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2019 DOE Hydrogen and Fuel Cells Program Review:

Methane Pyrolysis for Base-Grown Carbon Nanotubes and CO_2-free H_2 over Transition Metal Catalysts

James AC McDermott (PI, C4-MCP, LLC)
Robert Dagle (co-PI, PNNL)
Jianli (John) Hu (co-PI, WVU)
Ron Kent (SoCalGas)

Jamie Holladay (Presenter)

Pacific Northwest National Laboratory
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Project ID
h2045

Overview

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Timeline

- Project Start Date: 4/15/18
- Project End Date: 10/15/20
- Total Project Budget: $2.2M

Barriers

A. Reformer Capital Costs and Efficiency

Reduce criteria and other emissions from H_2 production from natural gas

Target: $2/kg Hydrogen Production

Budget

- Total Project Budget: $2.2M
  - Total Recipient Share: $1.2M (mix of cash & in-kind cost share)
  - Total Federal Share: $1.0M
  - Total DOE Funds Spent*: $370K (as of 3/15/19, includes sub-contract)

Partners

- Pacific Northwest National Laboratory
- C4-MCP, LLC
- Southern California Gas Company
- West Virginia University

Relevance

- **Objective**: Develop a new process for producing **CO_2-free hydrogen** and **solid carbon** from inexpensive and domestically available natural gas and reduce the net production cost of **H_2 to < $2/kg** with the sale of valuable byproduct carbon.
  - Development and use of co-products from hydrogen production
  - Carbon nanotubes produced via "base-growth" versus "tip-growth" mechanism, the conventional technology, offers potential for economic advantage
  - Low cost H_2 production is relevant to H2@Scale

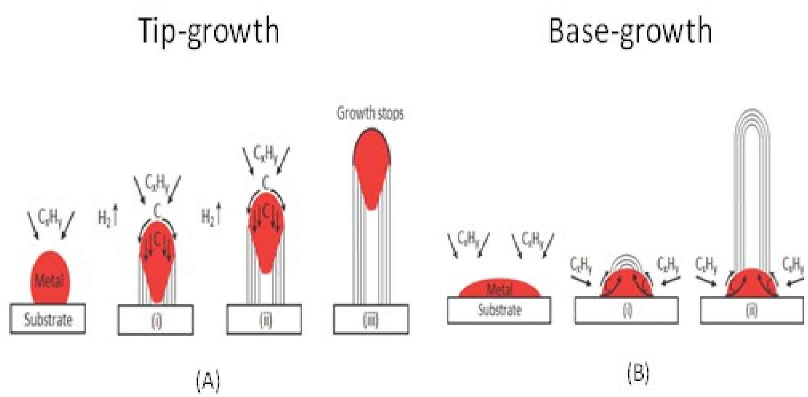

Illustration of (A) tip-growth and (B) base-growth carbon nanotube formation. This technology uses the more desirable base growth process.

Relevance

Market Analysis for Potential Carbon Products

(K= thousand, M= million, MT= metric ton)

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Type of Carbon	Types of Applications	Expected Price for Carbon	Size of the Market (current/ projected)	Corresponding Hydrogen Production[(a)]
Carbon black [79,80,81]	Tires, printing inks, high-performance coatings and plastics	$0.4–2+ /kg depending on product requirements	U.S. market • ~ 2M MT (2017) Global market • 12M MT (2014) • 16.4M MT (2022)	U.S. market • 0.67M MT Global market • 4M MT (2014) • 5.4M MT (2022)
Graphite [82]	Lithium-ion batteries	$10+/kg	Global market • 80K MT (2015) • 250K MT (2020)	Global market • 27K MT (2015) • 83K MT (2020)
Carbon fiber [83,84,85]	Aerospace, automobiles, sports and leisure, construction, wind turbines, carbon-reinforced composite materials, and textiles	$25–113/kg depending on product requirements	Global market • 70K MT (2016) • 100K MT (2020)	Global market • 23.3K MT (2016) • 33.3K MT (2020)
Carbon nanotubes [86,87]	Polymers, plastics, electronics, lithium-ion batteries	$0.10–600.00 per gram depending on application requirements	Global market • 5K MT (2014) • 20K MT (2022)	Global market • 1.7K MT (2014) • 6.7K MT (2022)
Needle coke [88]	Graphite electrodes for electric arc steel furnaces	~$1.5/kg	Global market • ~1.5M MT (2014)	Global market • ~0.50M MT (2014)

(a) Based on stoichiometric ratio of carbon to hydrogen present in methane. Does not take into account process efficiency or use of hydrogen to provide process heat or loss of hydrogen during hydrogen recovery.

