DOE Hydrogen Program

2021 Annual Merit Review and Peer Evaluation Meeting

C-ZERO

Decarbonizing Natural Gas

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Presenter: Fadl Saadi

Binary Chloride Salts as Catalysts for Methane to Hydrogen and Graphitic Powder

DE-EE0008845 AMR#P182

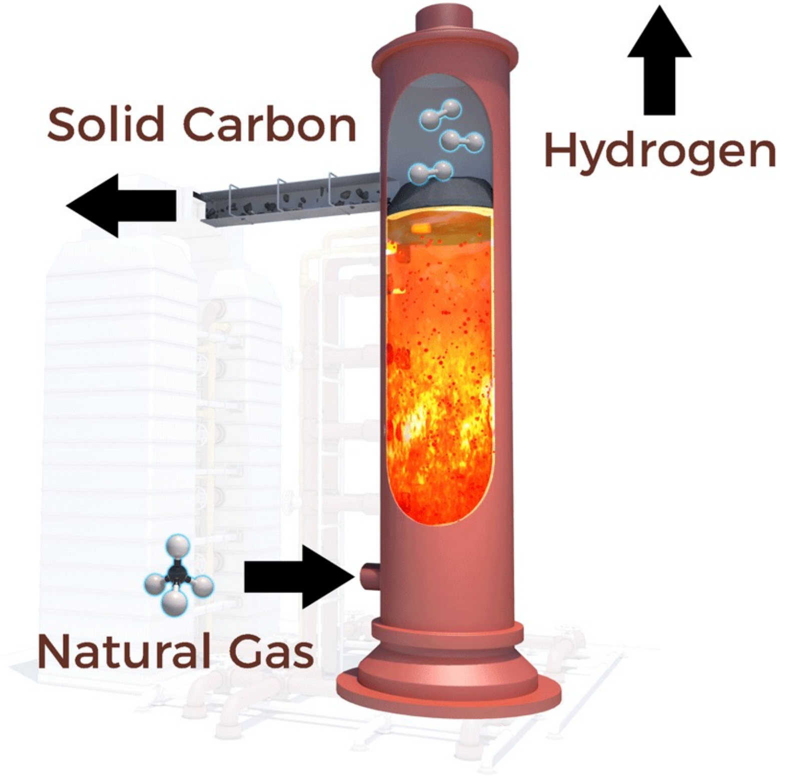
Project Goal & Approach

Idea

Key Challenges

- Carbon Removal
- Carbon Valorization
- Control Carbon
- Reactor Design
- Heat Integration
- Product Gas Cleanup

Goal



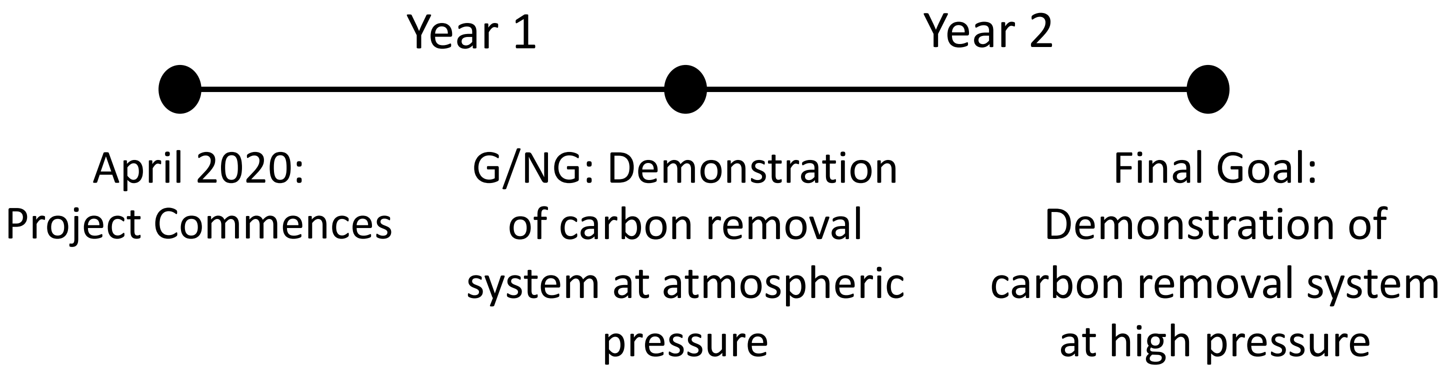
Project Goal: Develop scalable methane pyrolysis process that produces cheap low-emission hydrogen from natural gas

Overview

- Demonstration of stable, active, binary chloride melt system:
  - ≥ 90% H_2 selectivity
  - Graphitic carbon product that has properties favorable for battery anodes and additives
- Design and construct a carbon removal system capable of:
  - High Temperature (1000 C)
  - Continuous carbon removal (≥ 24 hours)
  - High Pressure (≥ 10 bar)

- Total Project Budget: $1.25MM
  - Total DOE Share: $999,878
  - Total Cost Share: $252,000
  - Total DOE Funds Spent*: $261,562
  - Total Cost Share Funds Spent*: $101,933

  * As of 02/28/2021



Team & Collaborators

UCSB

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Potential Impact

Project Goal: Demonstrate scalable methane pyrolysis process capable of carbon removal and valorization

Project Targets:

- Demonstration of stable, active, binary chloride melt system
- Design and construct a carbon removal system

