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## 2020 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)


Pacific Northwest National Laboratory
May 30, 2020

Project ID
H2045

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# Overview

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## Timeline

- Project Start Date: 4/15/18
- Project End Date: 10/15/20
  - 6 month no-cost extension to be requested due to Covid-19 shutdown
- 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 $H_2$ Production

## Budget

- Total Project Budget: $2.2M
  - Total Federal Share: $1.0M
  - Funds-in cost share: $0.7M
  - In-kind cost share: $0.5M

## Partners

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

# Relevance

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- **Objective:** Develop a new process for producing **low-$CO_2$ $H_2$** and **solid carbon co-product** from inexpensive and domestically available natural gas and reduce the net production cost of **$H_2$ to < $2/kg** with the sale of valuable co-product carbon.
  - Development and use of carbon co-products from $H_2$ production
  - Low cost $H_2$ production is relevant to H2@Scale

**Southern California Gas Company (SoCalGas) is motivated to rapidly develop this technology and then demonstrate on-site in California**

- Demonstrate technical feasibility
- Demonstrate that this low-$CO_2$ technology as a viable option to regulators

# Market Analysis for Potential Carbon Products

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

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**The U.S. produces 10M MT $H_2$ per year (primarily from steam methane reforming).**

| 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<br>• ~ 2M MT (2017)<br>Global market<br>• 12M MT (2014)<br>• 16.4M MT (2022) | U.S. market<br>• 0.67M MT<br>Global market<br>• 4M MT (2014)<br>• 5.4M MT (2022) |
| Graphite [82] | Lithium-ion batteries | \$10+/kg | Global market<br>• 80K MT (2015)<br>• 250K MT (2020) | Global market<br>• 27K MT (2015)<br>• 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<br>• 70K MT (2016)<br>• 100K MT (2020) | Global market<br>• 23.3K MT (2016)<br>• 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<br>• 5K MT (2014)<br>• 20K MT (2022) | Global market<br>• 1.7K MT (2014)<br>• 6.7K MT (2022) |
| Needle coke [88] | Graphite electrodes for electric arc steel furnaces | ~\$1.5/kg | Global market<br>• ~1.5M MT (2014) | Global market<br>• ~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.

**One strategy (of several) for producing low-$CO_2$ $H_2$ at scale, made possible with the sale of valuable solid carbon co-product(s).**

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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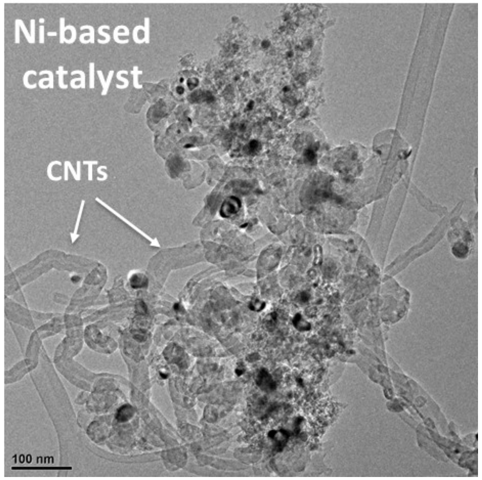
- **Background**: West Virginia University reported a promising new catalyst innovation for methane conversion to $CO_2$-free $H_2$ and highly crystalline solid CNTs.
- **Approach**: Build upon this prior research and:
  - Improve catalyst design to increase lifetime and yields
  - Develop the catalyst/carbon separation
  - Demonstrate the proof of concept for the reactor engineering that would enable a commercially viable process technology
  - Evaluate the overall techno-economics with rigorous process modeling

