SULFUR BASED THERMOCHEMICAL ENERGY STORAGE FOR SOLAR POWER TOWER

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GENERAL ATOMICS

Outline

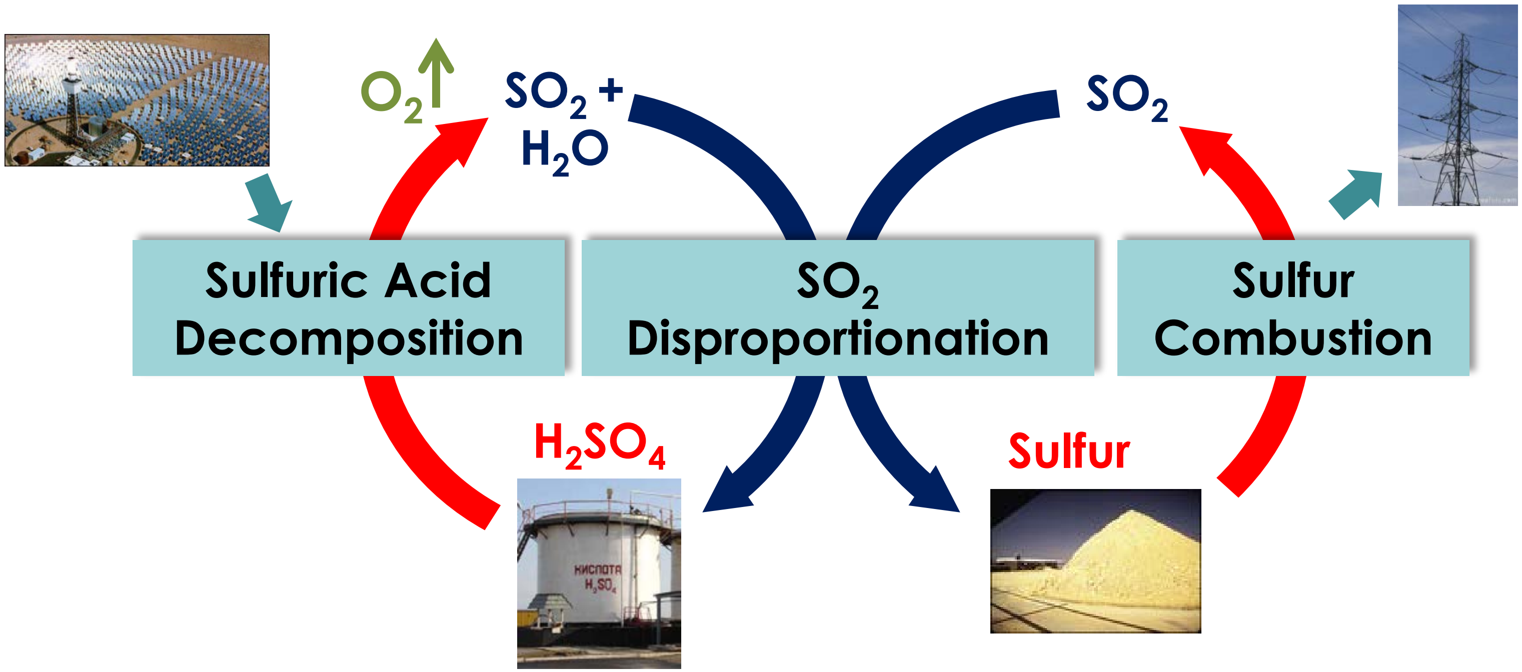
- Introduction – Sulfur Energy Storage
- Project Tasks – Risks and Barriers
- SO_2 Disproportionation Process Development
- H_2SO_4 Decomposer Development
- CSP Plant Design and Economics
- Summary and Future Work

Chemical energy storage can provide very high storage density

Media	Energy Density (kJ/kg)	Materials Cost ($/kWh$_t$)
Gasoline	45000	0.108
Sulfur	12500	0.018
Molten Salt (Phase Change)	230	7.56
Molten Salt (Sensible)	155	11.22
Elevated water Dam (100m)	1	-

- Energy storage using sulfur has very low material cost

Solar heat energy can be stored in elemental sulfur via a three step thermochemical cycle



	Reaction	Temp (°C)
H_2SO_4 Decomposition	$2H_2SO_4 \rightarrow 2H_2O(g) + O_2(g) + 2SO_2(g)$	800
SO_2 Disproportionation	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(l)$	150
Sulfur Combustion	$S(s,l) + O_2(g) \rightarrow SO_2(g)$	1200

Key risks and barriers of the proposed concept were identified and addressed

SO_2 Disproportionation (GA)

- Disproportionation rate
- H_2SO_4 conc.
- Sulfur separation
- Catalyst recovery

Sulfuric Acid Decomposition (DLR)

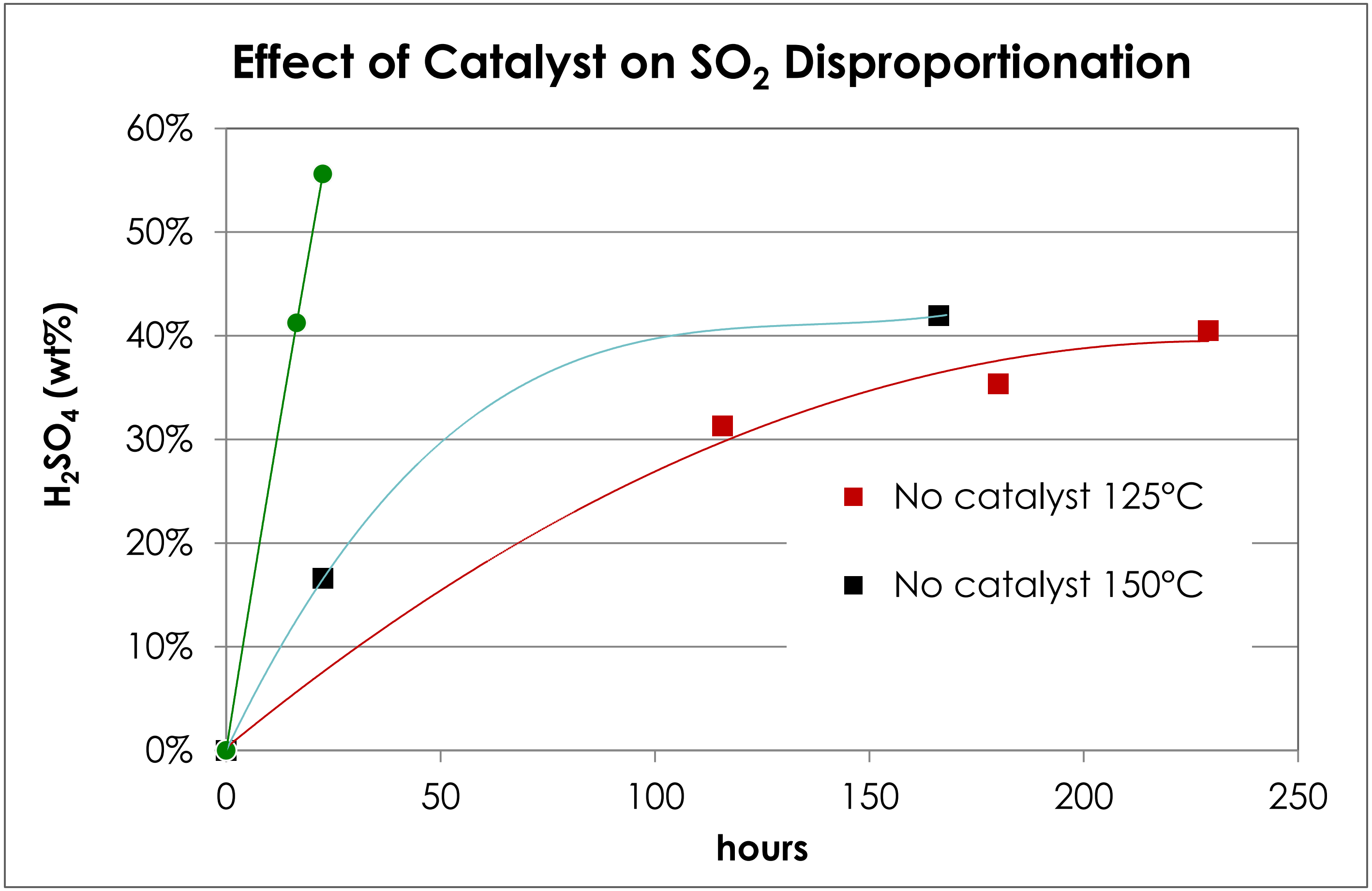
- Decomposer design and efficiency
- Catalyst performance

