Chemically Reactive Working Fluids for the Capture and Transport of Concentrated Solar Thermal Energy for Power Generation

SunShot CSP Program Review 2013

Argonne National Laboratory

Program Start Date: October 1, 2012

R. Brotzman (PI), M. Urgun-Demirtas, J. Libera

Presentation Outline

- Project Description
- Project Objectives and Goals
- Project Innovation Compared With Baseline
- Key Technical Results, Analysis, and Accomplishments to Date
  - CRWF candidates
  - CSP process simulations on CRWF candidates
  - Reaction test system (RTS)
- Conclusions

Project Description

- Project addresses cost barrier of power produced by CSP plants
- Specifically, the primary heat transfer fluid (HTF), which transmits the collected solar power to power cycle
- Evaluate Chemically Reacting Working Fluids (CRWFs) as HTFs in the range of 650°C–1200°C – *sensible, latent, and* ***chemical reaction heat***
- Work plan
  - Conduct thermodynamic and process simulations using Aspen Plus® – use simulations and published kinetic data to identify CRFW candidates and process window to enable reversible reactions in the temperature ranges of 650°C–1200°C
  - Design CRWF cycling experiments to demonstrate thermal capture, transport, and release between 650°C and 1200°C, below 160-bar
  - Test CRWF system to validate the models and to demonstrate that more than double the power output efficiency of current CSP systems is achievable, scalable, and robust

Project Objectives and Goals

- Demonstrate lab-scale feasibility of employing CRWFs as HTFs for CSP systems
- Program Goals
  - Identify CRFW candidates and process window to enable reversible reactions in the temperature ranges of 650°C–1200°C
  - Compare CRWF cycling experimental data with commercial HTF's DOWTHERM A® and Solar Salt
  - Compare CRWF cycling experimental data to systems that use air as the working fluid and to the models of super critical CO_2 as a working fluid
  - Determine CRWF compatibility with CSP system components, material availability, cost competitiveness, safety, environmental impact, and the need for catalysts
  - Develop predictive models to determine power production and efficiency given various designs, and process parameters
  - CRWF system will be tested to validate the models and to demonstrate that more than double the power output efficiency of current CSP systems is achievable, scalable, and robust

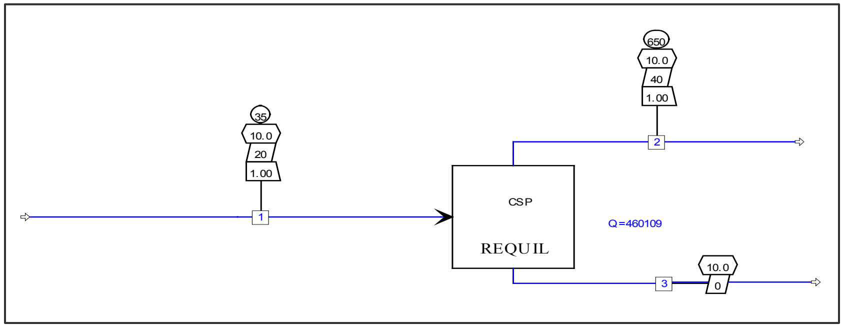
Project Innovation Compared With Baseline

- State-of-the-art CSP has a maximum solar-to-electric efficiency of 29.4% *
- Operationally, industrial-scale plants are < 15% efficient – primary HTFs absorb solar heat as sensible heat at near atmospheric pressure in solar collector and are pumped through heat exchangers to transfer heat to water to produce steam for power generation
- Innovation: Chemically reacting fluids (CRWFs) as HTFs
  - Sensible, latent, and ***chemical reaction heat*** of a reversibly reacting fluid
  - Sun's energy absorbed by ***endothermic decomposition*** of CRWF at high temperature
  - At lower temperature, ***exothermic regeneration*** of decomposition state releases heat absorbed at higher temperature
  - Enable substantially ***more heat/mass to be captured*** in the range of 650°C–1200°C
  - CRWF is cycled reversibly between different chemical states, dictated by chemical equilibrium, and coupled to standard steam cycle

* Washom, B., Paper No. 849516, Proceeding of the IECEC, San Francisco, CA (1984)

CRWF Candidates

- *Ethane and Hydrogen:* $0.95\ C_2H_6 + 0.05\ H_2 = 0.95\ C_2H_4 + H_2$
- *Methane and* CO_2: $CH_4 + CO_2 = CO + H_2$
- *Methane and* H_2O: $CH_4 + 2\ H_2O = CO + CO_2 + H_2$
- *Methanol and* H_2O: $CH_3OH + H_2O = CO + CO_2 + H_2 + H_2O + CH_4$
- *Ammonium Bisulfate:* $NH_4HSO_4 + 8\ H_2O = NH_3 + N_2 + H_2 + SO_2$
- *Ammonium Sulfate:* $(NH_4)_2SO_4 + 10\ H_2O = NH_3 + N_2 + H_2 + SO_2$
- *Ammonium Chloride:* $NH_4Cl + 8\ H_2O = NH_3 + HCl + N_2 + H_2$
- *Decalin:* $C_{10}H_{18} = C_{10}H_8 + H_2$
- SO_3: $SO_3 = SO_2 + O_2$
- *Ammonia:* $NH_3 = N_2 + H_2$
- N_2O_4: $N_2O_4 = NO + O_2 + NO_2$
- *Water:* $H_2O = H_2 + O_2$ *(comparative system)*



