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

April 3, 2024

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 fluctuation of gas flow rate and composition.

Project Overview

- ❑Electromagnetic sensitive catalyst development and scale up.
- ❑Microwave plasma pilot reactor test at capacity of 50-100 cft/hour (18-72 kg carbon nano materials/day)
- ❑Technoeconomic analysis.
- ❑Technology-to-market strategy, plan, and commercialization.

Technology Background-The Need

The Issue of Flaring Gas

Shale Gas Exploration

Wellhead Equipment

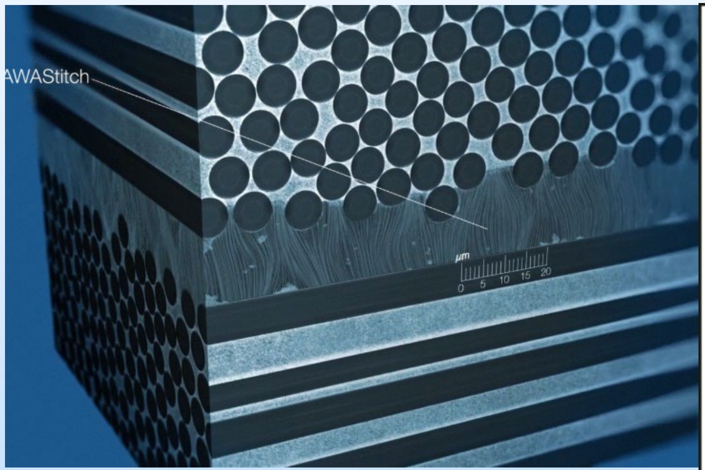
(Bakken, ND)

Natural gas flaring, venting up in Texas

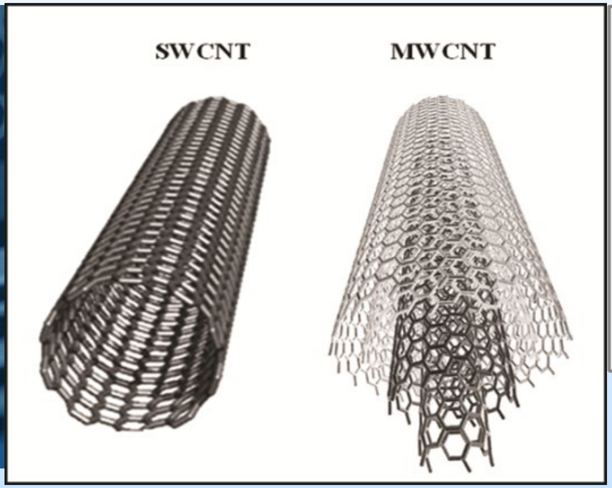
Zero-Carbon Dioxide Emission Hydrogen Production

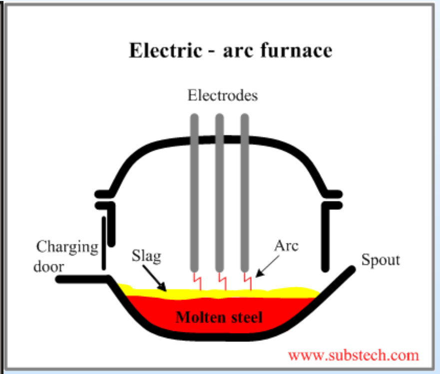
WVU patented technology turns natural gas into hydrogen and high value carbon without carbon dioxide:

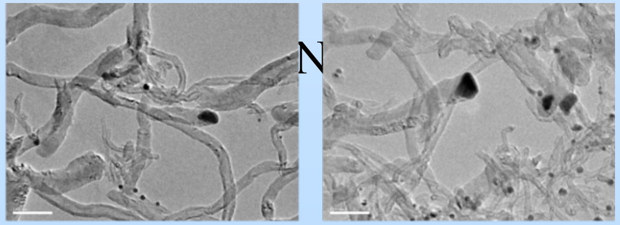
$$CH_4 \rightarrow C_s(Advnaced\ Carbon) + 2H_2$$