CSP Plant Design and Economics (GA)

- Process efficiency
- Plant safety

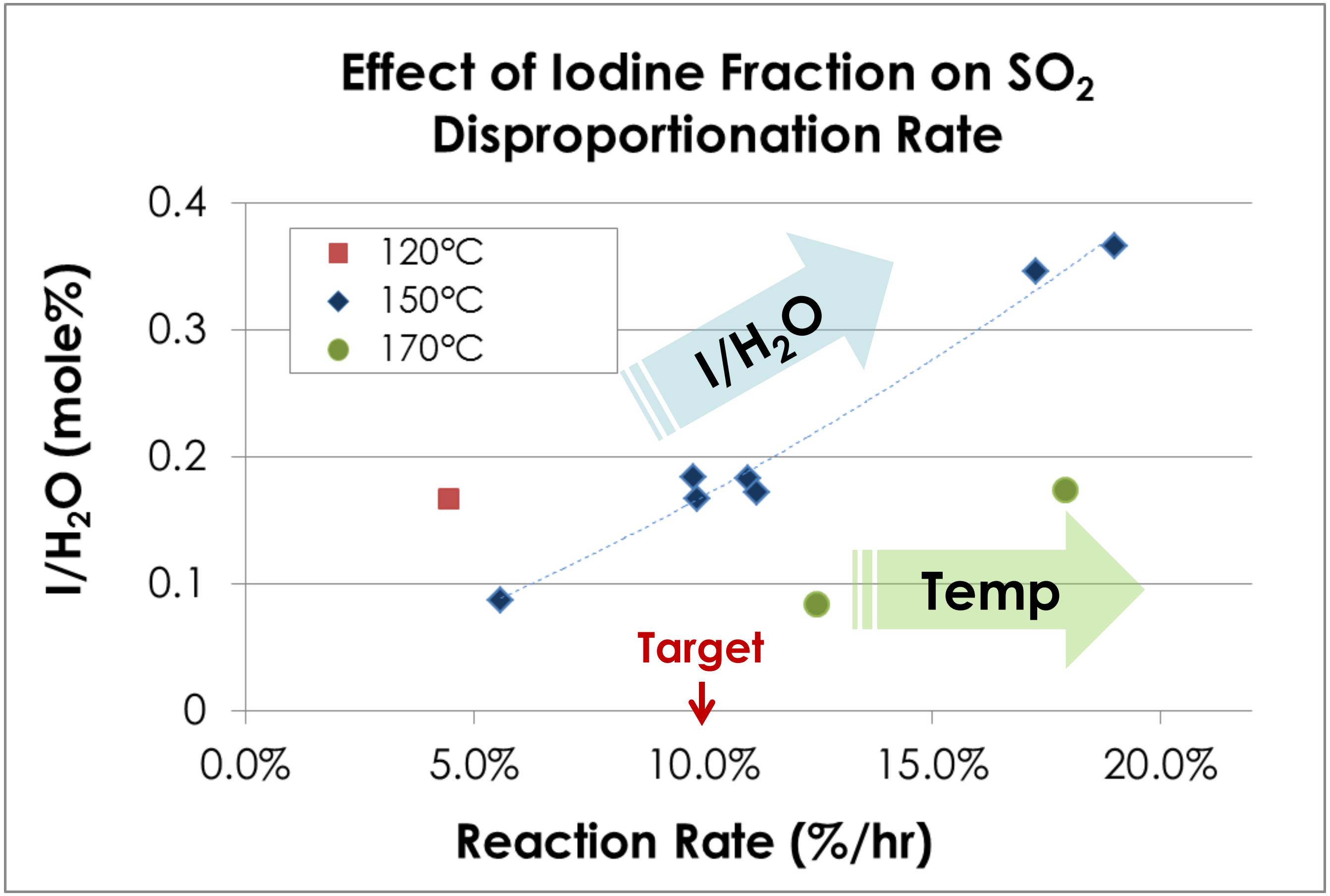
Phase I	Phase II	Phase III
09/10 – 03/12	08/12 – 10/13	10/13 – 03/15
Verification	Improvement & Design	Prototype

