9803 + 0.018(P/100) + 0.0017(P/100)^{2}$$
(C.16)

where P is pressure (psi).  $F_L$  is 1 for tube length of 20 ft.

### C.6 Electrolyzer

Cost of the electrolyzer is based on electrical performance. The H2A costing for the electrolyzer is \$723/m<sup>2</sup>. The electron efficiency is assumed to have an efficiency of 100%. And the current density, given by Electrosynthesis Company In. is 100 mA/cm<sup>2</sup>.

#### C.7 Reactors

The costing equation for the reactors is as follow:

$$C_{p} = F_{M}C_{V} + C_{PL} + V_{p}C_{PK} + C_{DR}$$
(C.17)

where  $F_M$  is the material factor,  $C_V$  is the cost of the vessel,  $C_{PL}$  is the cost for platforms and ladders,  $V_p$  is the volume of packing (ft<sup>3</sup>),  $C_{PK}$  is the installed cost of packing, and  $C_{DR}$  is the cost of liquid distributors required for obtaining satisfactory performance with packing. The material factor is 2.1 for stainless steel. The cost of a vertical cylindered vessel is calculated as follow:

$$C_{\rm V} = \exp[7.2756 + 0.18255\ln W + 0.02297(\ln W)^2]$$
(C.18)

where W is the weight (lb) of the vessel. Weight of vessel is calculated as follow:

$$W = pi^{*}(D+ts)^{*}(L+0.8D)^{*}ts^{*}p$$
(C.19)

where D is the diameter (in), ts is the shell thickness (in), L is length (in), and p () is the density of carbon steel. Volume is calculated with the assumption of a 5 minute liquid holdup time and liquid making up 50% of the total volume. Furthermore, L is assumed to be 4\*D. The shell thickness, ts, is calculated as follows:

$$ts = 1/8 in + tv$$
 (C.20)

where tv is the average wall thickness (in). The average wall thickness, tv, is calculated as follows:

$$tv = (tp + (tp+tw))/2$$
 (C.21)

where tp is the wall thickness (in) to withstand the internal pressure of the vessel, and tw is the necessary thickness (in) to withstand the wind load or earthquake at the bottom of vessel. tp and tw are calculated as follow:

$$tp = Pd*D/(2SE - 1.2Pd)$$
 (C.22)

$$tw = 0.22(D + 18)L^2/S/D^2$$
 (C.23)

where Pd is the design pressure (psi) of the vessel, S is the maxium allowable stress  $(lb/in^2)$  of the shell material at the design temperature, and E is the fraction weld efficiency. The design pressure is calculated as follows:

$$Pd = \exp[0.60608 + 0.91615\ln P_0 + 0.0015655(\ln P_0)^2]$$
(C.24)

where  $P_o$  is the operating pressure (psi). Cost of platforms and ladders is calculated as follows:

$$C_{PL} = 300.9(\text{Di})^{0.63316} (\text{L})^{0.80161}$$
(C.25)

where Di is the inside diameter (ft) and L is the length (ft). For 2 in ceramic berl saddles,  $C_{PK}$  is \$28/ft<sup>3</sup>. Furthermore, the cost of liquid distributors,  $C_{DR}$  is \$125/ft<sup>2</sup>.

#### **C.8 Separators**

Costing equation for separators is as follows:

$$C_p = F_M C_V \tag{C.26}$$

where  $F_M$  is the material factor and  $C_V$  is the cost of the vessel. The material factor is 2.1 for stainless steel. The cost of a vertical cylindered vessel is calculated as follow:

$$C_{\rm V} = \exp[7.0132 - 0.18255\ln W + 0.02297(\ln W)^2]$$
(C.18)

where W is the weight (lb) of vessel and is calculated with the same procedure shown in Section C.7.

### **C.9 Separation Columns**

Costing equation for separation columns is as follows:

$$C_p = F_M C_V + C_T \tag{C.27}$$

where  $F_M$  is the material factor,  $C_T$  is the cost of trays, and  $C_V$  is the cost of the vessel. The material factor is 2.1 for stainless steel. The cost of a vertical cylindered vessel is calculated as follow:

$$C_{V} = \exp[7.0132 - 0.18255 \ln W + 0.02297 (\ln W)^{2}]$$
(C.18)

where W is the weight (lb) of vessel and is calculated with the same procedure shown in Section C.7. Cost of trays is calculated as follows:

$$C_{\rm T} = N_{\rm T} F_{\rm NT} F_{\rm TT} F_{\rm TM} C_{\rm BT} \tag{C.28}$$

where  $N_T$  is the number of trays,  $F_{NT}$  is factor for number of trays,  $F_{TT}$  is tray type factor,  $F_{TM}$  is material factor for trays, and  $C_{BT}$  is base cost of trays.  $F_{NT}$  is 1 if the number of trays is less than 20.  $F_{TT}$  is 1 for sieve type trays.  $F_{TM}$  for stainless steel and  $C_{BT}$  are calculated as follow:

$$F_{\rm TM} = 1.401 + 0.0724 D \tag{C.29}$$

$$C_{BT} = 468 \exp(0.1739 D)$$
 (C.30)

where D is the diameter (in) of the tray.

