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Status of the solar sulfur ammonia thermochemical hydrogen production system for splitting water

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Abstract

A sulfur ammonia (SA) cycle for splitting water to produce hydrogen with solar energy was evaluated using the Aspen Plus® chemical process modeling tool. The hydrogen production step consists of electrolytic oxidation of ammonium sulfite and the oxygen evolution side is a molten salt sub-cycle. Laboratory testing for the thermochemistry of molten salts and electrolysis has indicated that the cycle is viable. The solar field, reactor configurations and continuous operation with storage have been evaluated. The SA cycle is an all-fluid cycle and the solar receiver operates below 1073 K. All of the electricity needed by the process is generated internally from waste heat. Using thermal energy storage, the system will operate continuously with no shut downs required due to the variability of solar energy.

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1. Introduction

Science Applications International Corporation (SAIC) with the support of the University of California San Diego, Electrosynthesis Company, Inc. and Thermochemical Engineering Solutions is developing an advanced thermochemical process based on a sulfur ammonia (SA) cycle for splitting water to produce hydrogen with solar energy through a DOE funded project. A variation of the hybrid sulfur thermochemical water splitting cycle (aka the “Hybrid Sulfur,” or “HyS” cycle) was developed by introducing ammonia as a working reagent (thus “sulfur-ammonia,” or “SA,” cycle) to allow more efficient solar interface and facile product separation steps. The SA thermochemical cycle was originally developed by the Florida Solar Energy Center [1].
The SA cycle considered in the study utilizes the oxidation of aqueous ammonium sulfite as the hydrogen production half cycle, and an all-liquid potassium sulfate/potassium pyrosulfate sub-cycle for oxygen production. The reactions for the present cycle are presented below, and Figure 1 shows a schematic of the electrolytic SA cycle presently being examined.

SO\(_2\) (g) + 2NH\(_3\) (g) + H\(_2\)O (l) → (NH\(_4\))\(_2\)SO\(_3\) (aq) (1 - chemical absorption) 298-323 K
(NH\(_4\))\(_2\)SO\(_3\) (aq) + H\(_2\)O (l) → (NH\(_4\))\(_2\)SO\(_4\) (aq) + H\(_2\) (g) (2 – electrolytic oxidation) 353-423 K
(NH\(_4\))\(_2\)SO\(_4\) (aq) + K\(_2\)SO\(_4\) (l) → 2NH\(_3\) (g) + K\(_2\)S\(_2\)O\(_7\) (l) + H\(_2\)O (g) (3 – adiabatic mixing) 673-723 K
K\(_2\)S\(_2\)O\(_7\) (l) → SO\(_3\) (g) + K\(_2\)SO\(_4\) (l) (4 – stored thermal) 1063 K
SO\(_3\) (g) → SO\(_2\) (g) + ½O\(_2\) (g) (5 – electric heat) 1123-1473 K

The net cycle reaction represented by reactions (1)-(5) is the decomposition of water to form hydrogen and oxygen. The electrolytic oxidation of the ammonium sulfite solution in reaction (2) occurs above ambient temperature at reasonably low pressures to yield hydrogen gas. Reactions (3) and (4) form a sub-cycle by which potassium sulfate is reacted with ammonium sulfate in the low-temperature reactor, to form potassium pyrosulfate. Potassium pyrosulfate is then fed to the medium temperature reactor where it is decomposed to SO\(_3\) and K\(_2\)SO\(_4\), again, closing the sub-cycle. The potassium sulfate and pyrosulfate form a miscible liquid melt that facilitates the separations and the movement of the chemicals in reactions (3) and (4). The oxygen production step (5) occurs at high temperature over a catalyst. Separation of the oxygen from SO\(_2\) occurs when SO\(_2\) is absorbed in water in reaction (1). Note, there are no gas-gas or liquid-liquid separation steps in this process. All of the reaction steps described above have been demonstrated in the laboratory and shown to occur without undesirable side reactions. By using an all liquid oxygen sub-cycle, materials handling problems could be reduced, molten salt storage could be used as will be described, and thermal energy recovery could be employed, resulting in easier continuous operation. First, the laboratory tests for the two sub-cycles will be discussed. Then the modeling of the chemical plant using Aspen Plus® and design and evaluation of the solar field and storage system will be described. The basis for the Aspen Plus® model was a chemical plant to generate 1.7X10^5 kg/day of hydrogen. However, as this is an extremely large plant, the system was reduced to a more reasonable unit size of 50 MWth maximum thermal input with an average hydrogen production of 5000 kg/day for the solar plant design and costing. This system would be replicated to meet the DOE target of ~10^5 kg/day.