Homogeneous iodide ions greatly enhance SO_2 disproportionation in water



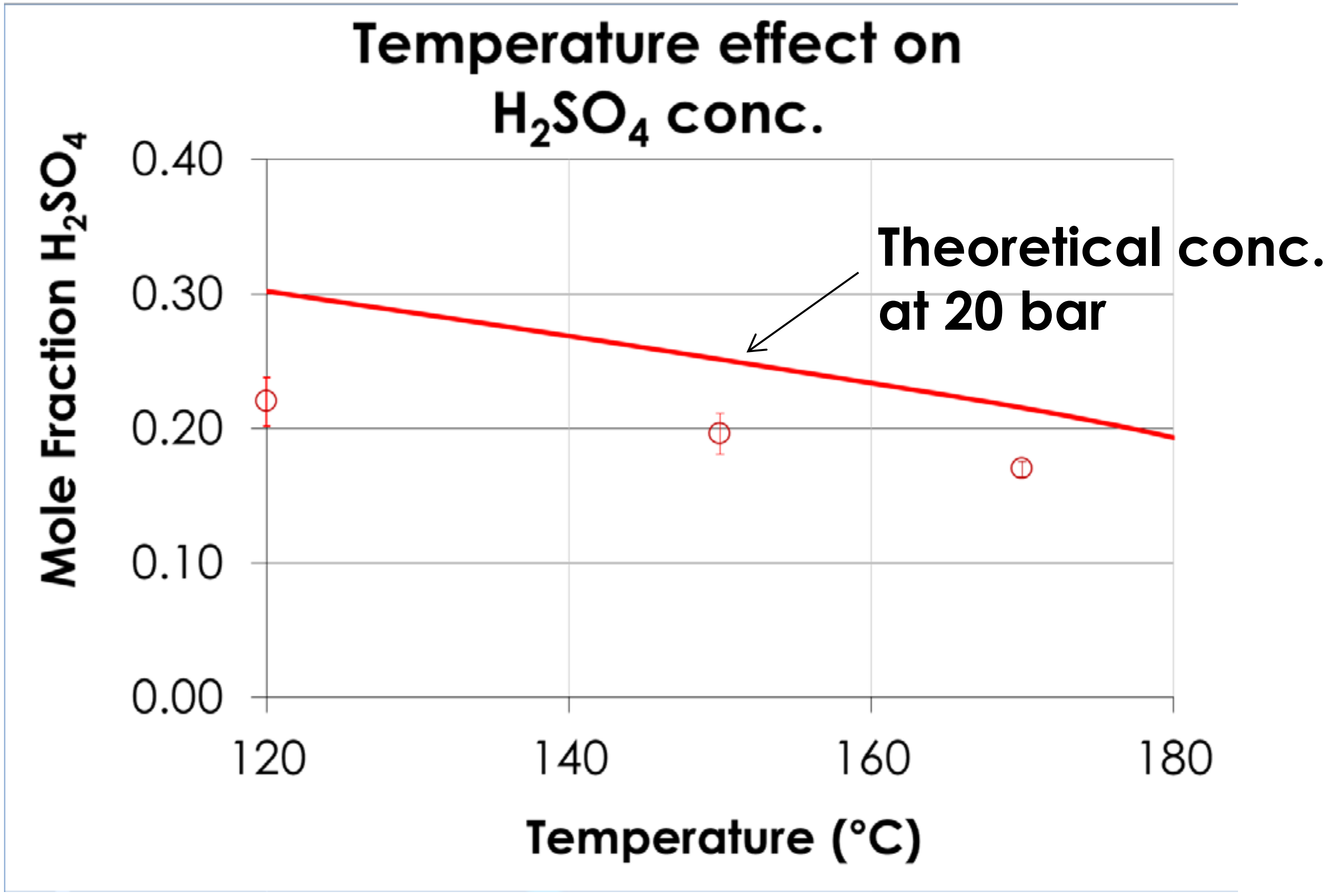
- **Both disproportionation rate and degree increased**
- **Final H_2SO_4 conc.: 40wt% vs. 57wt%**

Disproportionation rate increases with catalyst concentration and temperature



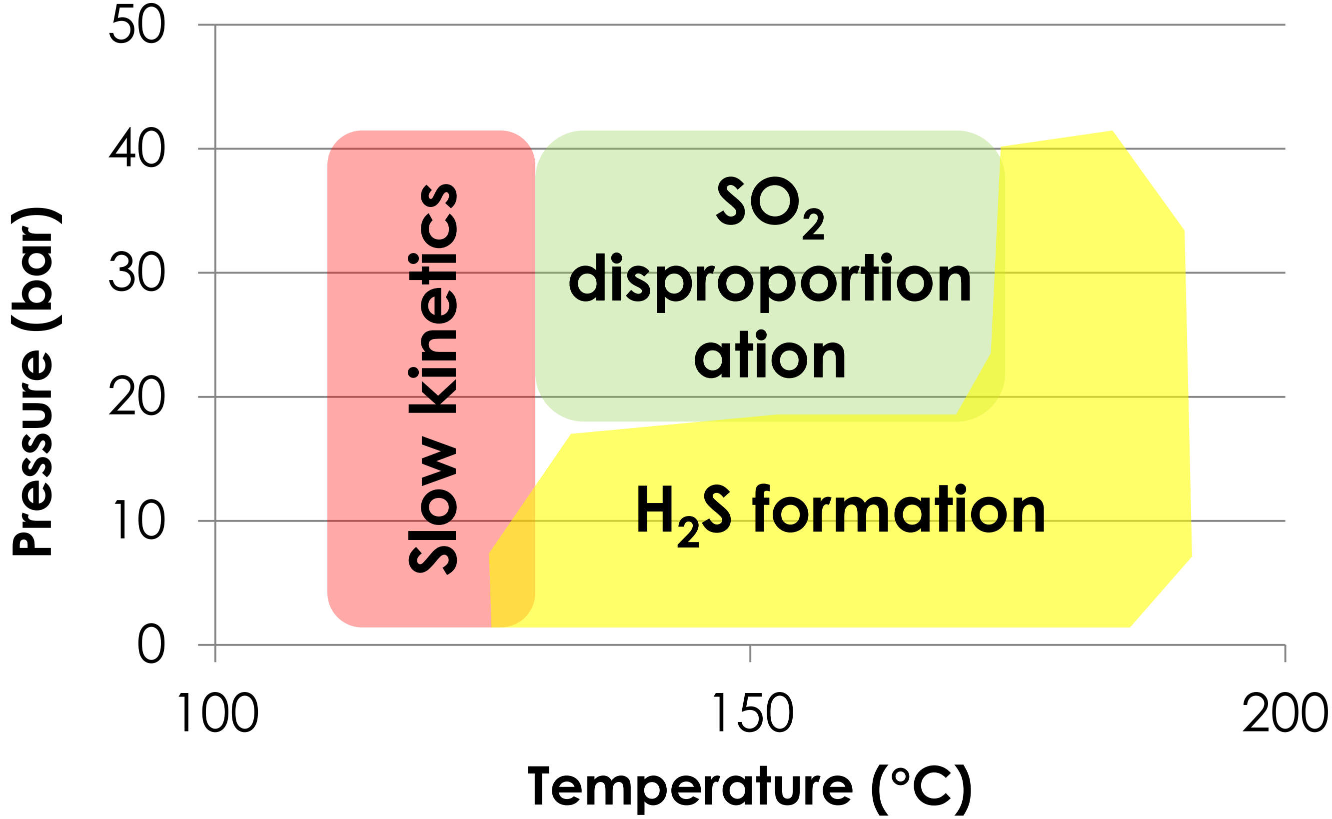
- **Post experiment formation of colloidal sulfur at 170°C → H_2S formation**

The degree of disproportionation decreases with increasing temperature



- Process conditions will need to be optimized by flowsheet modeling

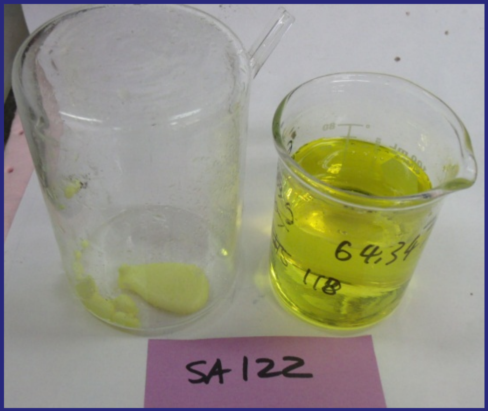
The optimal processing regime for SO_2 disproportionation has been identified