Aspen Plus® Receiver Simulations: Ethane and H_2

$0.95\ C_2H_6 + 0.05\ H_2 = 0.95\ C_2H_4 + H_2$

Exergy (B) is the maximum energy available to do work on the environment

$$B = E + P_R V - T_R S - \Sigma_i\ \mu_{i,R}\ N_i$$

$$H = E + PV$$

$$G = H - TS \Rightarrow \Delta G/\Delta H = 1 - \Delta(TS)/\Delta H$$

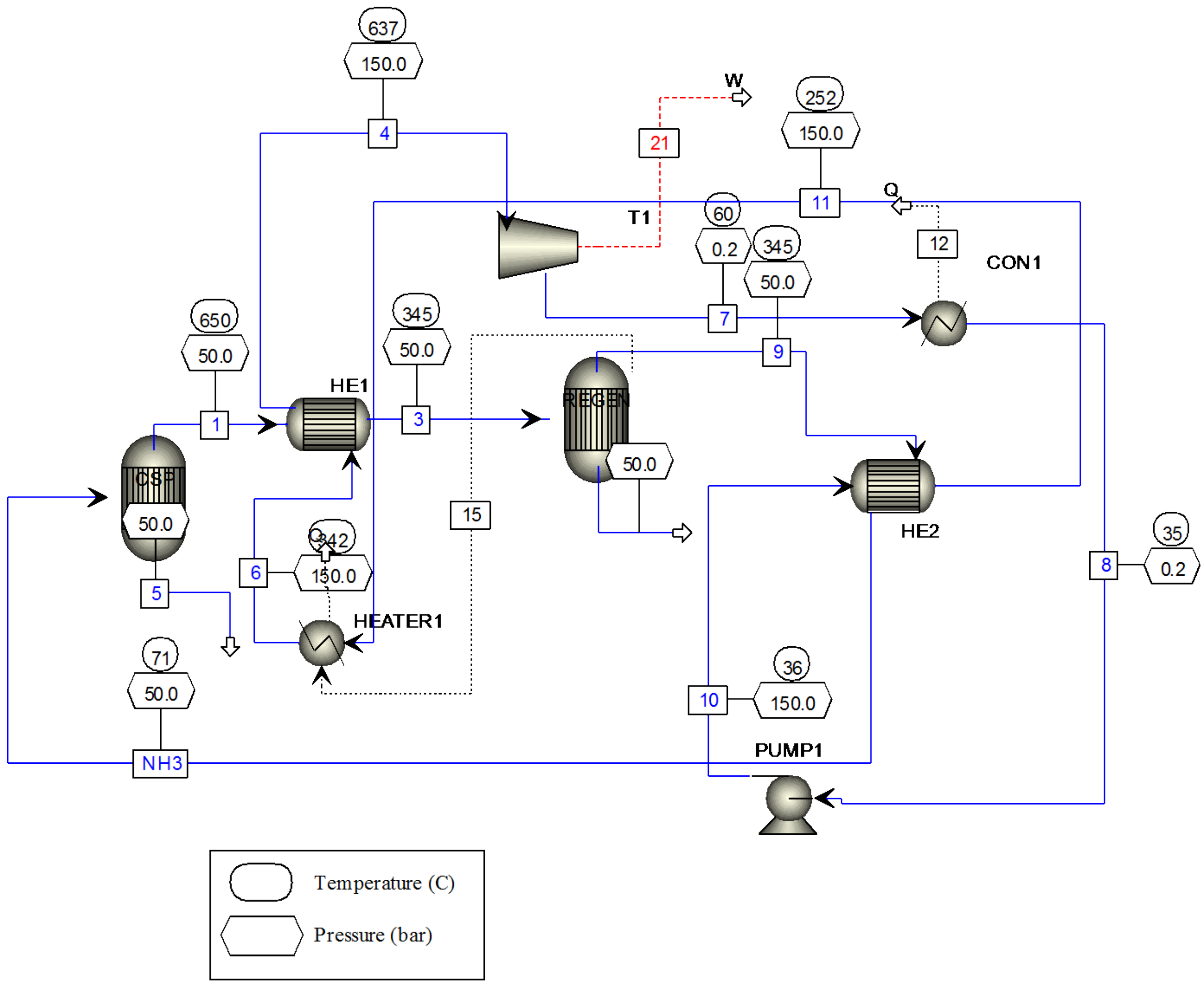
T-2 C	P Bar	Mole % C2H6-2 %	Mole % C2H4-2 %	Mole % H2-2 %	C2H6 Conversion %	Exergy kW	CSP Heat Duty kW	$\Delta G/\Delta H$
650	10	82.38	6.47	11.15	6.92	9.2	17.6	1.369
	50	90.73	2.19	7.08	2.24	8.2	16.5	1.625
	100	92.57	1.24	6.18	1.26	8.3	17.4	1.620
	150	93.31	0.86	5.82	0.87	8.3	17.4	1.668
800	10	50.60	22.77	26.63	29.48	19.0	31.5	0.845
	50	73.31	11.12	15.56	12.51	14.6	25.6	1.200
	100	80.18	7.60	12.22	8.23	13.7	25.2	1.290
	150	83.41	5.94	10.65	6.32	13.4	24.6	1.364
1000	10	12.66	42.23	45.12	73.09	37.2	56.0	0.467
	50	35.11	30.71	34.18	44.33	29.4	45.4	0.729
	100	47.07	24.58	28.35	32.59	26.3	42.1	0.854
	150	53.93	21.06	25.01	26.68	24.8	39.9	0.938
1200	10	2.51	47.43	50.06	90.23	48.4	70.2	0.317
	50	10.59	43.29	46.13	76.33	45.2	65.6	0.487
	100	17.93	39.52	42.55	65.36	42.4	62.7	0.576
	150	23.49	36.67	39.84	57.91	40.5	59.9	0.640