Fig. 1. Schematic of the Electrolytic SA Cycle.
Energy to fuel the cycle comes entirely from a solar collection system, using a phase-change NaCl storage medium to allow continuous operation of the process. Thermal energy from the storage system is introduced to the mid-temperature reactor for the $\text{K}_2\text{S}_2\text{O}_7$ decomposition. The low-temperature reactor is operated adiabatically powered by the sensible heats of the reactants. The chemical absorber generates enough heat of reaction to maintain its temperature. The energy recovery system produces electricity that is used to operate the electrolytic reactor and to heat the high-temperature reactor. Electric heating of the high-temperature reactor allows the solar collection system to be operated at a lower temperature, maximizing its efficiency, and optimizes the energy balances of the system.

2. Hydrogen generation sub-cycle – electrolysis

The voltage requirement for the electrolytic production of hydrogen is greatly reduced by using the oxidation of sulfite to depolarize the anode reaction. Indeed, in basic media the thermodynamic potential required to drive this reaction is estimated to be $-0.1 \text{ V}$ (depending on pH). We have demonstrated the process in electrochemical flow cells comprising a membrane electrode assembly (MEA) with a Pt/C cathode on a cation exchange membrane and a high surface area carbon felt anode. Despite the favorable thermodynamic potential required for the reaction, in practice the voltage required to drive the reaction is significantly higher. Using electroanalytical techniques such as linear sweep voltammetry, we have determined that the largest contributor to the cell voltage is the overpotential at the anode. In order to reduce this overpotential for sulfite oxidation, we have investigated a range of electrocatalysts and deposited these onto high surface area carbon felt materials. Moreover, we have shown that the kinetics of the oxidation reaction can be significantly improved by operating the cell at elevated temperatures (up to 403 K has been demonstrated in a pressurized reactor).

Figure 2 shows the cell voltage for a cell operating at 400 K as a function of current density for the oxidation of ammonium sulfite (2 M) to sulfate with hydrogen generation at the cathode. The anode was Pt/Co catalyst on carbon felt while the cathode was Pt/C MEA on a Nafion® 112 membrane. The data are shown for a range of sulfite to sulfate conversions up to 90% conversion. Cell voltages of approximately 0.7 V were observed at current densities of 100 mA/cm².

![Current density vs. cell voltage for the oxidation of ammonium sulphite](image)
Longer-term operation of this cell configuration showed that the Nafion® membrane becomes unacceptably permeable to sulfite species, which transport to the cathode leading to unwanted side reactions (sulfur reduction species). In order to eliminate these reactions we have identified alternate membranes that reduce the flux of sulfite by over two orders of magnitude. We have further demonstrated the long-term stability of the anode catalyst and cathode MEA through a series of batch electrolyses that accumulated over 550 h of electrolysis time. These tests utilized a flow cell comprising Pt/Co catalyzed anode and a Pt/C MEA on a Fumatech cation exchange membrane. The average cell voltage for the electrolyses was 1.1 V at a current density of 100 mA/cm² and 373 K; the coulombic current efficiency for hydrogen production was measured at >94%. The cell performance remained consistent from batch to batch demonstrating excellent stability of the catalyst and membrane materials over the entire test.

3. Oxygen generation sub-cycle thermochemistry experiments

Key steps in the oxygen generation sub-cycle were investigated experimentally to determine its feasibility. In order to avoid costly gas separations, NH₃ and SO₃ must be released separately in the sub-cycle. Thermogravimetric and differential thermal analysis (TG/DTA) were employed to study the thermal decomposition of the molten salts [2, 3]. Thermal decomposition of (NH₄)₂SO₄ + K₂SO₄ + 4 K₂S₂O₇ + Na₂SO₄ + 4 Na₂S₂O₇ showed that NH₃ and SO₃ could be released separately, but the process would require careful temperature control.