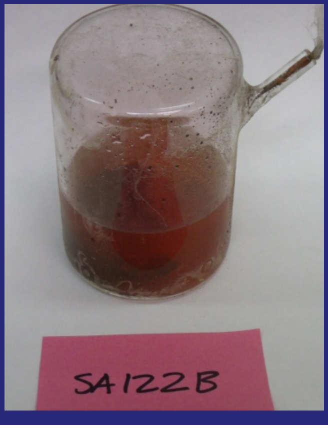


- **Catalyst quantity will need to be balanced against flowsheet design and work required for recovery**

Iodide catalyst oxidized to form elemental iodine as sulfuric acid concentration increases

3.5hr	8.5hr	10hr
31.6wt%	53.5wt%	56.9wt%





- **Iodine is extracted from H_2SO_4 and elemental sulfur using Bunsen reaction**

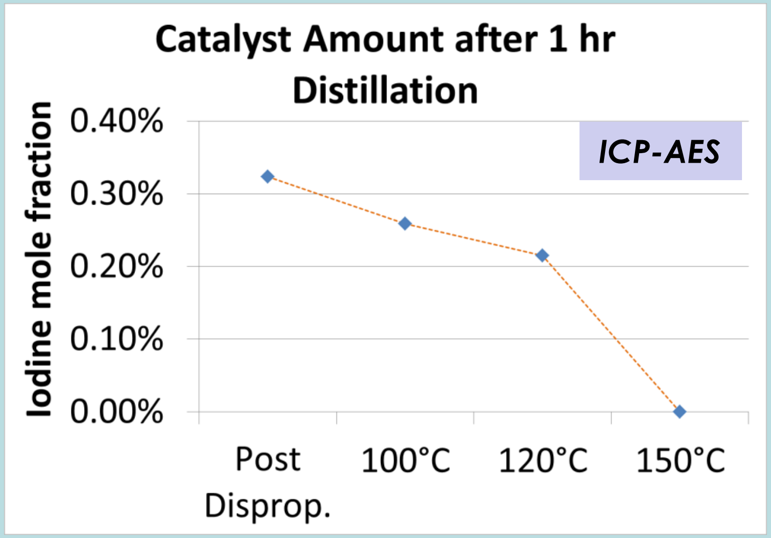
$$SO_2(g) + I_2(s) + 2H_2O(l) \Leftrightarrow 2HI(aq) + H_2SO_4(aq)$$