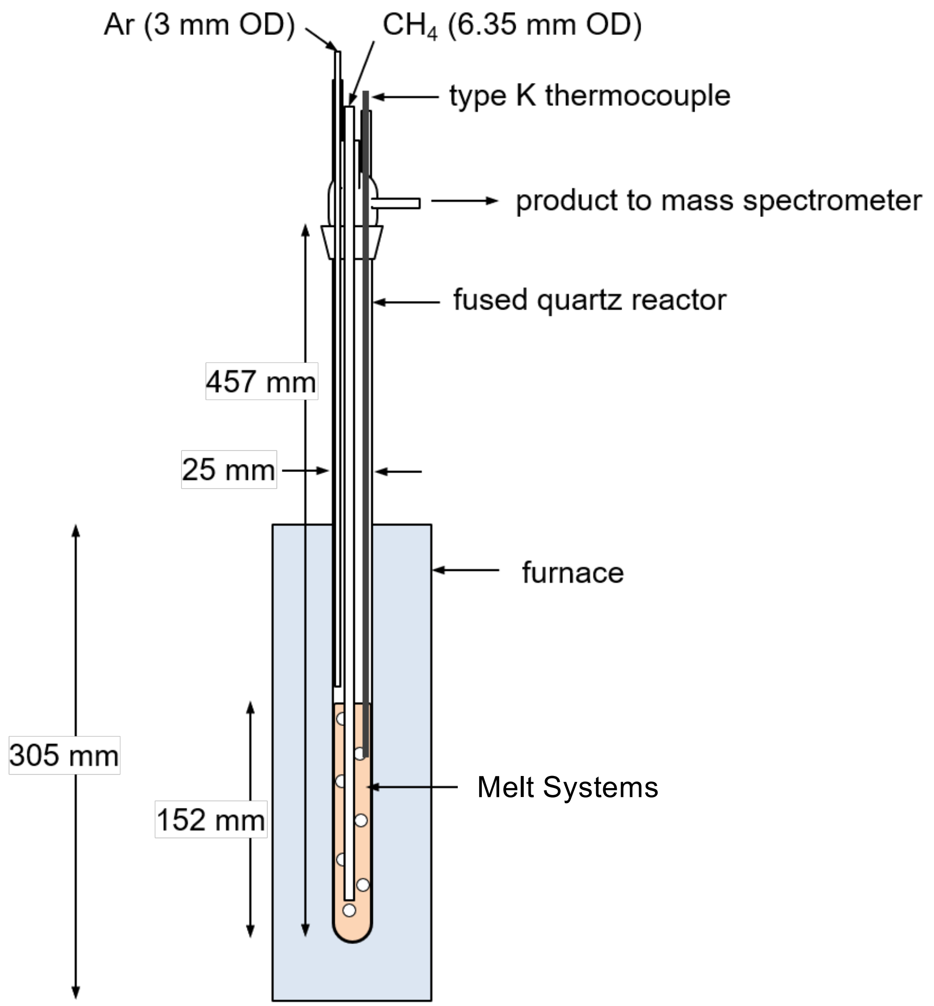
DOE Goal: Low-CO_2 emission Hydrogen <2 $/gge

Potential Impact

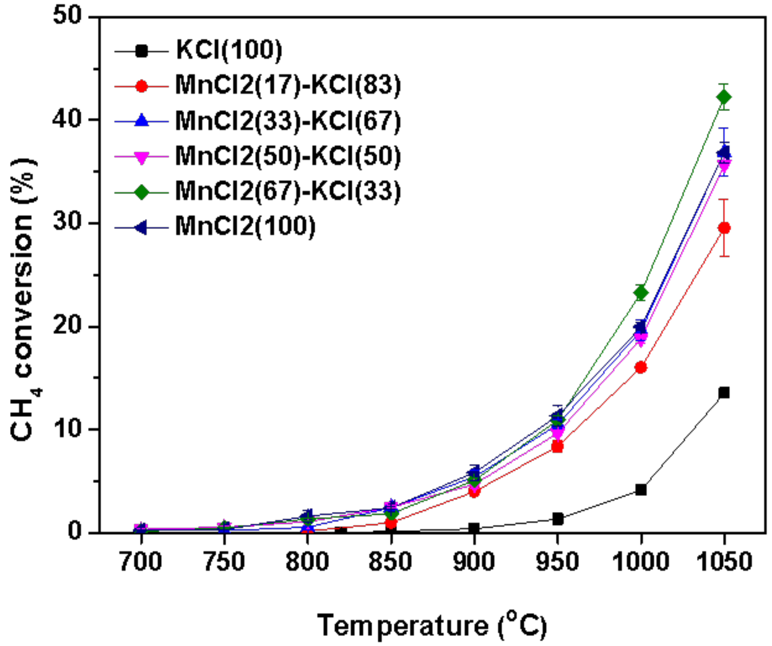
- 75+% reduction in CO_2 emission from hydrogen production from natural gas
- Ability to do 'carbon sequestration' in locations that are not amenable to CO_2 sequestration
- Provide employees with expertise in the oil & gas space opportunities to work on clean energy technologies

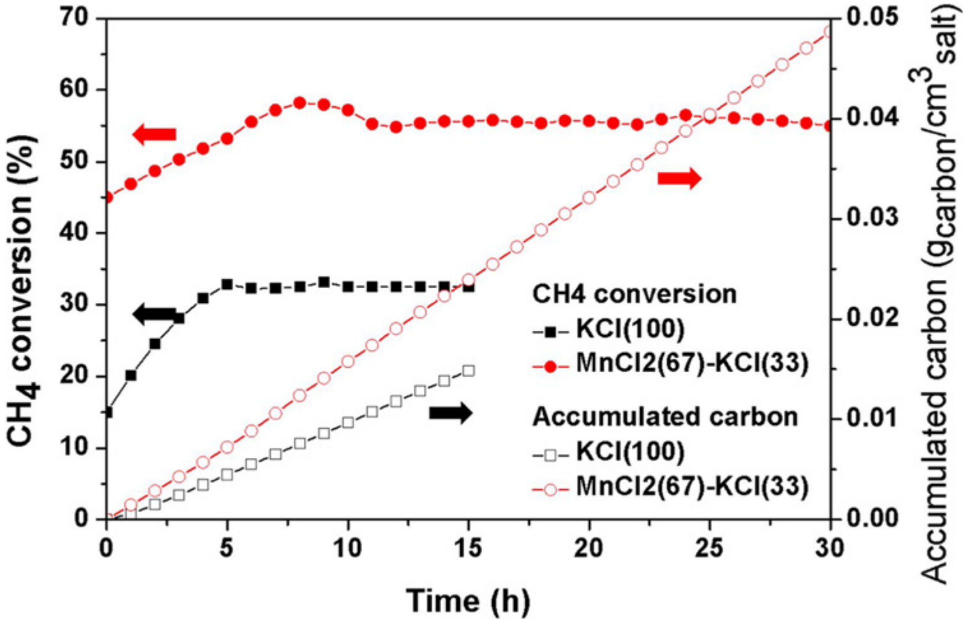
Melt System Activity Apparatus (Task 1)

- An apparatus for quantifying methane conversion to H_2 and solid carbon in a continuously-operating bubble column reactor was constructed and calibrated.
- The reliability of the apparatus for quantifying reaction rate parameters was verified using molten KCl as a test system.



