Sulfur Based Thermochemical Heat Storage for Baseload Concentrating Power

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Outline

- Project Description and Objectives
- Thermodynamic Modeling
- Laboratory Results
- Process Pathways and System Efficiency
- Summary
- Future Work

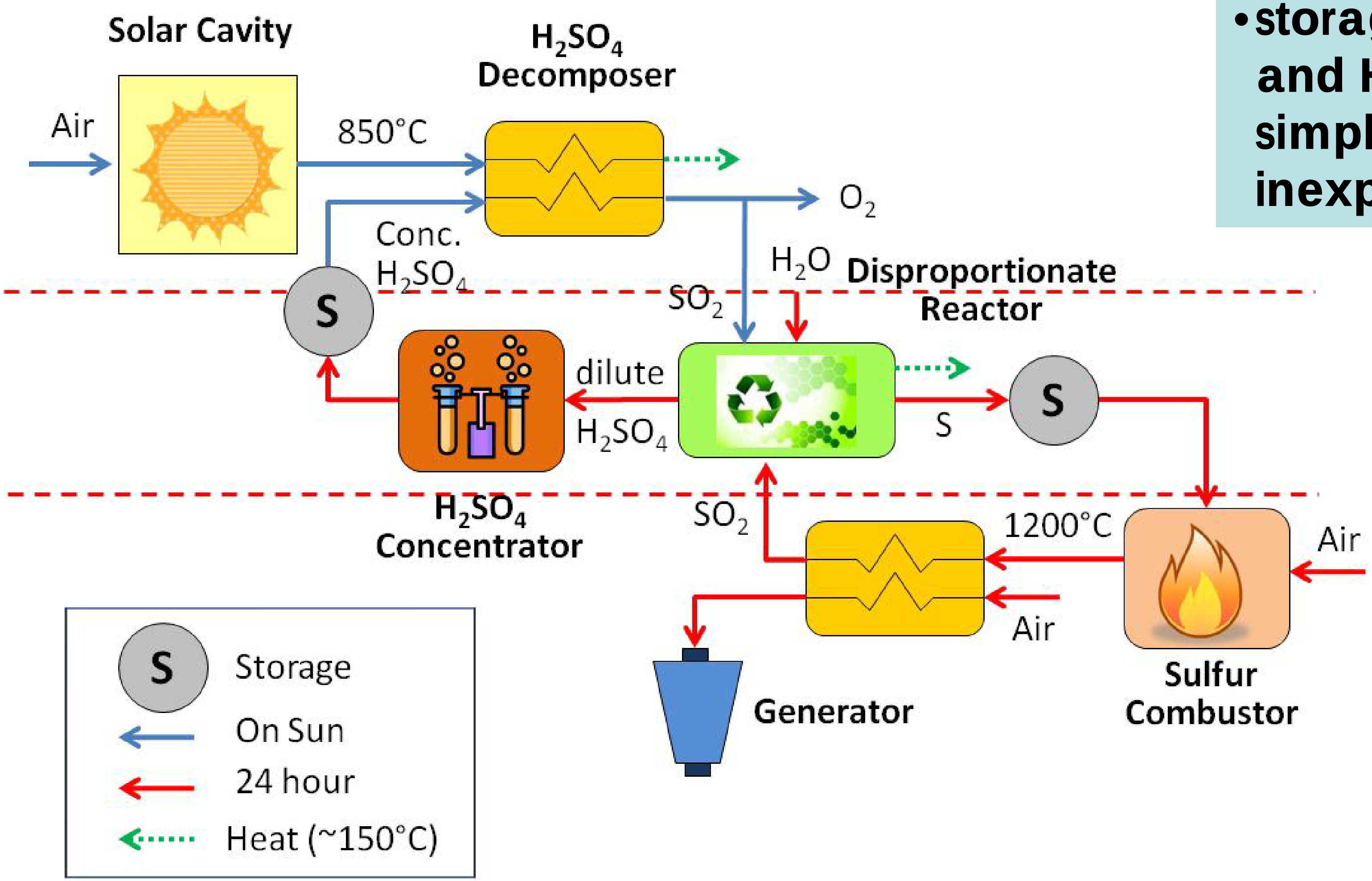
Project Goals

- **Demonstrate the engineering and economic feasibility of using sulfur to support baseload operation of a solar electricity plant**

