IEA/HIA TASK 25: HIGH TEMPERATURE HYDROGEN PRODUCTION PROCESS

Screening Analysis of Solar Thermochemical Hydrogen Concepts

Goals of Screening

The goal of this screening analysis is to identify solar thermochemical plant concepts that have a high likelihood of producing hydrogen at a lower cost than a normal (low) temperature electrolysis plant[1].

There are two conditions which make it likely that a solar thermochemical plant can beat the economics of a low temperature electrolysis plant:

1– The average annual solar-to-hydrogen conversion efficiency must be at least 30 % higher:

Thermochemical Cycle approaches are immature relative to low temperature electrolysis plant and are typically more complex. Efficiency is directly proportional to the cost of a solar hydrogen plant. So, to justify the R&D expense , the efficiency should be at least 30 % better.

↳For towers, the low temperature electrolysis plant S-H efficiency η is 14 % (HHV). Thus thermochemical plant efficiency must be > 1.3*14 % = 18 %

2 - The thermochemical plant must be scaled-up to a size similar to the largest low temperature electrolysis plant :

In fact, a bigger plant is supposed to improve economics, due to “economies of scale”.

↳Using a molten salt technology, a single 1400 MWt tower and storage system could power a low temperature electrolysis cycle with a 75 % capacity factor. This low temperature electrolysis solar plant would produce 83 000 kg/day of hydrogen in the Mojave Desert[10]. The thermochemical plant capacity must be similar.

The use of thermal storage systems in solar plants eases the management of the thermochemical plant allowing it to operate near design conditions both day and night.

Concentrating solar Approaches

Tower **Dish** **Trough**

Figure 1 : Solar tower, dish and trough power plants

Tower Concepts

A recent project estimated the efficiencies of many thermochemical cycles producing hydrogen[2]. These efficiencies and the required temperatures are shown in Table 1. Current molten-salt technology can be used to supply 600 °C heat to the Copper Chloride cycle (PID 191, Table 1). Up to 13 hours of molten salt can be economically stored in tanks to power the thermochemical plant "around the clock." Simulations suggest that up to a 75 % annual capacity factor can be achieved for a plant located in the Mojave Desert. A high capacity factor implies fewer startups of the thermochemical plant, which results in an improved annual efficiency of converting heat to hydrogen. To achieve the higher temperatures listed in Table 1 will require the development of new receiver concepts. Starting with a review of high-temperature solar power tower concepts introduced in the 1970s and 1980s for thermochemical and Brayton applications[3,4], many years of power tower development experience were used to identify candidate tower-receiver technologies that are capable of > 850 °C. The candidate receiver technologies are depicted in Figure 3.

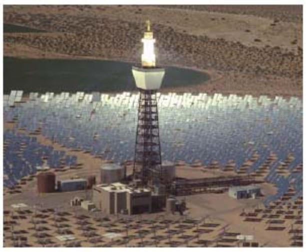

Figure 2: Tower

Tubular, heat pipe, and volumetric concepts appear to be feasible up to ~1000°C. Solid particle receivers may be feasible to ~ 1500 °C, but are better suited to < 1200 °C.

To achieve very high temperatures (>1500°C) with a good receiver efficiency, high solar concentrations (> 5000) are necessary; this necessitates the incorporation of a compound parabolic concentrator (CPC) at the entrance of the receiver[5].

Upon further examination, the remainder of the analysis thus focused on the solid particle and CPC receivers.

Referring to Table 1, the solid particle receiver is recommended for all thermochemical cycles in the range of 850 to 1500 °C. It is also recommended for high-temperature steam electrolysis (PID 106).

Referring to Table 1, the CPC receiver is recommended for thermochemical cycles above 1500 °C ; all of these are metal oxide cycles.

