West Virginia University

Microwave Catalysis for Process Intensified Modular Production of Carbon Nanomaterials from Natural Gas

DOE Project Number DE-FE-0031866

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U.S. Department of Energy

National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

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Project Overview

– Funding ($3 million DOE Funds and $790,000 Cost Share)

– Project Performance Dates: March 20, 2020 to March 19, 2023

Project Participants:

- ❑ Pacific Northwest National Laboratory
- ❑ North Carolina State University
- ❑ H-Quest Vanguard, Inc.
- ❑ SolCalGas
- ❑ C4-MCP

Project Overview
Goals and Objectives

The objective of the project is to develop a process intensified modular technology to convert flare gas or stranded gas to carbon nanomaterials and hydrogen (H_2). The proposed project is based on a WVU patented technology:

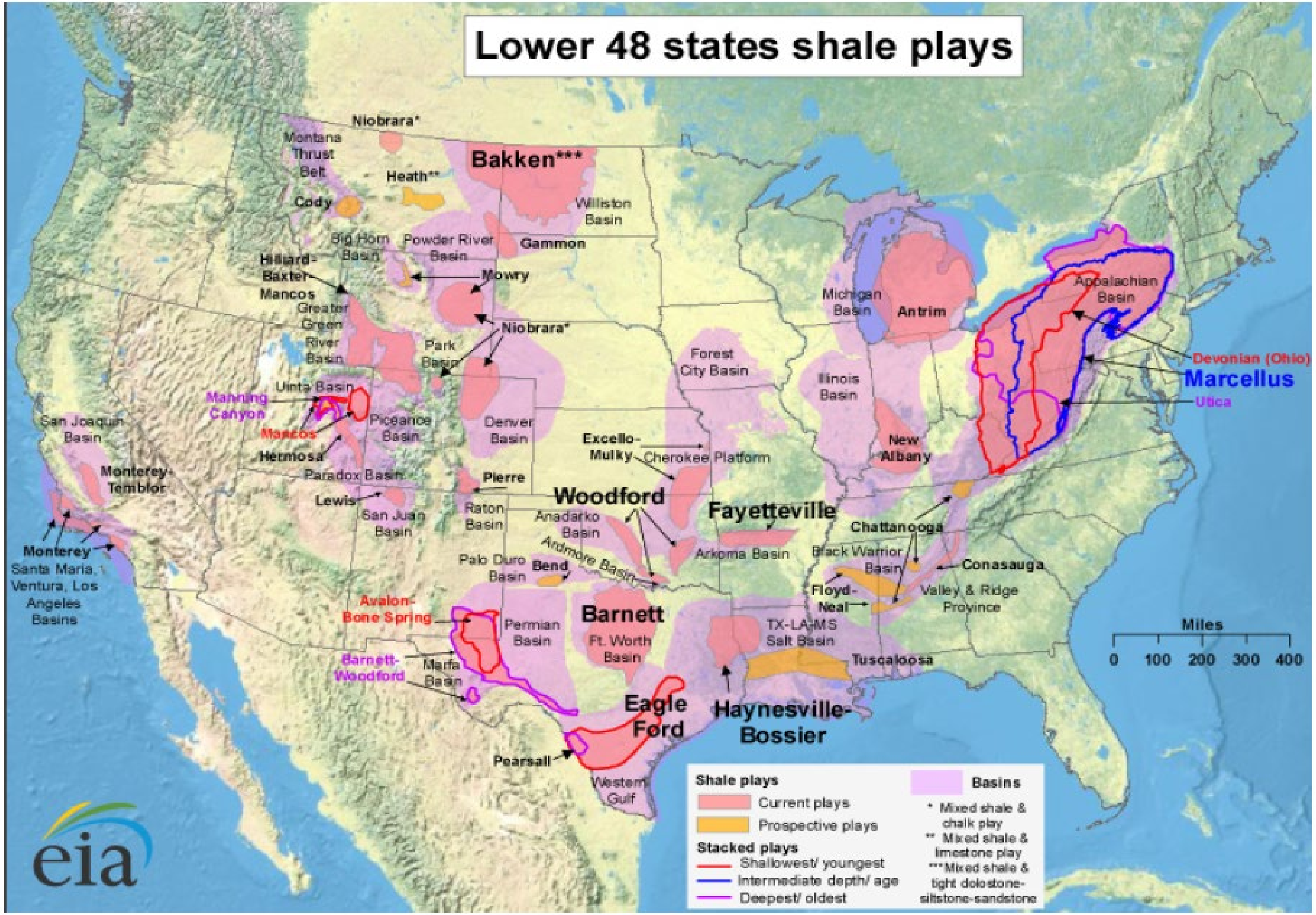
$$CH_4 \rightarrow H_2 + C \text{ (CNT, Carbon Fibers)}$$

Major focus:
- Process intensification at modular scales with the objective of deployment at flare gas location.
- Demonstrate the modular unit operation having a large turndown ratio which can operate under varying feed rate and composition.

Project Overview

- ❑Electromagnetic sensitive catalyst development, synthesis, scale up.
- ❑Microwave pilot reactor design and performance test at capacity of ~5 kg/day.
- ❑Modular component design, fabrication and pilot test for 100 hours
- ❑Commercial design flowsheet, Technoeconomic analysis.
- ❑Technology-to-market strategy, plan, and commercialization.

Technology Background



Lower 48 states shale plays
Niobrara*
Montana Thrust Belt
Bakken***
Heath**
Cody
Williston Basin
Big Horn Basin
Powder River Basin
Gammon
Hilliard-Baxter-Mancos
Mowry
Greater Green River Basin
Niobrara*
Park Basin
Uinta Basin
Manning Canyon
Mancos
Hermosa
Piceance Basin
Denver Basin
Paradox Basin
Pierre
Lewis
San Juan Basin
Raton Basin
San Joaquin Basin
Monterey-Temblor
Monterey
Santa Maria, Ventura, Los Angeles Basins
Excello-Mulky
Cherokee Platform
Forest City Basin
Woodford
Anadarko Basin
Ardmore Basin
Palo Duro Basin
Bend
Fayetteville
Arkoma Basin
Michigan Basin
Antrim
Illinois Basin
New Albany
Appalachian Basin
Devonian (Ohio)
Marcellus
Utica
Chattanooga
Black Warrior Basin
Conasauga
Valley & Ridge Province
Floyd-Neal
Avalon-Bone Spring
Permian Basin
Barnett
Ft. Worth Basin
Barnett-Woodford
Marfa Basin
TX-LA-MS Salt Basin
Tuscaloosa
Eagle Ford
Haynesville-Bossier
Pearsall
Western Gulf
Miles
0 100 200 300 400
Shale plays
Current plays
Prospective plays
Stacked plays
Shallowest/ youngest
Intermediate depth/ age
Deepest/ oldest
Basins
* Mixed shale & chalk play
** Mixed shale & limestone play
*** Mixed shale & tight dolostone-siltstone-sandstone
eia

Technology Background-The Need

The Issue of Flaring Gas

Shale Gas Exploration

Wellhead Equipment

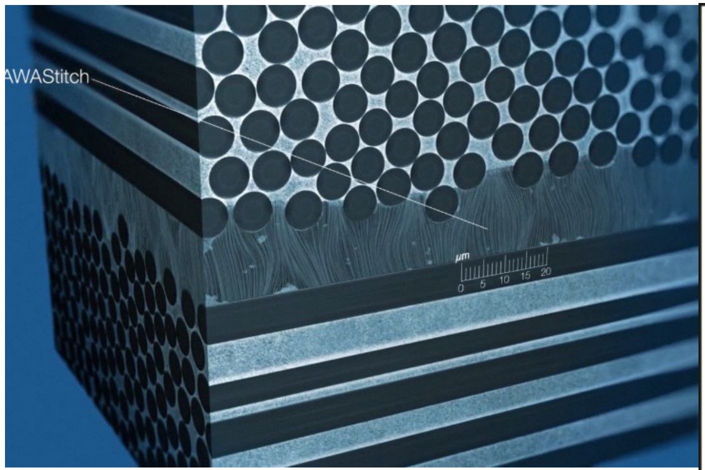
(Bakken, ND)

Natural gas flaring, venting up in Texas

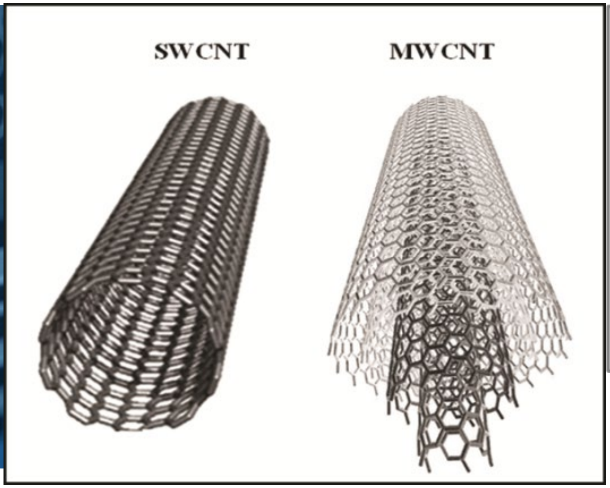
Zero-Carbon Dioxide Emission Hydrogen Production

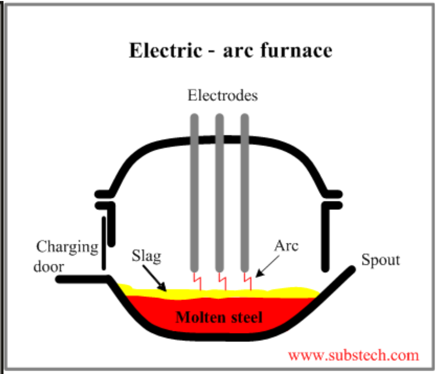
- **WVU patented technology turns natural gas into hydrogen and high value carbon without carbon dioxide:**

$$CH_4 \rightarrow C_s(Advnaced\ Carbon) + 2H_2$$



Carbon Composite





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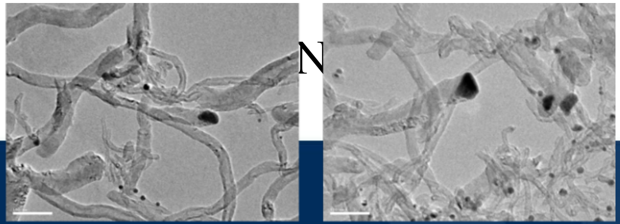

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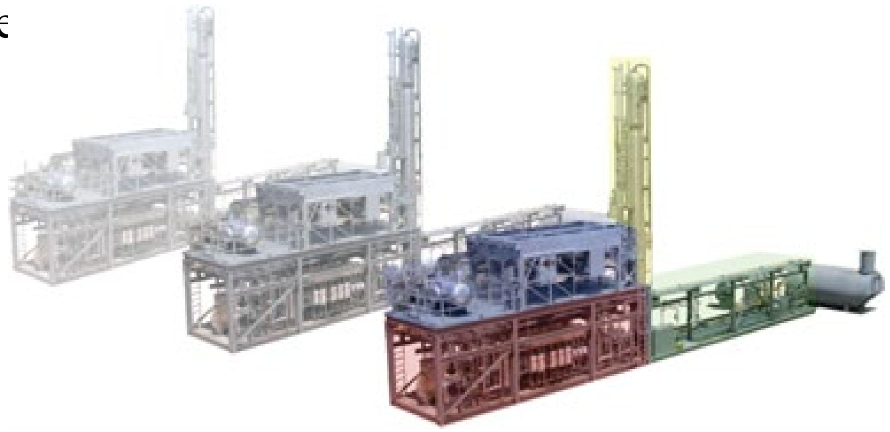
Technical Approach/Project Scope

Technical Approach-Microwave Catalytic Process

The development of process intensified modular systems provides a route for the direct conversion of flaring gas into value-added products. Modular systems are easily de
and transported to remote locations.



