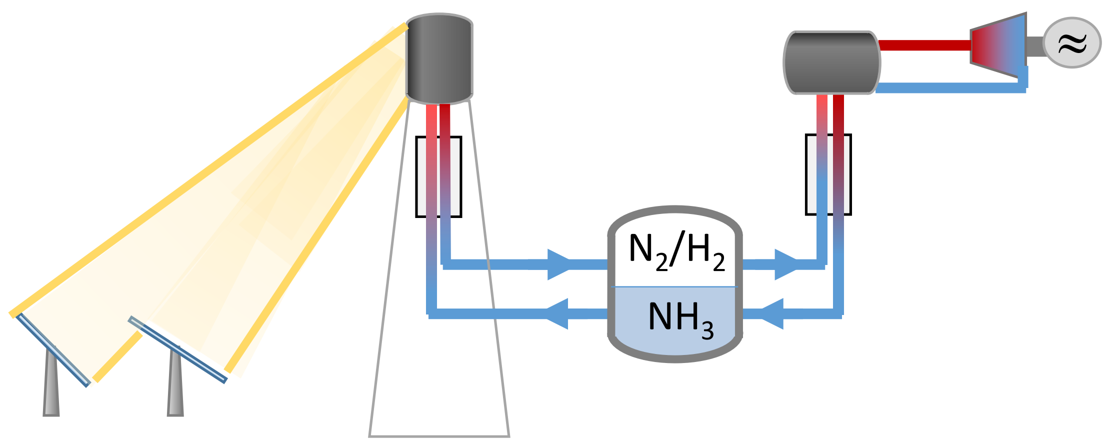
Thermochemical Energy Storage with Ammonia & Implications for Ammonia as a Fuel

Adrienne Lavine
Mechanical and Aerospace Engineering, UCLA
September 19, 2016

Other Contributors: Keith Lovegrove (IT Power Australia), Hamarz Aryafar, Chen Chen, Gabriela Bran Anleu, Bingjie Dang, Jenny Chieu, Jiahui Fu, Abdon Sepulveda, Dante Simonetti, Richard Wirz, Pirouz Kavehpour, Gopi Warrier



Overview of talk

- Introduce technology
- Discuss findings
- Pose questions: How our research may be relevant to synthesizing ammonia as a fuel

INTRODUCTION AND BACKGROUND

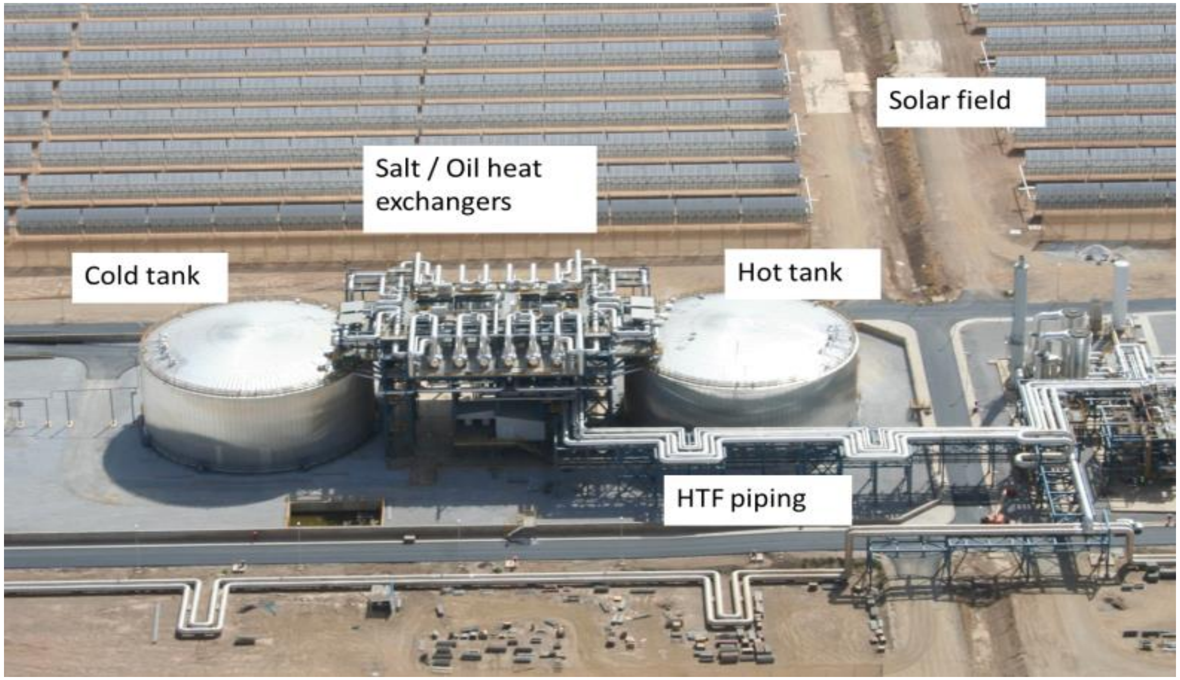
Concentrating Solar Power (tower configuration shown)

Ivanpah
400 MW_e, largest ever CSP plant

Crescent Dunes
110 MW_e, 10 hrs molten salt energy storage

Energy storage is CSP's competitive advantage

- Thermal storage enables electricity generation independent of time of day.
- Storage makes better use of the plant investment, can reduce LCOE.
- State of the art: two-tank molten salt storage.