PID	Cycle Name	Chemical Cycle Temp (°C)	Solar Plant	Solar Receiver & Size (MWt)	T/C η (HHV)	Optical η	Rcvr η	Annual S-to-H η
0	Conventional Electrolysis **BASELINE**	NA	Current Power Tower (PT)	Molten Salt 700	30%	57%	83%	14%
106	Hi-T Steam *Electrolysis*	850	Future PT	Solid Particle 700	45%	57%	76.2%	20%
191	Copper/Hybrid *Chloride*	600	Current PT	Molten Salt 700	49%	57%	83%	23%
67	Hybrid *Sulfur*	850	Future PT	Solid Particle 700	51%	57%	76%	22%
1	*Sulfur* Iodine	850	Future PT	Solid Particle 700	45%	57%	76%	19%
5	Cadmium/Hybrid *Metal Oxide*	1450	Future PT	Solid Particle 700	50% to 70%*	50%	67%	20%
182	Cadmium Carbonate *Metal Oxide*	1450	Future PT	Solid Particle 700	50% to 70%*	50%	67%	20%
6	Zinc *Metal Oxide*	1800	Future PT	CPC Si-G Reactor 46	45%	51%	72%	16.5%
110	Manganese *Metal Oxide*	1550	Future PT	CPC Si-G Reactor 46	50%	55%	78%	21%
131	Manganese *Sulfate* **	1500	Future PT	Solid Particle 700	42%	50%	67%	14%
147	Cadmium *Sulfate* **	1150	Future PT	Solid Particle 700	55%	54%	73%	22%
149	Barium Molybdenum *Sulfate* **	1400	Future PT	Solid Particle 700	47%	50%	67%	16%

* 60% was used in the calculation.

** After completing this screening analysis, sulfate cycles were eliminated from further consideration because experimental evidence indicated that the hydrolysis reaction did not work as originally suggested by analytical studies [2].

Table 1 : Solar Tower screening results[1]

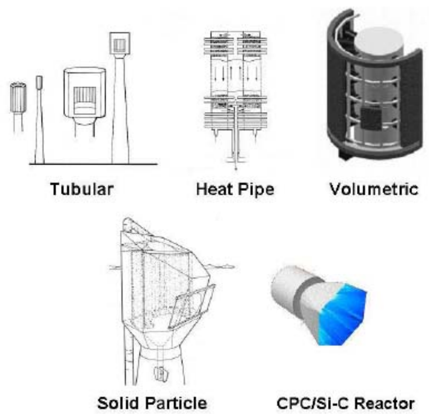

Figure 3: Tower receiver concepts

Dish Concepts

Current dish concentrators (Stirling Energy Systems, Figure 4) provide high-temperature heat at about 800 °C to high-performance Stirling engine induction generator power conversion units (PCUs) located near the focal point. State of the art solar concentrators typically operate with an average aperture concentration ratio in the range of 2000 to 3000 suns with high intercept factor (99 %). They are capable of 4000 suns with an intercept of 95 %. However, because of the relatively small scale and distributed nature of parabolic dishes and especially the need to accommodate variable orientations, the number of thermochemical cycles suitable for parabolic dishes is limited. Any thermochemical cycle for a parabolic dish must, therefore, be simple and the receiver/reactor must accommodate variable orientations relative to gravity, as well as the requirements of the thermochemical cycle.

Only the Ferrite cycles and high temperature steam electrolysis meet the requirements of parabolic dishes. The ferrite cycles can be powered by a rotating disk reactor now under development that is capable of operating in a variable gravity orientation environment.

The Ferrite cycles in Table 2 are representative of a potentially large number of viable thermochemical cycles based on iron oxide mixed with various amounts of nickel, manganese, magnesium, cobalt, zinc or combination oxides.

A high temperature steam electrolysis method of producing hydrogen could be accomplished by sending 900 °C steam created in the dish receiver to an electrolyser. The electrolyser would be electrically powered by a Stirling engine collocated within the same receiver.

Figure 4: Dish concentrators

PID	Cycle Name	Chemical Cycle Temp (°C)	Solar Plant	Solar Receiver & Size (kWt)	T/C η	Optical η	Rcvr H	Annual S-to-H η
00	Conventional Electrolysis **BASELINE**	NA	Current Dish	Stirling	26%	85%	86%	19%
106	Hi-T Steam *Electrolysis*	900	Future Dish	Stirling and Steam	35%	85%	84%	25%
2	Nickel-Iron Manganese *Ferrite*	1800	Future Dish	Rotating Disk	52%	77%	62%	25%
7	Iron Oxide *Ferrite*	2100	Future Dish	Rotating Disk	50%	74%	62%	23%
194	Zinc *Ferrite*	1800	Future Dish	Rotating Disk	52%	77%	62%	25%

Table 2 : Solar Dish screening results

Screening based on solar to hydrogen efficiency

The next step in the screening process was to estimate the solar-to-hydrogen efficiency for each proposed solar-thermochemical plant. This efficiency is the product of solar-collection and thermochemical-cycle efficiencies. Variations in weather, sun position, and sun intensity cause the efficiency of a solar plant to change throughout the day and throughout the year. Thus, it is necessary to estimate solar-collection efficiency on an annual basis. This effect is illustrated in Figure 5. For the thermochemical cycle efficiency a design point was used rather than an annual efficiency. This is a reasonable assumption at this point. For the power tower cycles that utilize thermal storage, we expect that the storage will buffer solar transients and allow the thermochemical cycle to operate close to design point during most of the year. The remaining metal oxide cycles are relatively simple and reactors and other internal heat transfer process should not degrade with turn down. These assumptions will of course need to be investigated in future studies. For each tower case we used the DELSOL[9] computer code to estimate the annual solar collection efficiency. This is done by performing hourly simulations of the heliostat-field optics and the receiver thermal performance for several representative days throughout the year. Annual efficiency is subdivided into optical and receiver efficiencies, as indicated in Tables 1 and 2.