Advantages of using MW heating

- Volumetric heating
- Selective material heating
- Rapid heating
- Non-contact heating
- Quick start-up and stopping

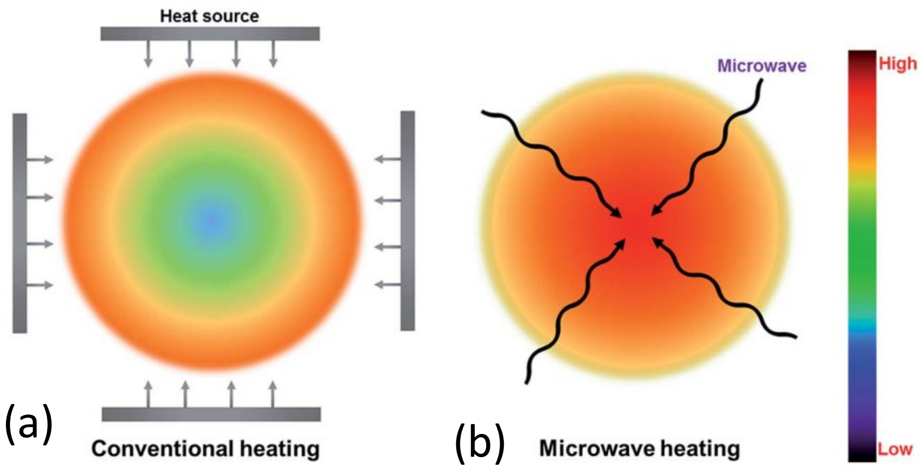


Fig 1. Schematic diagram of (a) conventional heating; (b) microwave heating

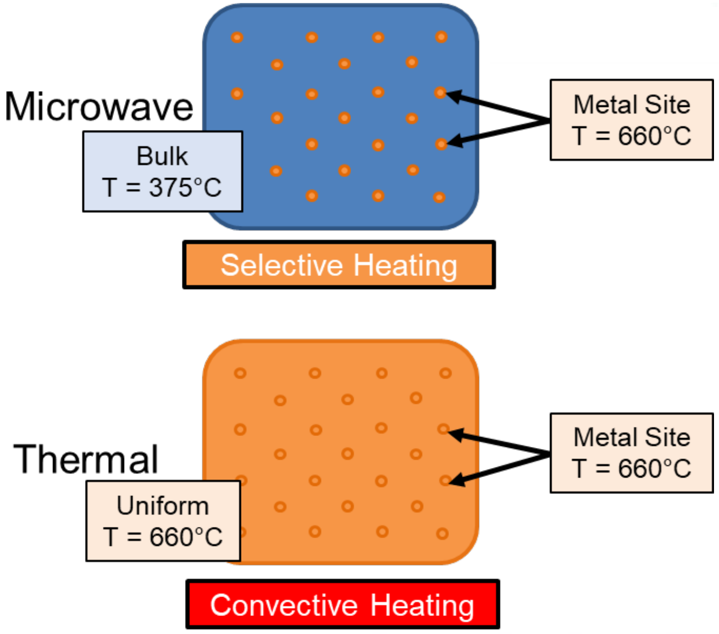
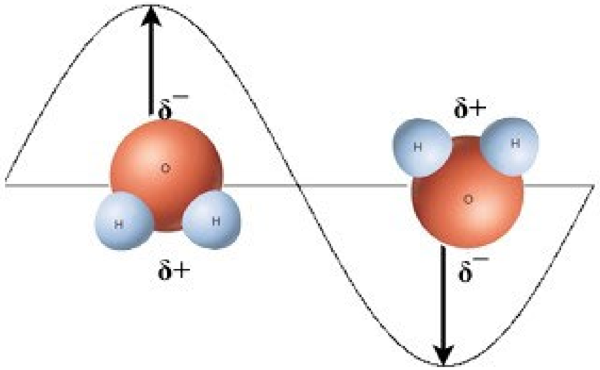
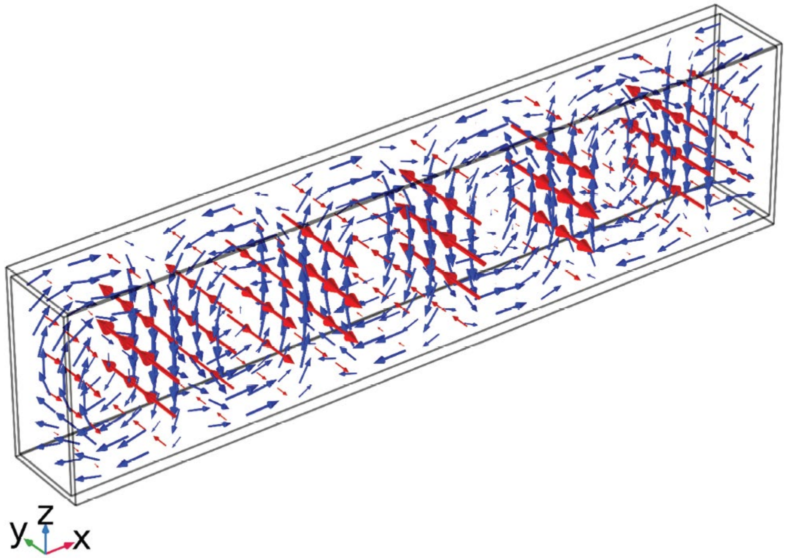


Fig 2. Selective material heating and reduce the bulk temperature

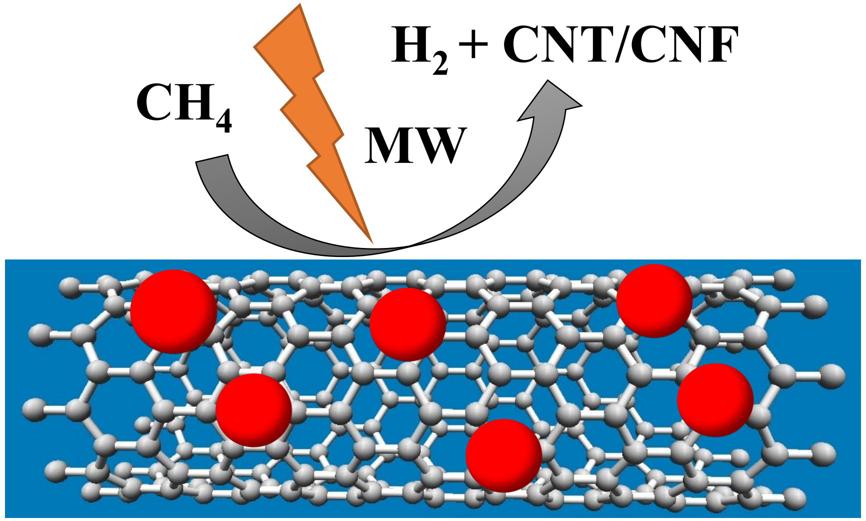
Approach: Overcome the Challenges

The proposed technology is based on microwave-enhanced, multifunctional catalytic system to ***directly*** convert the light components of stranded natural gas.





Field distribution of a TE10 waveguide (red arrows: electric field; blue arrows: magnetic field; the direction of wave propagation is −x; a larger arrow indicates a stronger field)[2].



- Selective heating: $T_{Metal} > T_{CNT}$
- Lower activation energy

Approach: Overcome the Challenges

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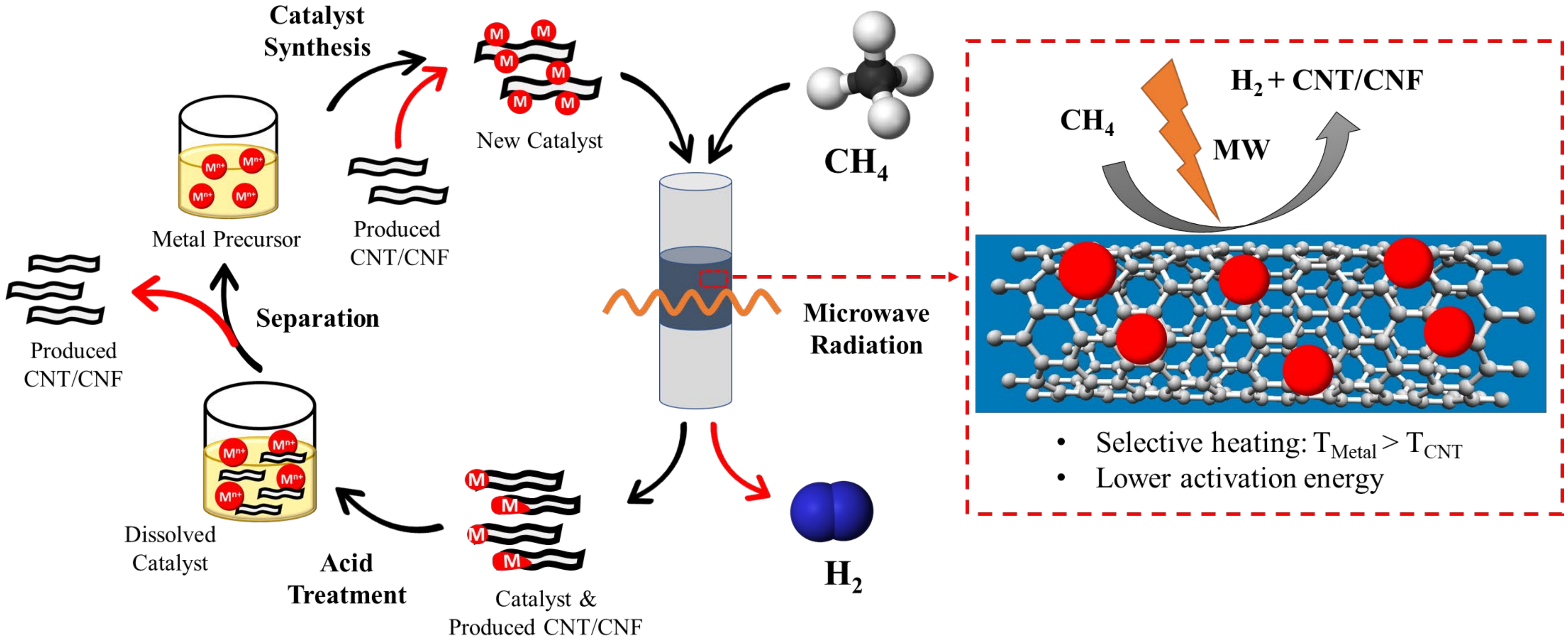
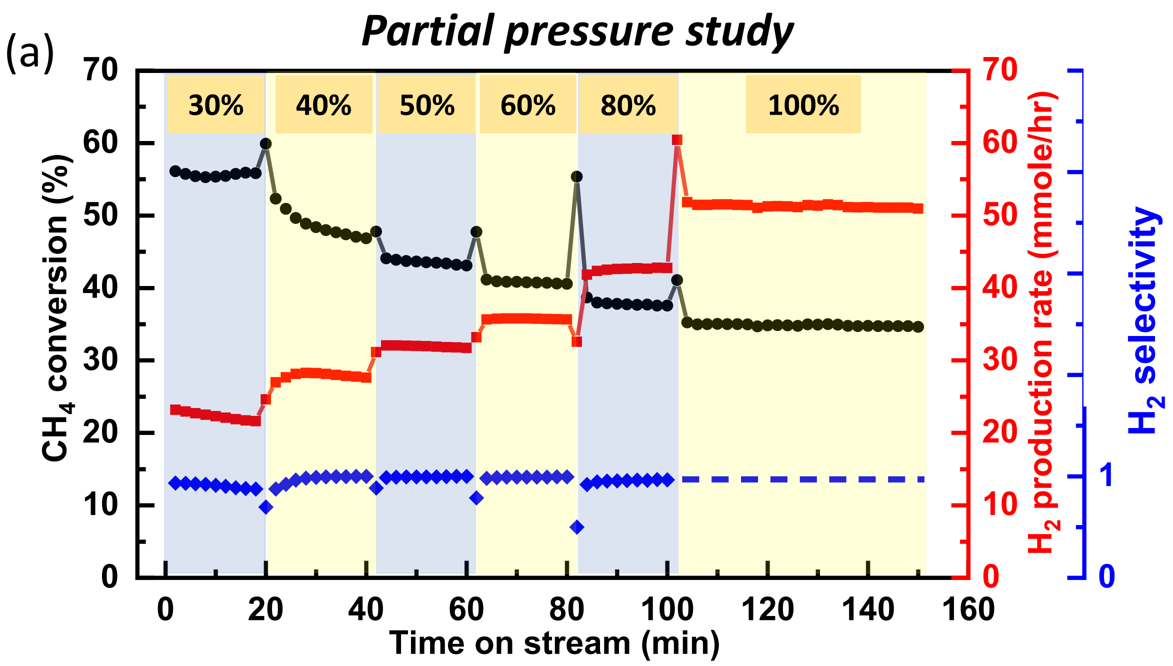
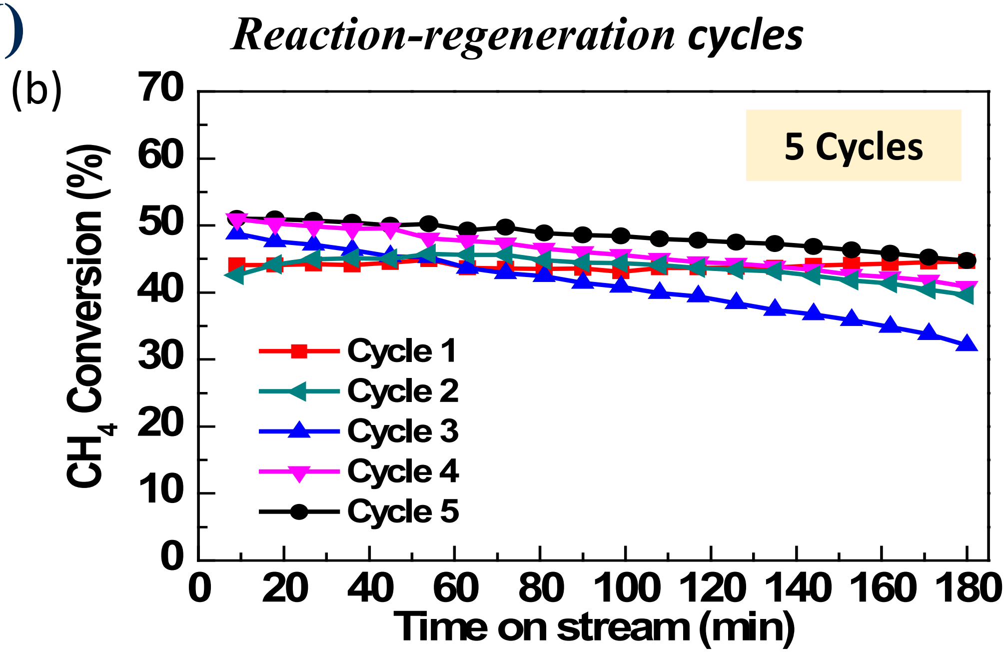
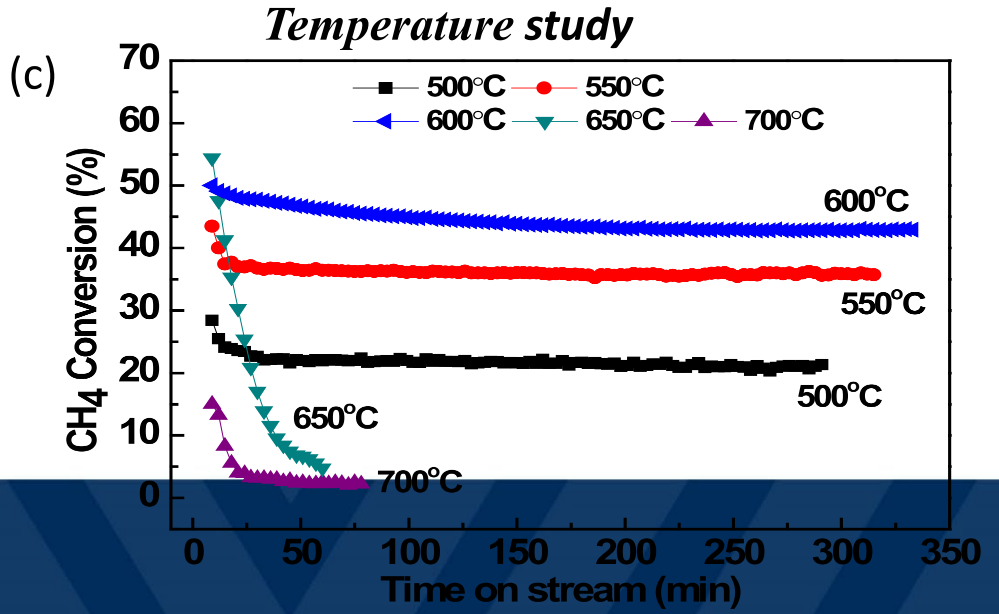