for 1 kmol/hr flow

Heat Duties/kmole/hr CRWF through CSP receiver CRWF Down Selection

CRWF Candidate	CSP Heat Duty (kW)/kmole/hr CRWF Flow in CSP Receiver @ 1000C - 10 bar
0.95 C_2H_6 and 0.05 H_2	56.0
SO_3	49.5
0.5 CH_4 and 0.5 CO_2	48.3
0.33 CH_4 and 0.67 H_2O	41.1
0.5 CH_3OH and 0.5 H_2O	40.4
1/9 NH_4HSO_4 and 8/9 H_2O	37.8
1/12 $(NH_4)_2SO_4$ + 11/12 H_2O	35.3
NH_3	34.7
N_2O_4	33.9
1/9 NH_4Cl and 8/9 H_2O	30.5
H_2O	22.5

CSP Process with CRWFs Simulated with Aspen Plus®



Aspen Plus® CSP Process Simulations: Ammonia $NH_3 = N_2 + H_2$

- Regeneration temperature dictates reverse equilibrium

NH_3							
T C	P Bar	SS Mole % NH_3	SS Mole % N_2	SS Mole % H_2	SS NH_3 Conversion	Regeneration Temp C	SS Work from Turbine kW/kmole/hr CRWF
650	50	27.5%	18.2%	54.4%	92.8%	345	3.56
	100	40.3%	14.9%	44.8%	89.5%		4.30
	150	48.8%	12.8%	38.4%	86.7%		4.69
800	50	27.5%	18.2%	54.4%	97.2%	345	4.64
	100	40.3%	14.9%	44.8%	96.0%		5.82
	150	48.8%	12.8%	38.4%	94.7%		6.52
1000	50	27.5%	18.2%	54.4%	98.8%	345	5.59
	100	40.3%	14.9%	44.8%	98.4%		6.91
	150	48.8%	12.8%	38.4%	98.0%		7.86
1200	50	27.5%	18.2%	54.4%	99.5%	345	6.53
	100	40.3%	14.9%	44.8%	99.3%		8.00
	150	48.8%	12.8%	38.4%	98.9%		9.05

CSP Reactor Conditons	550 C Regenaration			345 C Regenaration		
	NH3 Conversion	N2/H2 Conversion	Power, kW	NH3 Conversion	N2/H2 Conversion	Power, kW
650 C, 50 Bar	56%	4%	1.78	93%	41%	3.56
1200 C, 100 Bar	97%	12%	4.59	99%	57%	8
1000 C, 150 Bar	93%	17%	3.99	98%	65%	7.86