Opportunity to produce valuable solid carbon co-products with market size(s) commensurate with hydrogen production

R. Dagle et al. "R&D Opportunities for Development of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products", Technical Report, PNNL-26726, ANL-17/11, 2017.

Approach

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- **Background**: West Virginia University reported a promising new catalyst innovation for methane conversion to CO_2-free H_2 and solid carbon nanotubes
  - Produced via "base growth" mechanism offering potential for catalyst regenerability and high carbon product purity
- **Approach**: Build upon this prior research and:
  - Improve catalyst design
  - Develop the reactor engineering enabling a commercially viable process technology
  - Understand the produced carbon characteristics and market potential
  - Evaluate the overall techno economics

Date	Milestones	Completed
7/15/2018	Set-up methane pyrolysis experimental test stand apparatus, develop test protocol, and obtain required experimental testing permits.	✓
10/15/2018	Evaluate at least 10 different catalysts and select candidate formulation with highest conversion for harvesting and characterization studies. Report on ability to achieve >50% single pass conversion.	✓
1/15/2019	Determine catalyst regeneration and preliminary harvesting protocol conditions. Target at least 5 regeneration cycles, and with <10% activity loss if possible.	✓
4/15/2019	Characterize candidate catalysts using a least 3 techniques (e.g., TEM, TPR, and BET) in order to better understand reaction mechanism.	
7/15/2019	Characterize at least three carbon products produced from candidate catalyst(s) using at least 3 techniques to understand materials properties.	
10/15/2019	Update TEA to determine process efficiency and CAPEX and OPEX cost. Report on ability to achieve a projected H2 cost <$2/kg at a 25 kg/day scale.	

Baseline Catalyst Developed for Methane Pyrolysis

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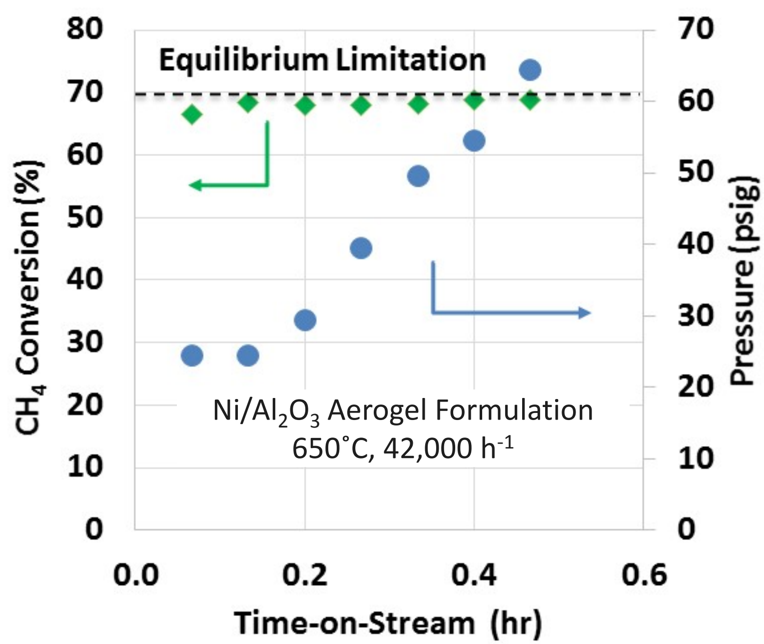
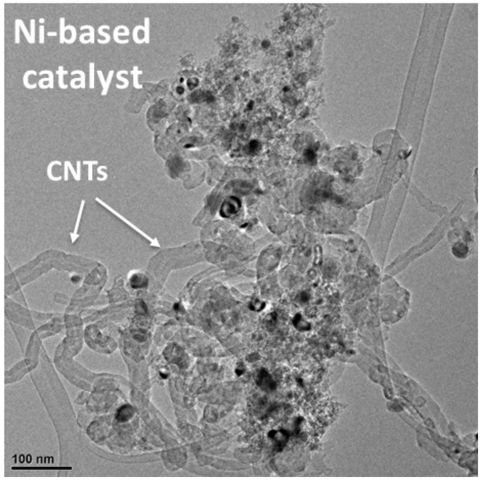
- Ni/Fe/Co metal and bimetallic catalysts evaluated for methane pyrolysis
  - Metal constituency key catalyst design variable
- Ni-based catalysts are the most active and selectivity towards CNT selectivity
  - > 20 catalyst formulations evaluated using microscale packed bed reactor