- Selective heating: $T_{Metal} > T_{CNT}$
- Lower activation energy

Performance Test: 10Ni-1Pd/CNT Catalyst (WVU)







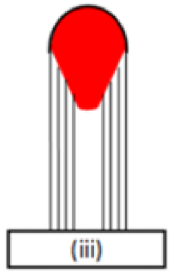
(a) Partial pressure test from 30%CH_4 to 100%CH_4 and the H_2 selectivity is close to 1 under different pressures.
(b) Each cycle shows similar activity and stability.
(c) Temperature test from 500^{o}C to 700^{o}C, and 600^{o}C is an ideal reaction temperature.

Novel Catalyst Synthesis for Base Growth-solving the challenge in CNT-metal separation

Route 1: traditional ex-situ surface deposition

Prefabricated MW heating host material → deposition → Prefabricated MW heating host material → Reduction → Prefabricated MW heating host material

Ni-Cu alloy particle



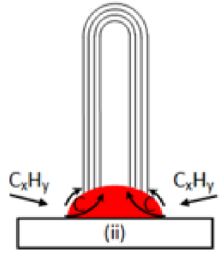
Tip-grown

Clean-cut interface between Ni-Cu alloy particle and host materials, tend to break-way

Route 2: new in-situ surface exsolution

Compound precursors → High T calcination → As-prepared single phase MW heating material → Surface exsolution → Reduced single phase MW heating material

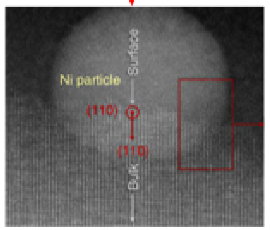
Ni-Cu alloy particle

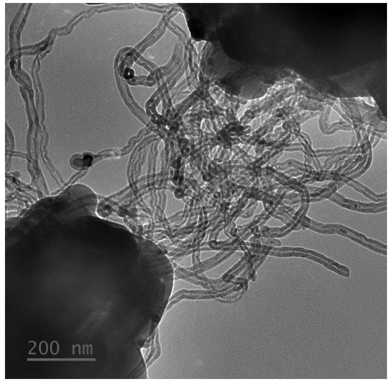


Base-grown

Deep-buried anchor between Ni-Cu alloy particle and host material, strong bond

Route 2 is potentially preferable for our goal of a robust, base-grown CNT catalyst





Surface catalyst exsolution control:

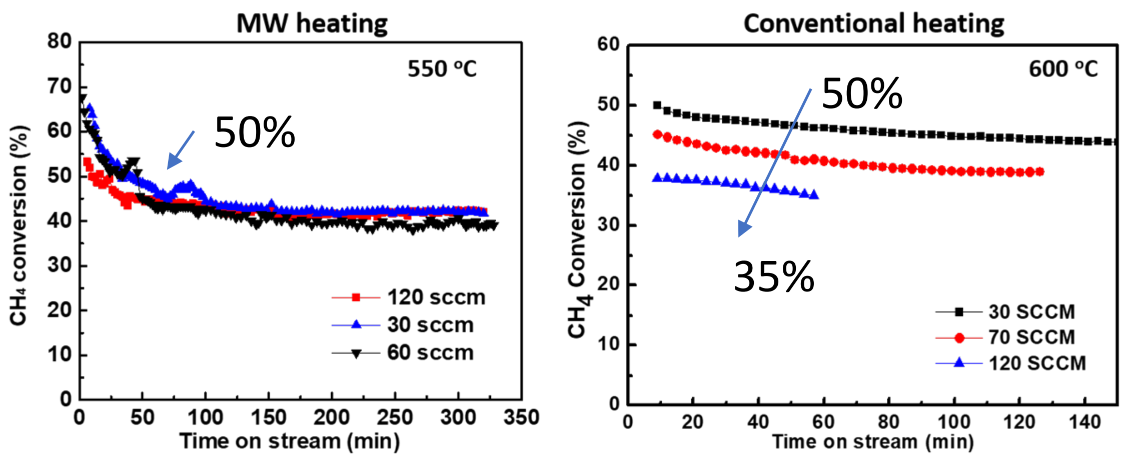
Dilute $H_2+(A_1A_2)(B_1B_2NiCu)O_3 \xrightarrow{\text{Intermediate T}} (A_1A_2)(B_1B_2)O_{3-\delta}+Ni\text{-}Cu+H_2O$

- ➢ High entropy compound as host tends to decrease to single oxides at intermediate T
- ➢ Higher reducibility of NiCuOx than other elements

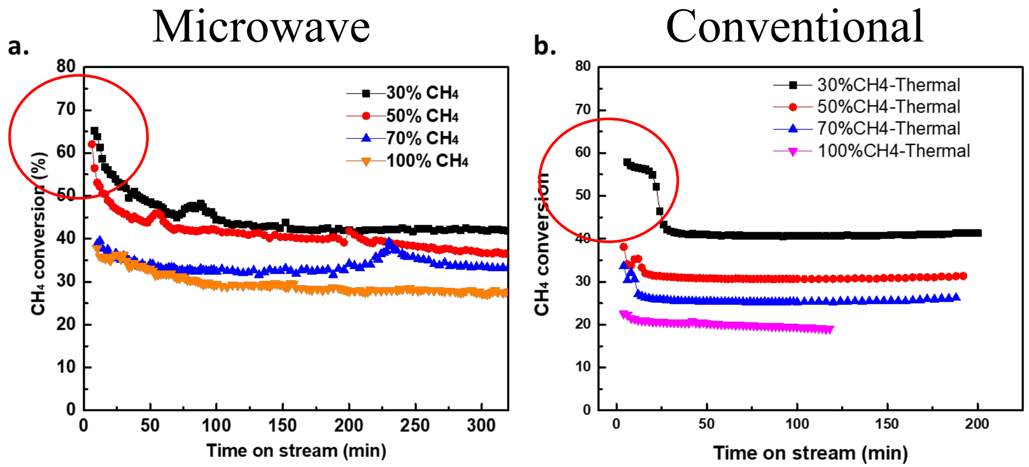
Progress and Current Status of Project

Accomplishments since last year's meeting.

Catalyst for Dielectric Heating: Ni-Pd supported by CNT

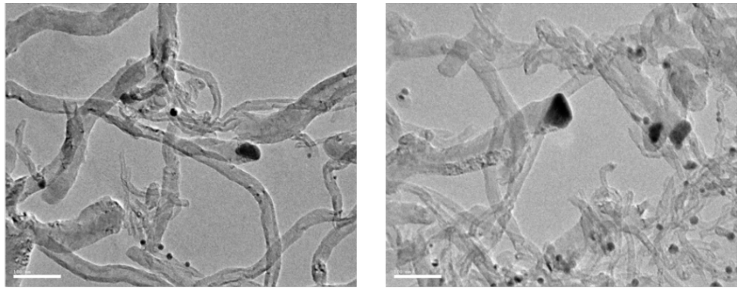


Effect of Flow Rate



Effect of Partial Pressure

- Under microwave irradiation, increase flow rate from 30-120 sccm doesn't decrease CH_4 conversion. Heat transfer mechanism improves catalyst turn over frequency.
- Under microwave irradiation, CH_4 conversion is higher for any concentration of methane.
- Similar trend is observed under MW vs conventional.