| Date | Milestones (abbreviated) | Completed |
|---|---|---|
| 9/30/19 | • Update TEA to determine process efficiency and CAPEX and OPEX cost. Report on ability to achieve a projected $H_2$ cost <$2/kg at a 25 kg/day scale.<br>• Assess risks and potential mitigation strategies for the production of carbon nanotubes as a potential toxicity hazard.<br>• Evaluate fluidized bed reactor operation and assess ability to maintain at least 20% conversion and determine catalyst stability for at least 2 hours' time-on-stream of continuous operation. | ✓ |
| 12/31/19 | Evaluate at least 3 different new catalyst formulations for methane pyrolysis and select candidate formulation for harvesting and characterization studies. Report on ability to achieve >50% single pass conversion for this catalyst type. Determine catalyst regeneration and ability for carbon harvesting. Target at least 3 catalyst regenerations with <10% activity loss. | ✓ |
| 3/31/20 | Characterize at least 3 spent catalyst samples using at least 3 techniques (e.g., TEM, XPS, and IR). Understand catalyst structure changes during methane pyrolysis and effect on catalyst regenerability. Understand catalyst active site structure-function relationship with catalytic performance. | ✓ |
| 6/30/20 | Evaluate at least 3 different carbon-supported catalyst formations for methane pyrolysis. Report on ability to achieve >50% single pass conversion for this catalyst type. Selective candidate formulation for carbon harvesting. Report on ability to retrieve at least 90% of carbon separated after at least one cycle. | |
| 9/30/20 | Update TEA using best results from the fluidized bed reactor operation. Determine process efficiency and CAPEX and OPEX cost. Report on ability to achieve a projected H2 cost <$2/kg. | |

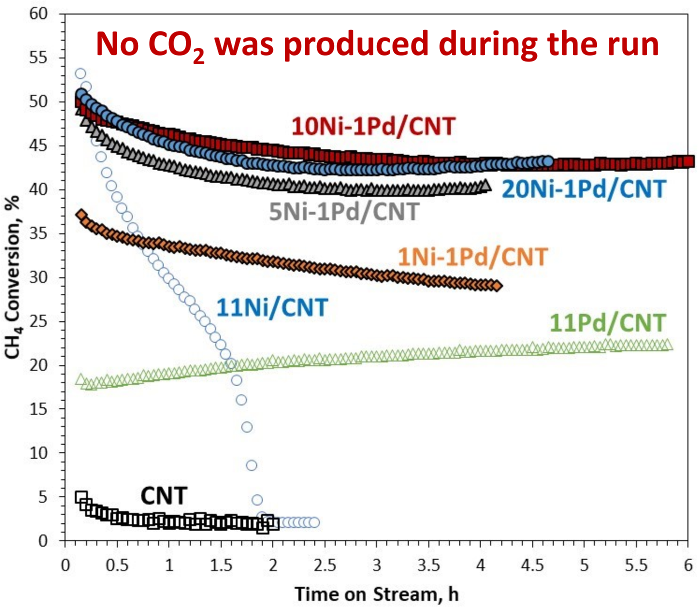
# Catalyst Development: Ni-M Bimetallic Catalysts Developed for Methane Pyrolysis



- The catalytic activity of supported and unsupported catalysts can be stabilized using Ni-Pd bimetallic alloys.
- Optimum Ni:Pd ratio determined for both supported and unsupported catalysts.
- Catalysts deactivated within 60 min of reaction if the catalysts are rich with either Ni or Pd
- Proprietary Ni-M bimetallic catalyst also developed without precious metal (not shown)




**Microscale Packed Bed Reactor Studies**
**(0.1 SLPM Scale)**




600 °C, 1 atm, 9,000 $h^{-1}$

**Ni-M bimetallic catalyst developed with favorable stability, activity, and selectivity towards crystalline carbon co-product.**