Additionally, the molten salts must be liquid and have a low enough viscosity to be pumped. Our laboratory experiments measured melting points and viscosities of various salt mixtures [2]. A combination of potassium sulfates and pyrosulfates with sodium sulfates and pyrosulfates resulted in a lower melting point than potassium or sodium sulfates and pyrosulfates by themselves. Because of the lower melting temperature, the salt mixture of K₂SO₄ + 4 K₂S₂O₇ + Na₂SO₄ + 4 Na₂S₂O₇, with a melting temperature of 646 K was chosen for the stream exiting the mid-temperature reactor which would be recycled to the low temperature reactor. The salt mixture of K₂SO₄ + 9 K₂S₂O₇ + Na₂SO₄ + 9 Na₂S₂O₇, with a melting temperature of 605 K, was chosen for the stream exiting the low temperature reactor to be recycled to the mid temperature reactor.

The viscosities of the two salt streams were measured as a function of temperature in order to check their ability to be pumped. The viscosity for K₂SO₄ + 4 K₂S₂O₇ + Na₂SO₄ + 4 Na₂S₂O₇ ranged from 3.3 mPa-s at 780 K to 9.3 mPa-s at 675 K, and the viscosity for K₂SO₄ + 9 K₂S₂O₇ + Na₂SO₄ + 9 Na₂S₂O₇ ranged from 2.6 mPa-s at 783 K to 8.3 mPa-s at 666 K [2]. The viscosity results revealed that these two salt mixtures would be suitable for pumping in the sub-cycle above their respective melting temperatures.

4. Aspen Plus® process modeling

Aspen Plus® was used to model the chemical plant by showing the convergence of material and energy balances, incorporating thermodynamics from literature into the process, incorporating internal electrical generation, and calculating the plant efficiency [4]. The model is for full-scale operation that would generate 1.7X10⁵ kg/day of hydrogen, which is equivalent to 355 MW on a lower heating value basis. Thermodynamic properties of chemical species obtained from the literature [5] and from the laboratory experiments [2] were entered into the model. Energy integration using pinch analysis and an internal power plant was integral to the design to ensure reasonable efficiency. Power requirements for the electrolyzer and the overall efficiency of the plant were determined based on a definition provided by DOE.

The DOE working definition of the efficiency is:

\[ \eta = -\Delta H_0^{\circ}(\text{H}_2\text{O}(g)) / (Q + E/\eta_s) \]

where Q is the total heat requirement of the three solar reactors, E is the electrical energy required to be purchased from outside the process and \( \eta_s \) is the efficiency at which solar electricity can be produced. The efficiency is based on the lower heating value of hydrogen.
The process flow sheet consists of the oxygen producing half-cycle, the hydrogen producing half-cycle, and the Rankine power recovery system. Figure 3 shows a simplified Aspen Plus® plant schematic.

Key plant parameters are summarized in Table 1. A pressure of 900 kPa was chosen as previous simulations were performed at this pressure [1,6]. The electrolyzer was specified to operate at 413 K with a concentration of ammonium sulfate in the electrolyzer product stream specified to be 3 M. The low temperature reactor was specified to operate at 673 K because our experimental studies showed that the production of ammonia gas occurred approximately at this temperature [3]. The mid-temperature reactor was specified to operate at 1063 K to ensure that heat will flow from the phase-change thermal-storage system, operating at 1073 K, to the reactor. The high temperature reactor was specified to operate at 1229 K such that there was sufficient energy generated by the Rankine power recovery system to run the entire thermochemical plant. The chemical absorber was specified to operate adiabatically and the operating temperature was determined by Aspen Plus®.