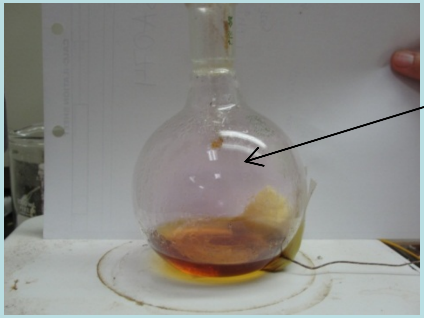
Iodine from Sulfur →

← *Iodide from H_2SO_4*

Options to recover iodine catalyst have been validated

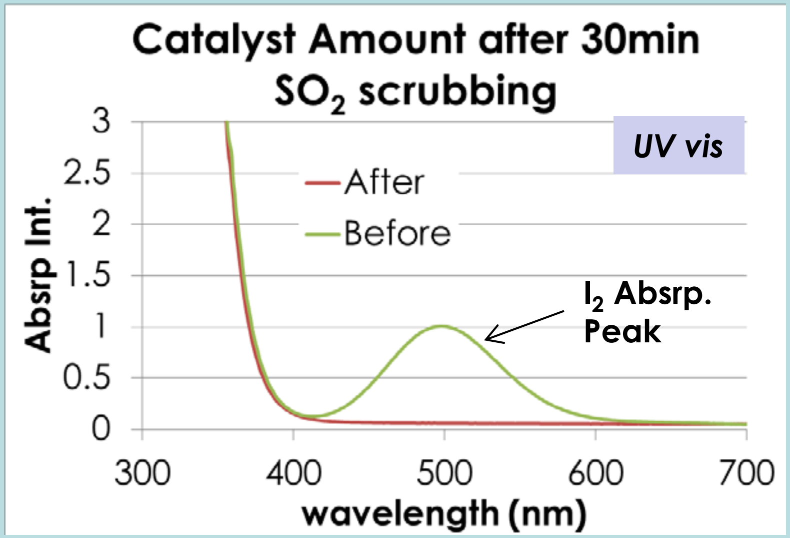
Recovery from H_2SO_4

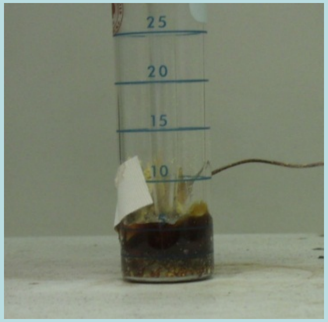




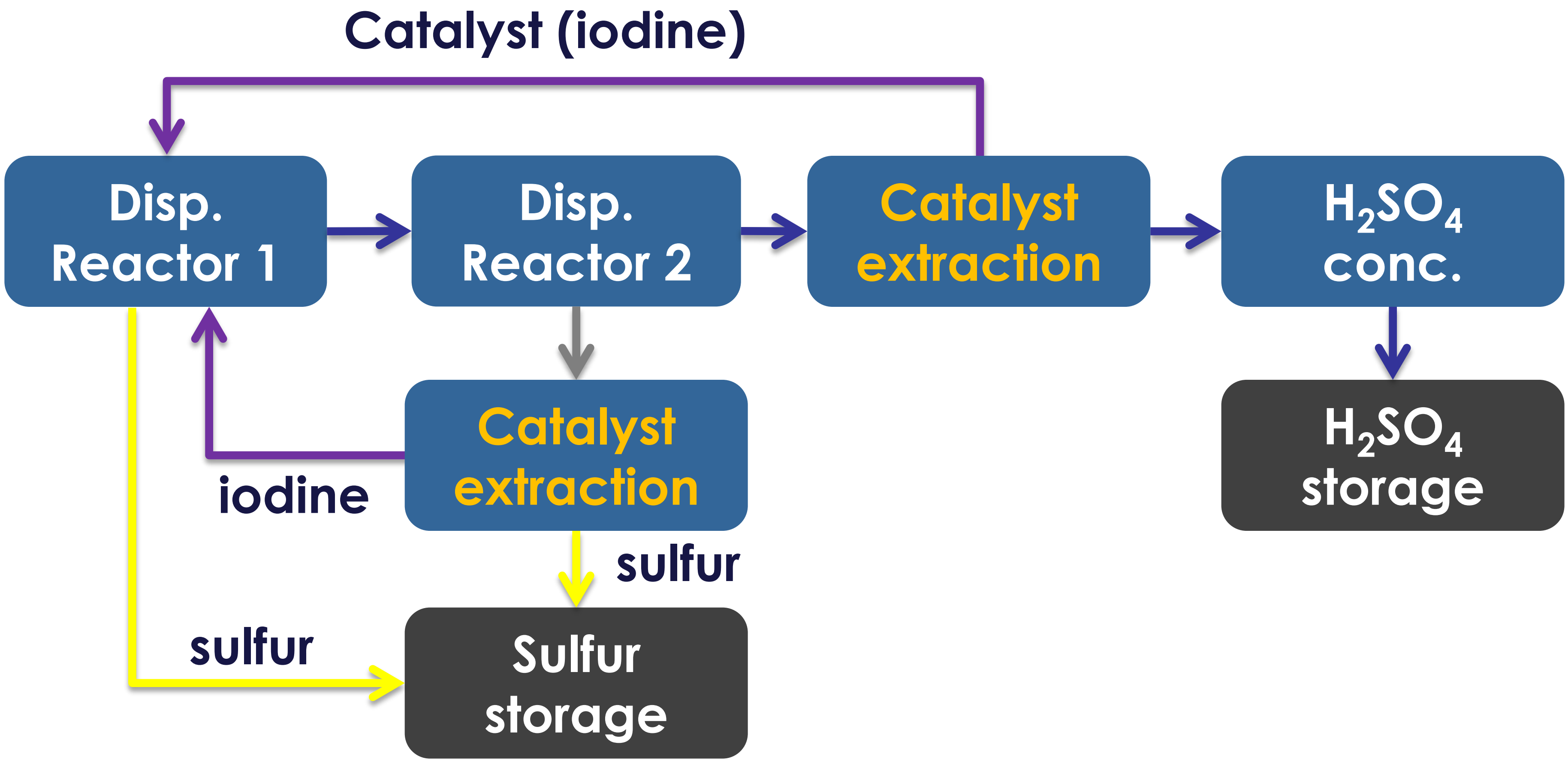
I_2 vapor from reversed Bunsen reaction

Recovery from Sulfur





SO_2 disproportionation process flow has been established using verified process steps



- Series reactors are used to minimize reactor volume and maximize pure sulfur output

Sulfuric acid decomposition is optimized with a two chamber solar receiver-decomposer

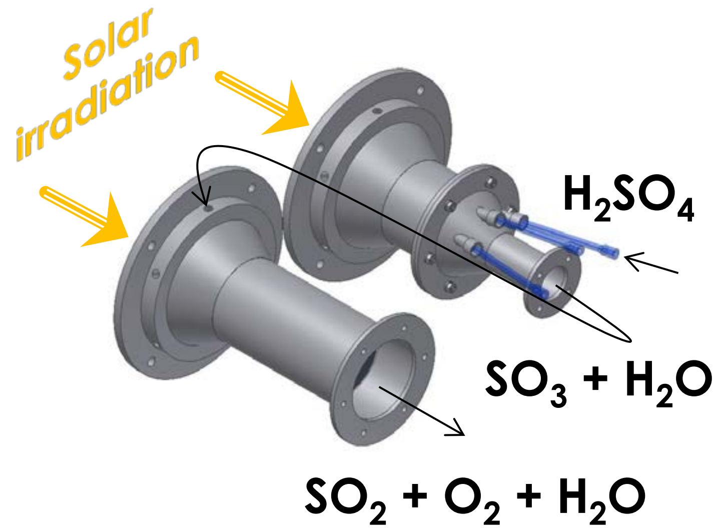
Evaporation at 400 °C
$H_2SO_4 \Rightarrow SO_3 + H_2O$

Decomposition at 650 – 850 °C
$SO_3 \Rightarrow SO_2 + ½ O_2$

Solar absorbers SiSiC foam

SiSiC honeycomb coated w/ catalyst

Receiver Rear View



Piping is constructed using high-alloyed steel

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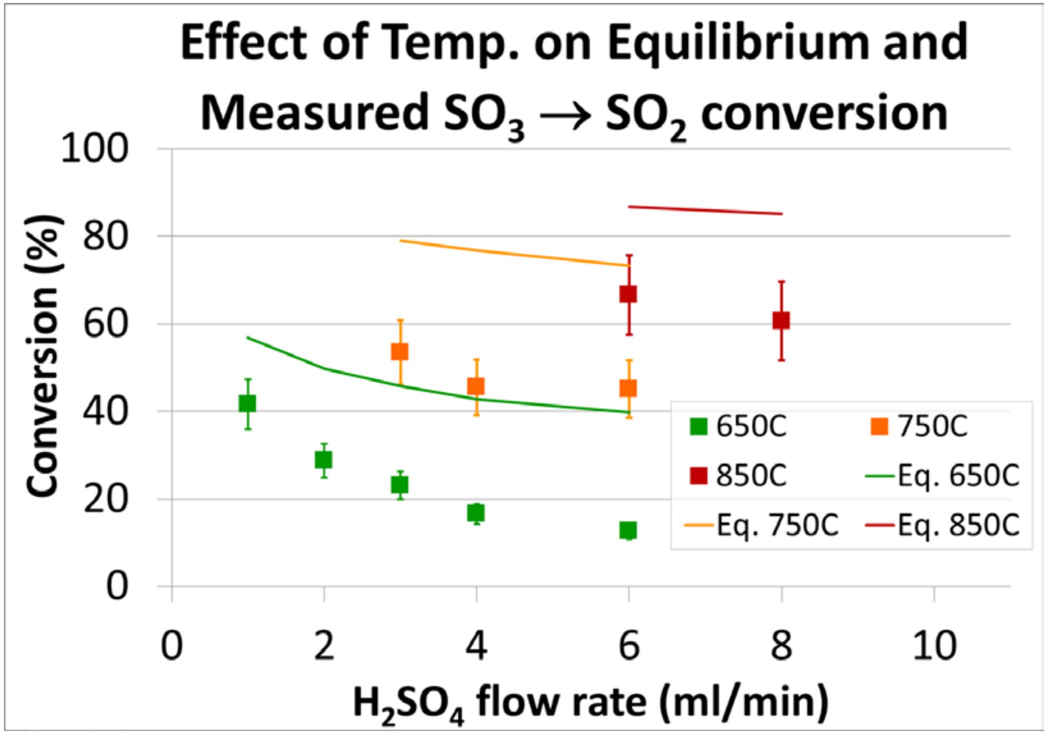
On sun testing and characterization of the sulfuric acid decomposer has been carried out



Catalyst: $FeCr_2O_4$, 94wt% H_2SO_4, τ_{res} = 0.5s

- **Conversion at 80% of equilibrium at 850 °C**
- **Poisoning of Fe-Cr oxide at 650 °C – vanadium oxide or Pt req.**
- **Thermal efficiency of receiver is at 50%**