	Reaction	Temp (C)	ΔH (kJ/mole)
Sulfuric Acid Decomposition	$2H_2SO_4 \rightarrow 2H_2O(g) + 2SO_3(g)$	450 – 500	560
	$2SO_3 \rightarrow O_2\,(g) + 2SO_2(g)$	700 – 800	
Disproportionation Reaction	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(s,l)$	50 – 200	-260
Sulfur Combustion	$S(s,l) + O_2(g) \rightarrow SO_2(g)$	500 – 1200	-300

- **All chemical reactions have been demonstrated**

The baseline concept decouples thermochemcial process from electricity generation



- storage of sulfur and H_2SO_4 is simple and inexpensive

Phase I Objective – Maximize the sulfur generation rate and establish a baseline system design

Phase I began in September 2010 and the duration is 18 months

Disproportionaton
- Improve Kinetics
- Thermodynamics Modeling
- Verify Process Feasibility
  - Catalysts
  - Sulfur Extraction

Decomposition (DLR)
- Decomposer Selection
- Concentration Construction Materials

→ **Flowsheet**
- Process Pathways Comparison
- System Design

→ **Project Performance**
- Capacity Factor
- LCOE

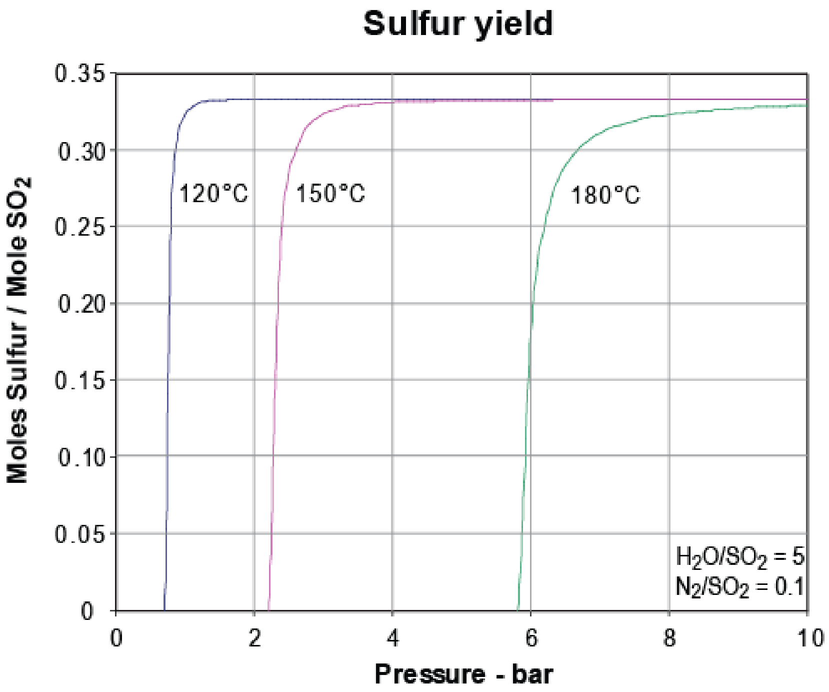
→ **GO NOGO**

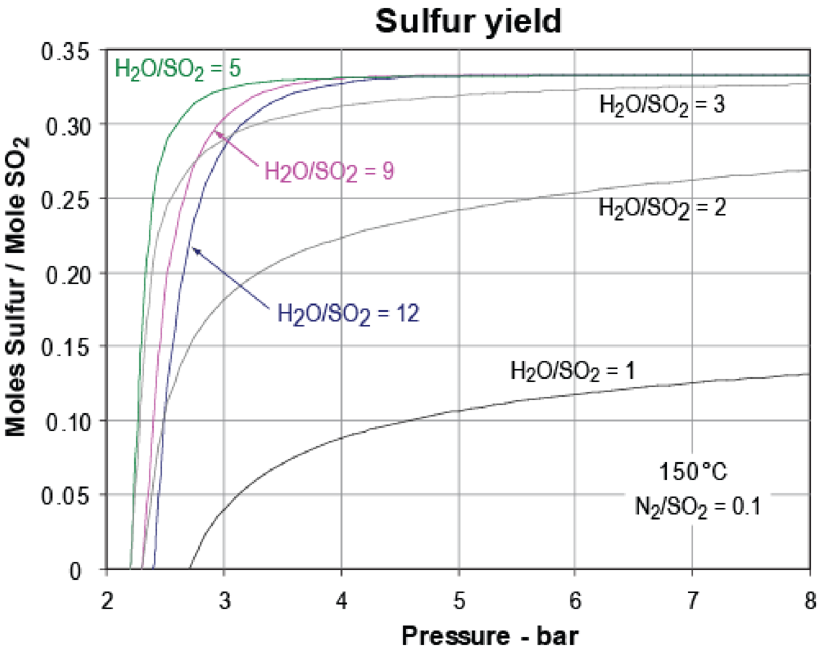
Thermodynamic modeling is used to guide disproportionation reaction experiments