Microscale Packed Bed Reactor Studies (0.1 SLPM Scale)





Ni/Al_2O_3 catalyst prepared via aerogel synthesis technique has the highest activity and CNT selectivity

- Baseline catalyst under further evaluation with fluidized bed reactor operation and carbon harvesting studies

Accomplishments and Progress
Methane Pyrolysis Studies Initiated Using Bench-Scale Fluidized Bed Reactor System Recently Commissioned

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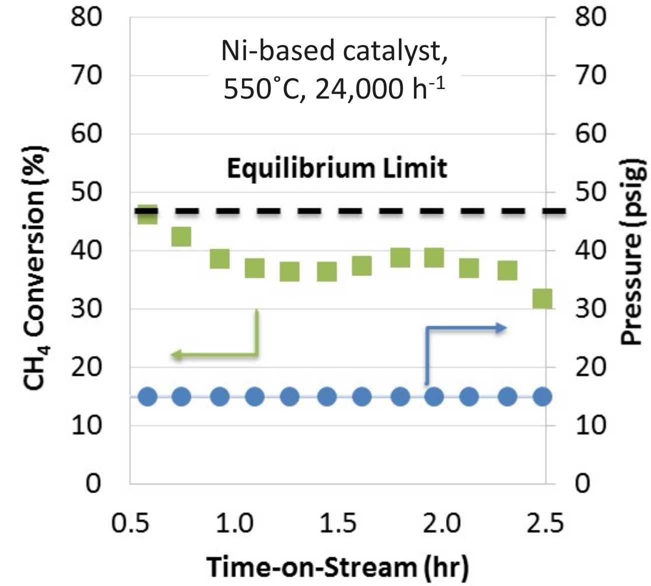
- Objective: Evaluate methane pyrolysis and CNT production and carbon harvesting protocols using research fluidized bed reactor
- Bench-scale (0.5" OD) fluidized bed reactor recently commissioned
- Operation relatively stable for methane pyrolysis (H_2 + C) for 2 hours using Ni catalyst
  - Near equilibrium methane conversion levels achieved
  - No pressure build-up
  - Spent catalyst contained 77 wt.% co-product carbon

Bench-Scale Fluidized Bed Reactor (2 SLPM Scale)

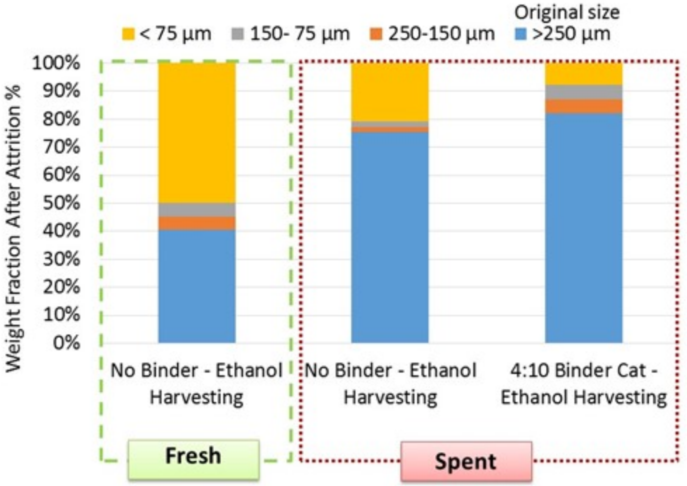


Bench-scale fluidized bed reactor system recently constructed and methane pyrolysis experiments initiated

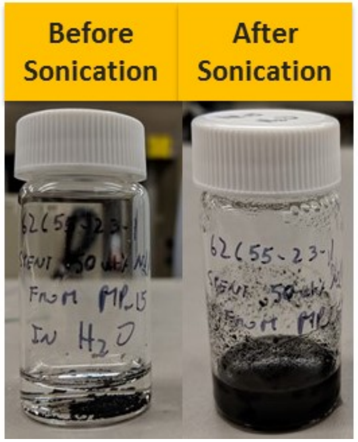
Carbon Harvesting Approaches via Non-Destructive Separation Evaluated

- Separation of solid carbon product and spent catalyst a key challenge; identifying a suitable carbon harvesting protocol is underway
- The use of binders improves attrition resistance of fresh and spent catalysts during carbon harvesting
- Separation using basic solvents (e.g. ethanol) followed by filtration maintained catalyst integrity, however, resulted in minimal carbon/catalyst separation