Carbon Composite







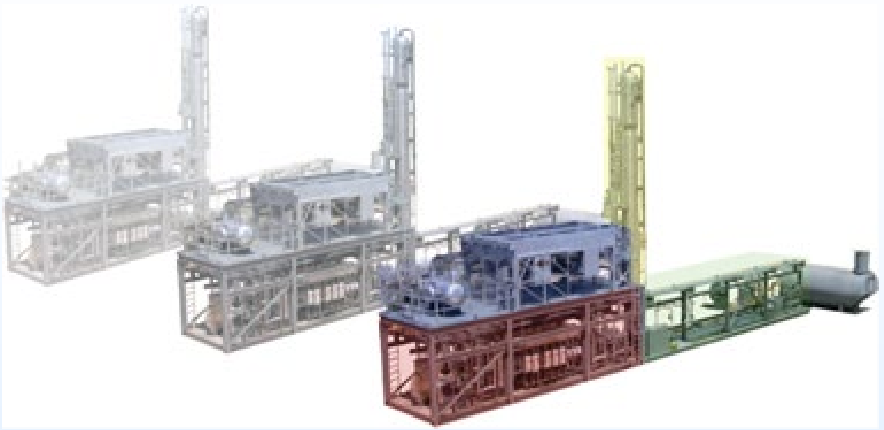
Scale bar = 100 nm

Technical Approach/Project Scope

Technical Approach-Microwave Catalytic Process

Advantages of using MW heating

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



Modular Unit

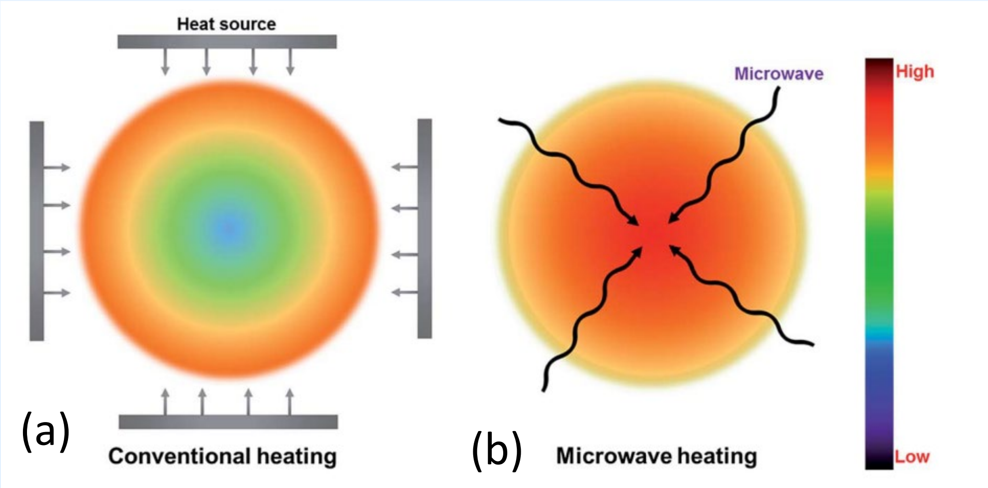