Table 1. Plant Parameters for Base Case

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Pressure (kPa)</td>
<td>900</td>
</tr>
<tr>
<td>Concentration of (NH₄)₂SO₄ in electrolyzer product stream (M)</td>
<td>3</td>
</tr>
<tr>
<td>Temperature of low temperature reactor (K)</td>
<td>673</td>
</tr>
<tr>
<td>Temperature of mid-temperature reactor (K)</td>
<td>1063</td>
</tr>
<tr>
<td>Temperature of high temperature reactor (K)</td>
<td>1229</td>
</tr>
<tr>
<td>Temperature of electrolyzer (K)</td>
<td>413</td>
</tr>
<tr>
<td>Temperature of chemical absorber (K)</td>
<td>434</td>
</tr>
</tbody>
</table>

The simulated thermochemical plant has the capacity to produce and deliver hydrogen at 2.5 MPa at a production rate of ~1.7 X 10⁵ 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% for the base case. The overall plant design can be linearly scaled by the thermal energy needed to operate the mid-temperature reactor to the thermal energy captured.
by the solar field.

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 crucial for extracting waste heat to be used in the Rankine power recovery system in which thermal energy is transformed into electrical energy.

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. A power recovery system, consisting of two Rankine cycles, was designed to convert waste heat generated by the thermochemical plant into electrical energy to be used in the process. Two cycles were designed such that all energy could be efficiently used without having temperature crossovers. Ammonia was chosen as the heat transfer fluid for both cycles due to its lower boiling point compared to water, its low cost, and since it was already present in the SA cycle.

In order to 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. Table 2 shows a summary of the required power needed to operate the plant and total power produced by the Rankine power recovery system. The 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; Rankine 1 produced a total power of ~283 MW and Rankine 2 produced a total power of ~26 MW. A total of 172 MW of energy was needed to drive the electrolytic reactor. 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>
<thead>
<tr>
<th>Table 2. Summary of Produced/Required Power for Base Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Power Produced from Rankine Power Recovery System [MW]</td>
</tr>
<tr>
<td>Power Needed for the Electrolyzer [MW]</td>
</tr>
<tr>
<td>Power Needed for the High Temperature Reactor [MW]</td>
</tr>
<tr>
<td>Power Needed for Pumps and Compressors [MW]</td>
</tr>
<tr>
<td>Excess Power [MW]</td>
</tr>
</tbody>
</table>

The solar thermochemical plant is a complex process with many inter-related process parameters that can affect the overall plant performance and efficiency. The 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. The reactor temperature was varied from 1173 K to 1473 K at an ammonium sulfate salt concentration of 3 M and plant pressure of 900 kPa. It was found that as the operating temperature of the high temperature reactor increased from 1173 K to 1473 K, the efficiency also increased from ~11% to ~15%. The plant pressure was varied from 7 bar to 13 bar and at each pressure, the reactor temperature was varied from 1173 K to 1473 K. At a reactor temperature of 1473 K, the efficiency at 7 bar was ~14%, while efficiency at 13 bar was ~15%. As the plant pressure increased from 700 to 900 kPa, the total required power increased from ~210 to ~260 MW. 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. Plant efficiency was varied as a function of ammonium sulfate concentration 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%. 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. This meant more ammonium sulfite was produced in the chemical absorber, and ultimately more hydrogen gas was generated in the electrolyzer, which increased the overall efficiency of the thermochemical plant. As the concentration of ammonium sulfite increased, less water was recycled throughout the process. The required power to operate the plant stayed relatively constant at ~240 MW. However, as concentration increased, power generation decreased. At concentrations greater than 3 M, imported electrical energy was needed to operate the plant.
5. Solar collector analysis and design

The proposed system for delivery of solar thermal energy to the SA hydrogen production process is shown schematically in Figure 4. The solar field consists of 231,600 m$^2$ of heliostats, each about 100 m$^2$, and each tracking to reflect the sun’s energy to the top of a 150 m tower. The heliostats are arrayed to the North of the tower over an area of about 1000 acres. At the top of the tower, a cavity receiver with an aperture 18 m wide and 14 m tall allows the energy to enter a receiver composed of multiple vertically-oriented sodium heat pipes. Above the receiver, the condenser ends of the heat pipes terminate in a vessel through which liquid sodium is circulated to collect the energy from the heat pipes. The sodium circulates down to the base of the tower, where the heat is used to melt NaCl in a storage tank at 1073 K.