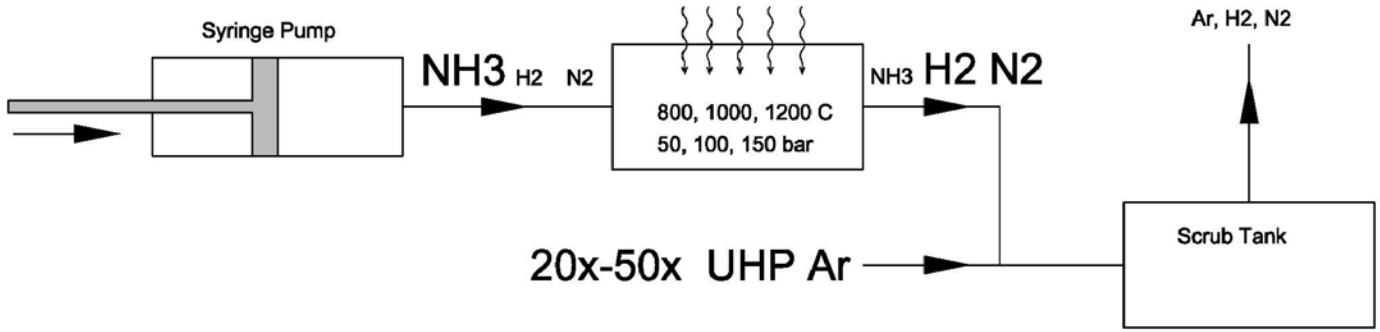
CRWF kW Turbine Power Generated per kmole CRWF flow at 1000°C and 50 bar

- Candidate CRWFs produce 20% to 100% more power, with the exception of NH_3

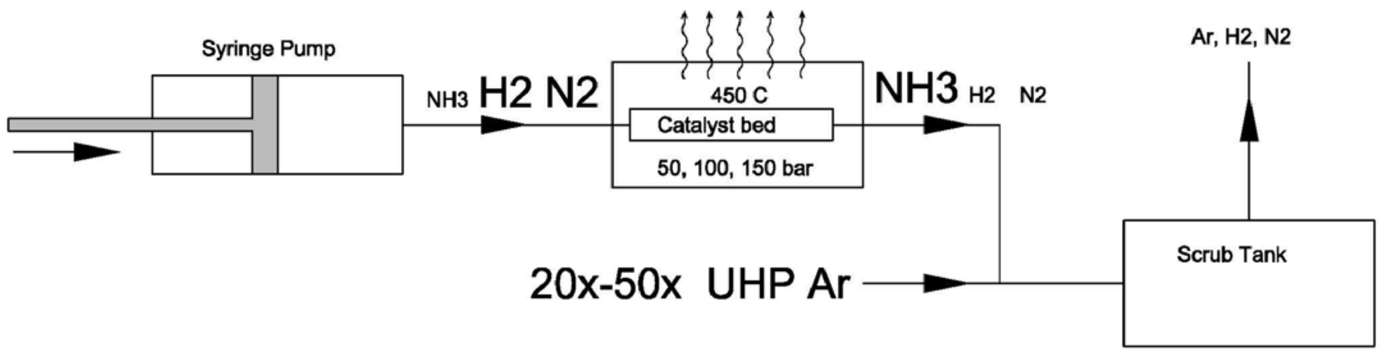
CRWF Candidate	kW turbine power/kmole CRWF/hr flow @ 1000C - 50 bar	Normalized to Water's Power
0.95 C_2H_6 and 0.05 H_2	18.15	2.03
SO_3	16.12	1.81
0.5 CH_4 and 0.5 CO_2	12.67	1.42
0.33 CH_4 and 0.67 H_2O	10.71	1.20
NH_3	5.59	0.63
H_2O	8.92	1.00

Reaction Test System – Test Sequence

High temperature decomposition: CWF endothermic decomposition



Lower temperature regeneration: CWF exothermically reacted



Reaction Test System - Challenges

- Materials of Construction
  - Strength at Temperature
  - Thermal Conductivity
- Inconel Alloy 601
- ASTM B 163-08: Standard Specifications For Heat Exchanger Tubes