Fig 1. Schematic diagram of (a) conventional heating; (b) microwave heating

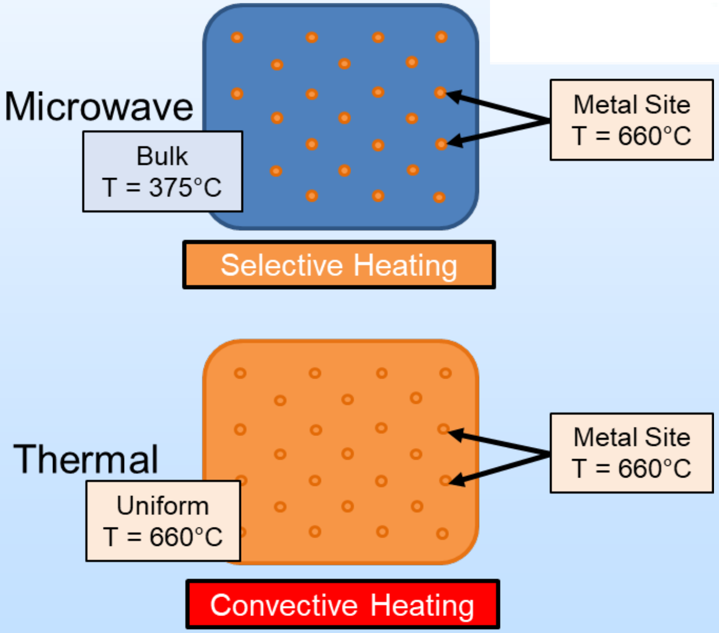
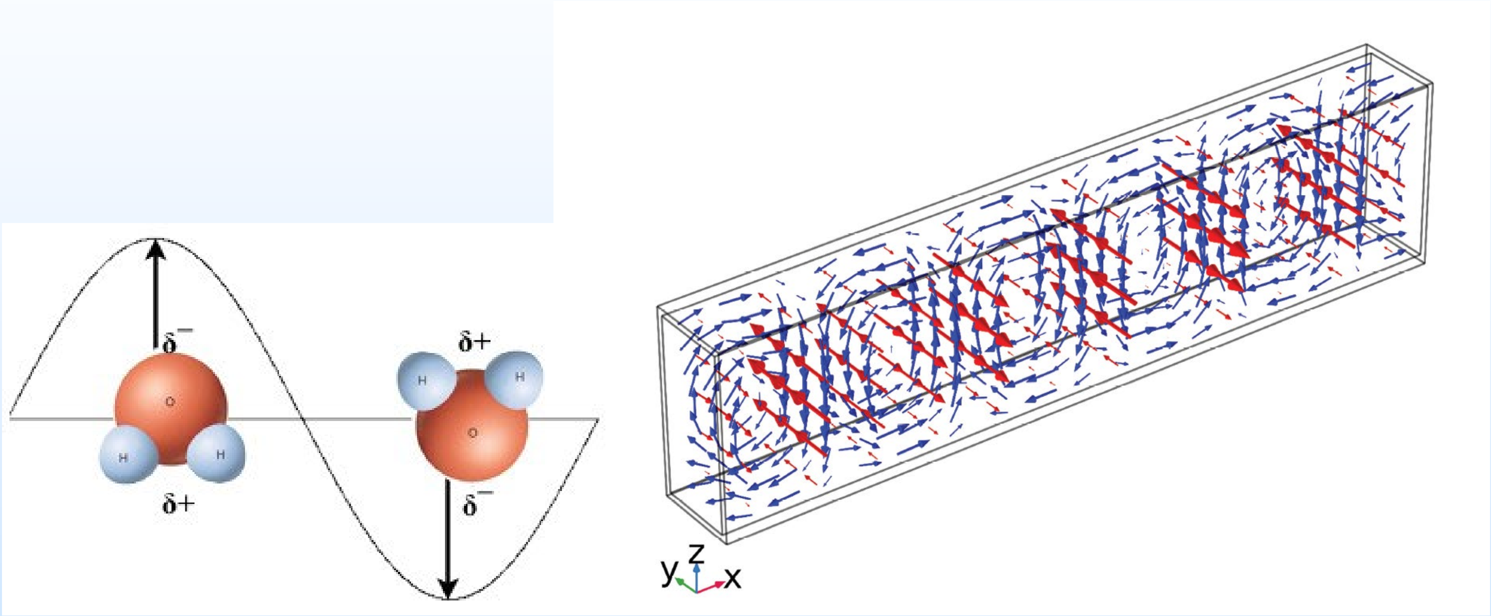
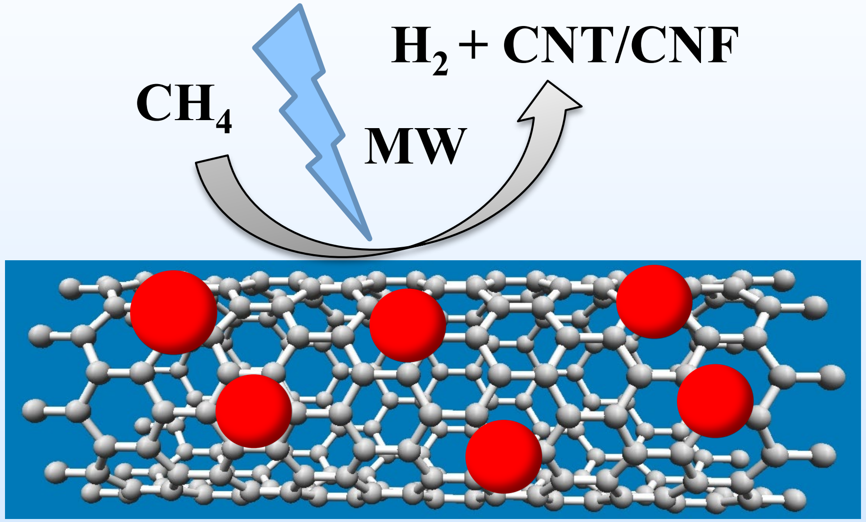


Fig 2. Selective material heating and reduce the bulk temperature

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.