MnCl2-KCl Activity (Task 1)





- Certain binary chloride salts show high catalytic activity for methane pyrolysis
  - Prolonged catalytic activity demonstrated (>24 hours)
- Activity of $MnCl_2$-KCl correlates to tetrahedrally coordinated $MnCl_4^{2-}$ molecular ion
- Surface mediated deep dehydrogenation demonstrated by isotope exchange

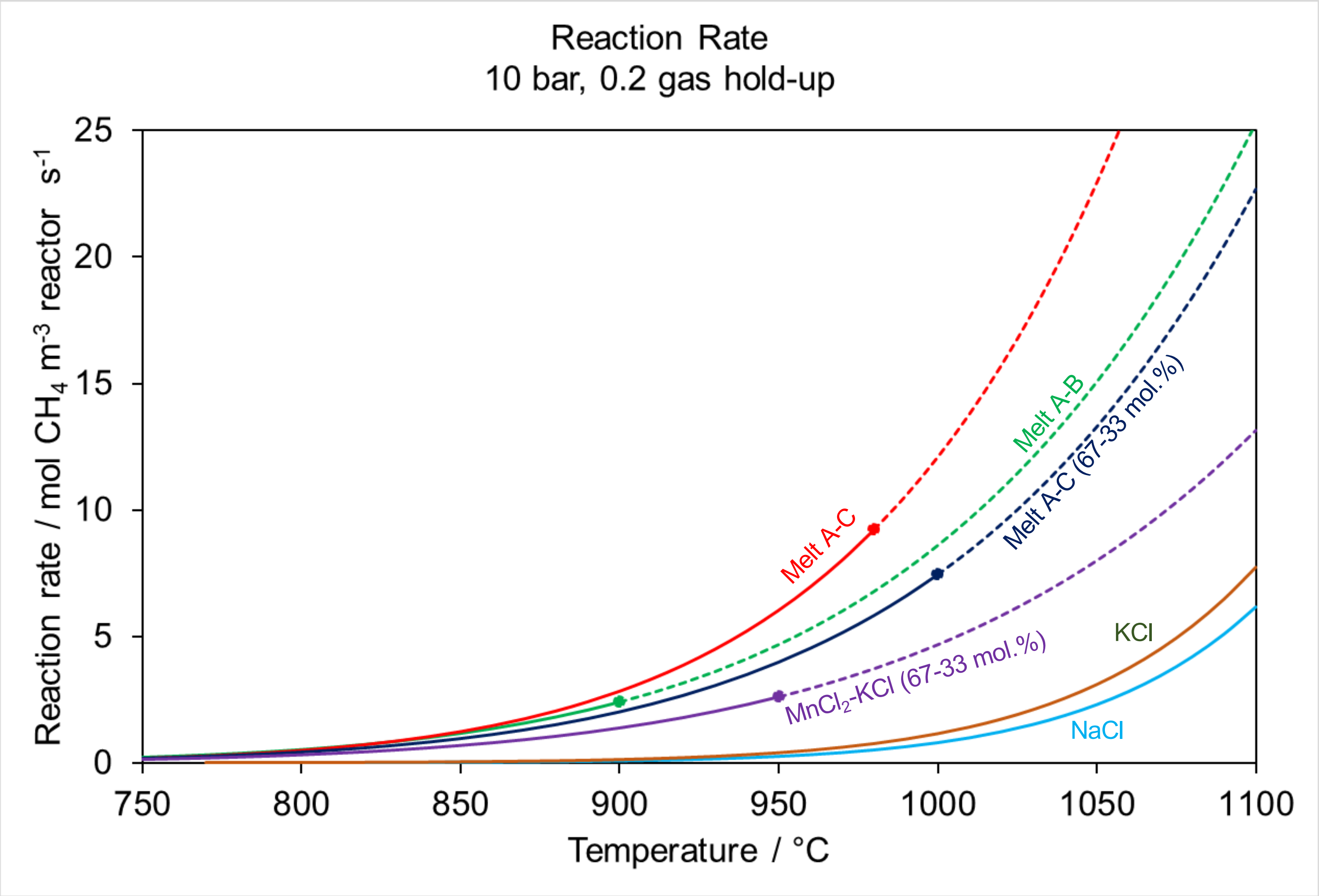
Novel binary salt systems (Task 1)

- A computational survey, using optimized thermodynamic solution models, of the phase stability and vapor pressures of Lewis acidic (catalytic) binary and ternary molten chloride salt systems was done to guide melt composition selection.
- New binary melt systems were identified as a promising and experimentally verified
- Calculated pseudo-first-order rate parameters:
- Accomplishment: Catalytic activity greater than milestone goals (<250 kJ/mol)

Composition	Temperature Range (°C)	Activation energy, E_a (kJ/mol)	Pre-exponential factor, k_0 (s^{-1})	ln(k_0) error
50-50 mol.% **Melt A-B**	700 - 900	168 ± 5	3.4×10^6	± 0.6
50-50 mol.% **Melt A-C**	700 - 980	190 ± 5	4.0×10^7	± 0.6
67-33 mol.% **Melt A-C**	700 - 1000	172 ± 4	4.7×10^6	± 0.4

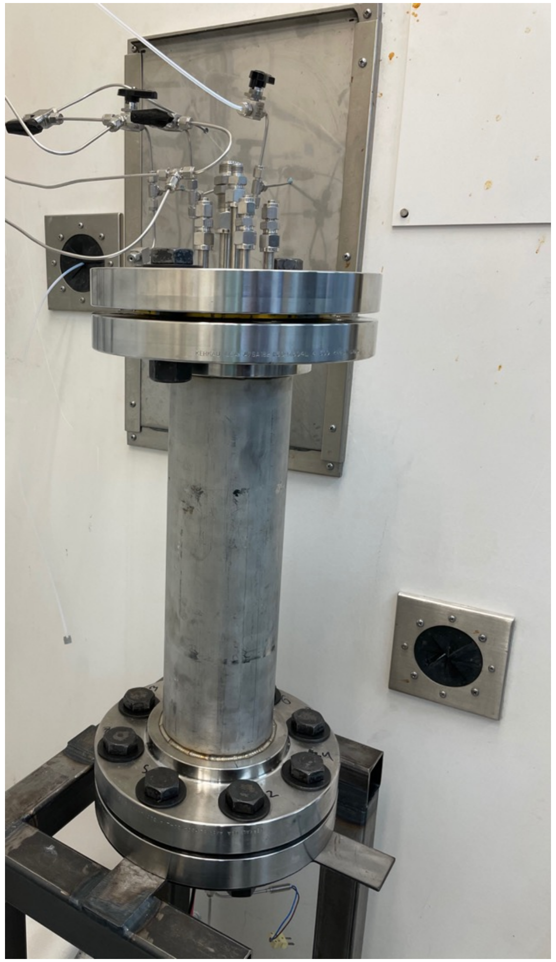
Melt System Comparison (Task 1)