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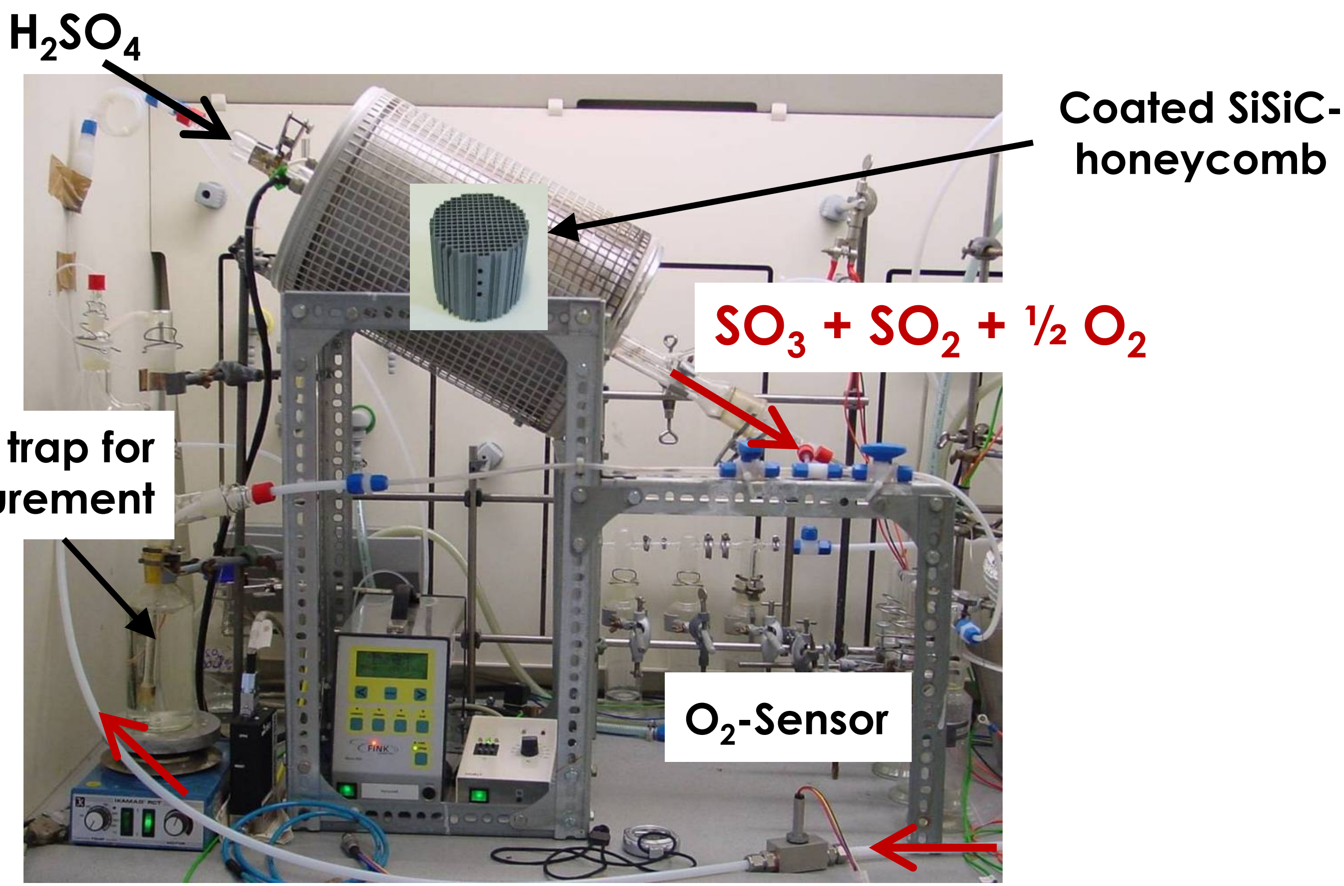
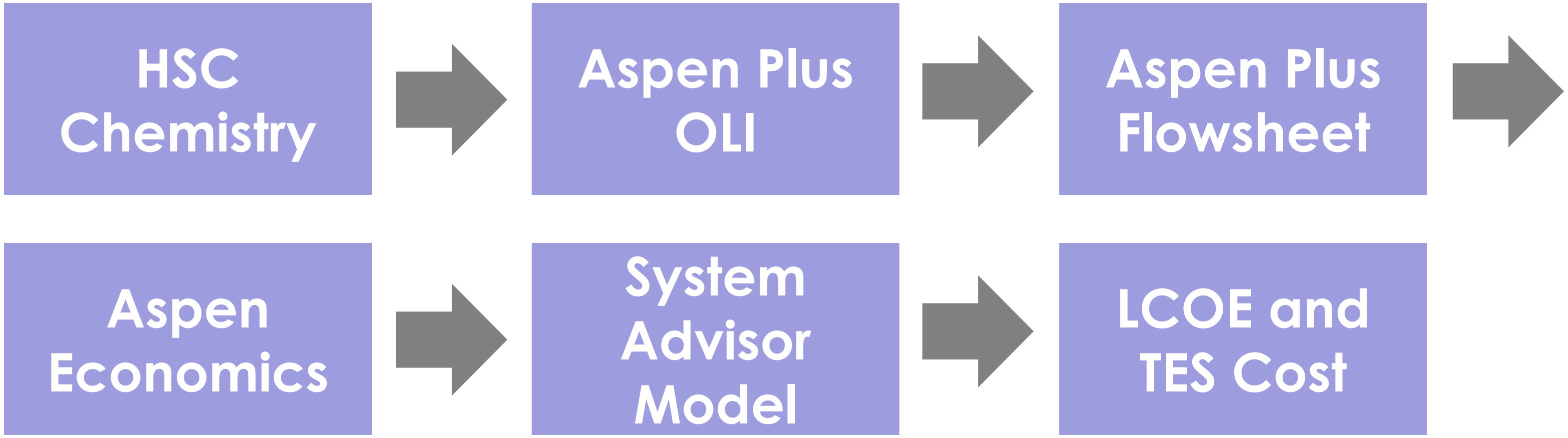
Long term performance testing of decomposition catalyst is currently on going



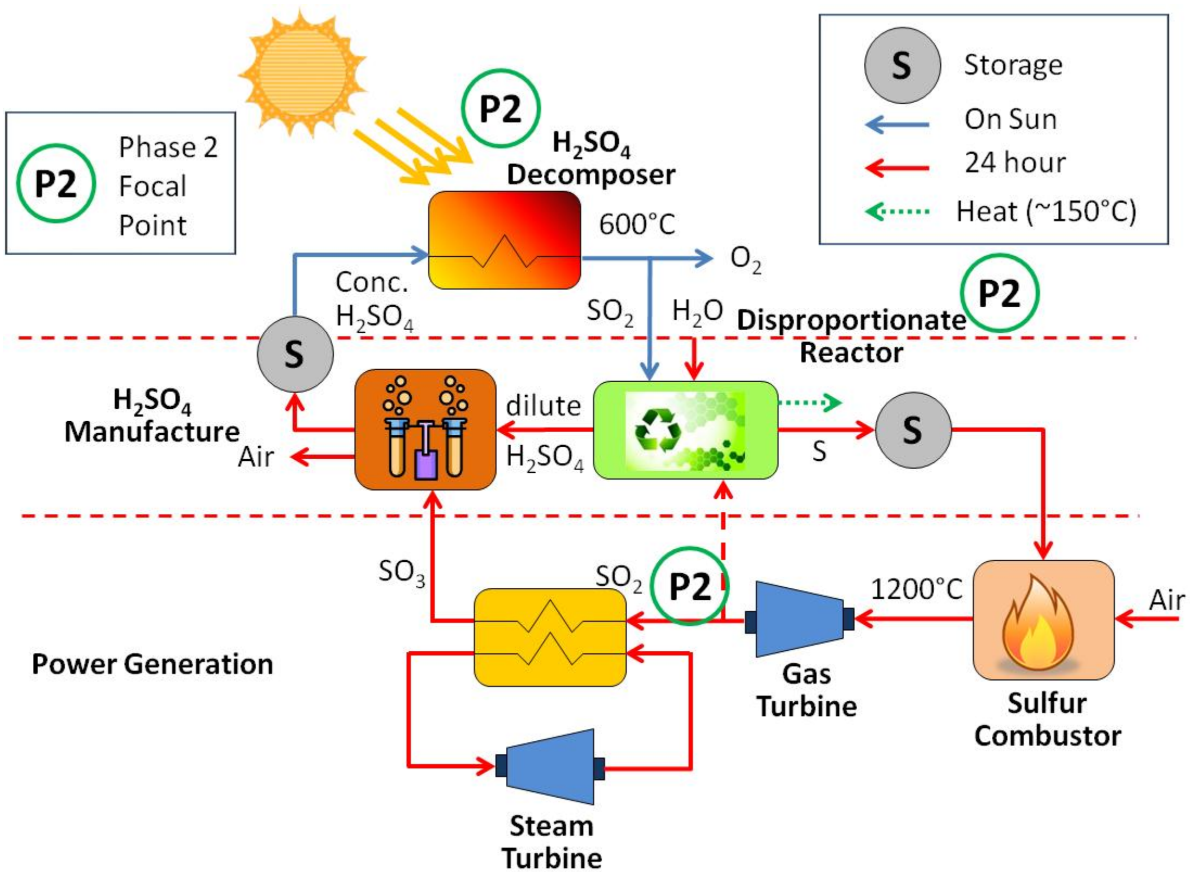
- **Goal – 1000hrs for Fe-Cr-O catalyst (850°C)**
  – 100hrs for low temp catalyst