Andasol 3
Courtesy Ferrostaal

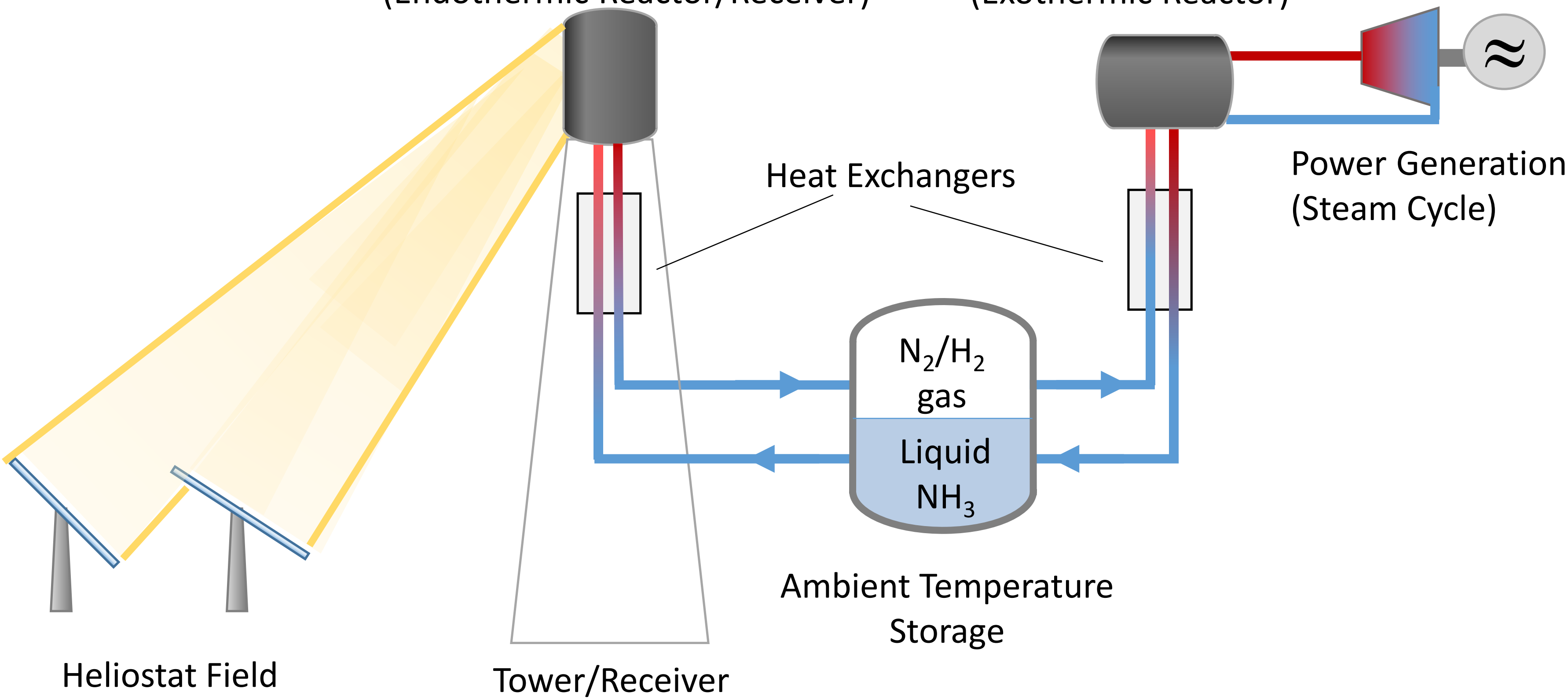

SOLARRESERVE


Salt itself is limiting cost factor
~ $25-40/kWh of energy stored

Project background

- U.S. Dept. of Energy SunShot supports research into energy storage for CSP
- Performance Goal: Recover heat at 650°C to enable advanced power block
- Target for Capital Cost: $15 per kWh of energy stored
  - not to be confused with LCOE
  - denominator not to be confused with energy for combustion of NH_3
- Many ideas, few are proven technologies
- Ammonia-based thermochemical energy storage has the potential to meet the performance and cost metrics

System overview



$$NH_3 + 66.6\ \text{kJ/mol} \rightleftharpoons \tfrac{1}{2}\, N_2 + \tfrac{3}{2}\, H_2$$

Pros and cons of ammonia TCES

Pros

- Extensive industrial experience
  - Haber Bosch
  - Catalysts available
  - Transportation routine
- Low cost medium
- Ambient temperature storage
- Automatic phase separation between products/reactants
- And more…