Carbon Harvesting Studies



On Catalyst (>250 µm)		After Harvest (>250 µm)	
Before Reaction	After Reaction	In H_2O	In Ethanol
Ni: 45 wt% C: 0 wt%	Ni: 19 wt% C: 69 wt%	Ni: 5.3 wt% C: 85 wt%	Ni: 6 wt% C: 83 wt%



Carbon harvesting studies evaluated, however, a protocol for carbon separation, while maintaining catalyst integrity, not yet suitable
- Now evaluating more severe acid wash approaches

Carbon Harvesting Method Identified for Carbon Removal and Regeneration of Catalyst

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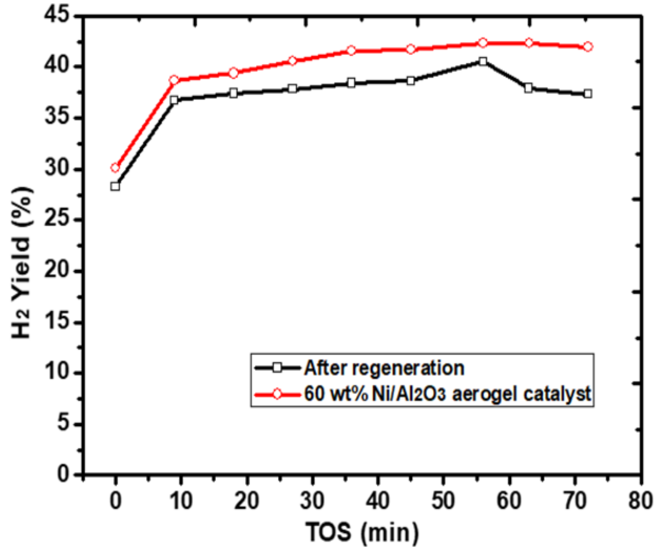
- Protocol for carbon harvesting identified
- Catalytic activity restored after full catalytic cycle
- Method enables restoration of catalytic activity, however, subsequent purification of solid carbon product still required
    - Future work item



Methane Pyrolysis
650˚C, 42,000 h^{-1}

Carbon harvesting method identified that enables restoration of catalytic activity after methane pyrolysis
- Additional purification of carbon product still required

Accomplishments and Progress

Process Model Developed and Performance Metrics Established via Technoeconomic Analysis

- Process performance models developed using commercial flow-sheeting software (Aspen Plus)
  - Supplied the heat and material balances needed to estimate production costs
- Fluidized bed reactor-based process modeled at different scales and assumed performances
- To produce H_2 at $2/kg, and assuming target performance metrics can be met, the required solid carbon co-product target selling prices range:
  - 4-10 $/kg carbon ➔1500 kg/day H_2 scale
  - 0.3-1 $/kg carbon ➔ 100,000 kg/day H_2 scale

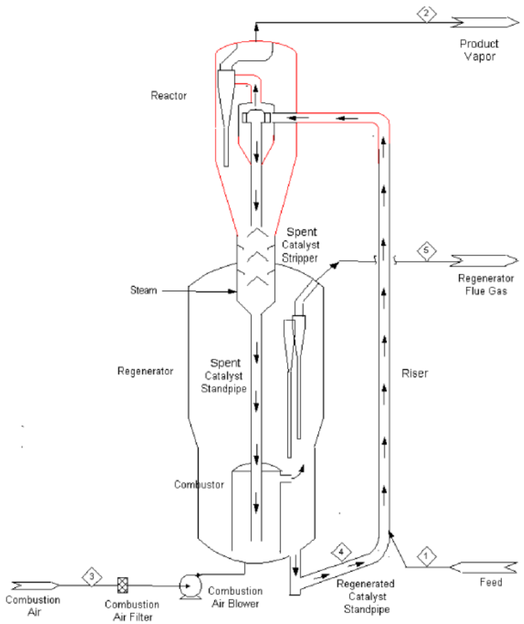


FIGURE 1-2 SMALL SCALE FCC DESIGN

<u>Market prices* (for comparison):</u>

- CNT: >$50/kg (price depending on application and purity)
- Needle coke: $1.5/kg

Detailed techno economic modeling performed, providing target performance metrics and resulting co-product selling prices necessary for achieving $2/kg H_2 production

* R. Dagle et al. "R&D Opportunities for Development of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products", Technical Report, PNNL-26726, ANL-17/11, 2017.