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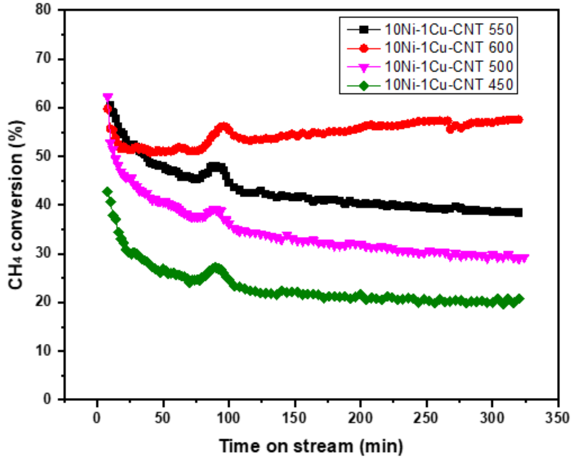
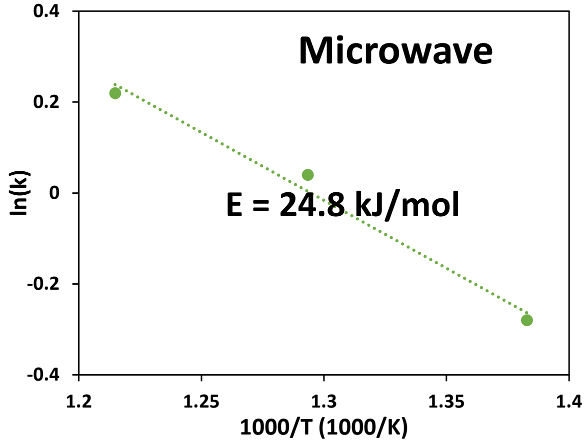
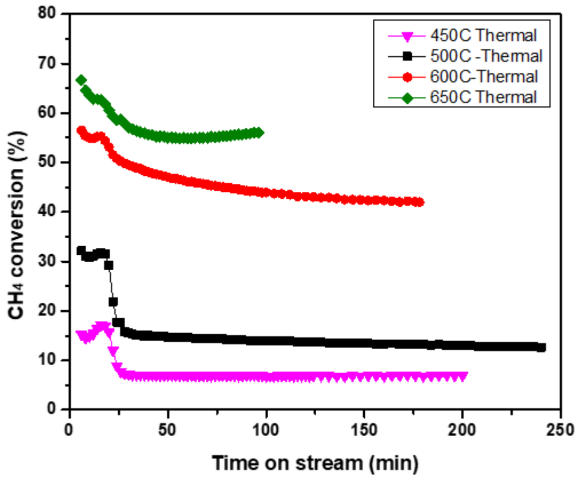
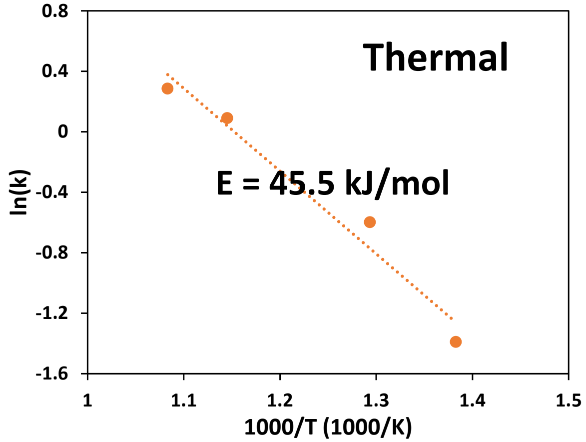
Kinetic Modeling Results- Microwave vs Thermal, Ni-Cu/CNT Catalyst





k_{0_MW}= 47.8 $mol^{0.4}L^{0.6}g^{-1}h^{-1}$





$k_{0\_Thermal}$= 545.0 $mol^{0.4}L^{0.6}g^{-1}h^{-1}$

Activation energy is lower under microwave reaction condition

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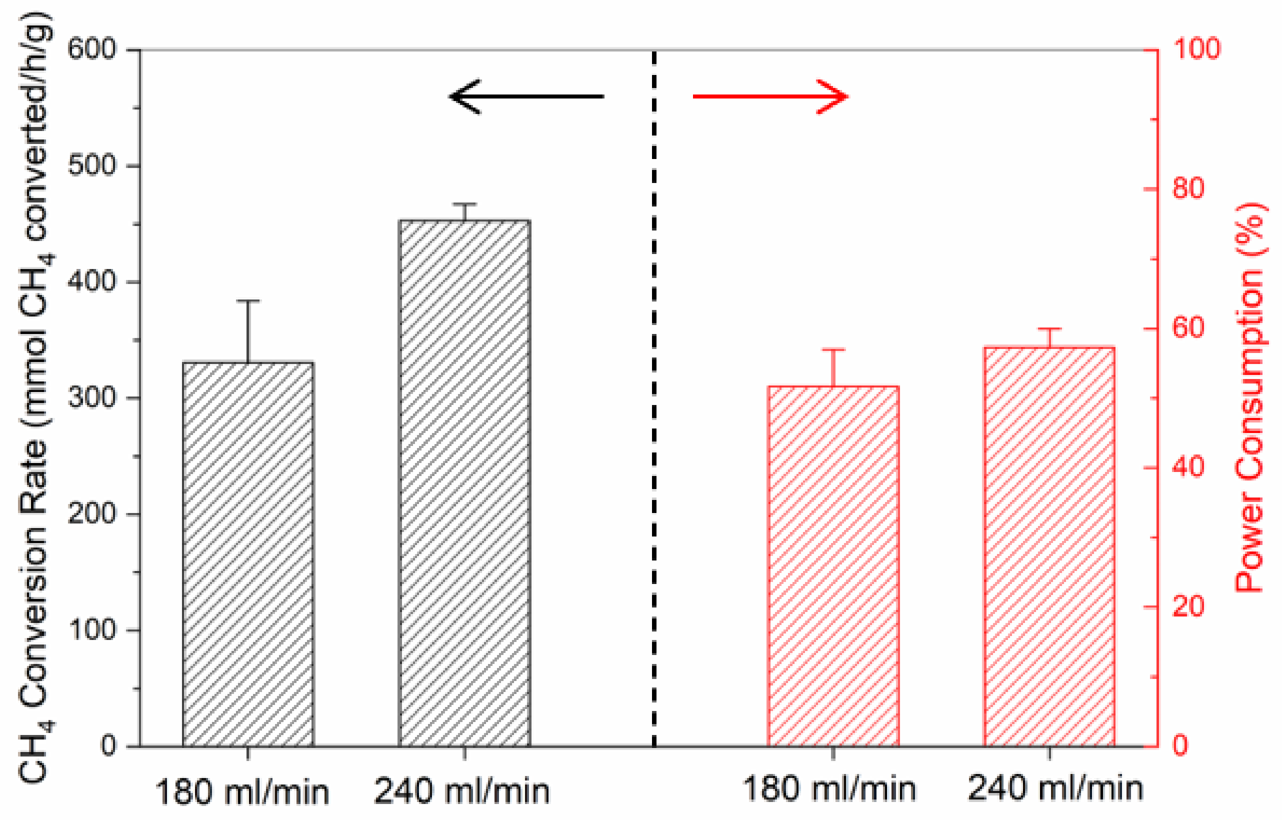
Conversion Rate vs Power Consumption



Overview Pilot Test

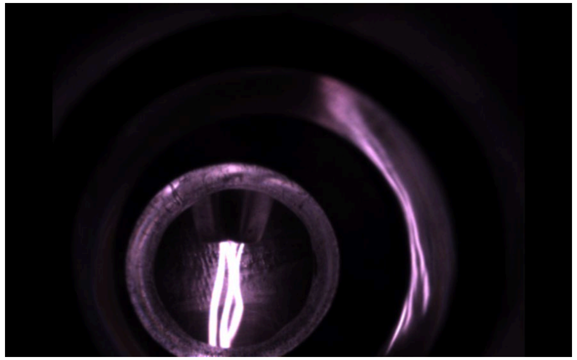
Current status:

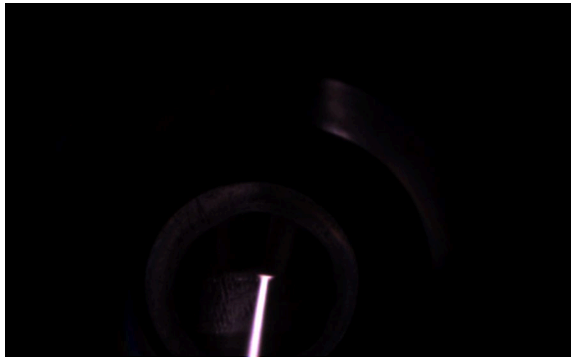
(1) tested spouted and fluidized bed reactor prototypes

(2) evaluated fluidization of multiple materials

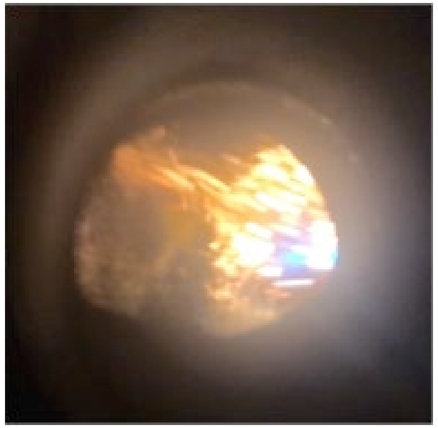
(3) shown MWCNT microwave plasma entrainment

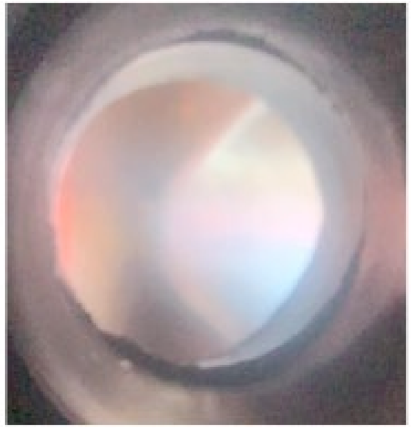
HQV Spouting Bed Microwave Plasma

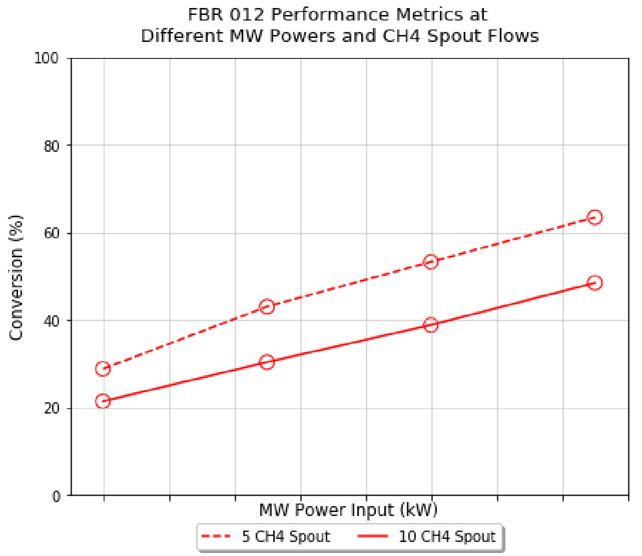


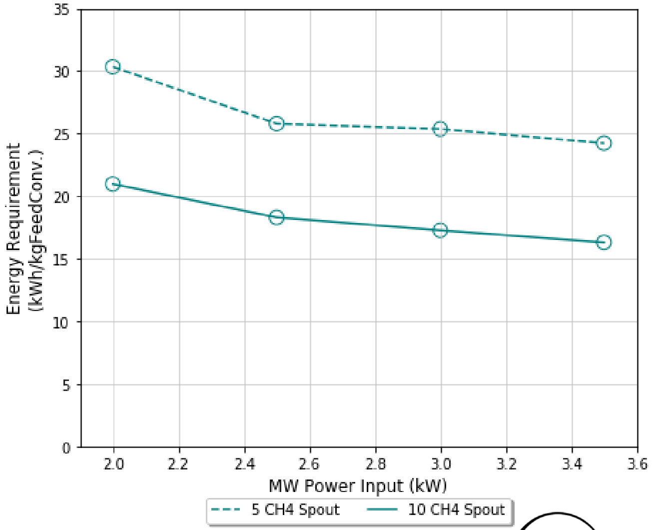


- *Fine control over plasma shapes and volumes.*
- *Significant (>60%) conversion of CH_4 in the unoptimized spouting bed plasma reactor.*
- *High C_2H_2 selectivity (>70%) at lower powers and feeds*