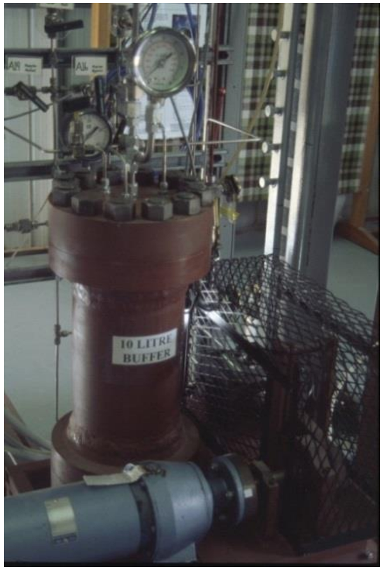
Cons

- Modest energy density
- Necessity of storing gaseous components
- High pressure process

Prior ANU research demonstrated complete loop

12 kW reactor/ receiver

20 m^2 dish concentrator



10 liter storage vessel

Synthesis reactor

Achieved wall temperature of 475°C

We want 650°C…

Key challenges identified and addressed

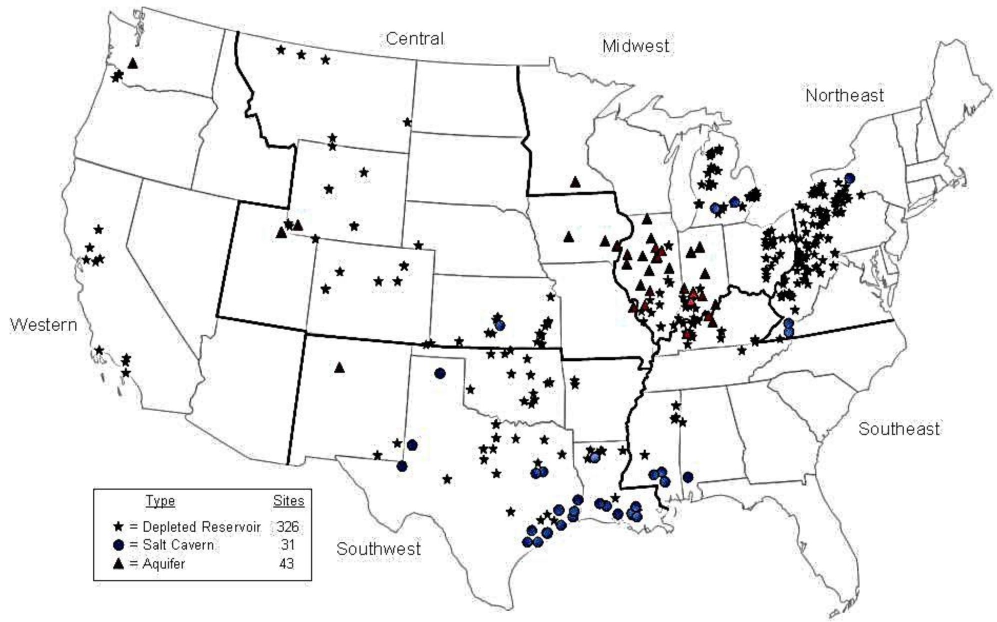
- Key challenges:
  - Can physical storage of high pressure nitrogen/hydrogen mixture be done cost-effectively?
  - Ammonia synthesis had never been used to heat supercritical steam to 650°C. Is it possible?

- Results presented today:
  - Gas storage
  - Heat recovery to supercritical steam at 650°C
  - Optimizing the synthesis reactor system

GAS STORAGE

Underground gas storage is prevalent

- Need to store ambient temperature, high pressure N_2+3H_2.
- Underground storage concept:
  - Surrounding geology provides bulk of pressure containment.
- Approaches considered:
  - depleted oil or gas wells
  - aquifers
  - salt caverns
  - rock caverns
  - tunnel drilling
  - shaft drilling