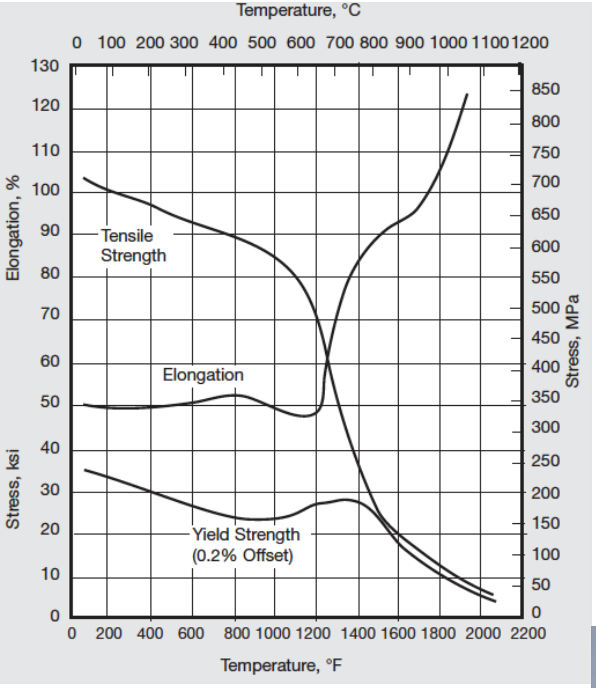
$P = 2\,S\,t\,/\,D$

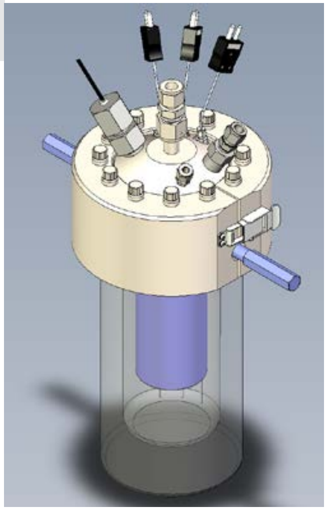
P = hydrodynamic test pressure, psi

S = allowable stress for material

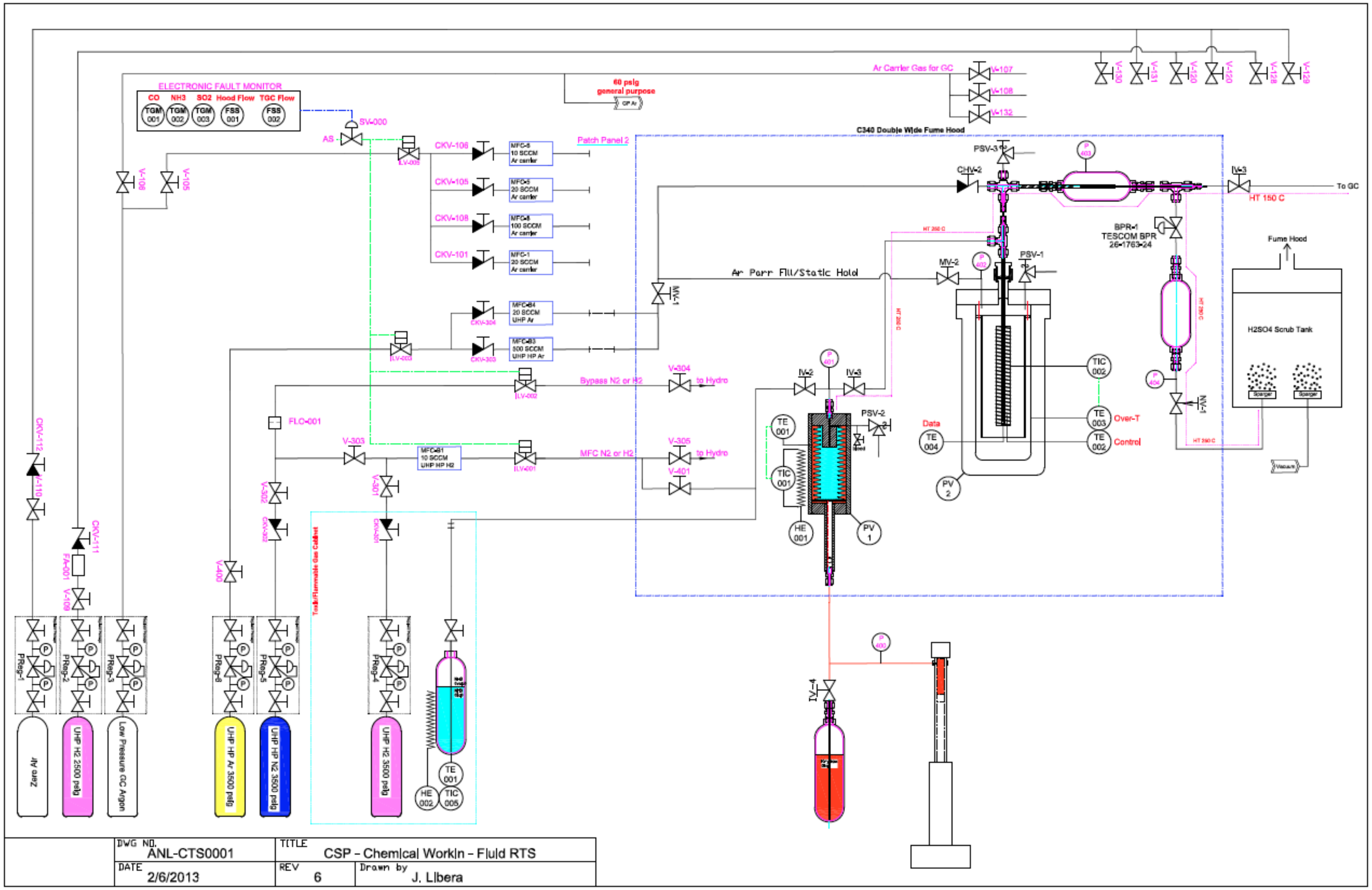
t = wall thickness

D = outside diameter



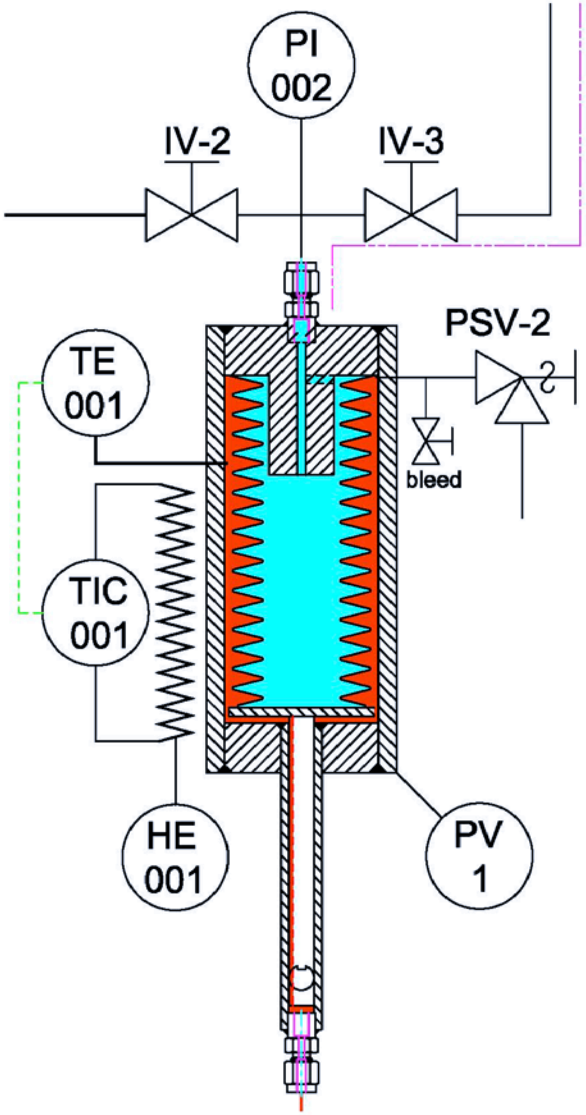