Wang et. al., *Energy & Environmental Science, Submitted*

Patent pending

# Catalyst Development: Large Metal Particle Sizes Favor Catalytic Activity and Stability

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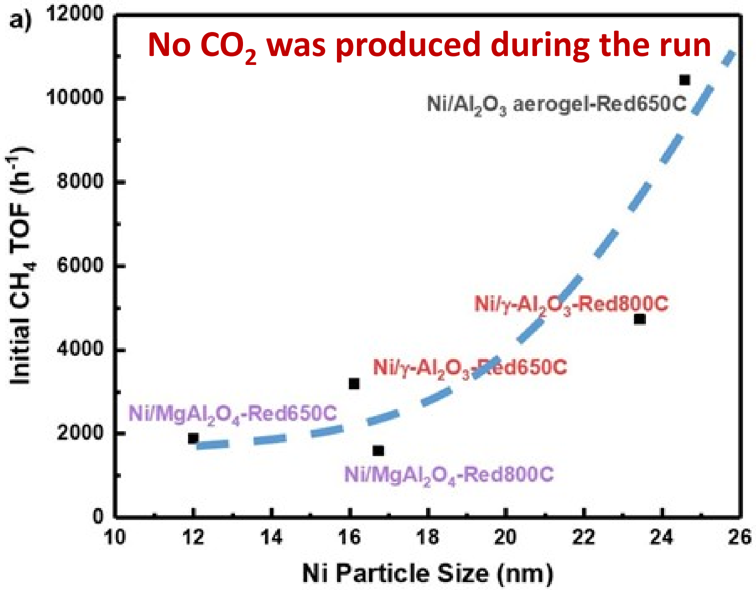
- Different particle sizes are obtained by changing support and synthesis conditions.
- Small (<10 nm) Ni nanoparticles show low activity because they quickly deactivate.
- Larger (> 20 nm) Ni nanoparticles show higher activity as they remain active for longer periods of time.

**Bench-Scale Fluidized Bed Reactor**
**(0.1 SLPM Scale)**




**Catalytic performance is directly correlated to metal particle size. Larger metal Ni nanoparticles favor CNT growth even in the absence of Pd.**

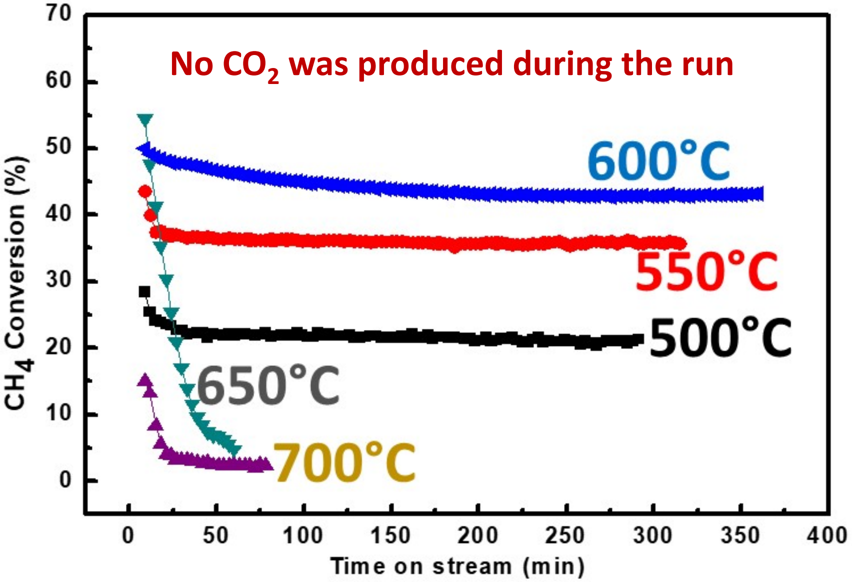
Xu et. al., Appl. Catal. B-Environ. In Preparation

# Process Development: Bimetallic Catalysts Provide Stable Catalytic Performance at 600°C



- The reaction temperature limits performance of the Ni-Pd bimetallic catalysts for both supported and unsupported systems.