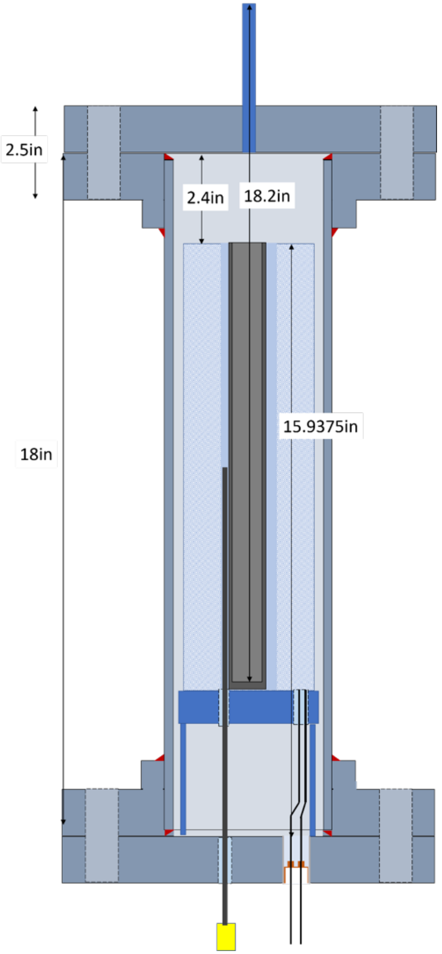
- Parameters
  - 10 bar pressure
  - 0.2 gas holdup
- Novel melt systems exhibit high CH_4 conversion rates
- Achieved Task 1 target metric



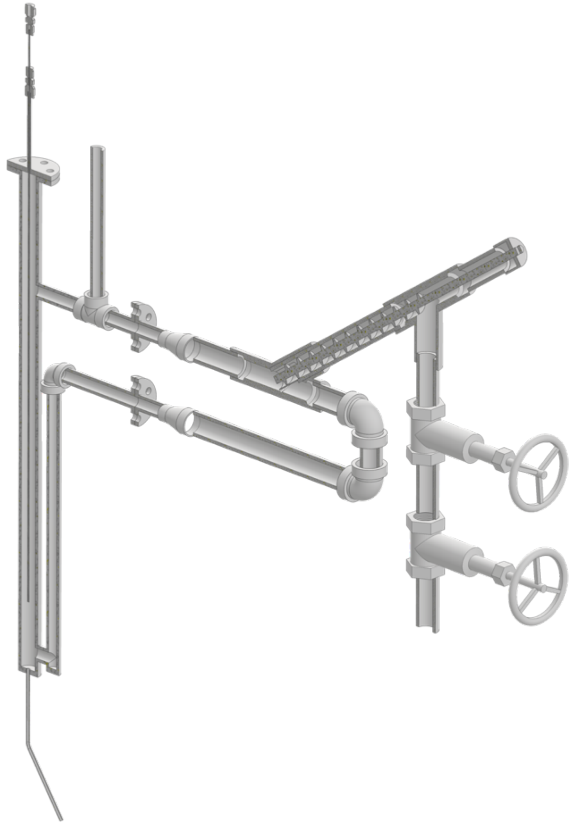
Fabrication and Testing of High Pressure Reactors (Task 1)

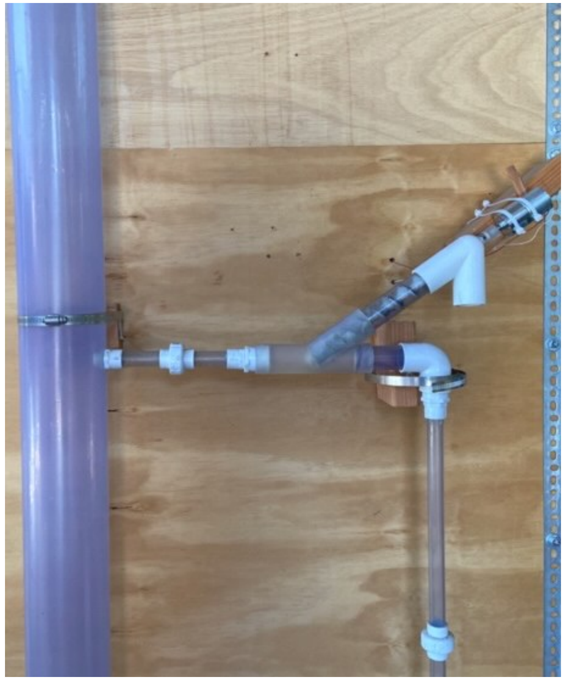
- Internally heated metal reactor fabricated in order to test systems at high pressure
- 1” dia fused quartz crucible with molten salt
- Vacuum/purge and pressurization with Ar gas
- Reactor was operated at 100-200 mL/min CH_4 flow at 17.7 bar (256 psig) and 1050-1100 C.
- The reactor functions as intended; wall temperature remains low enough under forced air cooling (<200 C) to allow for safe operation at >1100 C, 20 bar.
- Accomplishment: Operate molten salt system at High Temperature and Pressure

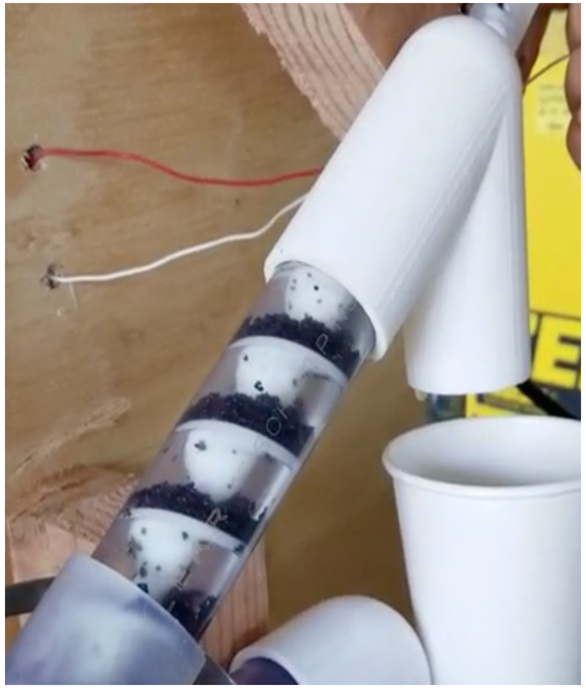




Carbon Removal via Screw Auger (Task 2)