HSC Chemistry → **Aspen Plus** → **Aspen Plus OLI**

- **Design of Experiments**
  - HSC Chemistry
  - Aspen Plus advanced sulfuric acid model
- **Preliminary optimization**
  - Aspen Plus advanced sulfuric acid model
  - OLI Systems electrolytes model
- **Final optimization**
  - Custom model based on experimental data

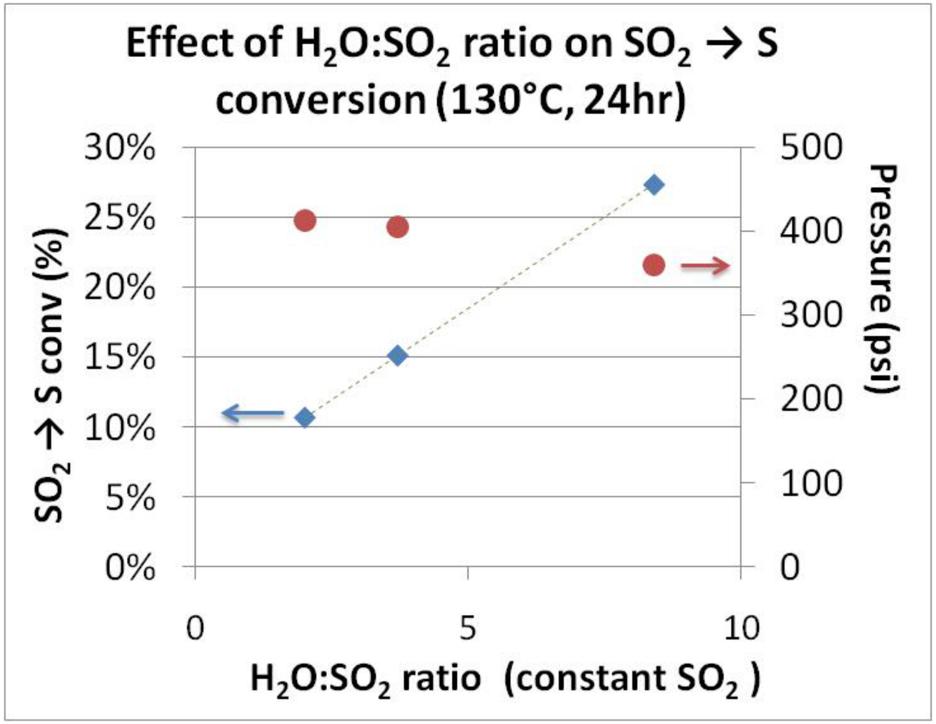
Aspen Plus results showed sulfur yield is suppressed by temperature but enhanced by pressure