**Bench-Scale Fixed Bed Reactor**
**(0.1 SLPM Scale)**




**Ni-Pd bimetallic catalysts are stable at temperatures at or below 600°C.**

Wang et. al., *Energy & Environmental Science, Submitted*

# Process Development: Demonstrated Carbon-Catalyst separation and Catalyst Recycling

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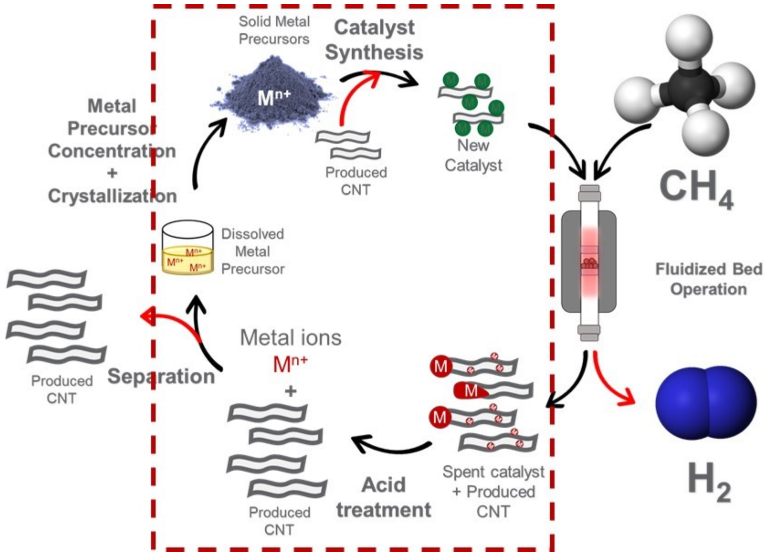


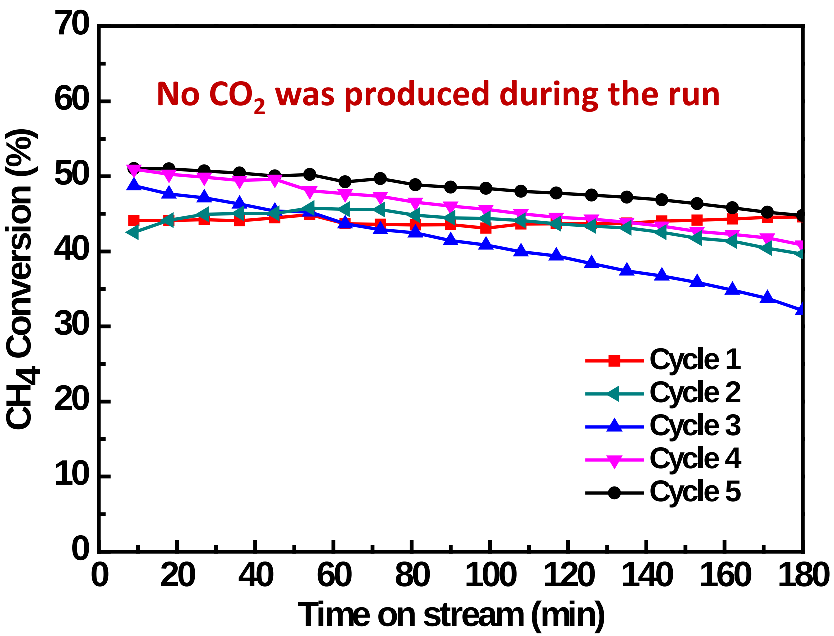


- Catalytic material can be harvested during the purification step to resynthesize catalyst: enabling pyrolysis-separation-catalyst re-synthesis
- Catalytic process was verified by continuously removing the metal and re-synthesis of catalyst.