GA uses multiple software tools to model and cost the sulfur TES process



- Initial Chemistries and Design of Experiments
  - HSC Chemistry
- Flowsheet Design
  - Aspen Plus for chemical plant
  - System Advisor Model (SAM) for solar plant
- Economic Calculations
  - Aspen Economics and SAM

A flowsheet for a 50MW$_e$ CSP plant integrated with sulfur based TES has been designed

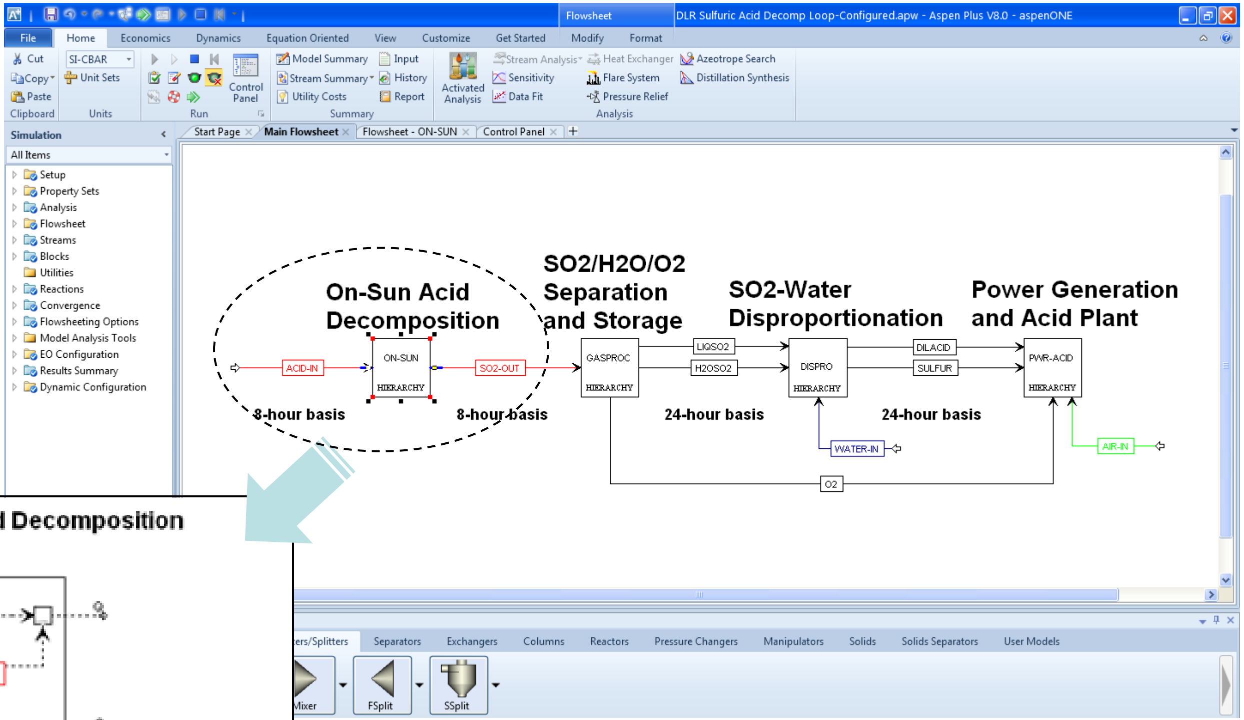


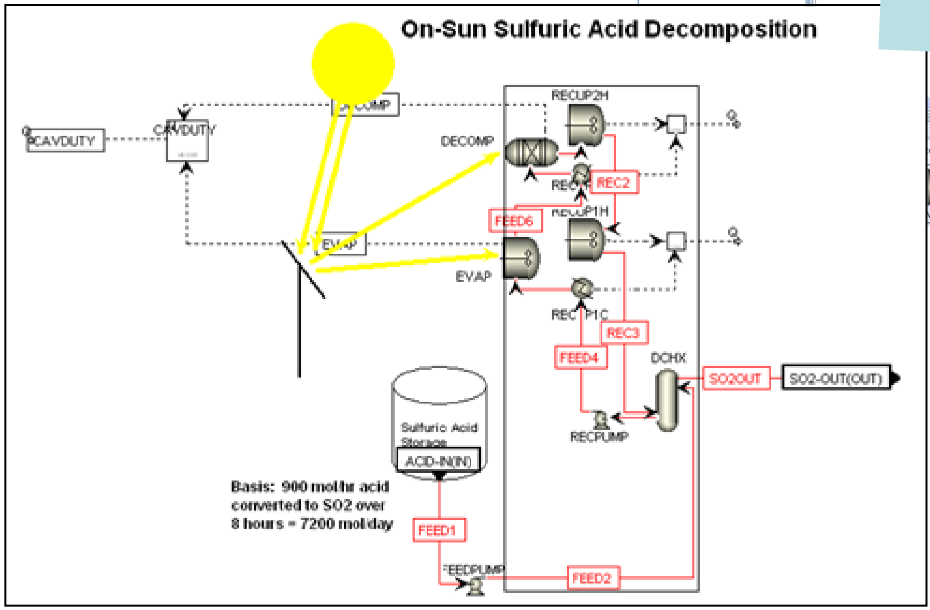
- TES portion is based on sulfuric acid plant
- Solar field and power block are independent
- 16 hours storage
- ~2000 Mton acid plant (~1100m^3) – 300m^3 of sulfur/day

- A 60% efficiency combined power cycle is used
- Minimize energy requirement for gas separation

Aspen Plus flowsheeting software was used to build a rigorous thermodynamic model of the cycle