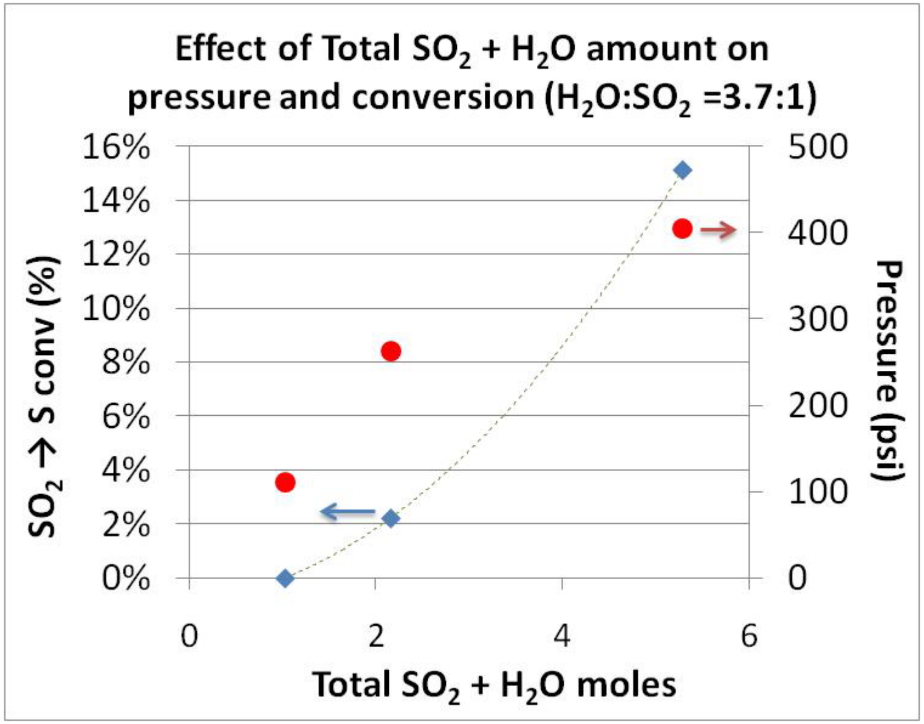




- Optimal H_2O: SO_2 ratio enhances sulfur yield
- Too much water can reduce SO_2 activity resulting in lower sulfur yield
- Too little water suppresses reaction resulting in lower H_2SO_4 formation

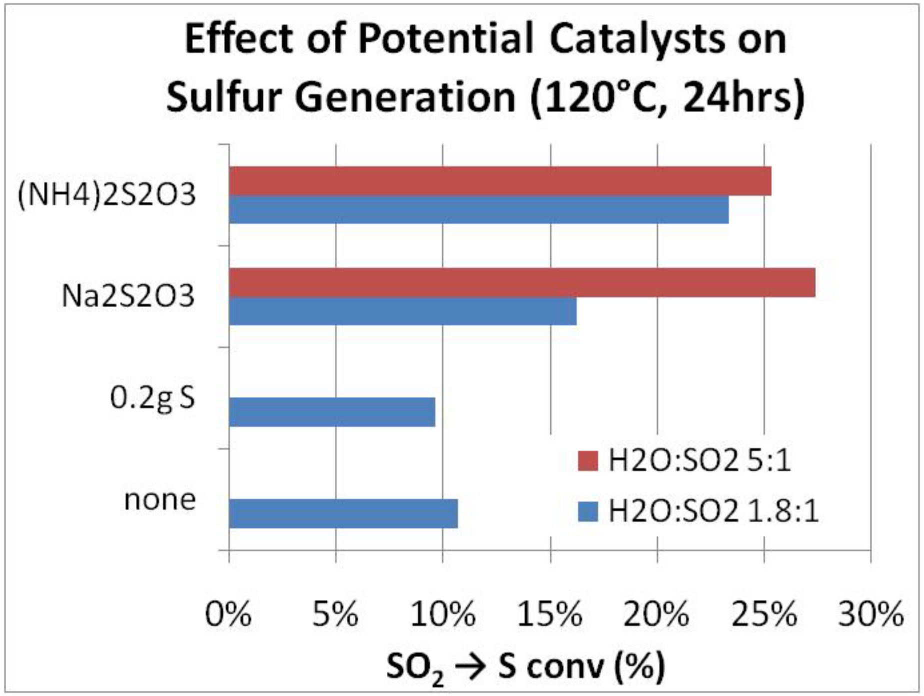
$H_2O:SO_2$ ratio and pressure effects predicted by thermodynamic model were qualitatively verified