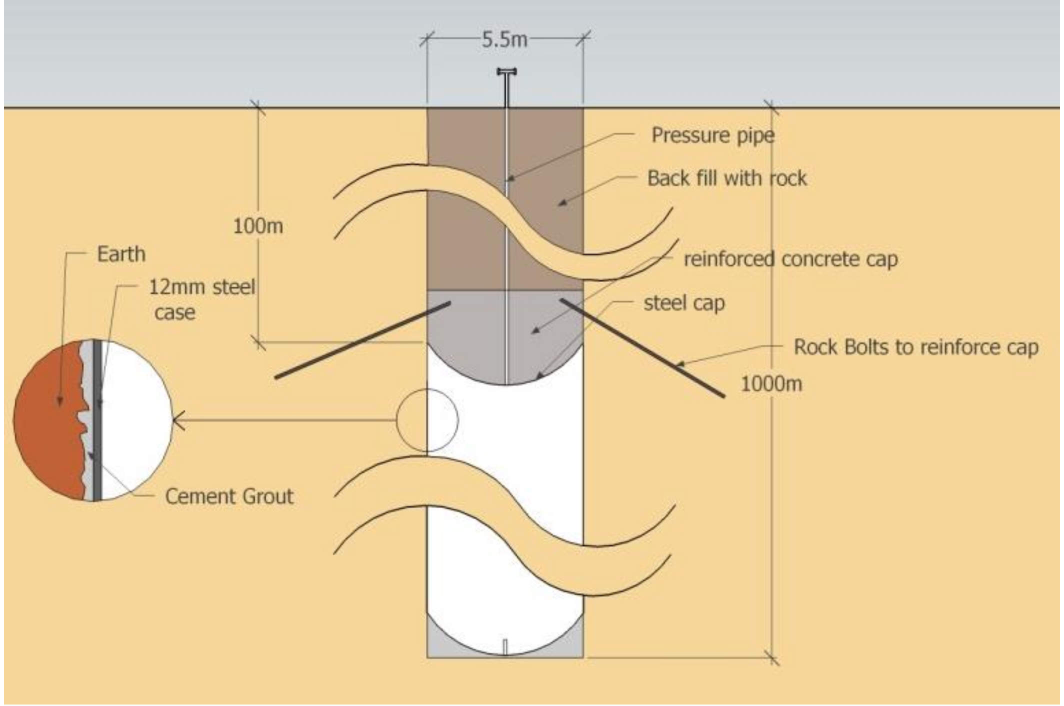
Underground natural gas storage sites in US

Salt caverns are inexpensive

- Solution mining of salt caverns is simple, established process
- Salt caverns widely used for storage:
  - Over 2000 salt caverns in North America alone for hydrocarbon storage.
  - Pure hydrogen or hydrogen-rich gas mixtures have been stored.
- Salt cavern conditions are suitable for our application:
  - Sufficient volume and pressure
  - Low permeability of rock salt
- Roughly $1/kWh to create storage space (for large projects).
- Available on every continent
  - but does present a site constraint.

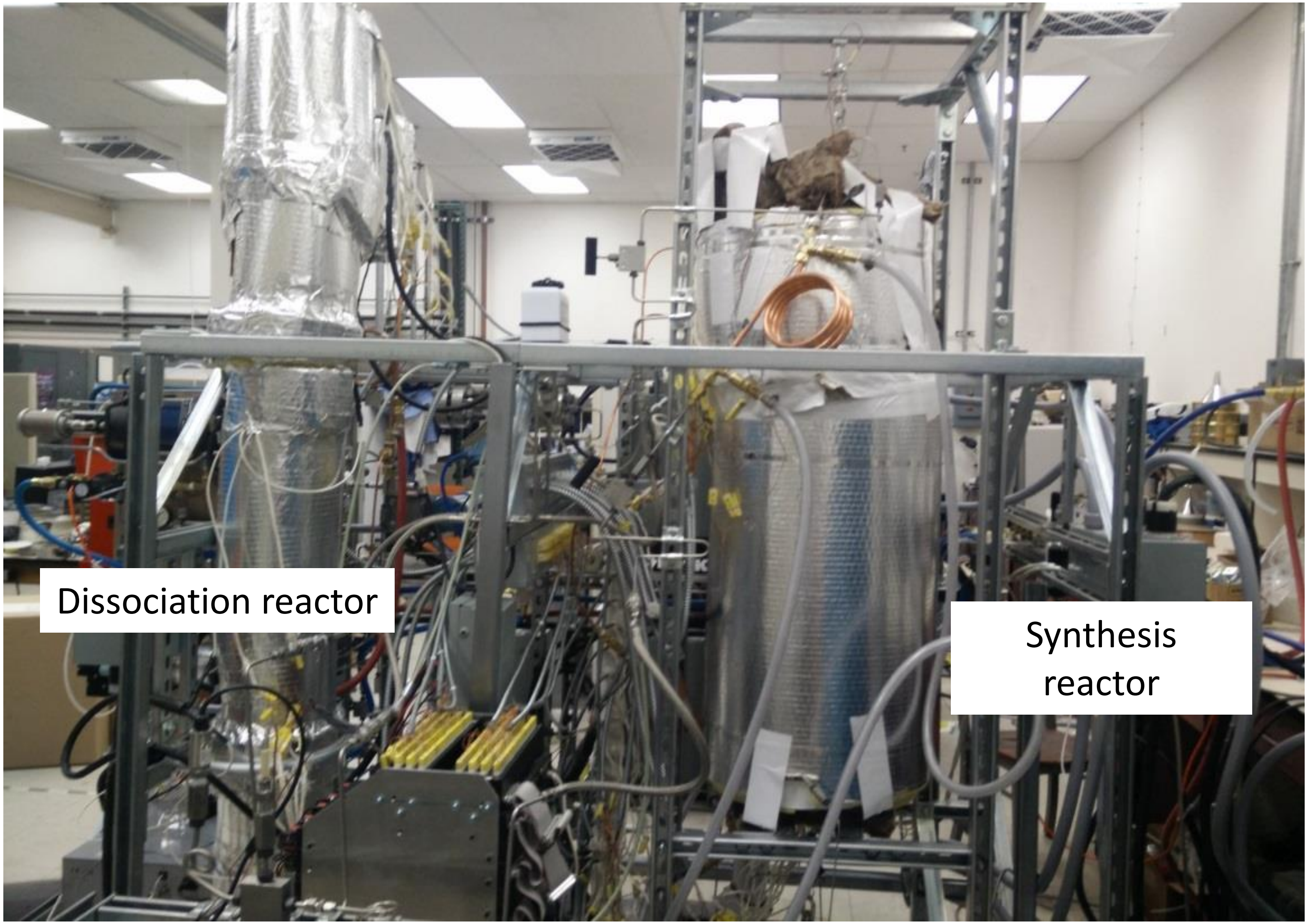
Large diameter drilled shafts provide another option