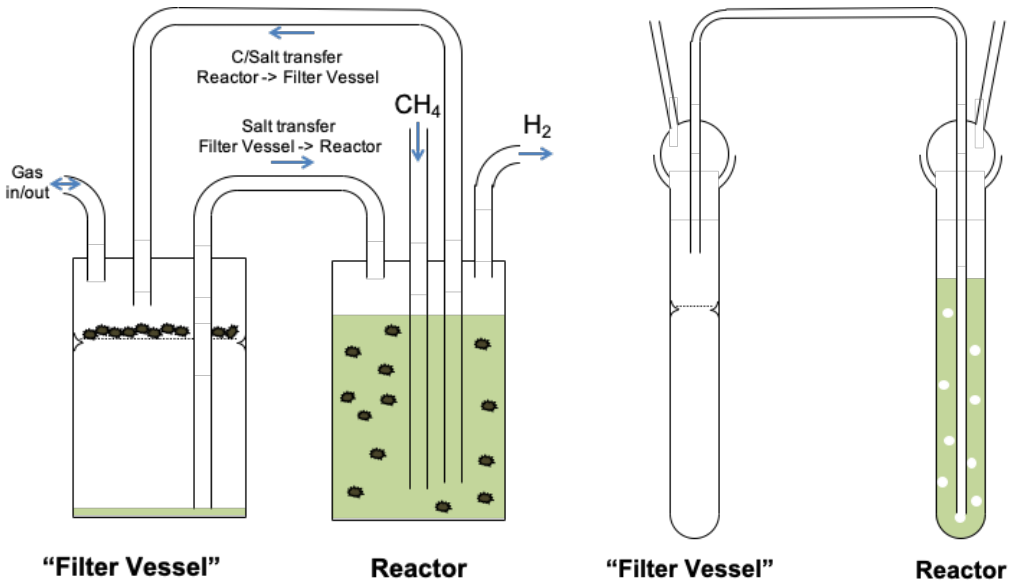


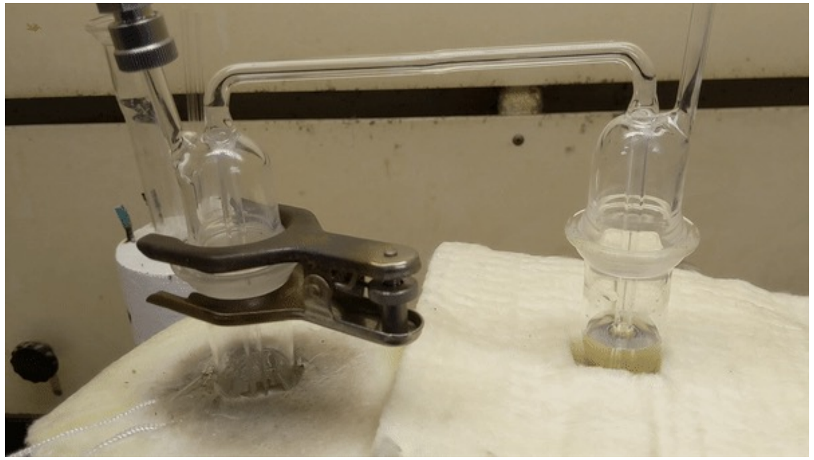


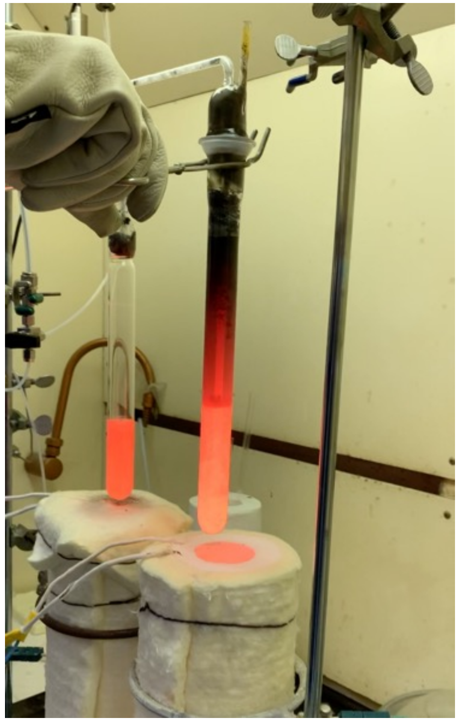


- Tested several different solid removal processes in room temperature aqueous systems
- Screw auger systems are used in waste management to remove solids from liquid media
- Accomplishment: Successfully removed carbon analog from aqueous system (~500 g/hr)

High Temperature Carbon Transfer (Task 2)



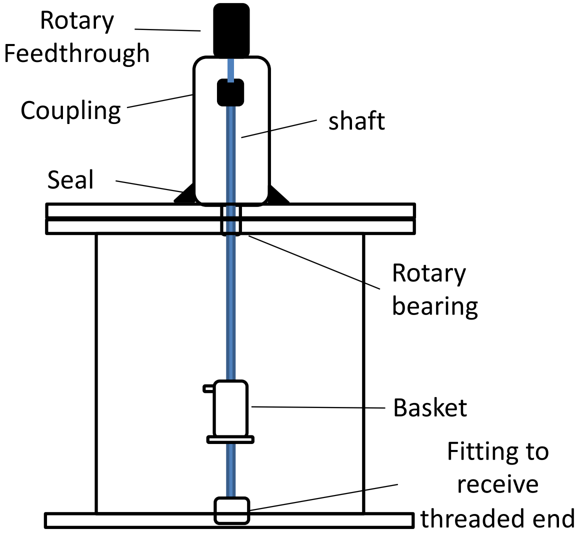




- Analyzed a semi-batch process to separate the solid carbon from the molten salt
- Allows for isolation of the filter cake and subjecting the filter cake to normal or reduced pressure evaporative drying
- Accomplishment: Successfully demonstrated in a high temperature molten salt system

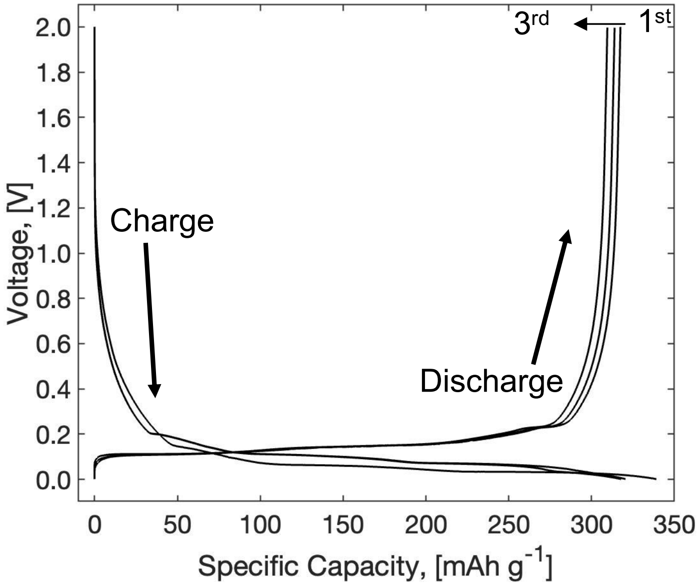
Centrifugal System (Task 2)