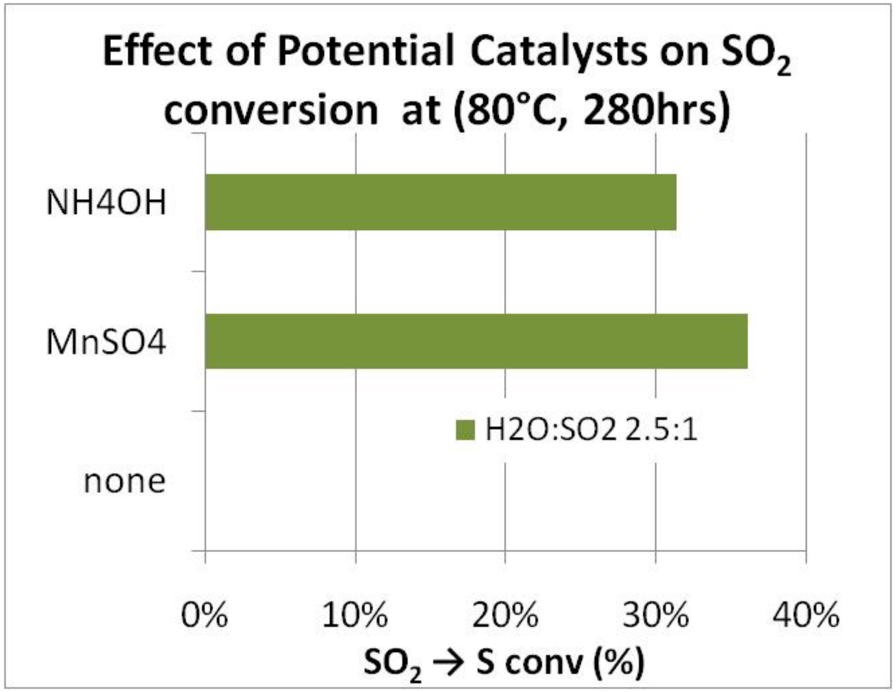




- High $H_2O:SO_2$ ratio enhance sulfur generation
- A minimum pressure is required for sulfur generation

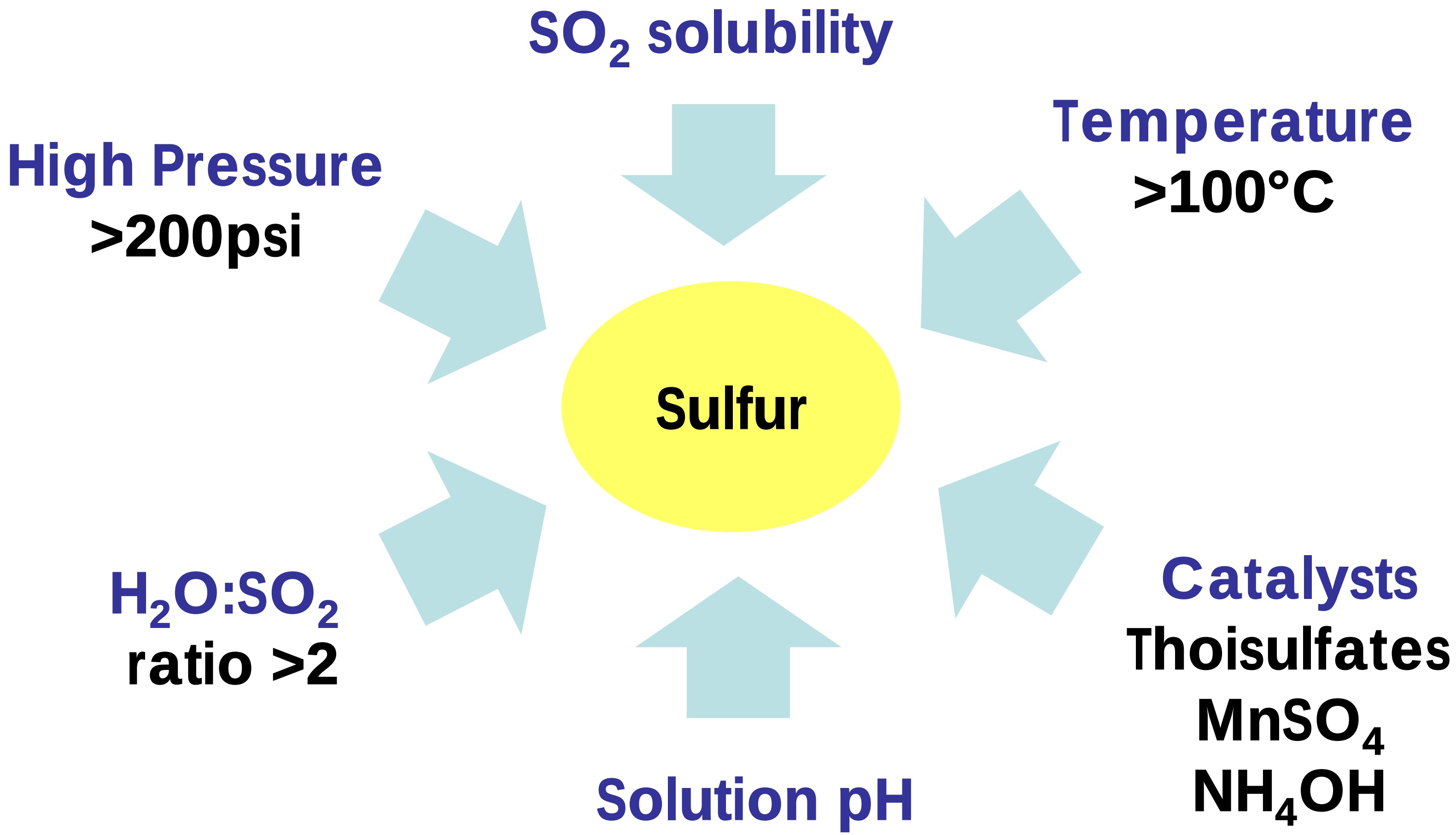
Catalysts have been used to enhance sulfur generation