- Removes site choice constraint.
- Shaft drilling routinely carried out at up to 7.5 m diameter and depths of 1000 m.
- In consultation with drilling company:
  - Cost roughly $5/kWh.
- Conceptual design developed.
- Details of hydrogen impermeable lining and endcaps required.

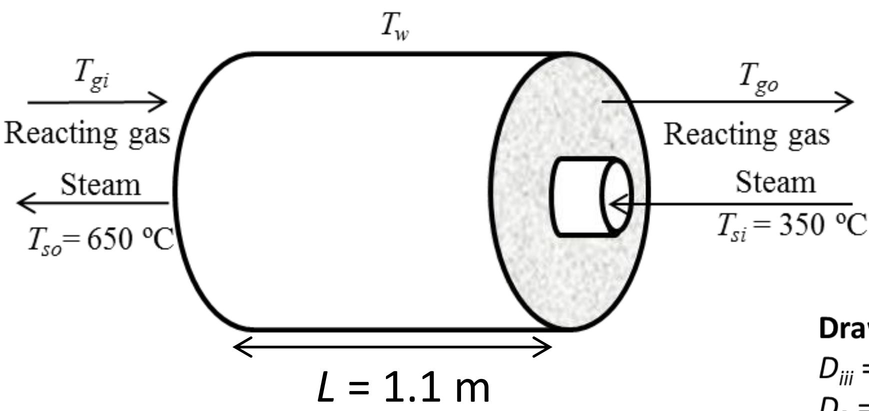


AMMONIA SYNTHESIS FOR HEAT RECOVERY TO SUPERCRITICAL STEAM

Experimental system in our lab

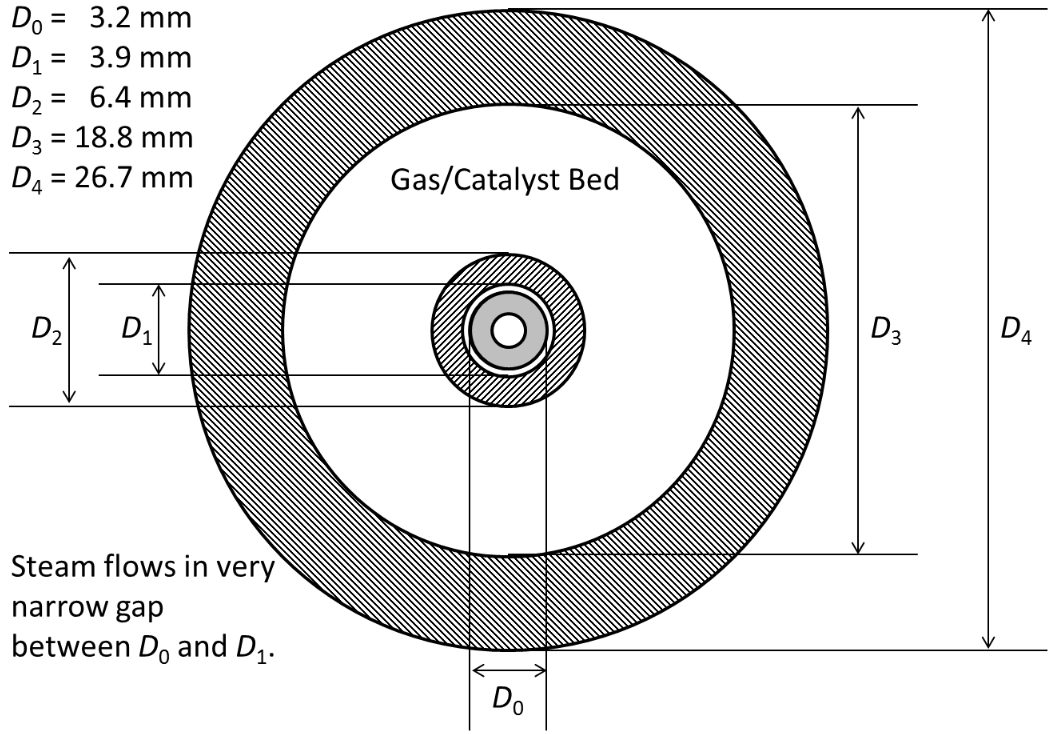


Reactor-hx configuration



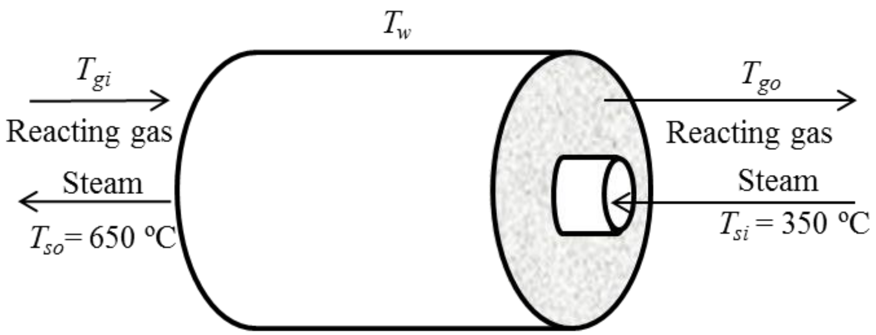
Drawn to scale.

D_{iii} = 1.4 mm
D_0 = 3.2 mm
D_1 = 3.9 mm
D_2 = 6.4 mm
D_3 = 18.8 mm
D_4 = 26.7 mm



Steam flows in very narrow gap between D_0 and D_1.

Reactor-hx model



Gas in Catalyst Bed