- A centrifugal removal system could allow for a removed carbon filter cake that is less 'wet' with salt.
- A filter centrifuge test apparatus was constructed and tested at high temperature up to 150 G's
- Salt content in carbon significantly reduced

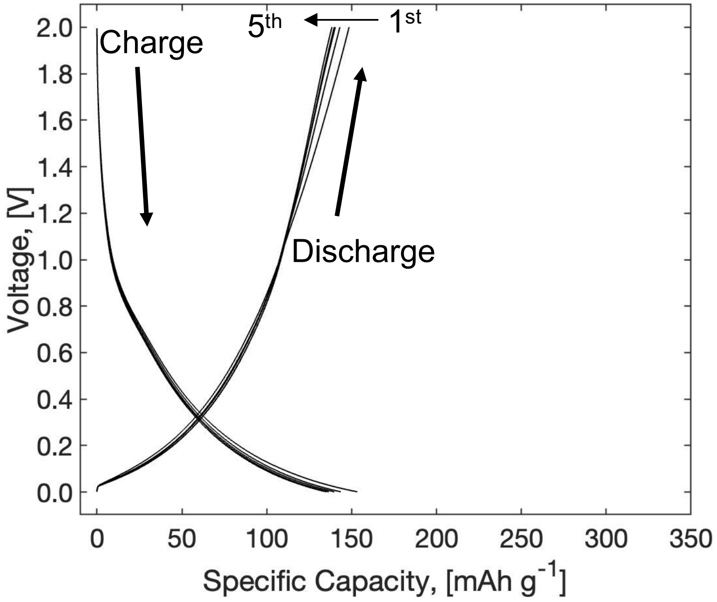


Electrochemistry Data for the Carbon (Task 4)

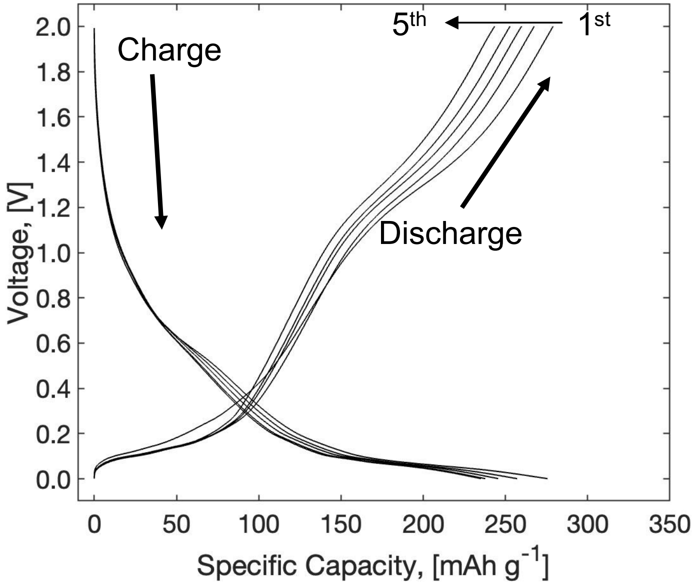
Commercial Graphite



Carbon produced with KCl at 1000 °C



Carbon produced with $MnCl_2$-KCl at 1000 °C



	Commercial Carbon	KCl Carbon	$MnCl_2$ Carbon
First discharge capacity	~315 mAh/g	~148 mAh/g	~279 mAh/g
Second charge coulombic efficiency	~99%	~93%	~97%
Capacity retention after 5 cycles	--	~93%	~87%

- $MnCl_2$ carbon more graphitic, as evidenced by electrochemical plateau below 0.2 V characteristic of Li^+ intercalation into graphite.
- $MnCl_2$ carbon shows potential to be used as an anode material for lithium-ion batteries.

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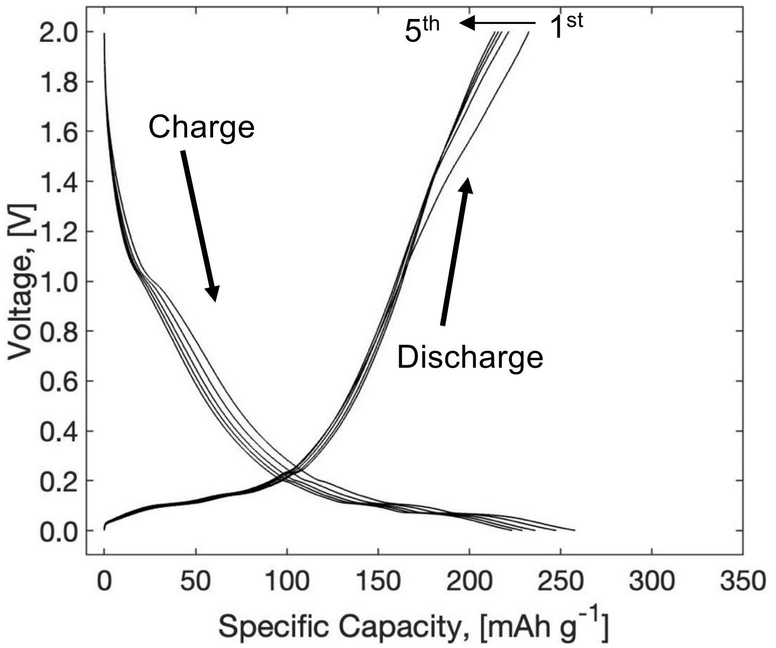
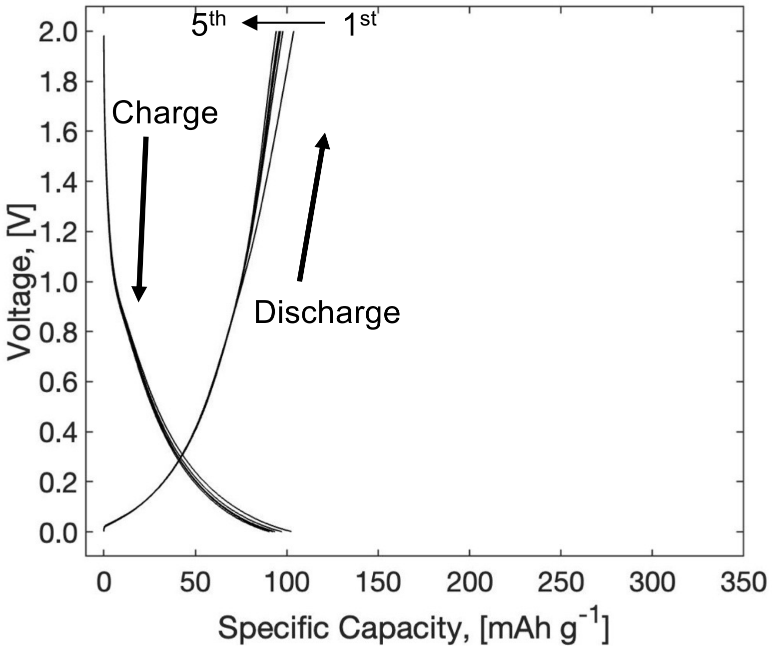
Electrochemistry Data for the Carbon (Task 4)