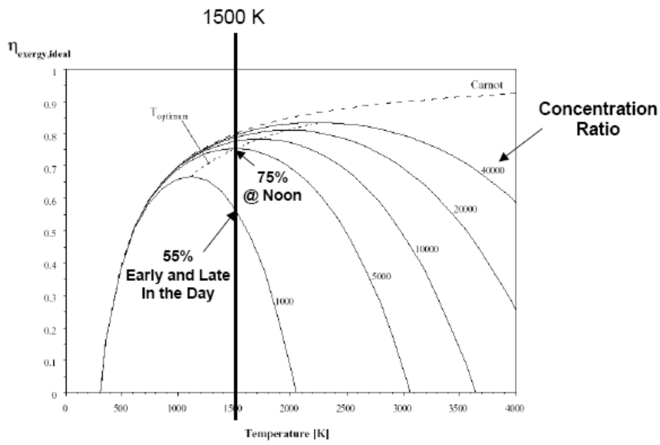

Figure 5: Solar collection efficiency. The efficiency of a solar receiver varies throughout the day because solar input is changing and thermal losses are constant. The highest efficiency occurs at noon when solar input is highest[5].

Molten-Salt Plant Calculations

The optimal molten-salt plant was very similar to the year 2008 case study investigated by Sargent & Lundy for the National Academy of Science[10]. This calculation was based on the following DELSOL input:

- Heliostats - 98 m² ; 1.3mrad slope/tracking error; 94 % reflectance; 95 % cleanliness; canted/ focused to slant range; cost is $ 120/m^2; heliostats surround the tower.
- Receiver - Reflectivity of receiver surface is 7 %; receiver absorbs 700 MW_t @ noon; 600 °C outlet temperature equates to thermal losses of 31 kW/m²; default cost algorithms for receiver and tower.

The optimal plant is predicted to use 1.31 km^2 of heliostats, a 210 m tower, and a cylindrical receiver with an absorber area of 1000 m^2. Interfacing this plant with the Copper Chloride cycle (PID 191) yields an annual solar-to-hydrogen efficiency of 23 %.

Solid-Particle-receiver Plant Calculations

This calculation was based on the following DELSOL input:

- Heliostats - 98 m^2; 1.3mrad slope/tracking error; 94 % reflectance; 95 % cleanliness; canted/ focused to slant range; cost is $ 120/m^2; heliostats are north of the tower.
- Receiver - Receiver absorbs 700 MW_t @ noon; 900 °C to 1500 °C outlet temperature equates to thermal losses of 290 to 680 kW/m^2; default cost algorithms for receiver and tower.

The solid-particle plant calculations were based on the same input assumptions as the molten-salt case, except that receiver thermal losses were increased due to the much higher operating temperatures. The optimal low-temperature plant (e.g., interfaced with PID 67) is predicted to use 1.34 km^2 of heliostats, a 360 m tower, and a cavity receiver with an aperture area of 400 m^2 and a downward tilt of 30 °C. The optimal high-temperature plant (e.g., interfaced with PID 131) is predicted to use 1.65 km^2 of heliostats, a 420 m tower, and a cavity receiver with an aperture area of 300 m^2.

Interfacing the solid-particle-receiver plant with the sulfur hybrid plant (PID 67) or the cadmium sulfate plant (PID 147) is predicted to yield a 22 % annual solar-to-hydrogen efficiency. Other combinations of the solid-particle plant and thermochemical cycles lead to lower efficiencies.

CPC Reactor Calculations

The molten-salt and solid-particle plants described above were sized to absorb 700 MW_t within a single receiver on a single tower. Large plants like this usually enjoy economies of scale over small plants. Given this rationale, it would be desirable to scale up the CPC plant to as large a size as possible. However, use of the CPC concentrators reduces the number of heliostats that can be aimed at a single tower. CU/NREL suggests that ~ 140 MW_t may be the optimal size for a single receiver/tower[11]. Thus, five towers would be required to absorb 700 MW_t.