# **D.** Complete Stream Table for Base Case Design

The following stream table was generated by Aspen Plus for the base case design.

		T	able D.1: B	ase Case Sti	ream Tabl	e			
Stream Name	1	2	3	4	4-1	5	9	L	8
To	P101	RECUPSIN	PREHEAT	HX4C1	HX4C2	T101	RECUPSR	C101	
From		P101	RECUPSIN	PREHEAT	HX4C1	HX4C2	T101	RECUPSR	C101
Mole Flow kmol/sec									
H2O	0	0	0	0	0	0	0	0	0
H2	0	0	0	0	0	0	0	0	0
02	0	0	0	0	0	0	0	0	0
NH3	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679
SO2	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
H2SO4	0	0	0	0	0	0	0	0	0
NH4+	0	0	0	0	0	0	0	0	0
-HO	0	0	0	0	0	0	0	0	0
$H^+$	0	0	0	0	0	0	0	0	0
HSO3-	0	0	0	0	0	0	0	0	0
HSO4-	0	0	0	0	0	0	0	0	0
SO4	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0	0
K2S2O7	0	0	0	0	0	0	0	0	0
AM2SO4	0	0	0	0	0	0	0	0	0
AM2SO3	0	0	0	0	0	0	0	0	0
AMHSO3	0	0	0	0	0	0	0	0	0
H2SO3	0	0	0	0	0	0	0	0	0
Total Flow kmol/sec	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679	73.22679
Total Flow kg/sec	1247.093	1247.093	1247.093	1247.093	1247.093	1247.093	1247.093	1247.093	1247.093
Temperature C	40	43.27735	59.80222	71.93913	166.5125	229.629	87.19535	53	39.99959
Pressure bar	16.24905	103.6117	103.6117	103.6117	103.6117	103.6117	16.24845	16.24845	16.24845
Enthalpy MW	-4781.499	-4759.588	-4657.64	-4579.705	-3209.567	-2941.78	-3226.342	-3328.295	-4781.502

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Stream Name	11	22	22-DUP1	22-DUP2	22-DUP3	33	77	55
То	P102	DUP3	HXELECTR	HXDUP3		T103	C102	
From		P102	DUP3	DUP3	HXDUP3	HXELECTR	T103	C102
Mole Flow kmol/sec								
H2O	0	0	0	0	0	0	0	0
H2	0	0	0	0	0	0	0	0
02	0	0	0	0	0	0	0	0
NH3	12.15996	12.15996	12.15996	12.15996	12.15996	12.15996	12.15996	12.15996
SO2	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0
H2SO4	0	0	0	0	0	0	0	0
NH4+	0	0	0	0	0	0	0	0
-HO	0	0	0	0	0	0	0	0
$\mathbf{H}^+$	0	0	0	0	0	0	0	0
HSO3-	0	0	0	0	0	0	0	0
HSO4-	0	0	0	0	0	0	0	0
SO4	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0
K2S2O7	0	0	0	0	0	0	0	0
AM2SO4	0	0	0	0	0	0	0	0
AM2SO3	0	0	0	0	0	0	0	0
AMHSO3	0	0	0	0	0	0	0	0
H2SO3	0	0	0	0	0	0	0	0
Total Flow kmol/sec	12.15996	12.15996	12.15996	12.15996	12.15996	12.15996	12.15996	12.15996
Total Flow kg/sec	207.091	207.091	207.091	207.091	207.091	207.091	207.091	207.091
Temperature C	40	43.29891	43.29891	43.29891	128	130.0034	42.00056	40.00056
Pressure bar	16.24887	104.1706	104.1706	104.1706	104.1706	104.1706	16.24887	16.24887
Enthalpy MW	-794.0107	-790.3489	-790.3489	-790.3489	-578.5042	-573.5756	-603.1987	-794.0101