HQuest

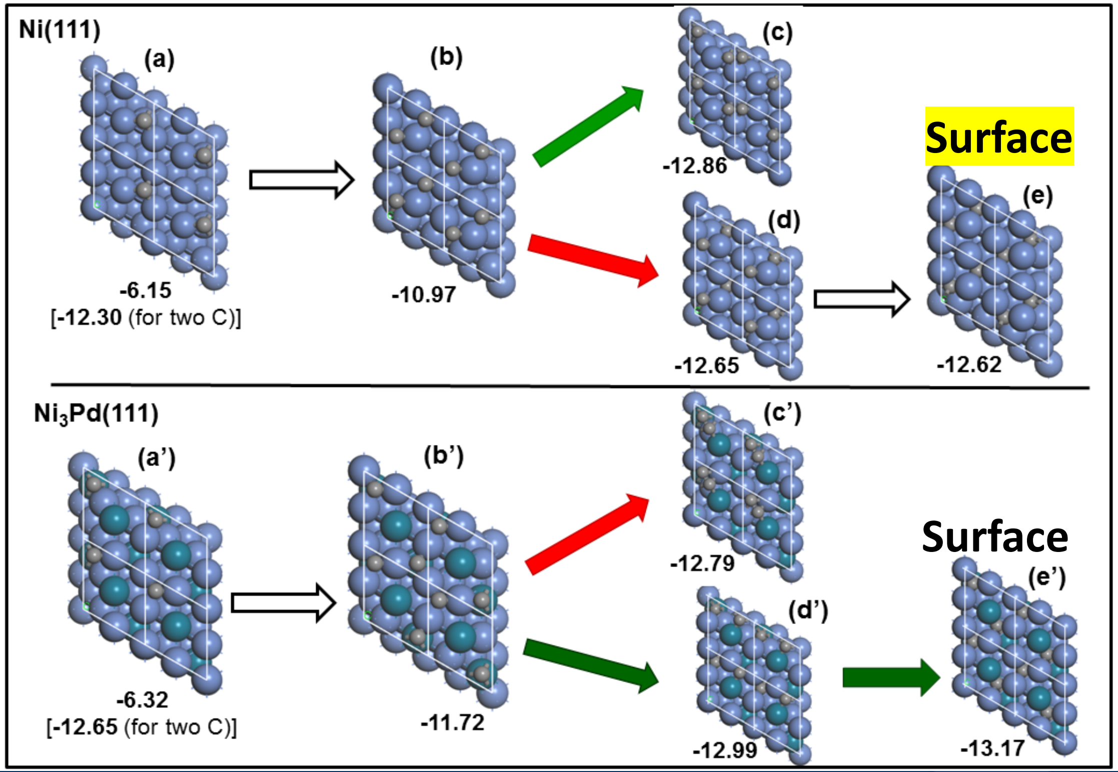
DFT Modelling-Carbon Diffusion

To study the catalytic stability

- Ni/CNT completely deactivates in 2 hrs
- Ni-Pd/CNT maintains the stability for 6 hrs

One of steps for CNT formation is carbon atoms diffuse into the sublayer and then precipitate out as CNT.

Why adding Pd or Cu can improve the stability ?



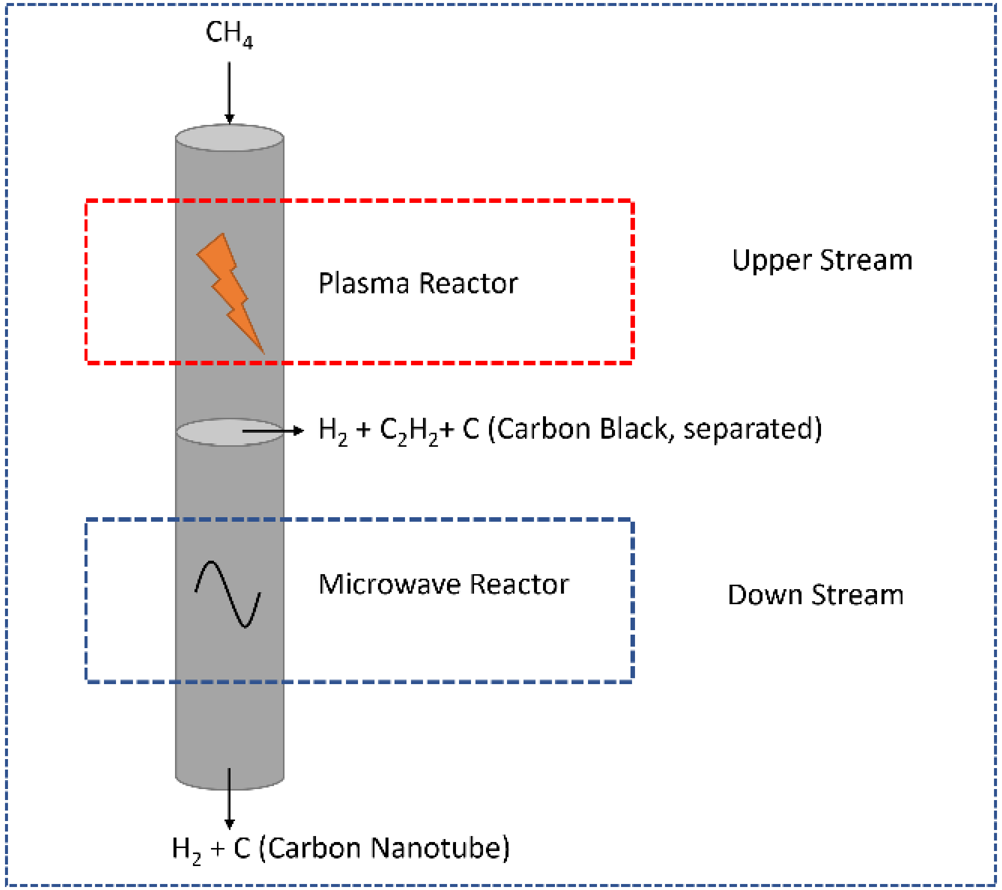
Surface → Deactivate

Sublayer

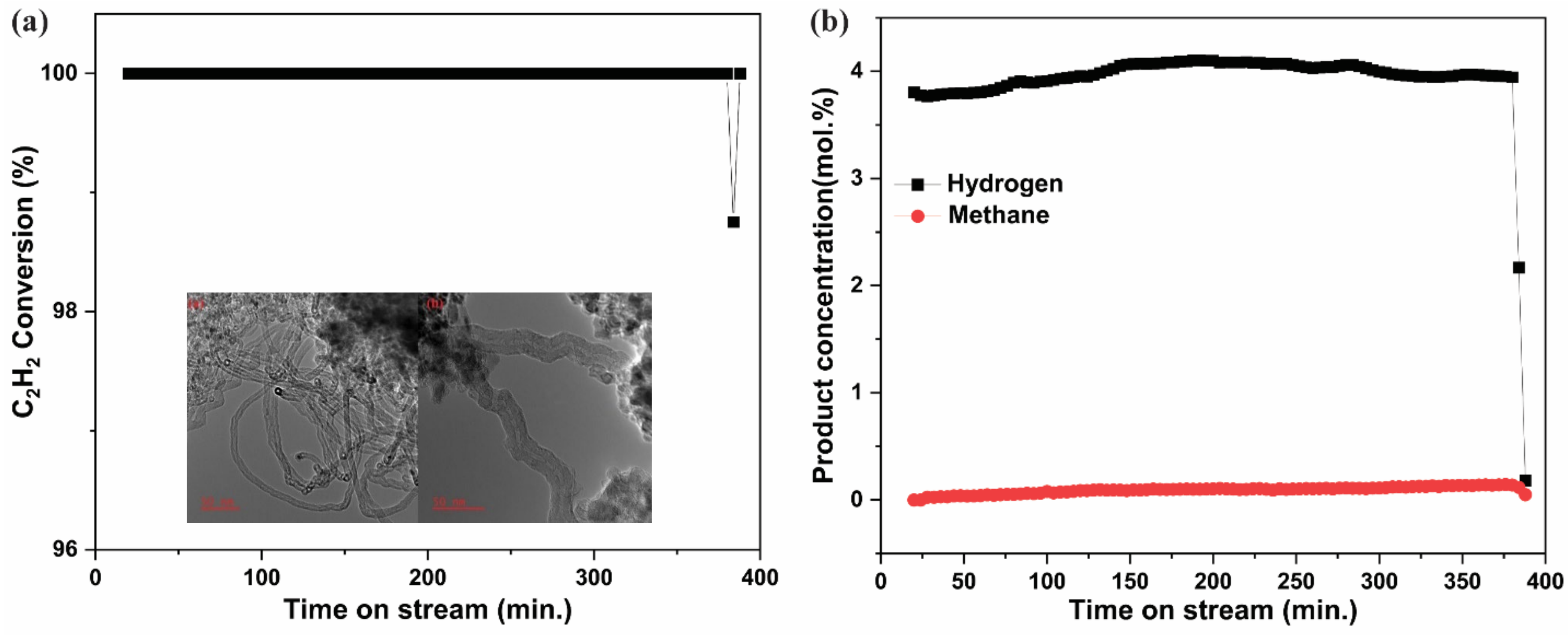
Sublayer → Still activate

DFT calculated energies for the competing routs for C_2 formation versus the dissolution of carbon over Ni and Ni_3Pd surfaces. Favorable route marked with green arrow.

Single Reactor Two-Stage Process



Second Stage Reaction-Pyrolysis of Acetylene



(a) Acetylene conversion and (b) product concentration over 10Ni-1Pd-CNT at 500 °C