Carbon produced with 3 wt% $FeCl_3$ in KCl at 1000 °C



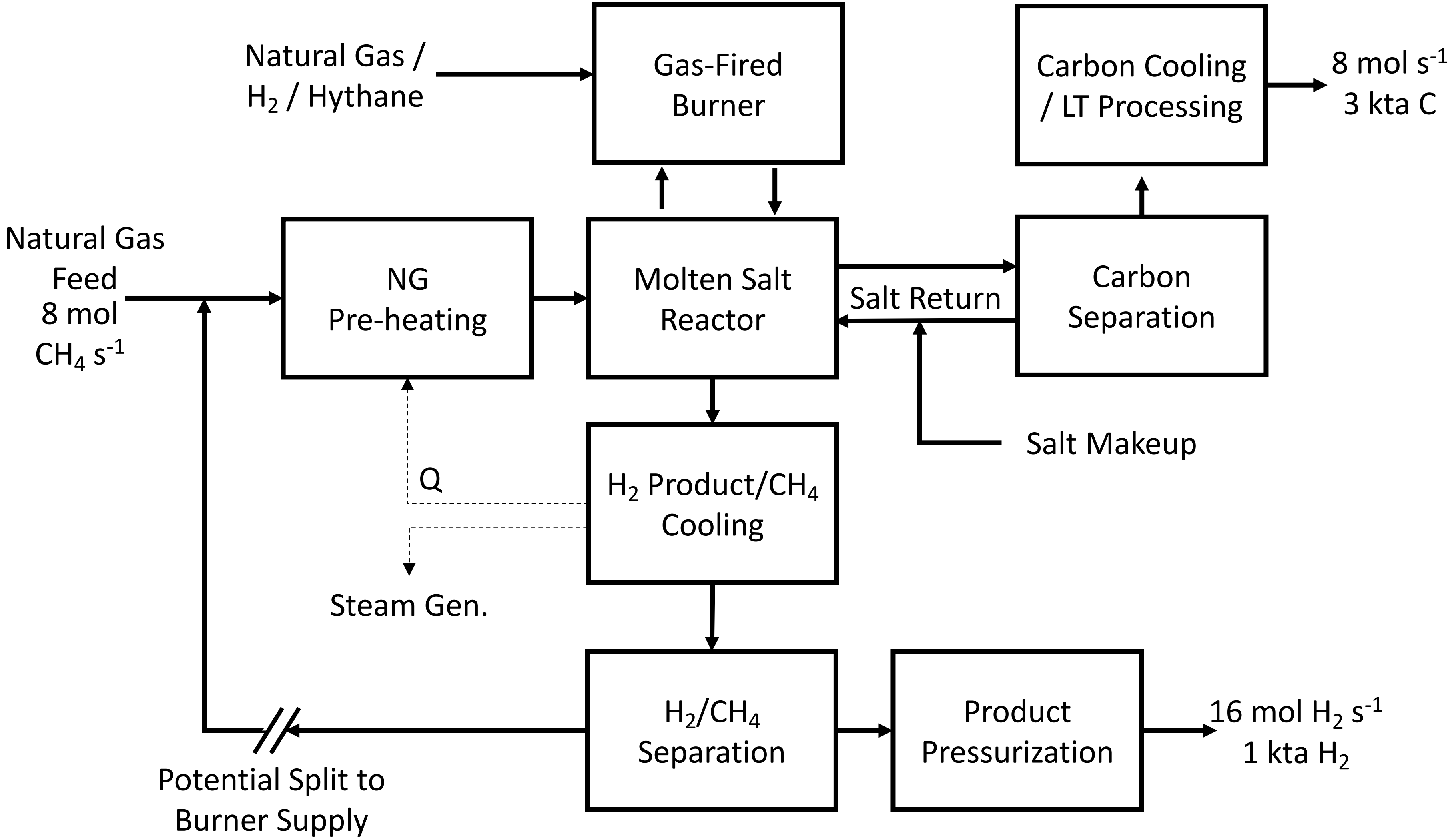
Carbon produced with NaBr at 1000 °C



	$FeCl_3$ Carbon	NaBr Carbon
First discharge capacity	~233 mAh/g	~104 mAh/g
Second charge coulombic efficiency	~86%	~95%
Capacity retention after 5 cycles	~92%	~91%

- NaBr carbon exhibits less reversible capacity and a higher average Li^+ intercalation potential: not optimal for lithium-ion battery applications.
- $FeCl_3$ carbon exhibits graphitic Li^+ intercalation features: good for lithium-ion battery applications.
- Electrochemistry from these four carbons (KCl, $MnCl_2$, $FeCl_3$, NaBr) seems to indicate that the presence of multivalent molten salt cations enhances graphitization.