Reactor Test System - PID



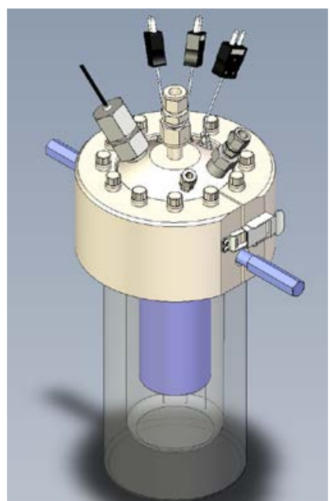
RTS Detail – Custom Transfer Bellows

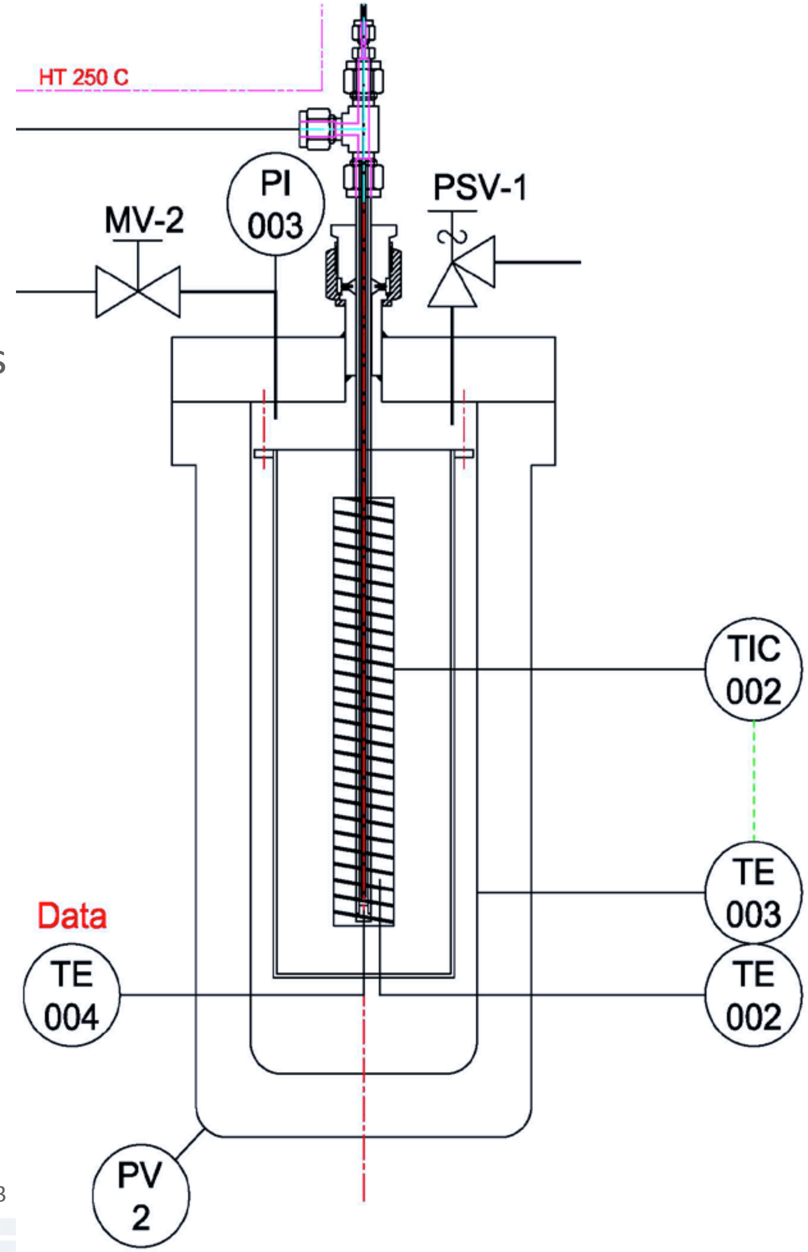
- Max Operating Pressure = 2500 psig
- Max Operating Temperature = 300°C
- Working Volume = 200 cm^3
- Stainless steel bellows isolation of SP (Krytox Oil) and process sides