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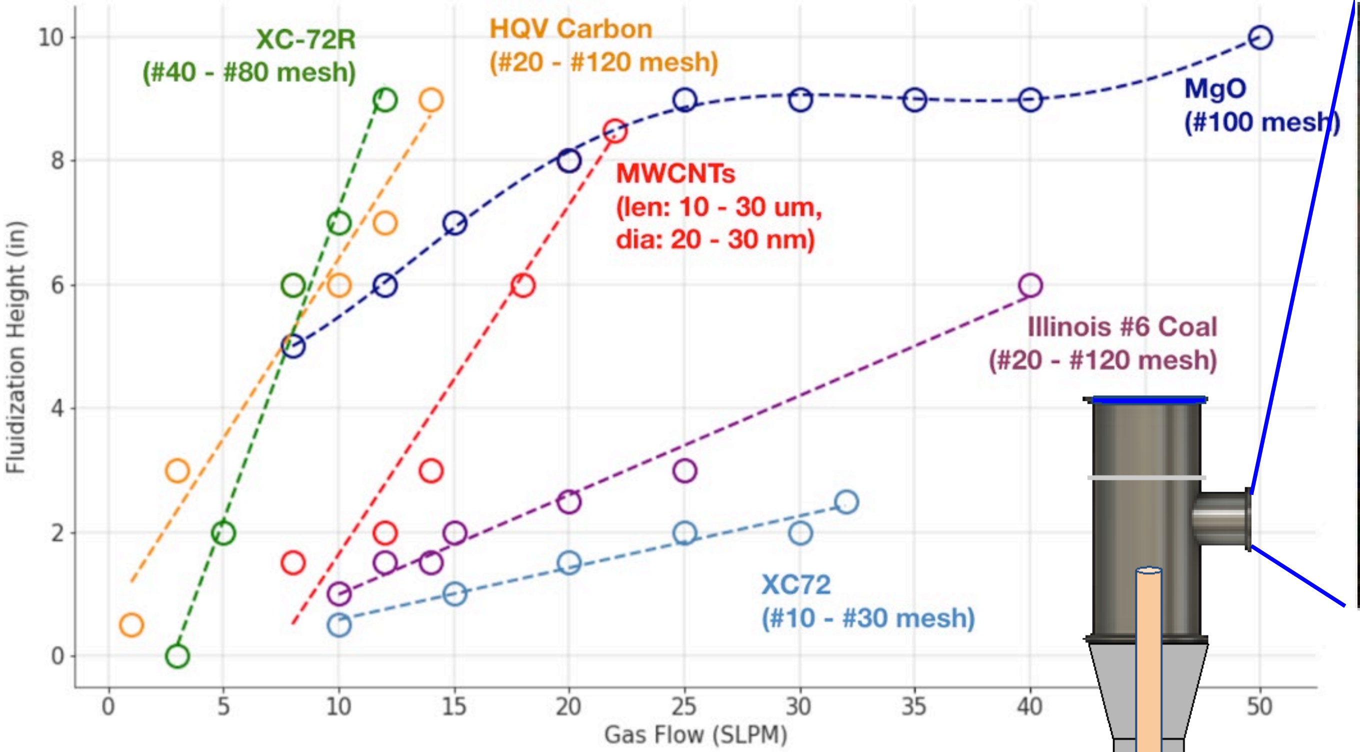
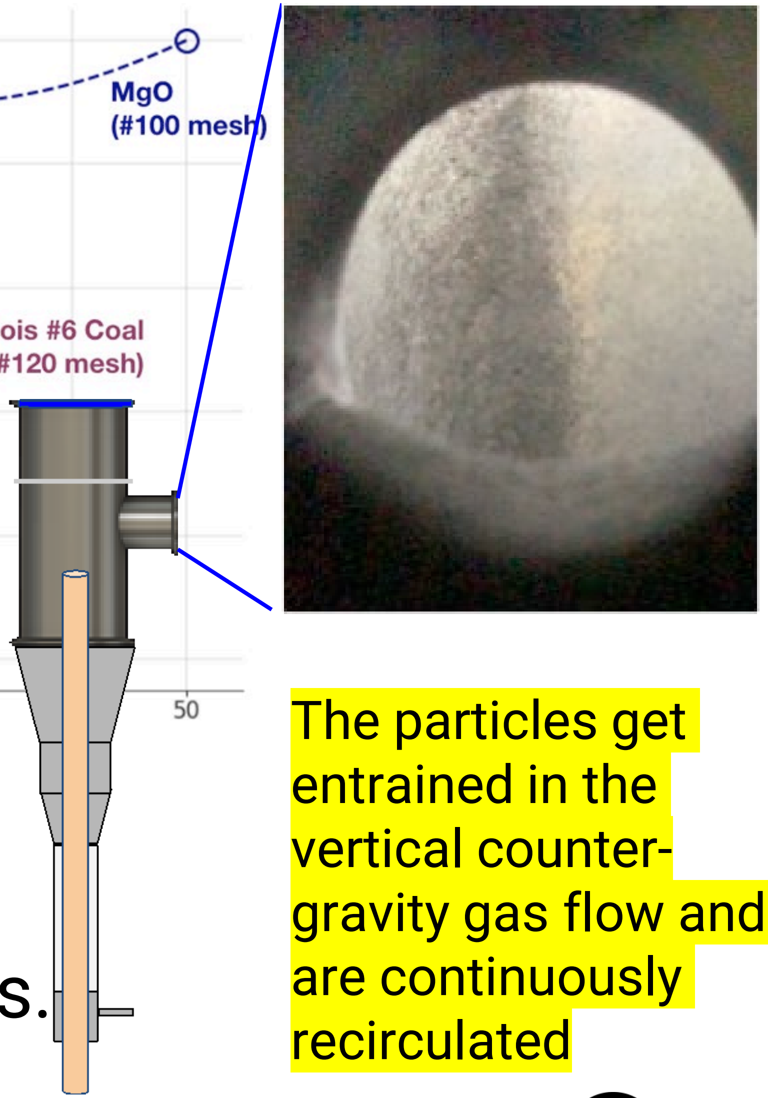
Prototype reactor characterization





Characterized fluidization of 6 materials, including MWCNTs, in two prototype configurations.

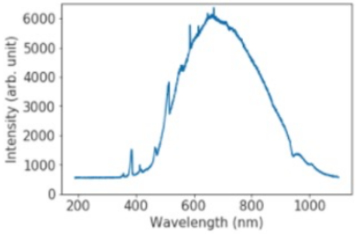
The particles get entrained in the vertical counter-gravity gas flow and are continuously recirculated

HQuest

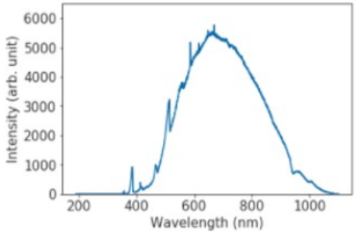
Plasma/Particle Temperature Measurements

