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

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September 19, 2016

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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.
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 NH₃
- Many ideas, few are proven technologies
- Ammonia-based thermochemical energy storage has the potential to meet the performance and cost metrics
System overview

Ammonia Dissociation
(Endothermic Reactor/Receiver)

Ammonia Synthesis
(Exothermic Reactor)

Heat Exchangers

Power Generation
(Steam Cycle)

Heliostat Field

Tower/Receiver

Ambient Temperature Storage

Liquid NH₃

N₂/H₂ gas

NH₃ + 66.6 kJ/mol ⇌ ½ N₂ + ⅓ H₂
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

- 20 m² dish concentrator
- 12 kW reactor/receiver
- 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

Dissociation reactor

Synthesis reactor
Reactor-hx configuration

\[ L = 1.1 \text{ m} \]

Steam flows in very narrow gap between \( D_0 \) and \( D_1 \).

Drawn to scale.

- \( D_w = 1.4 \text{ mm} \)
- \( D_0 = 3.2 \text{ mm} \)
- \( D_1 = 3.9 \text{ mm} \)
- \( D_2 = 6.4 \text{ mm} \)
- \( D_3 = 18.8 \text{ mm} \)
- \( D_4 = 26.7 \text{ mm} \)
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

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

Supercritical Steam

\[ (mc_p)_s \frac{dT_s}{dx} = hP (T_{iw} - T_s) \]

\[ Nu_b = CRe_b^m Pr^q \left( \frac{\rho_w}{\rho_b} \right)^{0.3} \left( \frac{\bar{c}_p}{c_{pb}} \right)^n \]
Success heating supercritical steam

- Supercritical steam heated from 350 to 650°C.
- Model agrees well with experiment.
- Illustrated run: 1.6 kW
- Best run to date (with larger system): 4 kW
DESIGN OPTIMIZATION
• 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: $V_w/\text{Power}$
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:** $V_w/\text{Power} \sim 0.7 \text{ cm}^3/\text{W}$

**Multi-parameter optimization results:**

- **Single module,** $V_w/\text{Power} = 0.09 \text{ cm}^3/\text{W}$
  - Smaller diameters (still commercially available)
  - Higher steam and gas flow rates per tube (but with reasonable $\Delta P$ constraints)

- **Three module design,** $V_w/\text{Power} = 0.05 \text{ cm}^3/\text{W}$
  - 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<sub>e</sub> 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<sub>e</sub> – 2019-2024
  – First trial of underground storage using shaft drilling technology.
• First full-sized system, 100 MW<sub>e</sub>, 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 $15/kWh\text{t}$ 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?