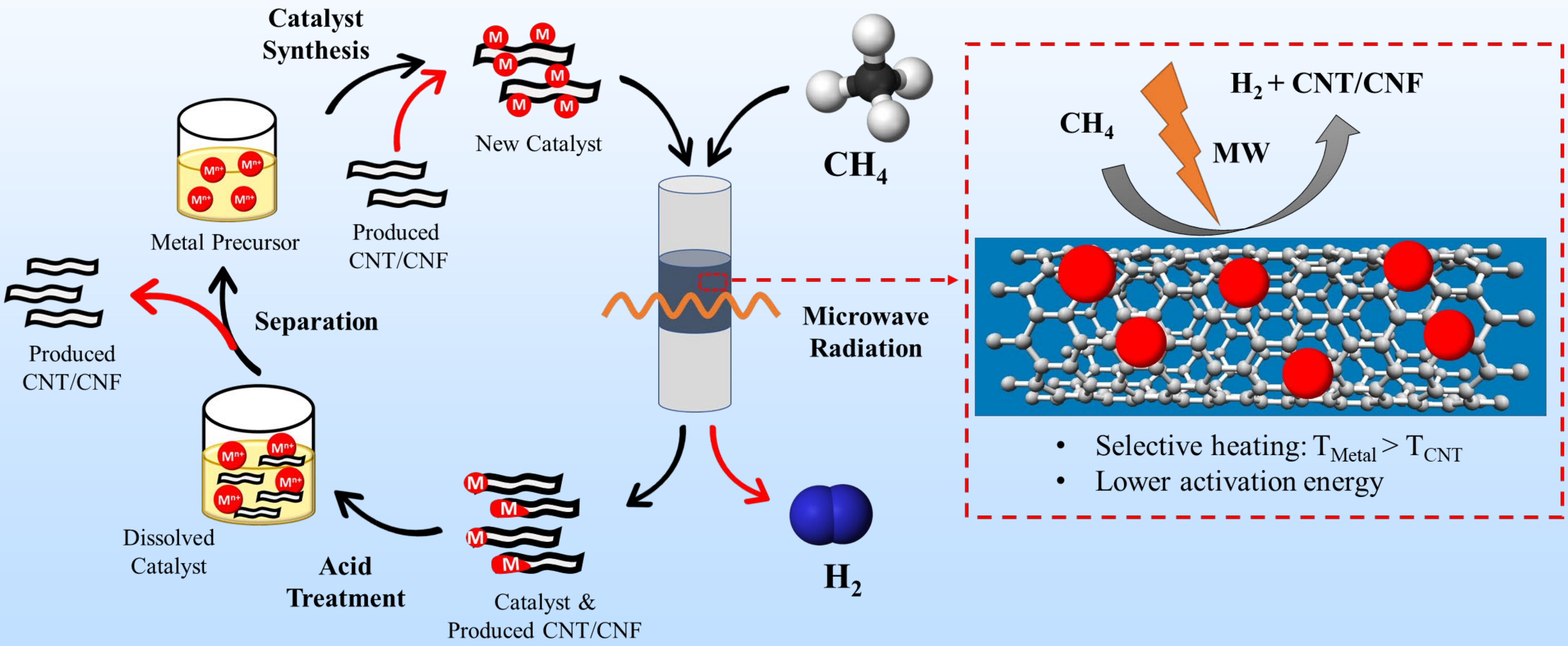




- Selective heating: $T_{Metal} > T_{CNT}$
- Lower activation energy

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.