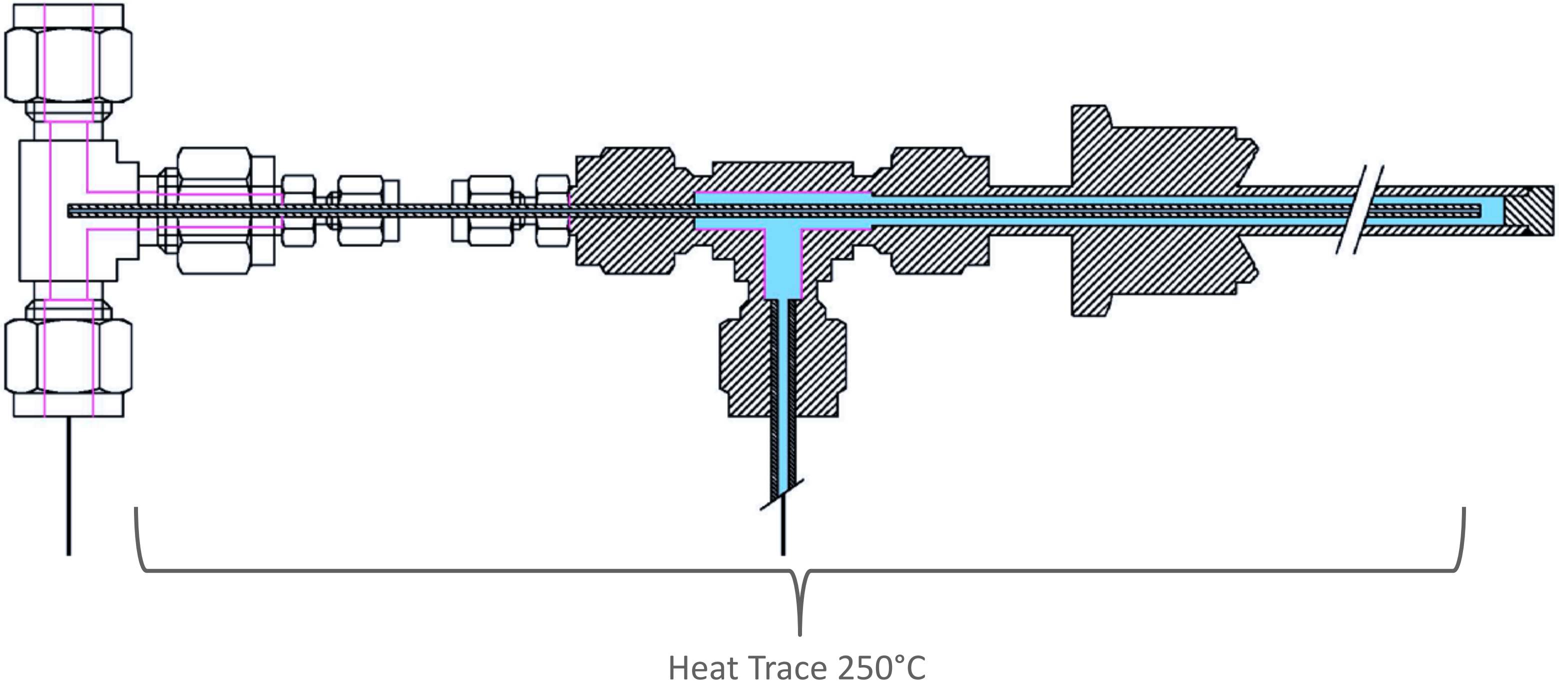
RTS Detail – Parr Pressure Vessel

- Max Operating Pressure = 2500 psig
- Max Operating Temperature = 300 C
- Argon gas filled + process fluid if test tube fails
- Design and Fabrication by Parr Instrument Co.
  - Use existing Parr 4572 vessel
  - Furnish modified head
  - Certified hydro-test