Flow-Sheet – 1 KTA H_2 (Task 5)



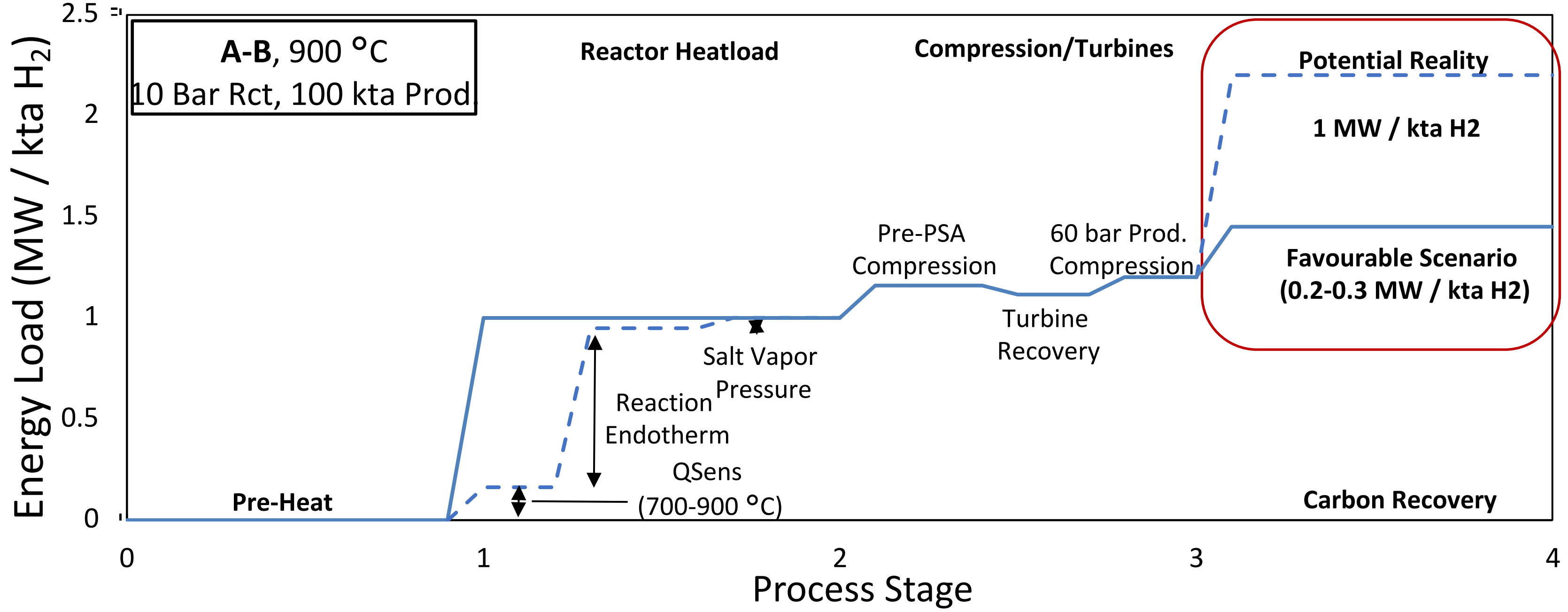
Task 5 Update System-Wide Energetics Modelling

100 KTA H_2 Production

Key Process Assumptions:

- ASPEN Plus V10
- 10 Bar Reactor Pressure (variations 5-30 bar);
- Reactor Operating Temperature of 900 °C;
- PSA Pressure 24 bar, H_2 product compressed to 60 bar (52% isentropic eff.);
- Single-pass CH_4 conversion of 80%, recycled CH_4 (and unseparated H_2) burned to supply Q_{rct} (H_2-fired options part of future work);
- Flow-sheet maximises high-pressure steam generation for turbine-work recovery;
- CO_2-equivalent footprint accounts for burner-eff. and electrical footprint process-wide

Task 5: A-B Melt, 10 Bar P, 100 KTA H_2



Key Points

- 700 C RCT Feed T, 900 C Op., 80% CH_4 single-pass conv.;
- PSA Feed Pres. 24 bar, 60 Bar H_2 Prod. Pressure

Takeaways

- Reactor Q_{Sens} and Q_{endo} account for overwhelming majority of energy required;
- Compression/Turbine work is essentially neutral - Higher P operation helps
- Carbon separation cost critical to reducing energy requirements

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Responses to Previous Year's Reviewer Comments

This project was not reviewed last year.

Proposed Future Work

- Task 1: Investigation of catalytic melt activity for the synthesis of carbon products
  - Measure stability of catalytic melts for >24 hours
- Task 2/3: Fabrication of high pressure carbon removal system
  - Demonstrate carbon removal system capable of operation at 1000 C and 10 bar for > 24 hours
- Task 4: Analysis of carbon for battery and additives usage
  - Test carbon produced for both battery anode use as well as for cement additives
- Task 5: Technoeconomic Analysis (TEA), Process Modelling, and Customer Discovery
  - Update and refine Aspen model as process goes on with the goal of a process showing < 2 $/gge hydrogen production and carbon production cost < 1 $/kg

Any proposed future work is subject to change based on funding levels

Summary

- Task 1: Identified novel Lewis acidic (catalytic) binary and ternary molten chloride salt systems and showed them to be highly active for methane pyrolysis
  - Achieved target of $E_a < 250$ kJ/mol

- Task 2: Constructed and tested several different carbon removal methods for methane pyrolysis
  - Work on high pressure systems also commenced with reactors operating at >15 bar

- Task 4: Analyzed several different carbons produced via methane pyrolysis for use as li-ion battery anodes
  - Significant differences in activity observed depending on molten chloride catalyst used with $MnCl_2$/KCl and $FeCl_3$/KCl systems

- Task 5: Modelled total system energy costs and determined critical steps that require energy optimization
  - Carbon separation cost critical to reducing energy requirements

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Decarbonizing Natural Gas

Thank You!

Technology Transfer Activities

- C-Zero is working on the design and commercialization of its methane pyrolysis technology
- C-Zero plans to complete the full design of the commercial reactor by 2022
- Current goal is engaging with potential customers to better understand their needs and requirements and identifying the optimal first market. We are interested in talking to:
  - Operators of natural gas turbines (combined and simple) for electricity production
  - Refinery operators (especially in California)
  - Current hydrogen generators
  - Existing customers of hydrogen and natural gas

Production Unit

6000 kg H_2 / day
10 MW Thermal

Progress toward DOE Targets or Milestones

Milestone Update		
Task	Project Milestones	Progress Notes
1	Identification of bimetallic salts with high activation energy for methane pyrolysis (Activation energy < 250 kJ/mol)	New catalysts identified that have targeted catalytic activity.
2	Demonstration of a plastic model of a carbon removal system at room temperature and pressure (>100 g/hr)	Several carbon analog removal systems have been built and tested at ~500 g/hr rate
	Demonstration of working carbon removal prototype operating at reaction conditions	First carbon removal prototype demonstrated at methane pyrolysis reaction conditions showing successful carbon removal
4	Optimization of carbon for battery anode applications	Carbons from different molten salt systems tested for activity in Li-ion cells with significant differences in activity showing importance of reaction conditions in carbon morphology
5	Process model for C-Zero process	Process energetics studied with carbon removal identified as a key process to minimize both energy use and CO2 emissions