**Proof of concept for acid wash and catalyst re-synthesis demonstrated for multiple cycles.**

Wang et. al., *Energy & Environmental Science, Submitted*

# Process Development: Separation Results in Highly Crystalline Carbon Product

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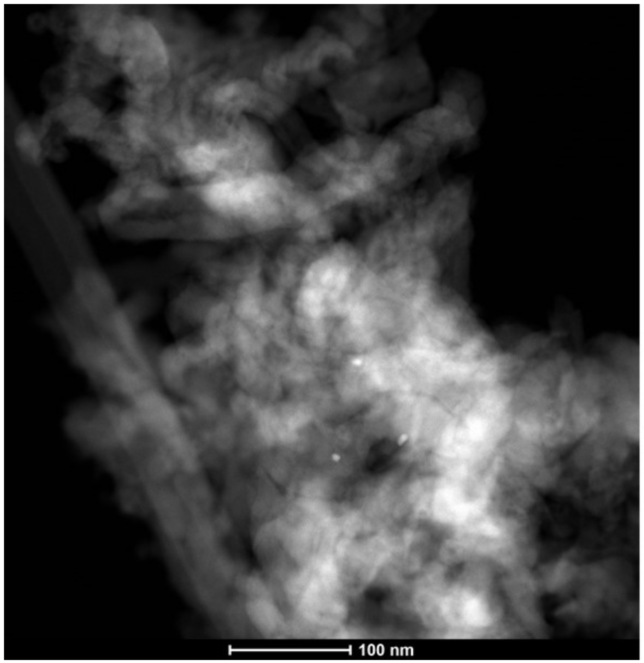


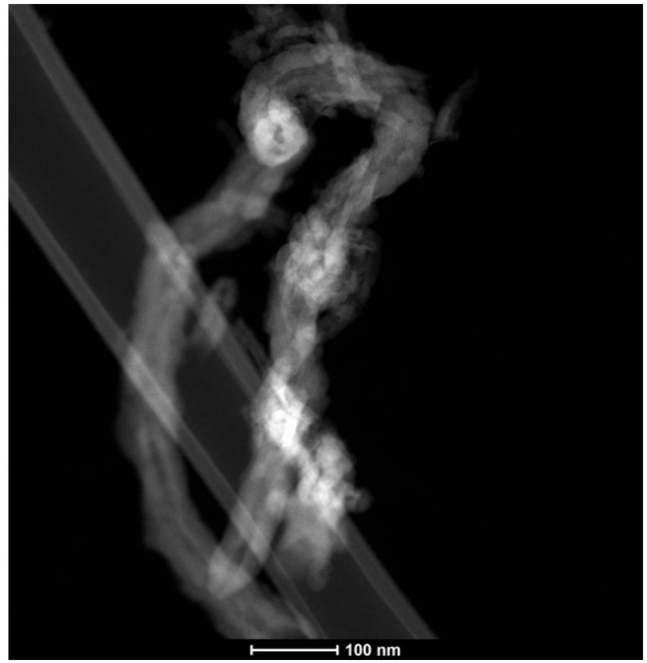


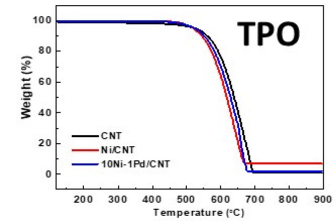


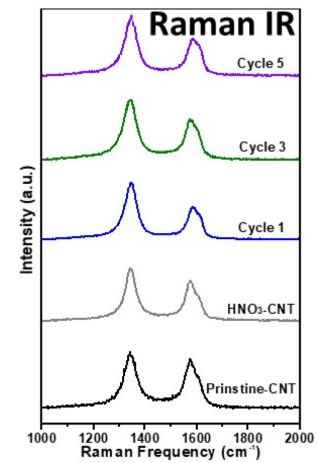


- Acid-wash of the carbon co-product shows complete removal of the metal nanoparticles.