The tank contains a sodium pool boiler/heat pipe arrangement that allows the heat from solidifying NaCl to be delivered to the chemical process as needed. The system is designed to provide a chemical plant with a maximum input of 50 MW of thermal energy on a continuous basis through the year. The following paragraphs summarize some of the design considerations that went into the selection of this plant configuration and selection of the components.

5.1. System sizing

From the beginning, it was clear that the DOE-specified nominal plant size of 100,000 kg/day of hydrogen production would be an extremely large plant. Initial sizing of plant components yielded huge components that were outside the normal range of chemical plant equipment, requiring large extrapolations to estimate the equipment costs. After discussing the costing of plant equipment it was decided to reduce the plant to a more reasonable size, and a unit size with a maximum thermal input of 50 MW$_{th}$ was chosen.

Fig. 4. Proposed Solar Interface for SA Hydrogen Process
5.2. Continuous plant operation

It has long been recognized that continuous plant operation is advantageous for the chemical plant. Start and stop cycles in high-temperature chemical processes lead to inefficient operation and to thermal stresses and materials issues. Running the chemical plant continuously also maximizes the capacity factor of the equipment, minimizing the size of equipment and thereby the capital cost of the plant.

Unfortunately, solar energy is inherently intermittent on a diurnal basis, and varies significantly on a seasonal basis. In order to operate any process using solar heat on a continuous basis, thermal storage on the order of at least one day’s thermal needs is needed. Seasonal variations in the solar resource also amount to a turndown ratio of about 35% from summer peak to winter minimum. If the chemical plant is unable to run at turn-down ratios of that magnitude, the plant might even have to operate in an intermittent basis in the winter, storing up heat over periods of days in order to operate for several days at a time, and then shutting down again.

Solar thermal electric plants have been designed and built with storage of up to about one day’s worth of energy. Energy is stored in the sensible heat of molten salts and used to provide electrical generation into the evening and in some cases through the night. This technology has been demonstrated and is commercially available. Such molten salt thermal storage systems have shown themselves to be very efficient, operating at 98-99% efficiency over short (e.g., 1-day) periods and delivering energy at temperatures of about 773 K.

An advantage of a solar plant containing large amounts of storage is that the operation of the solar system becomes more and more independent from the operation of the chemical plant. The solar plant operates when the sun shines to charge the storage, while the chemical plant can draw upon the storage independently as it needs energy. As long as the solar input and the chemical plant usage balance over a period of time comparable to the storage capacity, they can operate independently, each maximizing their efficiency based only on their own operating constraints.

5.3. Choice of Heliostat Configuration

Reaching temperatures of 1073 K requires high solar concentration in order to reduce the thermal losses from the receiver to make the collection of energy efficient. So, for example, trough collectors, with concentrations of up to about 100X, would not be feasible for this temperature level. High concentrations (up to ~2000X) can be reached easily in dish concentrators, and the solar efficiency of dishes is higher than any other type of collector at these temperatures. However, dishes are inherently modular, ranging in size from a few square meters up to a few hundred square meters, and power levels from a few kW to only a couple hundred kW. Since our system requires tens or hundreds of MW, a large number of dishes would be needed to provide the power our chemical plant requires. The cost and heat losses from high-temperature piping to and from such a field of dishes poses a major problem that generally precludes them from consideration for large systems. This leaves us with a central receiver as the only practical solar configuration for our system. Power levels up to a few hundred MW are feasible, and the collection of the energy at a central point makes it simple to interface to the chemical plant.

5.4. Solar plant design

The NREL SAM (System Advisor Model) [7] was used to produce a design for a heliostat field appropriate for our needs. SAM is a detailed modeling system that is mainly aimed at solar thermal electric systems, but includes optimization routines for the heliostat field and tower, as well as the most up-to-date cost data for solar thermal systems. The result of this design exercise was a preliminary heliostat field layout and design of a tower and receiver. Since our plant requires energy at 1073 K, the design was constrained to a North-side heliostat field with a cavity receiver at the top of the tower. A cavity receiver allows higher temperatures to be reached without unacceptable thermal losses.