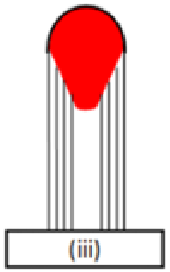


Novel Catalyst Synthesis for Base Growth-solving the challenge in CNT-metal separation

Route 1: traditional ex-situ surface deposition

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

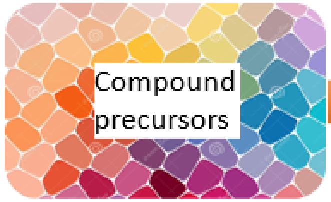
Ni-Cu alloy particle



Tip-grown

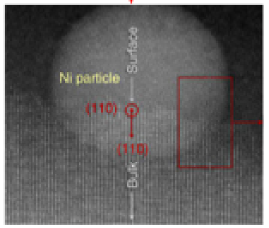
Clean-cut interface between Ni-Cu alloy particle and host materials, tend to break-way

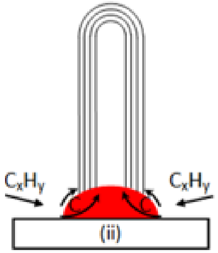
Route 2: new in-situ surface exsolution



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

Ni-Cu alloy particle





Base-grown

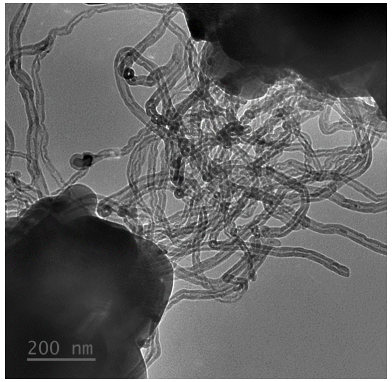
Deep-buried anchor between Ni-Cu alloy particle and host material, strong bond

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

Surface catalyst exsolution control:

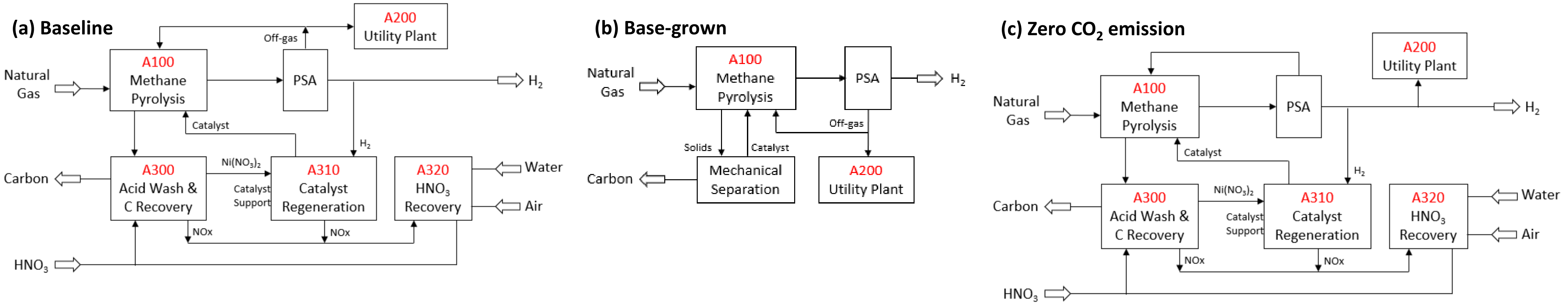
$$\text{Dilute } H_2+(A_1A_2)(B_1B_2NiCu)O_3 \xrightarrow{\text{Intermediate T}} (A_1A_2)(B_1B_2)O_{3-\delta}+Ni\text{-}Cu+H_2O$$