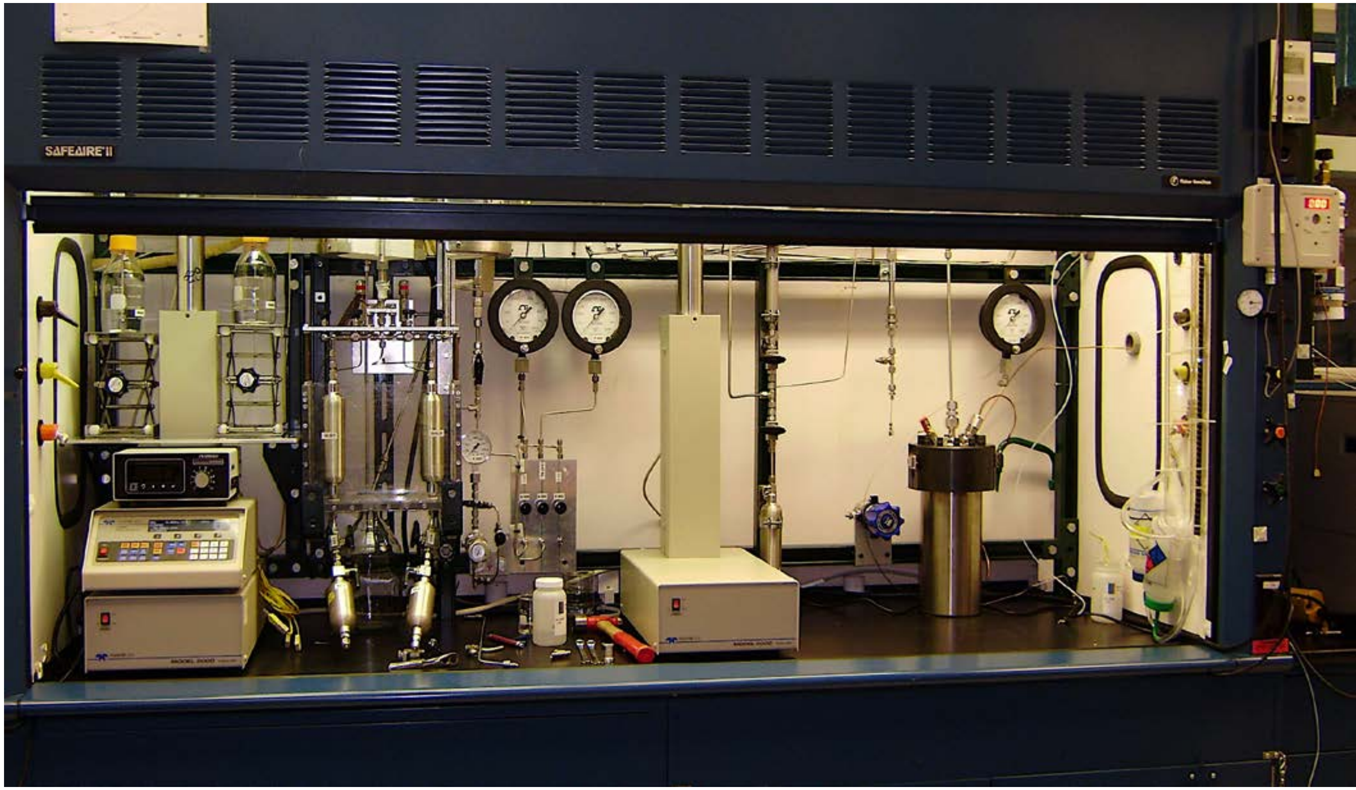




RTS Detail – Process Test Tube in Pressure Reactor



RTS Complete



CRWF Conclusions

- Future work planned
  - Experimentally validate CRWF systems at 650°C to 1200°C and 25-bar to 150-bar
  - Determine need for catalyst
  - Conduct postmortem evaluation of reactor materials
- Impact of work
  - Demonstrate feasibility of CRWFs as HTFs for CSP systems at lab-scale
  - Demonstrate that more than double the power output efficiency of current CSP systems is achievable, scalable, and robust
- Breakthroughs
  - Quantify process and metrics, including regeneration conditions, to maximize power output