- **Energy and mass flow are balanced wrt process conditions**



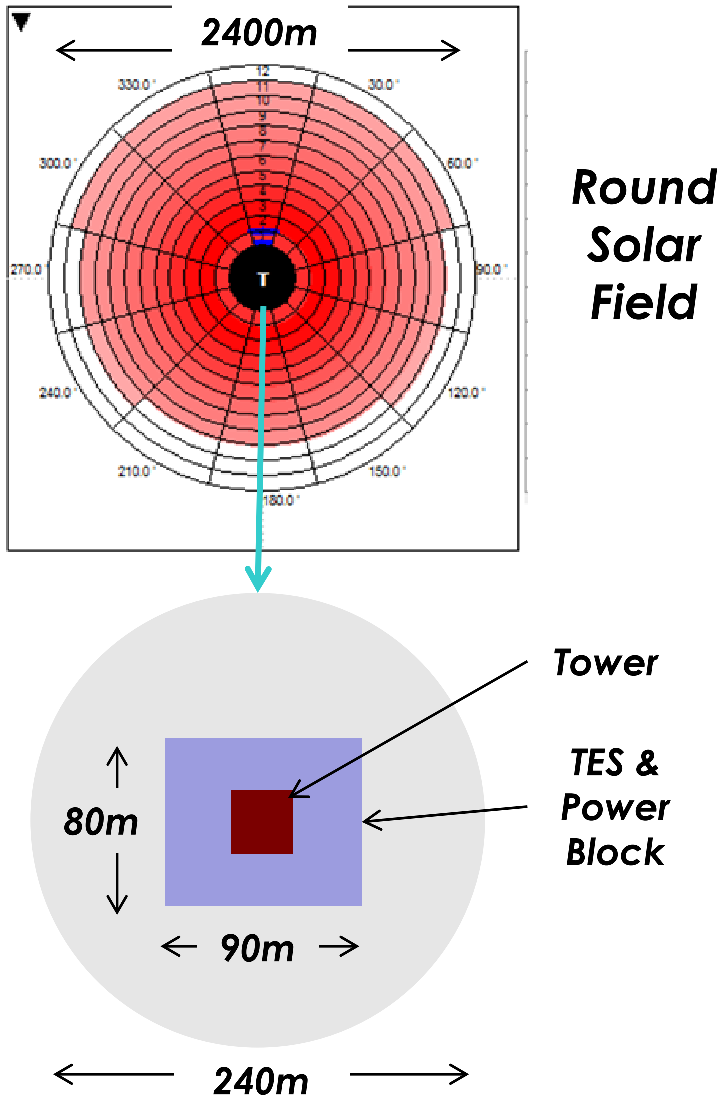


H_2SO_4 decomposition section expanded for details

System Advisor Model (SAM) does basic solar plant design and costing, and calculates LCOE

- **Daggett, CA was used as CSP plant location**
- **Heliostat field and tower configurations via SAM**
- **Takes Aspen chemical plant costs as input**
- **Calculates solar component costs and LCOE**

- Total heliostat area = 738,477m^2
- Number heliostats = 5115
- Single tower height = 161m
- Minimum distance from tower = 121m
- Maximum distance from tower = 1208m
- Total land area = 1041 acres



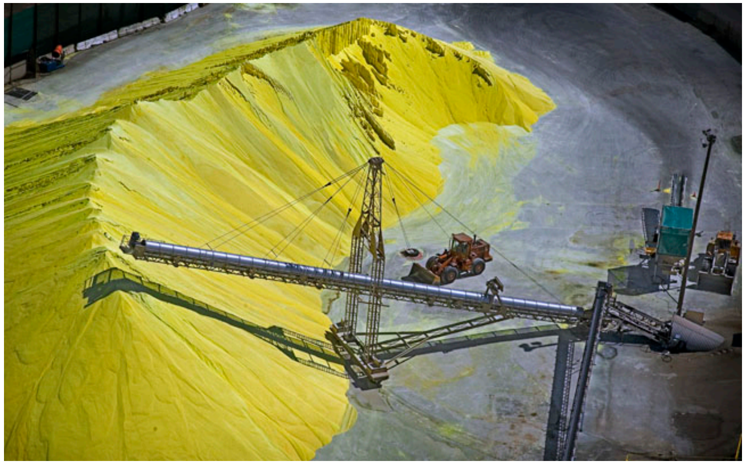
Storage cost and LCOE estimates for a CSP plant integrated with sulfur storage are competitive

DOE Metric	Capacity Factor	LCOE	Storage Cost
SunShot Target	75%	6.0 ¢/kWh_e	\$15/kWht
CSP w/Sulfur (SAM 2013)	>75%	8.7*¢/kWh_e	\$2/kWh_t
CSP w/Sulfur** (Sunshot Metrics)	>75%	>6¢/kWh_e	\$2/kWh_t

* heliostat costs taken from "Heliostat Cost Reduction Study", Kolb et al., 2007

** Acid decomposition temperature is 600°C.

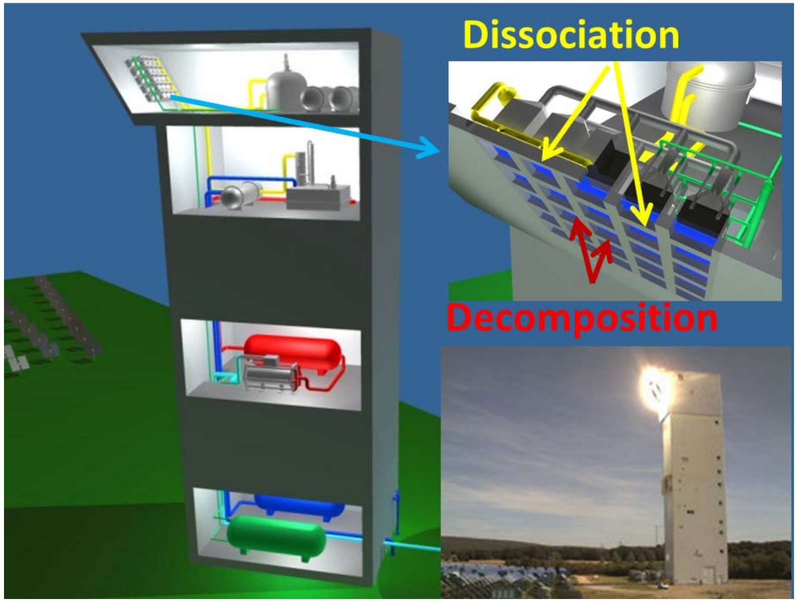
In summary, Sulfur TES is truly unique



- All process steps are verified
- Conceptual scale up for process equipment are established
- Potential CSP power generation at 1200ºC with 600ºC input
- Uncomplicated and cheap storage method
- Much of the process already proven economic at large scale by sulfuric acid plant
- Sulfur as a TES medium is literally dirt cheap

Future Work

- SO_2 Disproportionation processing parameters optimization (P2)
- Bench top prototype concept design and testing (P2)
- Catalysts testing (P2)
- Plants safety study (P2)
- 1MW on sun testing of scale up acid decomposer (P3)



Conceptual scale up of a modular decomposer on a solar tower

- On sun demo. component design and testing (P3)
- Solar-process integration design and optimization (P3)