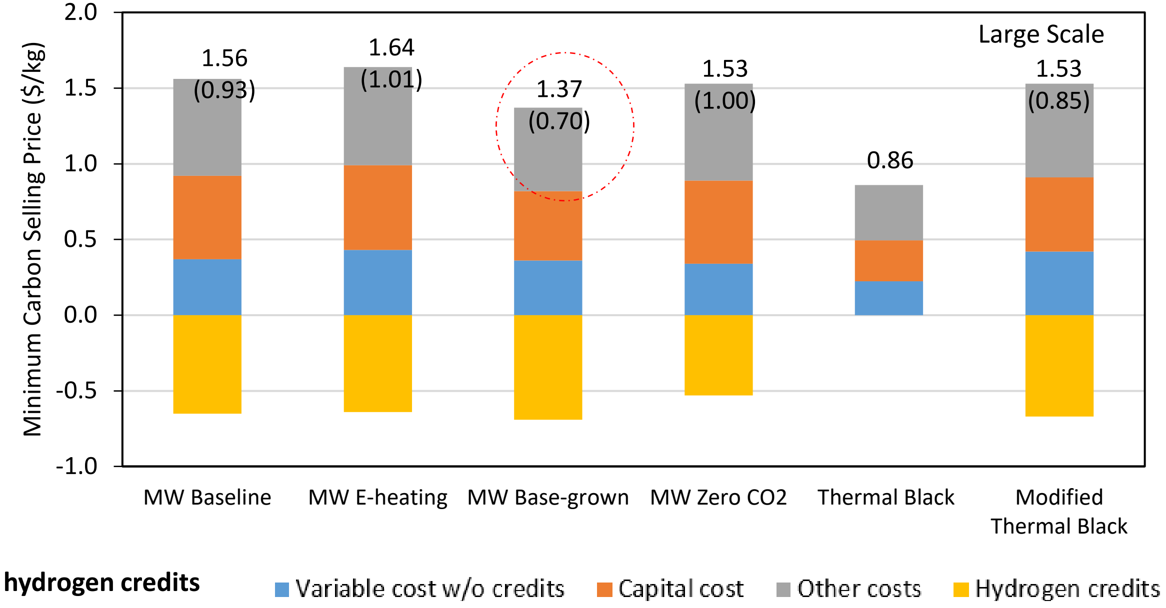
- High entropy compound as host tends to decrease to single oxides at intermediate T
- Higher reducibility of NiCuOx than other elements



Technoeconomic Analysis (TEA)