Stream Name	ELECPROD	H2	H2-2	H20FEED	H20FEED1	H2OFEED2	H2OGS	H2ORECYC	K2S2O7
To	H2-SEP		H2COMP	H2OPUP	O2WASH	H2OFDSP	GSOX	MIXER	HX2
From	ELECTROL	H2COMP	H2-SEP		H2OFDSP	H2OPUP	<b>H2OFDSP</b>	O2WASH	LOTEMRXR
Mole Flow kmol/sec									
H20	27.20025	0	0	1.225961	1.125495	1.225961	0.1004659	1.456164	0
H2	1.113519	1.113519	1.113519	0	0	0	0	0	0
02	0	0	0	0	0	0	0	1.15E-04	0
NH3	0	0	0	0	0	0	0	2.70E-03	0
S02	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
H2SO4	1.21E-04	0	0	0	0	0	0	1.47E-03	0
NH4+	0	0	0	0	0	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	0	0	0	0	0
HSO3-	0	0	0	0	0	0	0	0	0
HSO4-	0	0	0	0	0	0	0	0	0
SO4	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0	0.5798281
K2S207	0	0	0	0	0	0	0	0	26.75121
AM2SO4	1.47	0	0	0	0	0	0	0	0
AM2SO3	0.0772001	0	0	0	0	0	0	0	0
AMHSO3	0	0	0	0	0	0	0	0	0
H2SO3	5.12E-15	0	0	0	0	0	0	5.12E-15	0
Total Flow kmol/sec	29.86109	1.113519	1.113519	1.225961	1.125495	1.225961	0.1004659	1.460448	27.33104
Total Flow kg/sec	695.4894	2.24472	2.24472	22.08603	20.27611	22.08603	1.809921	26.42703	6904.527
Temperature C	140	335.4172	140	25	25.28257	25.28257	25.28257	137.1357	400.0019
Pressure bar	9	25.145	6	1	9	9	6	6	9
Enthalpy MW	-9268.674	10.07252	3.685097	-350.634	-321.876	-350.6079	-28.73185	-405.7395	-35398.97

Stream Name	K2S207-2	K2SO4	K2SO4-R	K2SO4SO3	MIXED	MIXED1	NH3-COLD	NH3-HOT	NH3DEW
To	MIDTEMRX	LOTEMRXR		SEP-MID	HX5	O2-SEP	ABSORBER	NH3-DUP	HXDEW
From	HX2		SEP-MID	MIDTEMRX	ABSORBER	HX5	HX4H	LOTEMRXR	NH3-DUP
Mole Flow kmol/sec									
H2O	0	0	0	0	27.20135	27.20135	28.7472	28.7472	28.7472
H2	0	0	0	0	0	0	0	0	0
02	0	0	0	0	0.561079	0.561079	0	0	0
SHN 3	0	0	0	0	2.70E-03	2.70E-03	3.0944	3.0944	3.0944
S02	0	0	0	0	0	0	0.0772	0.0772	0.0772
SO3	0	0	0	1.470121	0	0	0	0	0
H2SO4	0	0	0	0	0	0	0	0	0
NH4+	0	0	0	0	0	0	0	0	0
-HO	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	0	0	0	0	0
HSO3-	0	0	0	0	0	0	0	0	0
HSO4-	0	0	0	0	0	0	0	0	0
SO4	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
K2SO4	0.5798281	2.049828	2.049949	2.049949	0	0	0	0	0
K2S2O7	26.75121	25.28121	25.28109	25.28109	0	0	0	0	0
AM2SO4	0	0	0	0	0.3464927	0.3464927	0	0	0
AM2SO3	0	0	0	0	1.199358	1.199358	0	0	0
AMHSO3	0	0	0	0	0	0	0	0	0
H2SO3	0	0	0	0	0	0	0	0	0
Total Flow kmol/sec	27.33104	27.33104	27.33104	28.80116	29.31098	29.31098	31.9188	31.9188	31.9188
Total Flow kg/sec	6904.527	6786.833	6786.823	6904.527	693.1204	693.1204	575.534	575.534	575.534
Temperature C	405.6854	791.6199	791.62	791.62	160.7814	142	90	400.0019	400.0019
Pressure bar	9	9	6	9	9	9	9	9	9
Enthalpy MW	-35357.9	-32825.12	-32825.14	-33332.8	-8797.046	-8874.981	-8336.351	-6698.426	-6698.426