The interface to the chemical plant involved specification of a plant turn-down ratio and storage capacity, tied to a distribution algorithm. These parameters were adjusted to maximize the operation of the plant and minimize the
amount of storage needed. Initial runs assumed the plant would operate at a constant rate through the year. With a heliostat field of 140,000 m², this configuration provided 22.5 MW continuously, but had a storage requirement of about 31 days of thermal energy. This very large storage capacity essentially allowed energy from the summer to be stored through to the winter. This bounded the problem but did not represent a practical design.

Assuming that the chemical plant could be made to operate efficiently with a turndown ratio of 35% from summer to winter, the amount of storage needed drops dramatically. This represented eliminating “seasonal” storage of energy, so the storage was only used to make up for short-term (e.g., daily to weekly) variations in solar input. In that case, the energy to the process varied from 18 MW in winter to 27 MW in summer, and the storage requirement dropped to 9.3 days. Further refinements to the dispatch algorithm, in which the plant output was allowed to vary within limits on an hour-to-hour basis, eventually allowing configuration of a system that would deliver thermal inputs of 6 MW to 35 MW to the process and achieve continuous operation with only 3.3 days of storage. This still represented a large storage volume, so it was decided to limit storage to about 6 hours and to shut down the process as needed for periods of time.

5.5. Phase change storage system

Because the amounts of storage in our proposed system were large, and because our temperature level was significantly higher (1073 K vs. 773 K) than typical solar electric systems, a better thermal storage approach was sought. A phase-change NaCl storage system was identified that appeared to be ideal for our system, as shown in Figure 5. The melting point of NaCl is 1073 K, and the latent heat of fusion is quite high (481 kJ/kg) compared to the sensible heat capacity of typical solar salts (e.g. 1.5 kJ/kg/K) used in conventional solar thermal systems. The concept also used a unique method of extracting the heat from the molten tank of salt, involving a pool of liquid sodium floating on the NaCl liquid which acts as the evaporator of a heat pipe to deliver heat with nearly no loss to a condenser pipe containing our process fluids [8]. Finally, given that NaCl costs are about $80/ton, the cost of the storage material itself was quite reasonable at about $600/MWh. For example, for six hours of storage at 50 MW (e.g., 300 MWh), the salt cost is only about $180,000.

5.6. Solar heat transfer system

In order to absorb the energy from the proposed heliostat field, a receiver of about 140 MW is needed. A sodium-based receiver system is a good match. An approach to minimizing the risk of fire is to compartmentalize the sodium into small amounts. This leads naturally to the idea of using a bank of individual sodium heat pipes for

Fig. 5: Schematic of a Phase-Change Thermal-Storage System with NaCl [8]
the receiver. Each heat pipe is a sealed unit with only a small volume of sodium contained within it, capable of collecting and transferring tens or hundreds of kW of power. In a receiver composed of many of these pipes, failure of an individual pipe would not be catastrophic, and could be compensated for by radiative heat transfer to the pipes around it. Placing the heat pipes vertically leads to natural gravity-assisted circulation of the liquid sodium back to the bottom of the receiver tubes with no pumping required. Such a receiver, consisting of several banks of vertical sodium heat pipes, is therefore both safe and robust.

To deliver the energy from the top of the tower to the storage container (presumably at the bottom of the tower), a liquid sodium flow loop would be used. The condensers of all the heat pipes from the receiver would be terminated in a heat-exchange vessel containing sodium liquid, and the heat absorbed could be transferred either as sensible or latent heat down to the storage container. Likely, the flow would be kept liquid so that the system would operate with a siphon-return flow to limit the pressure needed from the circulation system. If a latent-heat, heat-pipe flow were used, the circulating pump(s) would have to overcome the entire head to pump the fluid to the top of the 150 m tower (although the flow rate would be much less than with an all-liquid system since the latent heat of sodium would be used). The fire danger from this loop would be minimal, since it would be only transporting heat from one heat exchanger to another, and would not be exposed to solar flux or other stresses. For safety and redundancy, multiple circulation loops operating in parallel may be used.