**TPO, Raman IR, and HRTEM indicate crystallinity is not affected by acid wash.**

Wang et. al., *Energy & Environmental Science, Submitted*

## Accomplishments and Progress

# Process Models for Methane Pyrolysis Indicate >80% Reduction in GHG Possible

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| | Raw Material | | Utility | Byproduct | Performance | |
|---|---|---|---|---|---|---|
| | Natural gas ($kg/kg\ H_2$) | $HNO_3$ ($kg/kg\ H_2$) | Electricity ($kWh/kg\ H_2$) | Carbon ($kg/kg\ H_2$) | $CO_2$ Emission ($kg/kg\ H_2$) | Efficiency (%, LHV) (d) |
| SMR (a, b) | 3.42 | | 0.28-2.10 | | 9.6-11.5 | 70-80 |
| SMR+CCS (c) | 3.68 | | 0.60 | | 2.98 | 71.4 |
| C1 Pyrolysis | 4.65 | 0.18 | 3.13 | 3.05 | 1.67 | 53.5 |

(a) PEP Yearbook, Hydrogen production by steam reforming of natural gas, 1E-586, 2014.
(b) PEP Yearbook, Hydrogen small scale by steam reforming, 1E-573, 2014.
(c) NREL, case study: central natural gas, future central hydrogen production from natural gas with $CO_2$ sequestration version 3, 2018.
(d) Carbon product is excluded.

- Process models developed comparing this pyrolysis process and baseline SMR and SMR + CCS cases.
- Raw material cost and stoichiometry disfavor ANY methane pyrolysis technology over steam reforming:
  - Pyrolysis: $CH_4 \rightarrow C + 2H_2$
  - Steam Reforming: $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

**Emission reductions and sale of carbon co-product are benefits for pyrolysis. Methane pyrolysis technologies being developed MUST produce a value-add carbon co-product to compete with SMR on a purely cost basis (although regulations could provide additional incentive).**

Wang et. al., *Energy & Environmental Science, Submitted*

## Accomplishments and Progress

# Technoeconomic Analysis Provides Carbon Co-Product Target Selling Price Range of $1.0-1.5/kg C

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- The sale of solid carbon co-product is key to lower the $H_2$ MSP below that of SMR.

| | Methane Pyrolysis | | SMR | SMR+CCS |
|---|---|---|---|---|
| Scale (kg $H_2$/day) | 1500 | 100,000 | 100,000 | 100,000 |
| Carbon production rate (kg/day) | 4538 | 3,025,500 | N/A | N/A |
| Total ISBL capital cost (MM$) | 34.9 | 434.1 | 132.6 | 225.49 |
| Raw material cost ($/kg $H_2$) | 1.20 | 1.20 | 0.70 | 0.70 |
| Utility + O&M cost ($/kg $H_2$) | 4.70 | 0.76 | 0.21 | 0.35 (4) |
| Capital cost ($/kg $H_2$, 15% ROI (1)) | 11.49 | 2.14 | 0.74 | 1.06 (4) |
| Other cost (2) ($/kg $H_2$) | 12.33 | 2.25 | 0.80 | 0.80 |
| Minimum carbon selling price ($/kg @ $2.0/kg $H_2$ price) | 8.89 | 1.37 | | |
| Minimum $H_2$ selling price ($/kg @ no carbon credit) | 29.72 | 6.35 | 2.45 (3) | 2.91 (3) |

(1) ROI = Return on Investment

(2) Including plant overhear, taxed and insurance, depreciation, general and administrative, sales and research cost

(3) The minimum hydrogen selling price at 380,000 kg $H_2$/day scale is $1.80/kg and $1.99/kg in 2014 pricing basis

(4) The operating and capital costs of the CCS section was reported by NREL, case study: central natural gas, future central hydrogen production from natural gas with $CO_2$ sequestration version 3, 2018

**Techno-economic analysis indicates that a carbon co-product selling price range of $1.0-1.50/kg C will enable $2/kg $H_2$ production (different sensitivities were performed).**

