Molten-Salt Methane Pyrolysis Optimization Through in-situ Carbon Characterization and Reactor Design

Fabrication & demonstration of a high temperature, high pressure molten salt methane pyrolysis reactor.

| Total project cost: | $2.3M |
| Length             | 24 mo. |

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

Production and continuous removal of graphitic powder from a molten salt methane pyrolysis reactor.

| Total project cost: | $1.2M |
| Length             | 24 mo. |

Eric McFarland, C-Zero

Additional team members in attendance: Zach Jones, Sam Shaner, Fadl Saadi
Molten-Salt Methane Pyrolysis Optimization Through \textit{in-situ} Carbon Characterization and Reactor Design

\textbf{C-Zero LLC (Santa Barbara, CA), Prof. Eric McFarland}

\textbf{EXECUTIVE SUMMARY}

C-Zero is requesting assistance in its effort to commercialize a novel process for transforming methane into hydrogen and valorized carbon cement additive using high temperature liquids in a multi-phase pyrolysis reactor. ARPA-E support is requested to allow C-Zero to better understand and control the methane decomposition and carbon formation processes as well as model and demonstrate an optimized methane pyrolysis prototype. This will assist C-Zero in de-risking its process sufficiently to attract the additional private sector capital required for commercialization.

In particular, the proposed work will allow C-Zero to:

1. Monitor and control the molecular and morphological structure of the carbon formed during the methane pyrolysis process
2. Identify reaction parameters that generate structural carbon that can be used as additives in cement

\textbf{NOTICE OF RESTRICTION ON DISCLOSURE AND USE OF DATA}

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The Team

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Board Chair, CTO

Prof. Ches Upham
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Arnie Smith
Fluor, Executive Director of Process Engineering

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December 8, 2019

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Fluor, Executive Director of Process Engineering

Philip Grosso
Kaiser Chemicals, Former Vice President
Lab & Setup
Objectives for ARPA-E Project

- Demonstrate in-situ spectroscopic measurements of carbon formation under methane pyrolysis reaction conditions.

- Design and construct a 10 liter methane pyrolysis molten salt reactor with:
  - $\geq 70\%$ CH$_4$ conversion
  - $\geq 90\%$ H$_2$ selectivity
  - $\geq 5$ mol H$_2$/m$^3$s
  - $\leq 2.5\%$ wt salt in carbon product
  - High Pressure ($\geq 5$ bar)

Begin Project 2020 G/NG: Demonstration of 10 liter reactor at atmospheric pressure

Final Goal: Demonstration of 10 liter reactor at high pressure 2021
Objectives for H₂@Scale Project

- Demonstration of stable, active, binary chloride melt system:
  - ≥ 90% H₂ 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)
Liquid metal catalysts showed very high activity for methane pyrolysis.

*Ab initio* molecular dynamics calculations support activation of host (Bi→Bi⁺) by the electrophile (Ni→Ni⁻).

Carbon purity and catalyst recovery costs were identified as technical and economic challenges.
Liquid Catalysts: Simple Salts

Monovalent salts have similar activities and produce similar disordered carbon

Experiments in excellent agreement with gas-phase, radical mediated kinetic pathway
Liquid Catalysts: Binary Salts

- Certain binary chloride salts show high catalytic activity for methane pyrolysis
  - Prolonged catalytic activity demonstrated (>24 hours)
- Activity of MnCl₂-KCl correlates to tetrahedrally coordinated MnCl₄²⁻ molecular ion
- Surface mediated deep dehydrogenation demonstrated by isotope exchange
High hydrogen selectivity (>98%) at 40% methane conversion

Graphitization of carbon in MnCl2-KCl significantly higher compared to KCl
  – Indicative of carbon formation on the catalytic surface

Moving Forward: Further investigation of binary chloride salts focused on identifying melt systems that are:
  – Highly catalytic
  – Produce graphitic carbon
  – Low cost and non-toxic
Carbon nucleation and growth on the surface of the molten salt, 1000 C
Direct Visualization of Carbon Deposition on Salt Surfaces

- Insulating properties of molten salts allow for direct imaging of methane pyrolysis and carbon formation.
- Moving Forward: Extend apparatus capabilities for \textit{in situ} spectroscopic analyses of molten salt during methane pyrolysis by Raman, IR, and UV/Vis.
  - Help elucidate pyrolysis mechanisms for different systems.
  - Allow for rational design of reaction conditions for optimized hydrogen and specific carbon production.
Reactor Modeling & Design

› Constructed aqueous circulating fluid bubble column of sufficient size to avoid wall/entrance effects.
› Evaluated multiple gas sparger designs.
› Moving Forward: Continue building Eulerian multiphase CFD model to enable a verified predictive capability for building and scaling up methane pyrolysis bubbly flow reactor. Construct model system with continuous solid particulate removal capabilities.
Challenges and Potential Technical Partnerships

- Biggest challenge to date has been the generation of a clean carbon product
  - Metal contamination was a major issue early on
  - Moved to molten salt catalysts which have the advantage of:
    • Lower catalyst cost
    • Ability to tune carbon morphology
- Another challenge is identifying suitable materials of construction (MOC)
  - Designing rapid MOC testing of several different potential materials.
- Looking for technical partnerships with entities that have expertise in carbon modification and characterization
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.

We are looking for partnerships/collaborations with:
- Current consumers of natural gas
- Experts in delayed cokers
- Hydrogen producers and consumers
- Refineries (especially in California)