(pseudo - homogeneous model)

$$\rho_g v_g C_{P,g} \frac{\partial T_g}{\partial x} = \frac{1}{r}\frac{\partial}{\partial r}\left(k_{eff}\, r \frac{\partial T_g}{\partial r}\right) + \dot{r}'''\Delta H$$

$$\rho_g v_g \frac{\partial f_{NH3}}{\partial x} = \rho_g D_{eff} \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial f_{NH3}}{\partial r}\right) + \dot{r}'''$$

k_{eff} from Argo and Smith, 1953

Temkin - Pyzhev Rate Equation

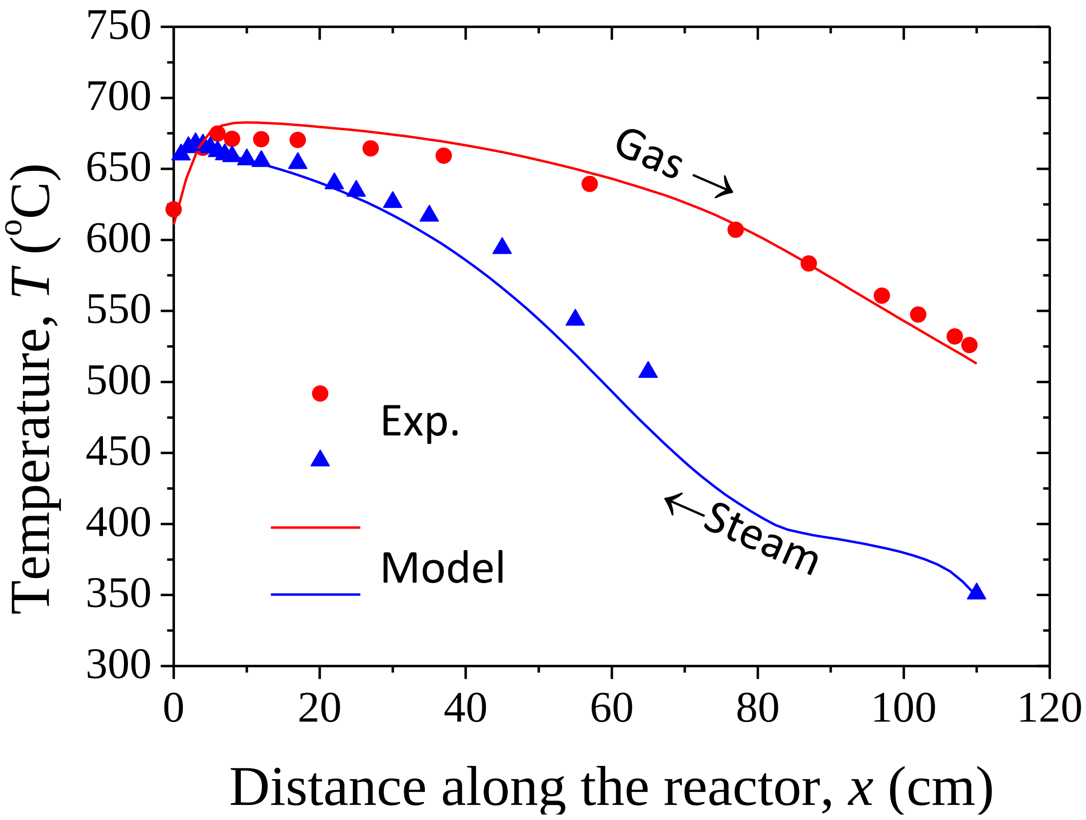
$$\dot{r}''' = \eta k_{0,m} \exp\left(-\frac{E_a}{R_u T}\right) \times \left[K_p^{-1} p_{N2} \left(\frac{p_{H2}^3}{p_{NH3}^2}\right)^{\alpha} p_o^{-(1+\alpha)} - \left(\frac{p_{NH3}^2}{p_{H2}^3}\right)^{1-\alpha} p_o^{(1-\alpha)} \right]$$