Collaboration & Coordination

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Partner	Project Roles
C4-MCP, LLC	Management lead, project coordination, tech-to-market plan
Pacific Northwest National Laboratory	Techno economic analysis, bench-scale reactor processing, catalyst design, carbon harvesting and characterization
West Virginia University	Catalyst synthesis and performance evaluations, and characterization
Southern California Gas Company	Sponsor, industrial advisor, stakeholder

- C4-MCP, LLC is a company specifically created to commercialize technology for the conversion of natural gas to hydrogen and solid carbon products.
- SoCalCas has a strong interest in using their natural gas infrastructure to mitigate emissions of greenhouse gases (GHG) and local criteria pollutants.
  - California's mandates significant GHG, NO_x, and particulate matter emission reductions.
  - Converting natural gas or biogas to H_2 while simultaneously producing high-value carbon materials as described in this project may represent a cost-effective means of decarbonizing H_2 production.
  - Supporting the use of fuel cells in electric vehicle and distributed power generation markets by providing low-cost hydrogen could substantially reduce, NOx, and particulate emission.

Future Work

- Further improve catalyst design for enhancing selectivity towards base grown CNT formation
- Further develop identified approach for carbon removal and catalyst regeneration and reuse
- Develop processing for purification of carbon product
- Update the flow sheet and process model with updated economic projections

Critical Assumptions

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Assumption	Validation or Mitigation
Carbon harvesting via physical separation/agitation technique is suitable for catalyst/CNT separation (FCC type reactor)	Validation: Evaluate assumption on physical separation feasibility via bench scale reactor experimentation. Mitigation: Evaluate alternative acid wash technique known in the literature to separate CNTs; evaluate impact of additional cost on economics
Value and/or market size of produced CNTs is sufficient to enable favorable economics	Validation: Evaluate techno economics via model. Mitigation: Evaluate upgrading of produced CNTs to more valuable product (e.g., carbon fibers) and assess additional cost in techno economic model
Produced CNTs versus amorphous carbon ratio is high enough to yield sufficient valuable product	Validation: Evaluate techno economics via model. Mitigation: Develop research approach to design catalyst for increased CNT/amorphous carbon product ratio (research execution would likely require additional scope).

Summary

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- **Objective**: Develop a new process for producing **CO_2-free hydrogen** and **solid carbon** from inexpensive and domestically available natural gas and reduce the net production cost of **H_2 to < $2/kg** with the sale of valuable byproduct carbon.
- **Relevance**: H2@Scale project for development and use of co-products from hydrogen production.
- **Approach:** Build upon innovative catalytic material reported at West Virginia University (WVU) and:
  - Improve catalyst design
  - Develop the reactor engineering enabling a commercially viable process technology
  - Understand the produced carbon characteristics and market potential
  - Evaluate the process techno economics
- **Accomplishments**:
  - Catalyst developed with high activity and selectivity towards carbon nanotube production, however, increased selectivity towards "base growth" versus "tip growth" mechanism, which offers potential for catalyst regenerability and high product purity, is still desired
  - Promising carbon harvesting approach identified, however, carbon separation and overall improvements to the process is required
  - Process model developed and performance metrics established via technoeconomic analysis
- **Collaboration:**
  - Pacific Northwest National Laboratory
  - West Virginia University
  - C4-MCP, LLC
  - Southern California Gas Company

Technology Transfer

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- C4-MCP, LLC will be providing technical guidance and at the successful completion of the work may commercialize the technology
- This is a CRADA

Data management plan

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- PNNL will actively protect all intellectual property (IP) and will publish the inventions after patents are submitted.
- All unclassified and non-export controlled data will be published in peer reviewed journals, presentations, and / or publically available reports
  - The journal articles will be sufficiently detailed to enable someone skilled in the field and with similar equipment and set-up be able to replicate the experiments
  - Manuscript metadata will be submitted to OSTI along with a document or link to a publicly accessible, full text version of the accepted manuscript available on an institutional repository.
  - Technical reports, journal article-accepted manuscripts, software, and scientific research datasets may be submitted to OSTI through the DOE Energy Link System: https://www.osti.gov/elink.
- When part of an EMN, consortium, or when a DOE data base is available for a topic (i.e. hydrogen storage materials), we will provide the data to the database per our contracts.
- PNNL has an active data management and electronic storage system so when the project is completed, data, lab notebooks, reports, etc. will be electronically archived and preserved.
- PNNL has an “information release” procedure to review all public release of information (abstracts, presentations, public reports, journal articles etc.) prior to release. The information is reviewed by a peer knowledgeable in the area, the responsible staff member’s manager, the project manager, the IP manager, and where appropriate derivative classifier or export control specialist to ensure no classified or export controlled material is publically released. All personally identifiable information is removed from the documents.
- Partners. When PNNL is working with a industry or academic partner, they provide copies of material to be publically released to the partner for review and approval prior to release.