- **Thiosulfates, metal sulfates and hydroxides have all shown catalytic activities in this system**

Disproportionation reaction is affected by a number of factors

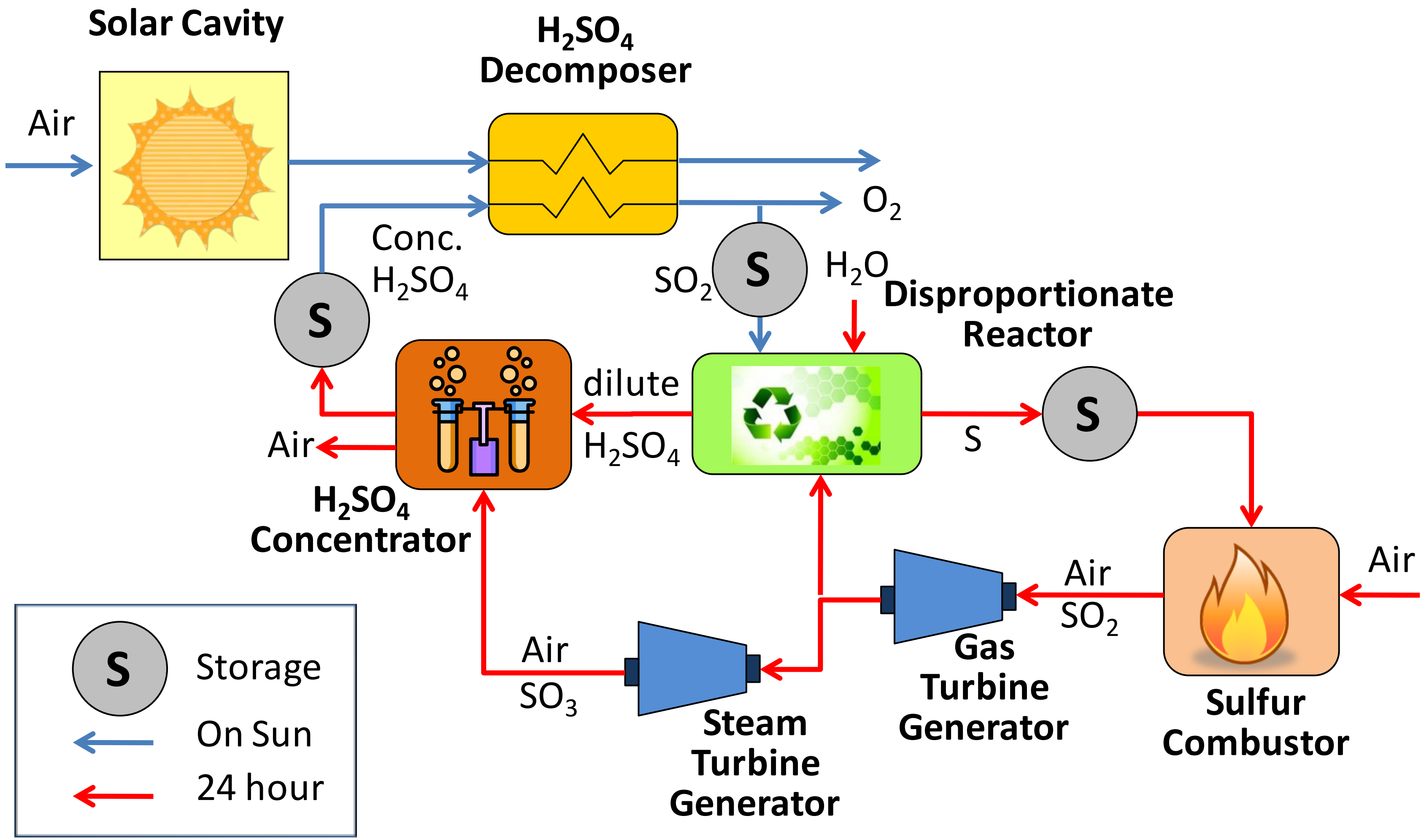


- Laboratory studies to find the optimal parameters for fast reaction kinetics is on going