Optical Emission Spectroscopy Setup and Pipeline

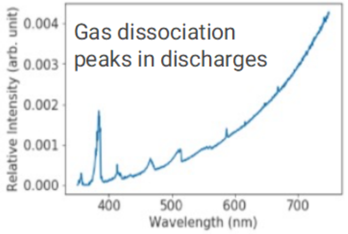
Spectral Analysis Pipeline



Unprocessed spectra



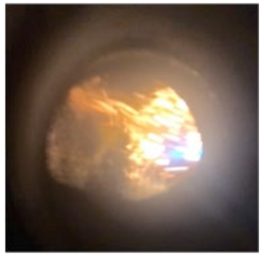
Black-pixel corrected spectra



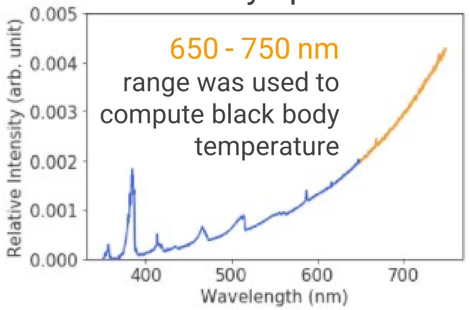
Response factor corrected spectra

Entrained plasma temperatures are too high for catalytic CNT growth

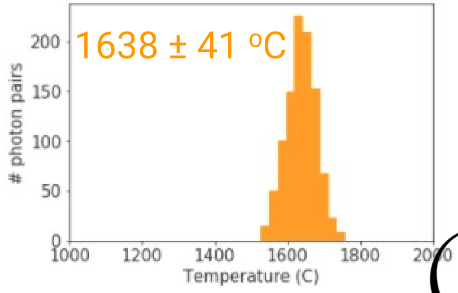
Plasma and entrained particles



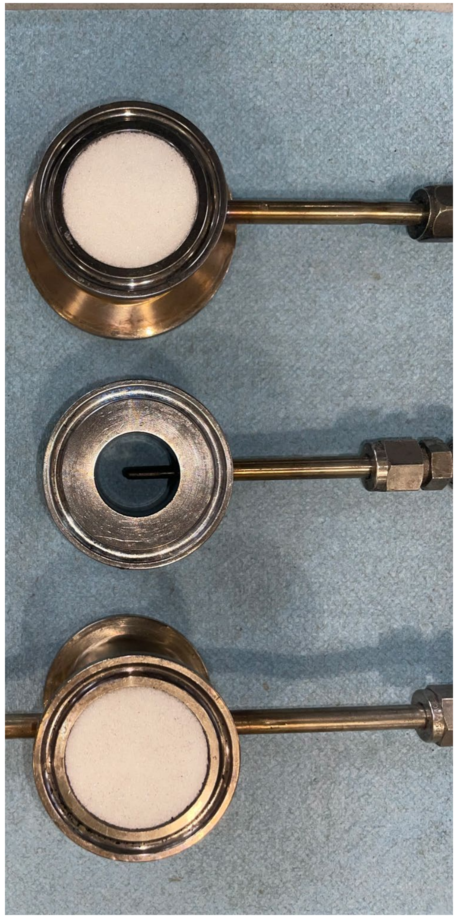
Blackbody spectra

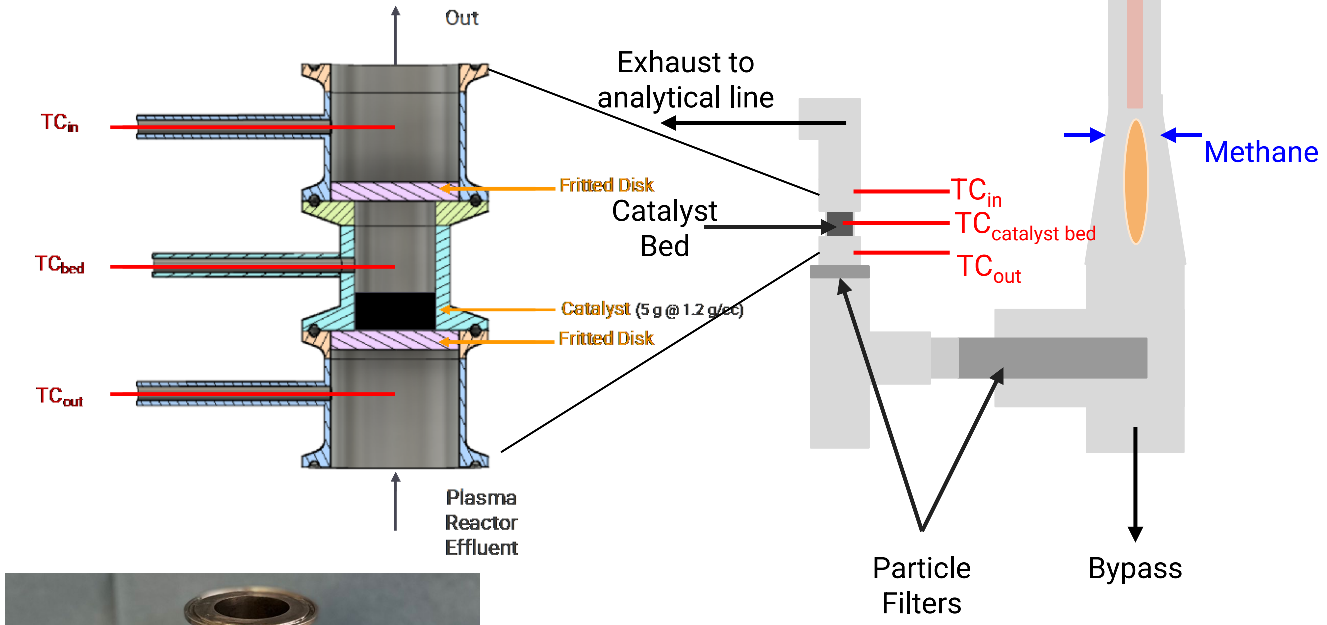


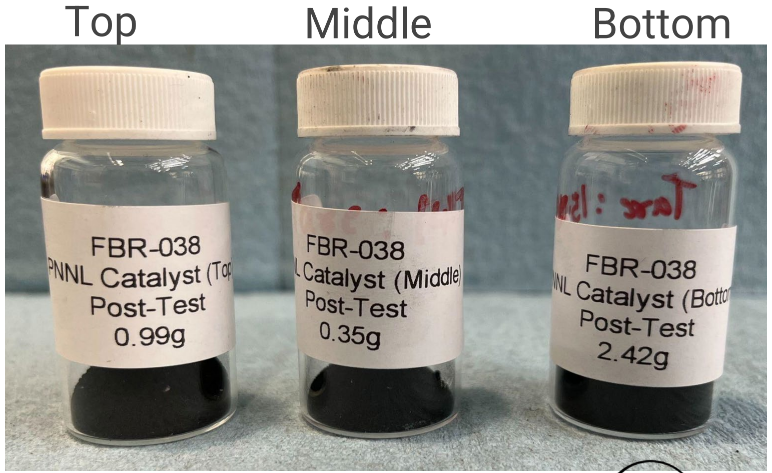
Computed temperature



Redesign to reduce reaction temperatures



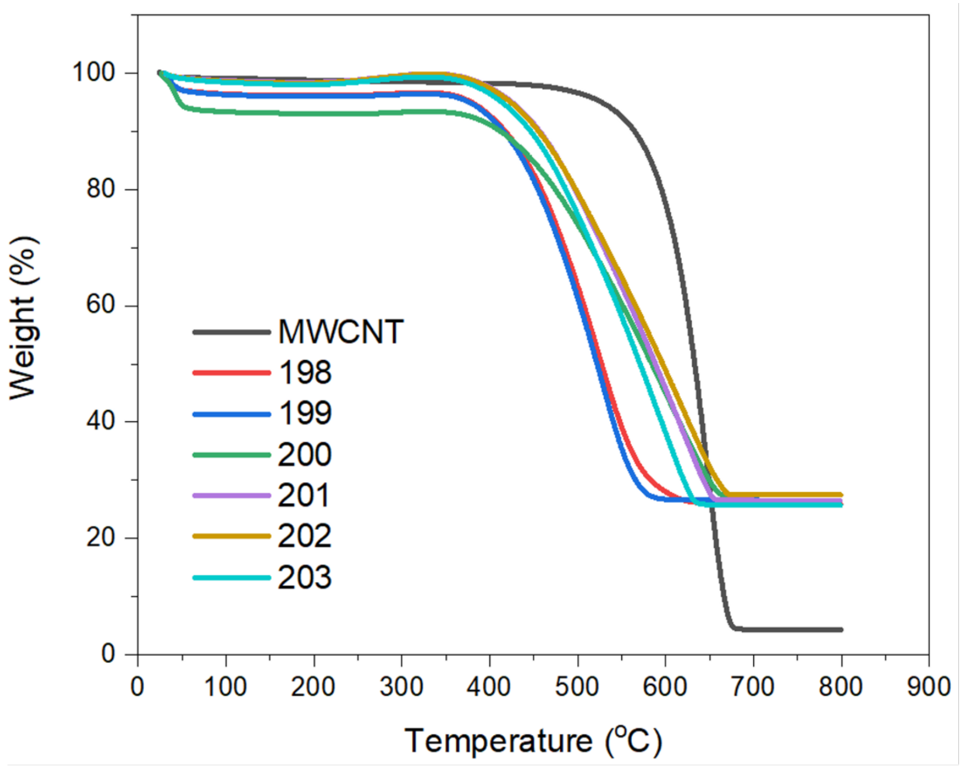


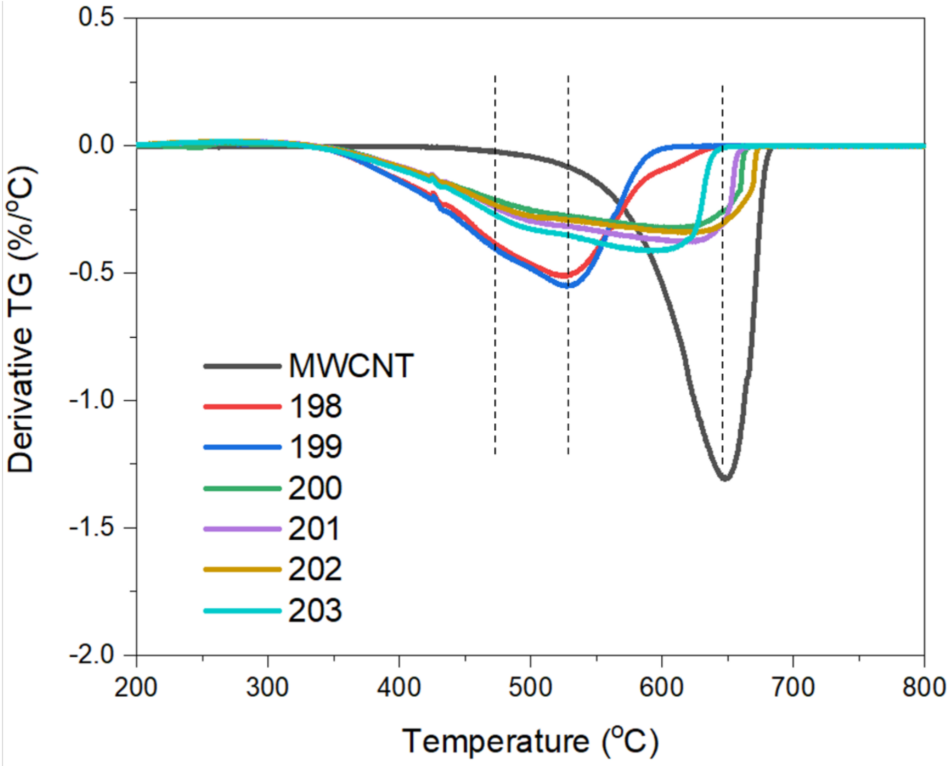


- Catalyst bed is separated from the plasma reactor
- Acetylene assumed to be primary reactant
- Temperature control via three thermocouples
- CNTs sampled from bottom (entry), middle, and top (exit) levels.

H Quest Pilot Plant- Carbon Characterization

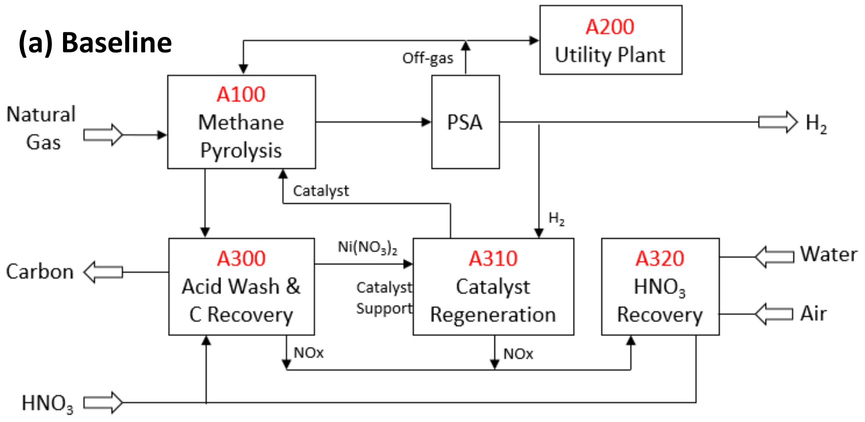
Single reactor methane → Acetylene → CNT

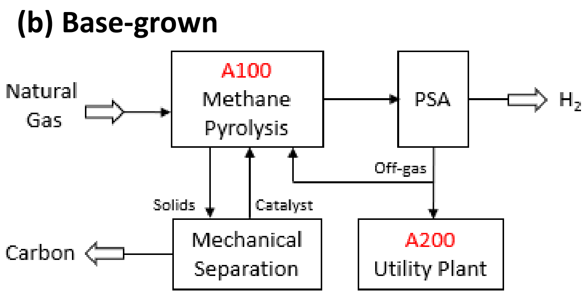


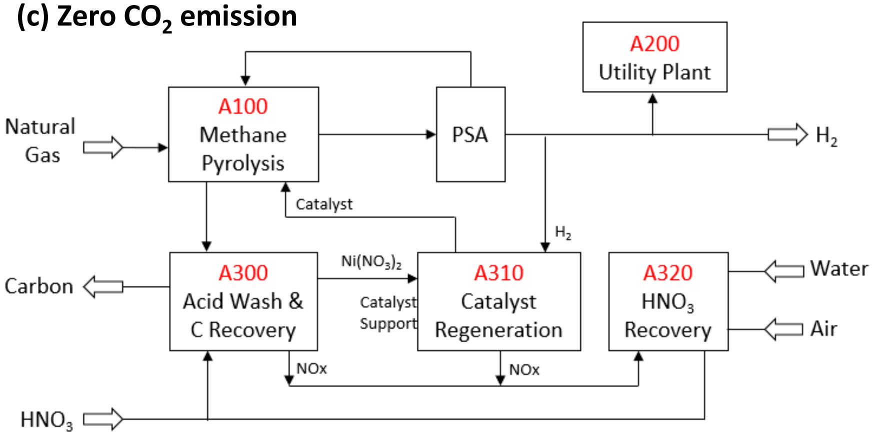


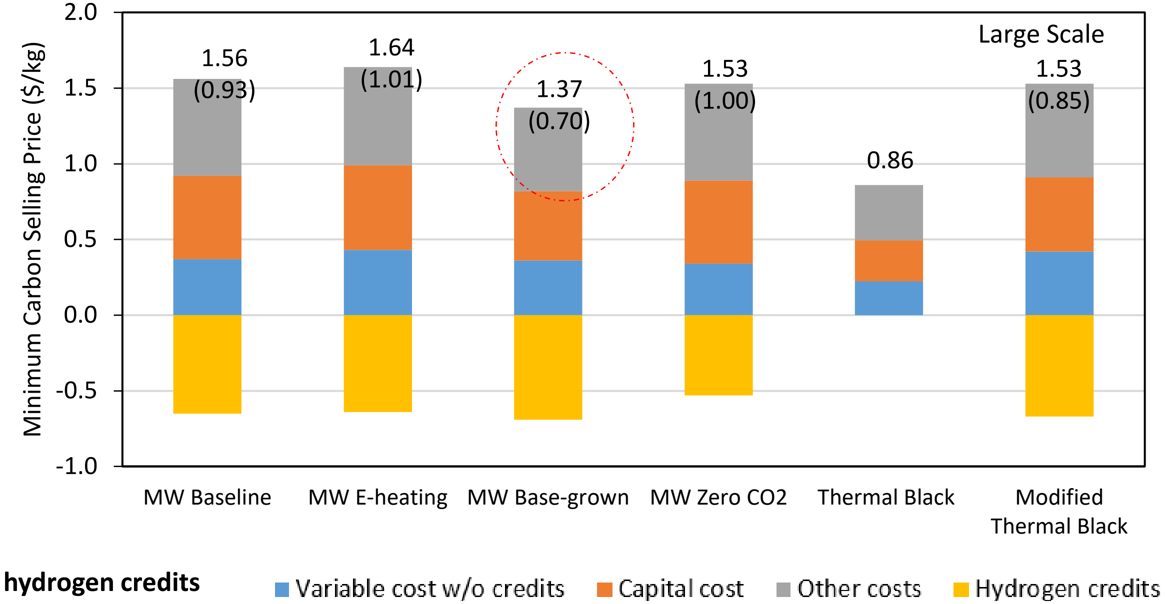
TPO Results: CNT and CNF, no amorphous carbon