Wang et. al., *Energy & Environmental Science, Submitted*

# Reviewer Only Slides



- Response to Previous year reviewers – this CRADA project was not reviewed last year
- Publications and Presentations
  - Xu et. al. “Insights into the Effects of Ni-Support Interactions on Selectivity of Solid Carbon and $CO_x$-free $H_2$ Production from Thermocatalytic Decomposition of Methane." Presented by M. Xu at 2019 AIChE Annual Meeting, Orlando, Florida, November 14, 2019.
  - Lopez-Ruiz et al., "Methane Pyrolysis for Base-Grown Carbon Nanotubes and $CO_2$-free $H_2$ over Transition Metal Catalysts." Presented by Robert Dagle and Juan Lopez-Ruiz at the H2@Scale Consortium Working Group Meeting, Online Conference, February 28, 2020.
  - Wang et. al., “Production of low-$CO_2$ $H_2$ and carbon nanomaterials from methane decomposition using a recyclable catalyst and self-sufficient process”, *Energy & Environmental Science, submitted.*
  - Xu et. al., “”Structure Sensitivity of Supported Ni Catalysts in Thermocatalytic Decomposition of Methane into CO2-free $H_2$ and Carbon Nanotubes, *Applied Catalysis B: Environmental, in preparation.*

# 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 $H_2$ and solid carbon co-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 $H_2$ could substantially reduce, NOx, and particulate emission.

# Remaining Challenges and Barriers

- More rigorously understand and demonstrate the the carbon separation using recycled metal salts and for multiple cycles.
- Better understand produced carbon co-product characteristics and understand the potential current markets and develop new markets (e.g., building materials).
- De-risk the technology for commercial adoption by developing and demonstrating the scalable fluidized-bed processing with continuous carbon/catalyst removal.
- Demonstrate processing at the pilot-scale.

# Proposed Future Work

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- Continued catalyst development to further improve catalyst stability and increase single pass yield.
- Optimize carbon wash and catalyst regeneration and demonstrate multiple cycles using recycled metals.
- Expand carbon co-product characterization activities to better understand its properties, and identify existing carbon markets and develop new carbon product markets (e.g., building materials).
- Fluidized bed reactor development.
- Pilot scale demonstration of methane pyrolysis and with continuous solid product removal and separation.
- Update process models and projected economics for a 100,000 kg $H_2$/day centralized $H_2$ generation facility.
- Obtain a preliminary front-end loading ~ 1.5 package with cost estimates for a 1500 kg $H_2$/day plant, which is of relevance to SoCalGas who would like to demonstrate at this scale commercially.


**Extension of the current CRADA for 2 years (through FY22) has been proposed.**

# Technology Transfer



- This is a CRADA project.
- C4-MCP, LLC will be providing technical guidance and at the successful completion of the work may commercialize the technology.
- A patent application was filed in the past year.
  - "Methods and compositions for producing $CO_2$-free hydrogen and carbon nanomaterials by methane decomposition", provisional patent application filed on 10/30/19.

# Summary

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- **Objective**: Develop a new process for producing **$CO_2$-free $H_2$** 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 co-product carbon.
- **Relevance**: H2@Scale project for development and use of co-products from $H_2$ production.
- **Approach:** Build upon innovative catalytic material reported at WVU and:
  - Improve catalyst design to increase lifetime and yields
  - Develop the catalyst/carbon separation
  - Demonstrate the proof of concept for the reactor engineering that would enable a commercially viable process technology
  - Evaluate the overall techno-economics with rigorous process modeling
- **Accomplishments**:
  - Catalyst developed with high activity and selectivity towards carbon fibers production.
  - Computational methods were used to rationalize the stability of our designed catalysts.
  - Carbon product and catalyst separation approach developed and demonstrated for 5 cycles developed
  - Techno-economic analysis shows that the \$2/kg $H_2$ production goal can be met assuming the sale of solid carbon co-product in the range of \$1.0 - 1.5/kg C
- **Collaboration:**
  - Pacific Northwest National Laboratory
  - West Virginia University
  - C4-MCP, LLC
  - Southern California Gas Company