At the bottom of the tower, the solar-heated sodium flow would simply be circulated through pipes near the bottom of the NaCl tank, causing melting of the salt. NaCl increases in volume by about 30% as it melts, so the liquid salt would quickly separate and rise to the surface, meaning that the NaCl tank would be well stirred by the phase change activity. Routing the sodium pipes in from the top of the tank would ensure that passages would be formed for the liquid that extended from the top to the bottom of the tank, eliminating the potential for pressure buildup and “burping” of the liquid. It would also eliminate any penetrations through the sides or bottom of the tank, improving the effectiveness of the tank insulation and making the tank less liable to leak.

6. Cost analysis

Plant cost estimation was performed to determine projected costs of hydrogen based on the process flow diagram at base case conditions in Table 1. Costing was performed using the H2A Version 3 model [9] and the equation-based Guthrie method [10] based on 50 MWth of chemical plant unit size. 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 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 projected cost in 2020, including several technology improvements and cost reductions was $7.67/kg of hydrogen.

<table>
<thead>
<tr>
<th>Average Hydrogen Plant Production</th>
<th>5000 kg/day</th>
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<tbody>
<tr>
<td>Solar Plant Module Cost (with storage)</td>
<td>$55 million</td>
</tr>
<tr>
<td>Thermochemical Plant Cost (including Electrolytic reactor)</td>
<td>$17 million</td>
</tr>
<tr>
<td>2015 Hydrogen Production Cost: Capital</td>
<td>9.77</td>
</tr>
<tr>
<td>Fixed O&amp;M</td>
<td>2.07</td>
</tr>
<tr>
<td>Other</td>
<td>0.05</td>
</tr>
<tr>
<td>Total: $11.89/kg Hydrogen</td>
<td></td>
</tr>
<tr>
<td>2020 Estimate</td>
<td>$7.67/kg Hydrogen</td>
</tr>
</tbody>
</table>

Currently, the most expensive component of the entire hydrogen production plant is the solar field, representing 76% of the total plant cost. Figure 6 illustrates the cost distribution of the thermochemical plant. The electrolyzer is the most expensive component of the chemical plant, representing 38% of thermochemical plant cost, excluding the cost of the solar field.
7. Conclusion

The SAIC team has made significant progress toward developing a cost-effective and efficient hydrogen production technology based on a solar thermochemical water-splitting cycle. A sulfur family cycle having ammonia as the working fluid and reagent has been developed. The long term stability of the complete electrochemical system has been demonstrated with a 500+ hour extended run. New membranes have been identified with up to two orders of magnitude lower sulfite fluxes (vs. the Nafion 112 membrane initially used) even after treatment at 413 K. The high-temperature oxygen generation step is an all fluid process requiring no solid particle handling. Lab results prove the sub-cycle feasibility. The NH₃ and SO₃ can be evolved separately without complicated membrane separation. A lower salt melting temperature was achieved and molten salts have low enough viscosity to be pumped. The decomposition of SO₃ is proven technology. The entire process consists of elementary chemical engineering unit operations that have been in widespread industrial use for over 100 years. The Aspen Plus® modeling was used to significantly optimize the SA process. Due to the variability of solar energy, a phase-change thermal-storage system with NaCl was incorporated allowing continuous plant operation at 1063 K. Rankine power cycles were designed to recover excess heat to efficiently generate electricity. Overall plant pressure was varied to optimize plant efficiency and power recovery. The solar configuration is focused on a 50 MW(thermal) central receiver system with NaCl molten salt storage to allow continuous operation. The H2A economic model was used to optimize and trade-off SA cycle configurations. Although the chemical plant efficiency of 13% reported for the base case seems low, parametric studies have indicated higher efficiencies of ~20% [4] and identified areas for further research and study for future improvements to the cycle.

The SA cycle is a renewable and sustainable process that is unique in that it is an all-fluid cycle (no solids handling). It is a relatively low temperature plant with the solar receiver operating at 1073 K. All electricity needed is generated internally from waste heat. While the SA cycle appears to be complex it consists of only 3 chemical reactions plus absorbers, scrubbers and heat exchangers. The plant would operate continuously with low cost storage and it is a good potential solar thermochemical hydrogen production cycle for reaching the DOE cost goals.
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