In the DELSOL analysis we studied the performance of only the north-facing CPC within the 140 MW_t receiver, the most efficient of the three CPCs. This CPC absorbs ~ 1/3 of the total power, or 46 MW.

This calculation was based on the following DELSOL input:

- Heliostats - 98 m^2 ; 1.3 mrad slope/tracking error; 94 % reflectance; 95 % cleanliness; canted/ focused to slant range; cost is $ 120/m^2; heliostats are north of the tower within a +/- 24 degree sector of land.
- Receiver - CPC at receiver entrance with an acceptance angle of +/- 24 degrees, a geometric concentration of 6.2, and a throughput of 89 %; receiver absorbs 46 MW_t @ noon; 1550 °C to 1800 °C outlet temperature equates to thermal losses of 620 to 1010 kW per m^2 of CPC exit area; default cost algorithms for receiver and tower.

The optimal field for the 1550 °C case is predicted to use 88 400 m^2 of heliostats, a 160 m tower, and a CPC tilted downward at 30 ° with an entrance diameter of 9.5 m and an exit diameter of 3.8 m.

Interfacing the CPC plant with the manganese metal oxide cycle (PID 110) yields an annual solar-to-hydrogen efficiency of 23 %. Interfacing with the higher temperature zinc cycle (PID 6) results in an efficiency of 16.5 %.

Dish plant Calculations

Like the power tower hydrogen efficiency calculations, the thermochemical design point efficiency was assumed to be equal to its annual efficiency. Because of the direct heating of the ferrite material and improved recuperation and reactivity expected at low turn down, we believe that this is a reasonable assumption, at least at this point.

To calculate dish annual efficiency, an Excel spreadsheet computer program utilizing typical meteorological year (TMY2) data for Dagget, California, Las Vegas, Nevada, and Albuquerque, New Mexico, were used. TMY2 data includes direct normal insolation, wind speed, ambient temperature, and other meteorological data compiled on an hour-by-hour basis for a number of locations throughout the United States[12]. Using this data the receiver efficiency was calculated on an hour-by-hour basis, and from these results we calculated the radiation and convection losses and efficiencies and the net amount of energy delivered to the thermochemical process over the year.

Calculation of dish optical efficiency is relatively straightforward compared to power towers.

It is important to note that the very high operating temperature of 1800 °C for the mixed-metal Ferrite cycles results in a low annual receiver efficiency of only 62 %. If the receiver temperature could be reduced to 1500 °C, as recent experimental results suggest they might, receiver efficiency increases to 76 % (i.e. a 22 % increase). Given the uncertainty in the receiver temperature requirements and the sensitivity of annual system efficiency to receiver temperature, especially for the very high temperature cycles, it is important not to place too much faith on the precision of these results.

CONCLUSIONS

The screening analysis identified a number of concepts that potentially could produce hydrogen at efficiencies significantly higher than low-temperature electrolysis.

Some general qualitative conclusions can also be drawn:

- No parabolic trough concepts were identified. Nevertheless, it is possible, coupling a trough plant, to provide heat at < 550 °C (ca. for example 80 % of total heat for the SI process) with a tower plant to provide the highest T heat.[14]
- Although CSP systems are capable of operating at very high temperatures, to maximize annual efficiency operating temperatures are limited by radiation losses. The following are general temperature limits for tower and dish receiver concepts:
  - Surround tower, molten salt ~ 600 °C
  - North facing tower, solid particle ~ 1200 °C
  - North facing high performance tower, CPC ~ 1600 °C
  - Parabolic dish, rotating disk reactor ~ 1800 °C.
- The solar collection efficiency (i.e. product of optical and receiver efficiencies) of the CPC plant exceeds the solid particle plant above ~ 1400 °C.
- The efficiency of high-temperature steam electrolysis concepts are similar to the best thermochemical concepts.
- For the very high temperature cycles (> 1500 °C), radiation losses dominate and receiver efficiency is extremely sensitive to temperature.

IEA/HIA task 25: High Temperature Hydrogen Production Process

Screening Analysis of solar thermochemical hydrogen concepts

Contacts:

- Gregory J. KOLB (SNL), gjkolb@sandia.gov
- Alberto GIACONIA (ENEA), alberto.giaconia@enea.it

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Main initiatives

USA: The Sandia National Laboratory, www.sandia.gov
EC: HyCycleS - Materials and components for HYdrogen production by sulphur based thermochemical CYCLES www.dlr.de
Italy: ENEA (TEPSI: Technologies and Innovative Processes for the Transition to the Hydrogen System future) www.enea.it

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