Stream Name	NH3DEW 1	NH3HOT1	02	O2-SEP	SFITPRD	SFITPRD2	SO2-O2-1	SO2-O2-2	SO2-O2-3
То		HX4H		O2WASH	MIXER	ELECTROL	HX1	HX2	HX3
From	HXDEW	NH3-DUP	<b>HSAWSH</b>	O2-SEP	O2-SEP	MIXER	HITEMRXR	HX1	HX2
Mole Flow kmol/sec									
H2O	28.7472	28.7472	0.1120755	0.3437486	26.8576	28.31376	0	0	0
H2	0	0	0	0	0	0	0	0	0
02	0	0	0.5567595	0.5568747	4.20E-03	4.32E-03	0.5616406	0.5616406	0.5616406
NH3	3.0944	3.0944	4.31E-07	2.70E-03	8.40E-16	2.70E-03	0	0	0
S02	0.0772	0.0772	0	0	0	0	1.123281	1.123281	1.123281
SO3	0	0	0	0	0	0	0.3468395	0.3468395	0.3468395
H2SO4	0	0	6.09E-55	0	0	1.47E-03	0	0	0
NH4+	0	0	0	0	0	0	0	0	0
-HO	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	0	0	0	0	0
HSO3-	0	0	0	0	0	0	0	0	0
HSO4-	0	0	0	0	0	0	0	0	0
SO4	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0	0
K2S2O7	0	0	0	0	0	0	0	0	0
AM2SO4	0	0	0	1.54E-95	0.3464927	0.3464927	0	0	0
AM2SO3	0	0	0	1.03E-95	1.199358	1.199358	0	0	0
AMHSO3	0	0	0	0	0	0	0	0	0
H2SO3	0	0	5.76E-255	0	0	5.12E-15	0	0	0
Total Flow kmol/sec	31.9188	31.9188	0.6688354	0.903322	28.40766	29.8681	2.031761	2.031761	2.031761
Total Flow kg/sec	575.534	575.534	19.83471	24.05801	669.0624	695.4894	117.704	117.704	117.704
Temperature C	176.5083	400.0019	110.3477	142.0029	142.0029	141.6273	955.785	801	410
Pressure bar	9	9	9	9	9	9	9	9	9
Enthalpy MW	-6966.212	-6698.426	-25.44457	-80.11509	-8794.855	-9200.595	-378.3836	-395.2631	-436.3357

Stream Name	SO2-02-4	SO2-02-5	SO3	SO3-1	SOX-1	SOX-2	SULFATE	<b>SULFATE1</b>	SULFATER
To	SO2SP	ABSORBER	HXI	HITEMRXR	GSOX	O2WASH	LOTEMRX	HX3	
From	HX3	SO2SP	SEP-MID	1XH	SO2SP	GSOX		H2-SEP	HX3
Mole Flow kmol/sec									
H20	0	0	0	0	0	0.0989957	27.2	27.20025	27.20025
H2	0	0	0	0	0	0	0	0	0
02	0.5616406	0.561079	0	0	5.62E-04	0	0	0	0
NH3	0	0	0	0	0	0	0	0	0
S02	1.123281	1.122158	0	0	1.12E-03	2.71E-17	0	0	0
SO3	0.3468395	0.3464927	1.470121	1.470121	3.47E-04	2.78E-25	0	0	0
H2SO4	0	0	0	0	0	1.47E-03	0	1.21E-04	1.21E-04
NH4+	0	0	0	0	0	0	0	0	0
OH-	0	0	0	0	0	0	0	0	0
H+	0	0	0	0	0	0	0	0	0
HSO3-	0	0	0	0	0	0	0	0	0
HSO4-	0	0	0	0	0	0	0	0	0
SO4	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0
K2SO4	0	0	0	0	0	0	0	0	0
K2S2O7	0	0	0	0	0	0	0	0	0
AM2SO4	0	0	0	0	0	0	1.47	1.47	1.47
AM2SO3	0	0	0	0	0	0	0.0772	0.0772001	0.0772001
AMHSO3	0	0	0	0	0	0	0	0	0
H2SO3	0	0	0	0	0	5.12E-15	0	5.12E-15	5.12E-15
Total Flow kmol/sec	2.031761	2.02973	1.470121	1.470121	2.03E-03	0.1004659	28.7472	28.74757	28.74757
Total Flow kg/sec	117.704	117.5863	117.704	117.704	0.117704	1.927625	693.2284	693.2447	693.2447
Temperature C	150	150	791.62	939.7462	150	82.45292	147.8697	140	147.8635
Pressure bar	9	9	9	9	9	9	9	6	9
Enthalpy MW	-461.1521	-460.6909	-505.5612	-488.6817	-0.4611521	-29.193	-9272.281	-9297.299	-9272.483

# References

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- [2] Seider, W., Seader, J.D., Lewin, D., Widagdo, S., "Purchase Costs of the Most Widely Used Process Equipment," Product and Process Design Principles, 3<sup>rd</sup> ed. John Wiley & Sons, Inc.: NJ, 2009, p. 558-596