Supercritical Steam

$$(\dot{m}c_p)_s \frac{dT_s}{dx} = hP\left(T_{iw} - T_s\right)$$

$$Nu_b = C Re_b^m Pr^q \left(\frac{\rho_w}{\rho_b}\right)^{0.3} \left(\frac{\bar{c}_p}{c_{p_b}}\right)^n$$

Success heating supercritical steam



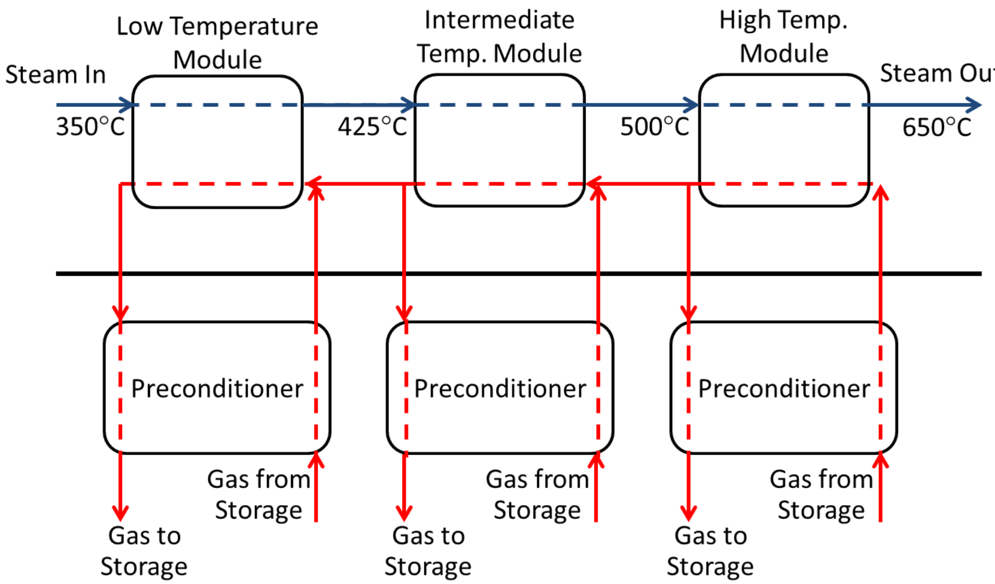
- Supercritical steam heated from 350 to 650°C.
- Model agrees well with experiment.
- Illustrated run: 1.6 kW_t
- Best run to date (with larger system): 4 kW_t