TEA-Minimum Carbon Selling Price







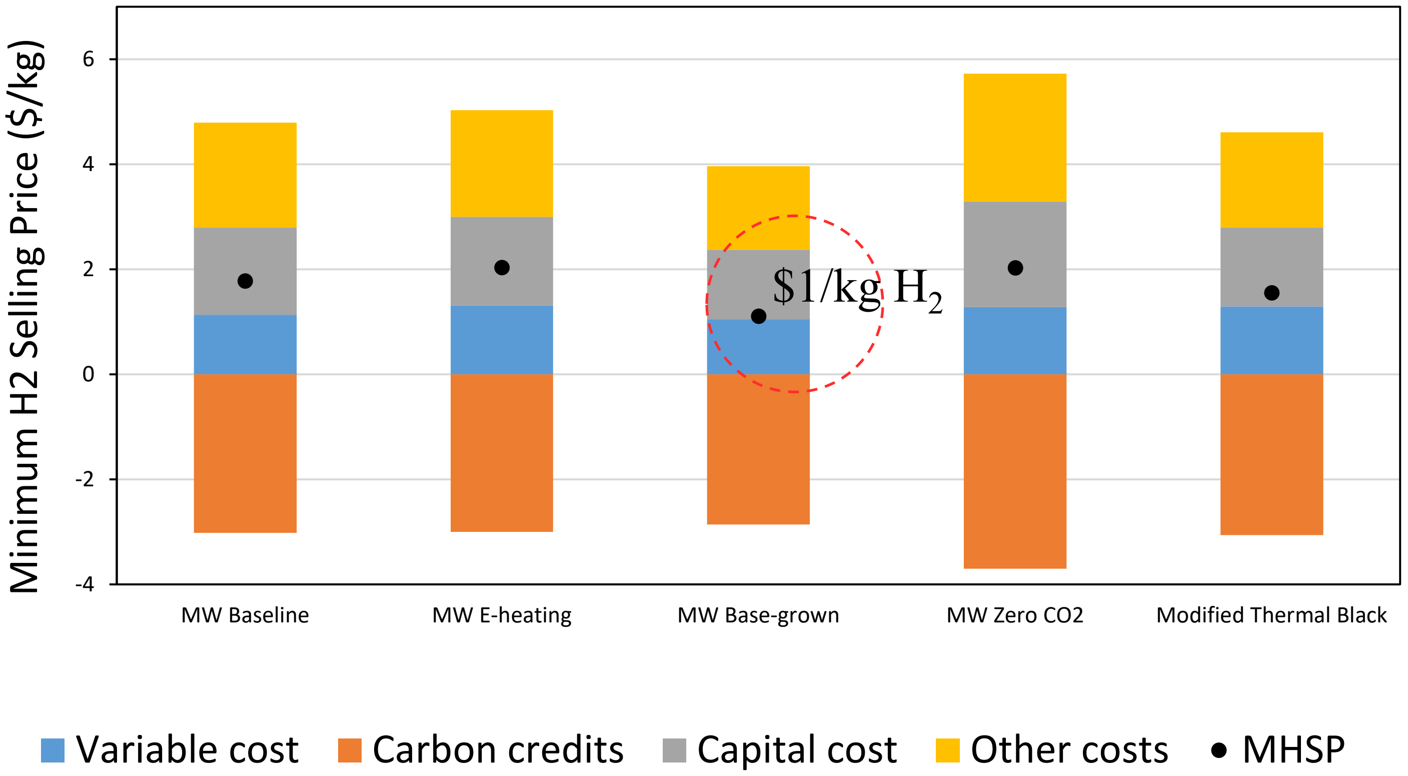


*() MCSP w/ hydrogen credits

- **The crystalline carbons from our technology will need to be sold at price similar or even lower than carbon black $0.7-1.0/kg**
- **We know these carbon can be sold at price much higher than carbon black.**
- **If benefit from CO_2 tax is considered, economic benefit will be even better.**

Minimum selling price has 15% return built in already

TEA-Minimum H_2 Selling Price



Conclusion:
Hydrogen price can be lower than $1/kg H_2

- Minimum selling price has 15% return built in already
- Carbon credit is set at low grade carbon black price
- Carbon tax is not included in TEA

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Minimum selling price has 15% return built in already

Plans for future testing/development/ commercialization

- ❑ Scale-up catalyst synthesis protocol to kg per batch
- ❑ Pilot scale microwave plasma reactor test at H-Quest, 100 hours demonstration
- ❑ Carbon characterization as electrode for electric arc steel making, additives to concrete and polymers.

a. **In this project**: Scale up to 5 kg/day.
b. **After this project**:
    - ❑ Industrial partners
    - ❑ Clean Energy Institute
    - ❑ H_2 Hub
c. **Scale-up potential:** modular approach , wellhead or stranded gas field deployment.

Outreach and Workforce Development Efforts or Achievements (If Applicable)

- ❑Graduate, undergraduate students, postdocs are working on the project.
- ❑First generation college students in West Virginia
- ❑Plan to work with industrial partners to train community college students in south Charleston areas.
- ❑Women, minority Chemical Engineering undergraduate students are trained to operate microwave reactors

Project Summary

- ❑ Gen 1 catalyst formulation Ni-Pd and Ni-Cu are developed and tested. Precious metal Pd is replaced by Cu.
- ❑ Reaction-regeneration cycles are being demonstrated.
- ❑ Gen 2 catalyst formulation featured “base-growth” is developed which will lower the CAPEX and OPEX.
- ❑ Two U.S. patent applications, two journal articles and several conference papers.
- ❑ Process simulation and TEA model developed and updated.
- ❑ Kinetics model has been completed.
- ❑ Microwave plasma pilot plant commissioning
  - ❖ Tested spouted and fluidized bed reactor prototypes
  - ❖ Evaluated fluidization of multiple catalytic materials
  - ❖ Single reactor two-stage process is being demonstrated


Thank You

Appendix

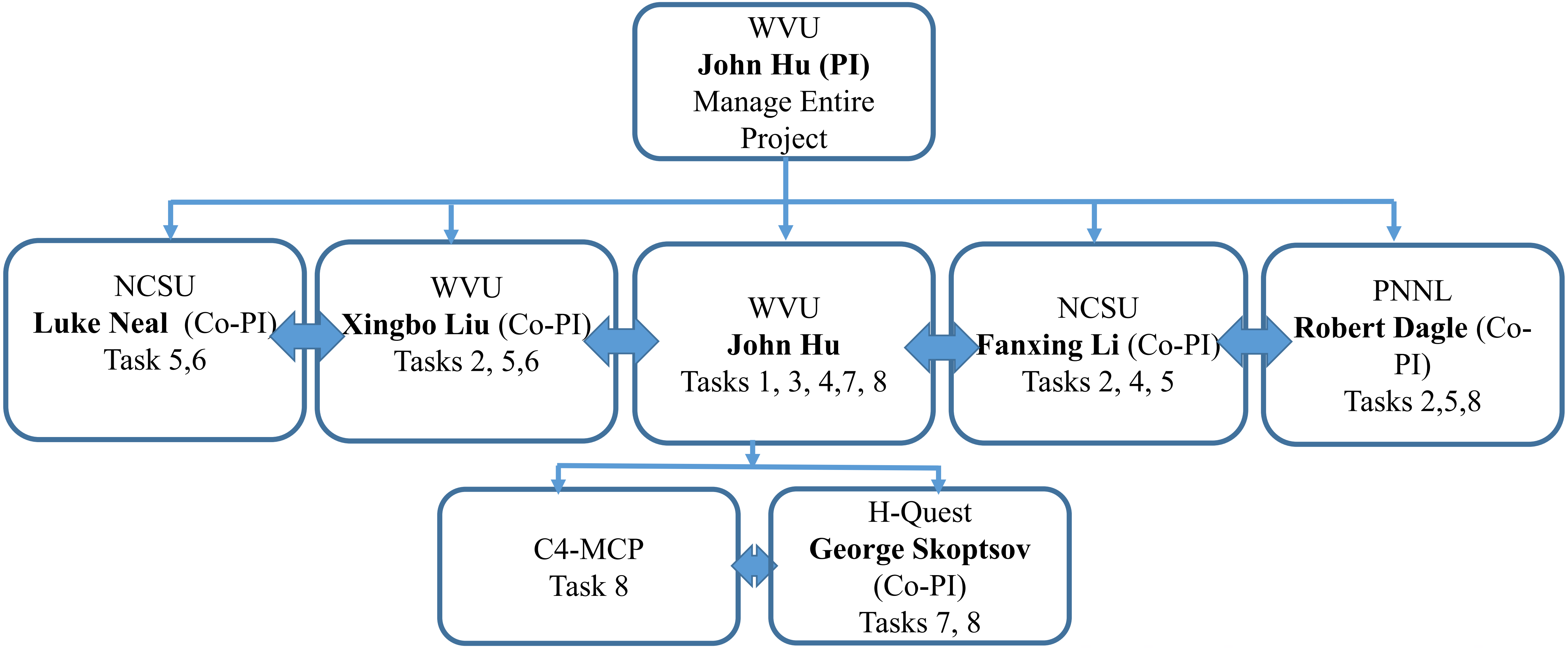
– These slides will not be discussed during the presentation but are mandatory.

Organization Chart

- Describe project team, organization, and participants.
  - Link organizations, if more than one, to general project efforts (i.e., materials development, design, systems analysis, pilot unit operation, management, risk/cost analysis, etc.).

- Please limit company specific information to that relevant to achieving project goals and objectives.

Project Organization Chart



Gantt Chart

Table 4.1. Updated Project Timeline **Green**=original schedule, **Orange**=task extension into BP-2

Task Name	**Assigned Resources**	Year 1 (Qtr)				Year 2 (Qtr)				Year 3 (Qtr)			
		1	2	3	4	1	2	3	4	1	2	3	4
Task 1. Project Management and Planning	Hu	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Task 2. Catalyst Design, Synthesis and Characterization	Li/Liu/Dagle	Green	Green	Green	Green	Green	Green	Green	Green	Orange	Orange		
Subtask 2.1. Explore Supported and Unsupported Bimetallic Catalysts	Li/Liu	Green	Green	Green	Green								
Subtask 2.2 Effect of Promoters on the Formation of CNTs/CNFs	Li/Liu/Dagle			Green	Green	Green	Green	Green	Green	Orange	Orange		
Task 3. Variable Frequency Microwave Reactor Test	Hu	Green	Green	Green	Green	Green	Green	Green	Green	Orange	Orange		
Subtask 3.1 Study Effect of Reaction Variables	Hu	Green	Green	Green	Green								
Subtask 3.2 Evaluate the Effect of Reactor Configurations on the Process Performance	Hu			Green	Green	Green	Green	Green	Green	Orange	Orange		
Subtask 3.3 Evaluate Effect of Feedstock Composition on the Process Performance	Hu					Green	Green	Green	Green	Orange	Orange		
Task 4. Separation of Catalyst-CNTs & CNFs and Catalyst Regeneration	Li/Hu	Green	Green	Green	Green	Green	Green	Green	Green	Green			
Task 5. Intrinsic Nature of Metal-Support Interaction for CNT and H_2 Formation	Liu/Li/Dagle	Green	Green	Green	Green	Green	Green	Orange	Orange	Orange	Orange		
Task 6. Kinetic Modeling	Neal/Liu		Green	Green	Green	Green	Green	Orange					
Task 7. Pilot Demonstration with a 6 kW Microwave Plasma Reactor	Skoptsov	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Task 8. Reactor Modeling, Commercial Process Flowsheet, Technoeconomic Analysis (TEA) and Tech-to Market	C4-MCP							Green	Green	Green	Green	Green	Green

Gantt Chart

- Provide a simple Gantt chart showing project lifetime in years on the horizontal axis and major tasks along the vertical axis. Use symbols to indicate major and minor milestones. Use shaded lines or the like to indicate duration of each task and the amount of work completed to date.

Timeline and Schedule

Task Name	Assigned Resources	Year 1 (Qtr)				Year 2 (Qtr)				Year 3 (Qtr)			
		1	2	3	4	1	2	3	4	1	2	3	4
Task 1. Project Management and Planning	Hu	■	■	■	■	■	■	■	■	■	■	■	■
Task 2. Catalyst Design, Synthesis and Characterization	Li/Liu/Dagle	■	■	■	■	■	■	■	■				
Subtask 2.1. Explore Supported and Unsupported Bimetallic Catalysts	Li/Liu	■	■	■	■								
Subtask 2.2 Effect of Promoters on the Formation of CNTs/CNFs	Li/Liu/Dagle			■	■	■	■	■	■				
Task 3. Variable Frequency Microwave Reactor Test	Hu	■	■	■	■	■	■	■	■				
Subtask 3.1 Study Effect of Reaction Variables	Hu	■	■	■	■								
Subtask 3.2 Evaluate the Effect of Reactor Configurations on the Process Performance	Hu			■	■	■	■	■	■				
Subtask 3.3 Evaluate Effect of Feedstock Composition on the Process Performance	Hu					■	■	■	■				
Task 4. Separation of Catalyst-CNTs & CNFs and Catalyst Regeneration	Li/Hu	■	■	■	■	■	■	■	■	■			
Task 5. Intrinsic Nature of Metal-Support Interaction for CNT and H2 Formation	Liu/Li/Dagle	■	■	■	■	■	■						
Task 6. Kinetic Modeling	Neal/Liu		■	■	■	■	■						
Task 7. Pilot Demonstration with a 6 kW Microwave Plasma Reactor	Skoptsov	■	■	■	■	■	■	■	■	■	■	■	■
Task 8. Reactor Modeling, Commercial Process Flowsheet, Technoeconomic Analysis (TEA) and Tech-to Market	C4-MCP WVU							■	■	■	■	■	■

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