Several process pathways were considered in devising the initial Sulfur TES flowsheet

- Rankine steam power cycle
  - High process heat available (~900ºC) not an optimal fit for steam cycle alone
- Supercritical CO_2 power cycle
  - Large gas-gas heat exchangers may be required for high efficiency
  - Development work remains
- Methods for sulfuric acid concentration
  - Solar trough heat
  - SO_2 conversion to SO_3

The current Sulfur TES flowsheet is based upon a combined-cycle power plant with SO_2 conversion



The combined cycle power plant concept is well established and is very efficient

- **Electrical conversion efficiency of heat supplied to the power plant is ~50%**
- **Overall efficiency of electricity generation from solar heat supplied to thermochemical process is about 27%**
- **Losses in disproportionation reactor and in sulfuric acid decomposer account for the difference**

Sulfuric acid concentration can be done via conversion of SO_2 to SO_3

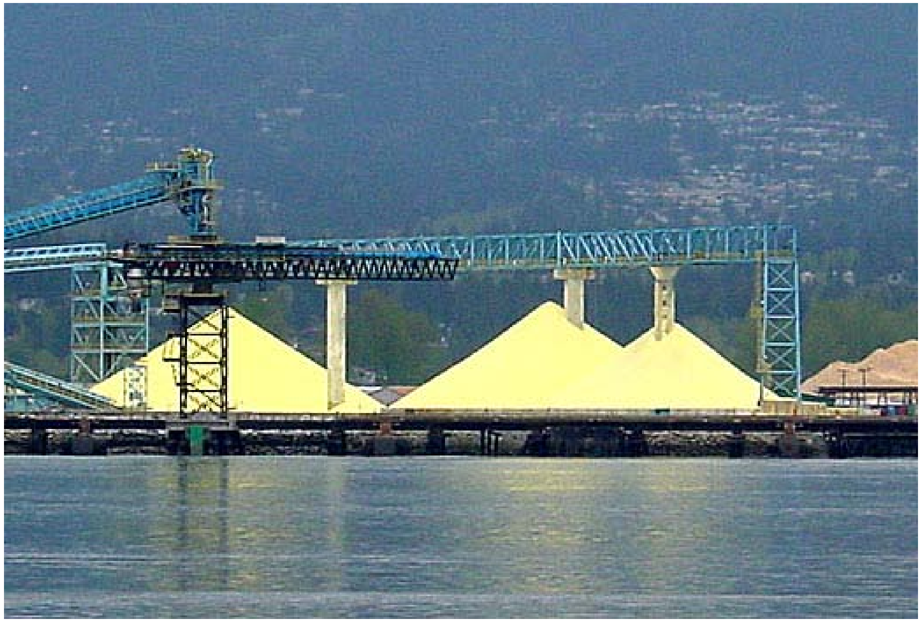
- **Avoids construction of a separate solar trough plant**
- **Allows this process to leverage established sulfuric acid production equipment and techniques**
- **SO_2 converter units generate recoverable heat, increasing efficiency**

TES is done via storage of dry sulfur

- Hot (molten) sulfur storage not necessary

- Dry sulfur delivered via hopper to combustor

- Sulfur is melted in combustor before atomizing/spraying into burner



Summary

- Process parameters boundaries were defined by thermodynamic models
- Laboratory results qualitatively agreed with thermodynamic models
- Sulfur yield was enhanced by using catalysts
- Flowsheet design focused on minimizing impact of thermochemical losses

Future Work

- Define the pressure, temperature and $H_2O:SO_2$ ratio for optimal reaction kinetics and system design
- Identify the catalyst(s) to be used
- Demonstrate a sulfur extraction methodology
- Establish reactor and system design concepts
- Determine the economics of the proposed system

Sulfur as a TES medium is truly unique

- Provides process heat at temperatures higher than collected at solar receiver

- Uncomplicated storage method

- Allows for seasonal storage if desired