DESIGN OPTIMIZATION

Multi-parameter optimization can improve design

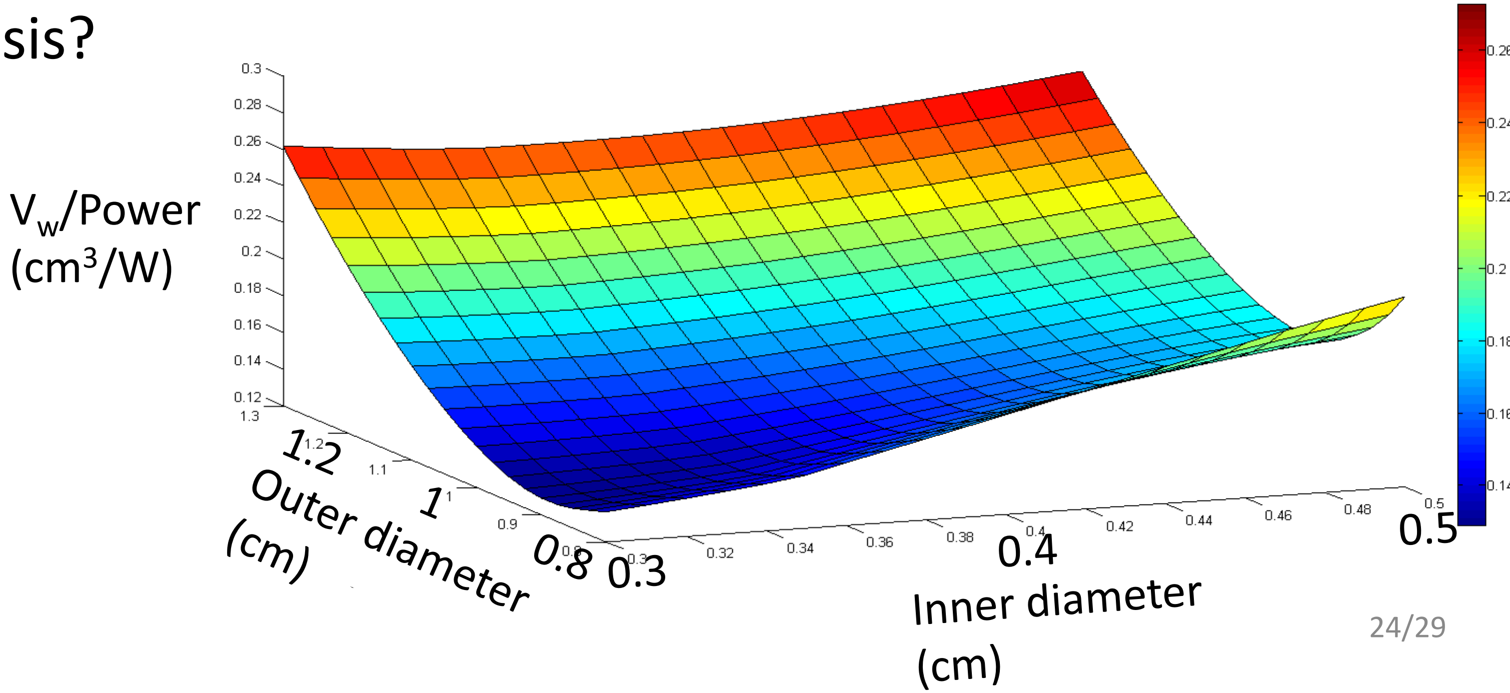
- Consider entire synthesis system:
  - Synthesis reactor
  - Preconditioning subsystem
- Modular system with different reactor designs for different temperature regimes
- Multi-parameter optimization problem with tens of parameters.

- Largest cost is wall material.
- Minimize objective function: V_w/Power



Optimization drives to small scale

- Optimize inner and outer diameters – small is best.
- Not surprising – small scale improves heat transfer.
- How small can we go?
  - Pressure drop, pumping power considerations.
  - Manufacturing costs.
- Could micro-channel reactors be considered for ammonia synthesis?



Optimization results to date

Preliminary design: V_w/Power ~ 0.7 cm^3/W

Multi-parameter optimization results:

- Single module, V_w/Power = 0.09 cm^3/W
  - Smaller diameters (still commercially available)
  - Higher steam and gas flow rates per tube (but with reasonable ΔP constraints)
- Three module design, V_w/Power = 0.05 cm^3/W
  - Smaller gas flow rates in high temperature/high reaction rate region
  - Higher gas flow rates in lower temperature/lower reaction rate regions

Full-scale system, 220 MW_t:

- 11 m^3 wall material volume

Further optimization in progress.

Path to market

- Identification of partners – current to next 12 months
- Solar-driven closed-loop experiment – 2017-2019
- Pilot 1 MW_e system – 2018-2021
  - Gas storage fabricated above ground using pressure pipe.
  - Heat recovery synthesis reactor designed for supercritical steam, but throttled for small off-the-shelf subcritical steam turbine.
- First utility scale demonstration, 10 MW_e – 2019-2024
  - First trial of underground storage using shaft drilling technology.
- First full-sized system, 100 MW_e, 10+ hrs storage – 2022-2027
  - Underground storage either salt cavern or drilled shaft.
  - Potential for supercritical steam turbine.

Conclusions

- Gas storage in salt caverns or drilled shafts appears feasible within the \$15/kWh$_t$ budget.
- Ammonia synthesis can be used to heat supercritical steam to 650°C, according to experiments and modeling.
- Design optimization of the synthesis reactor system is underway:
  - Small diameter tubes are desirable.
  - Multi-parameter optimization of modular design has significantly decreased wall material volume.
- A proposed path-to-market could achieve a full-scale system by 2027.

Relevance to ammonia as a fuel

- If ammonia is synthesized using intermittent energy sources (seasonal or diurnal), syngas storage may be needed.
  - Underground storage in salt caverns or drilled shafts might suit.
- Might the small-scale approach be useful for Haber-Bosch ammonia synthesis?
  - In the short-term before advanced technologies are developed?
  - To provide an approach that can scale down?
- Could high temperature heat recovery provide an advantage?
  - To supply heat for hydrogen production?
  - For efficient power generation?
- Is there merit to CSP-driven hybrid ammonia/electricity plant with storage?
  - 24-hr operation, optimizing time of electricity vs. ammonia production

Acknowledgments

- The information, data, and work presented herein was funded by the Office of Energy Efficiency and Renewable Energy, U.S. Dept. of Energy, Award No. DE-EE0006536. The authors gratefully acknowledge the support.

QUESTIONS?