TEA-Minimum Carbon Selling Price



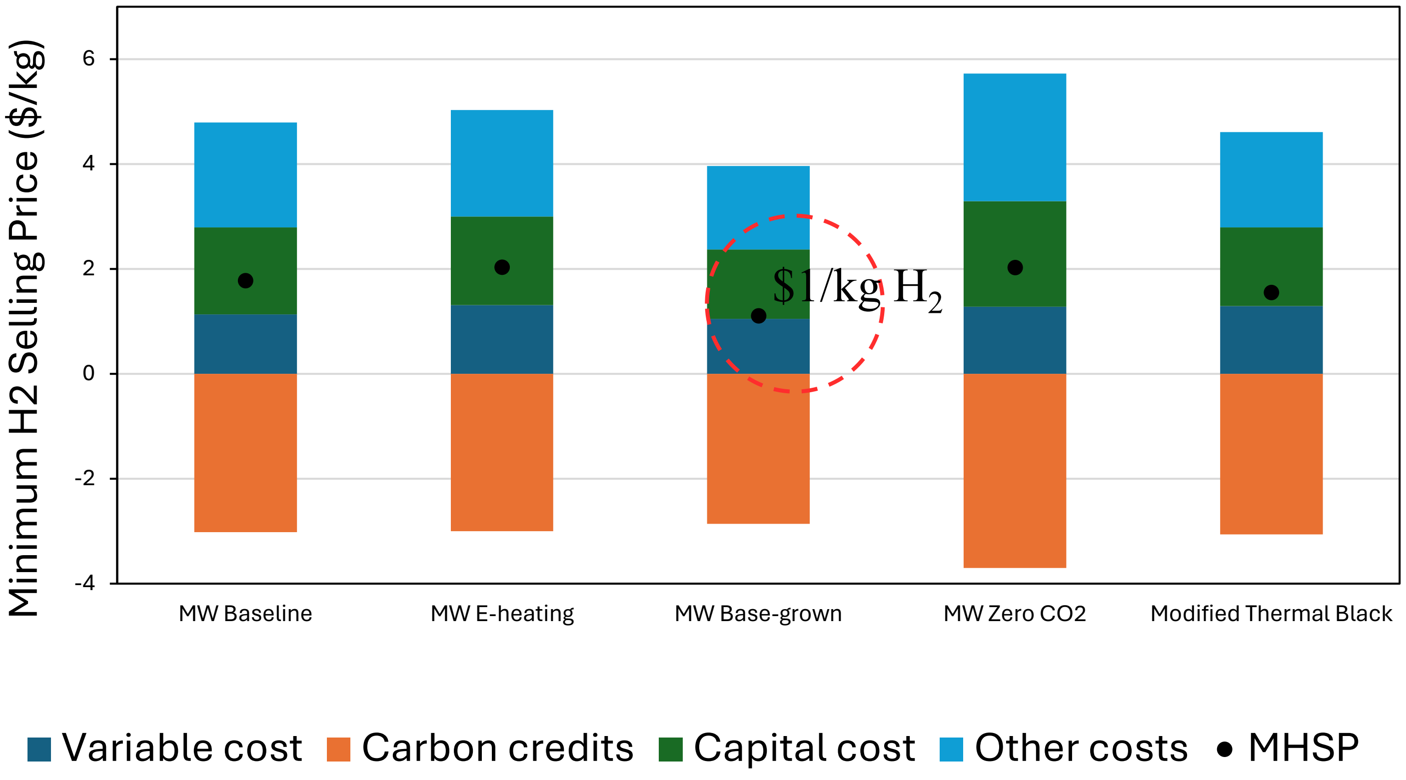


*() MCSP w/ hydrogen credits

- **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

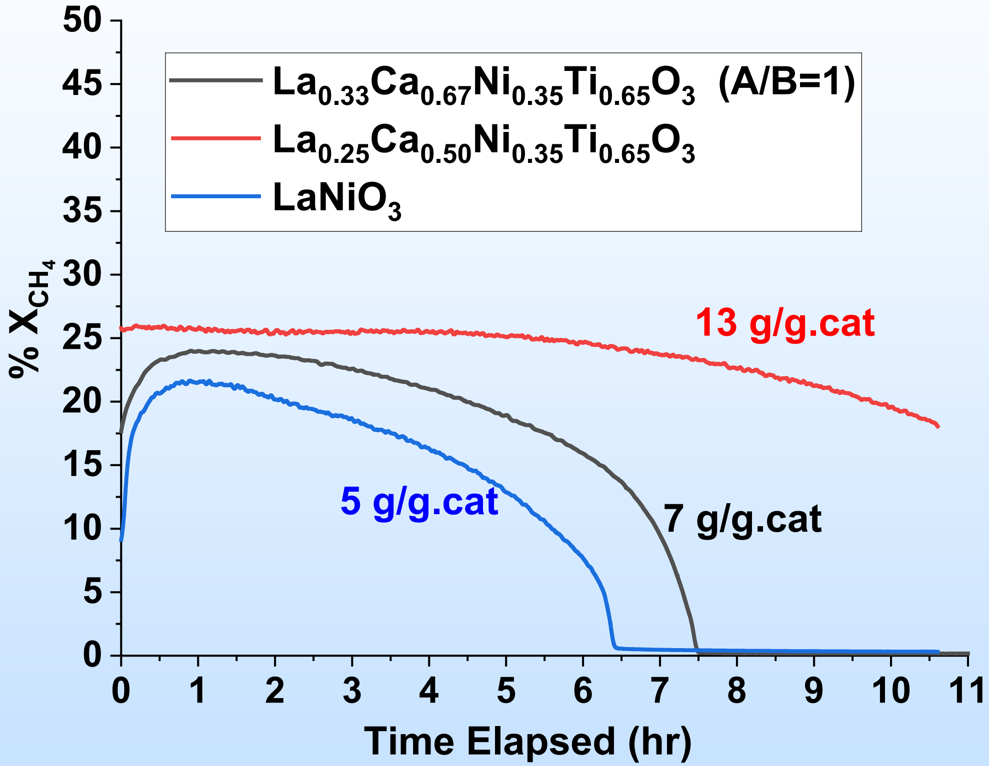
- Minimum selling price has 15% return built in already
- Carbon tax is not included in TEA

Ind. Eng. Chem. Res. 2022, 61, 5080−5092

Progress and Current Status of Project

Accomplishments since last year's meeting.

Methane Pyrolysis Over Perovskite Type Mixed Oxides: The Effect of Non-Stoichiometry



Conditions:
Catalyst loading :200mg
Reduction at 600°C for 1 hr in 10% H_2
CDM Reaction at 600°C with 90% CH_4

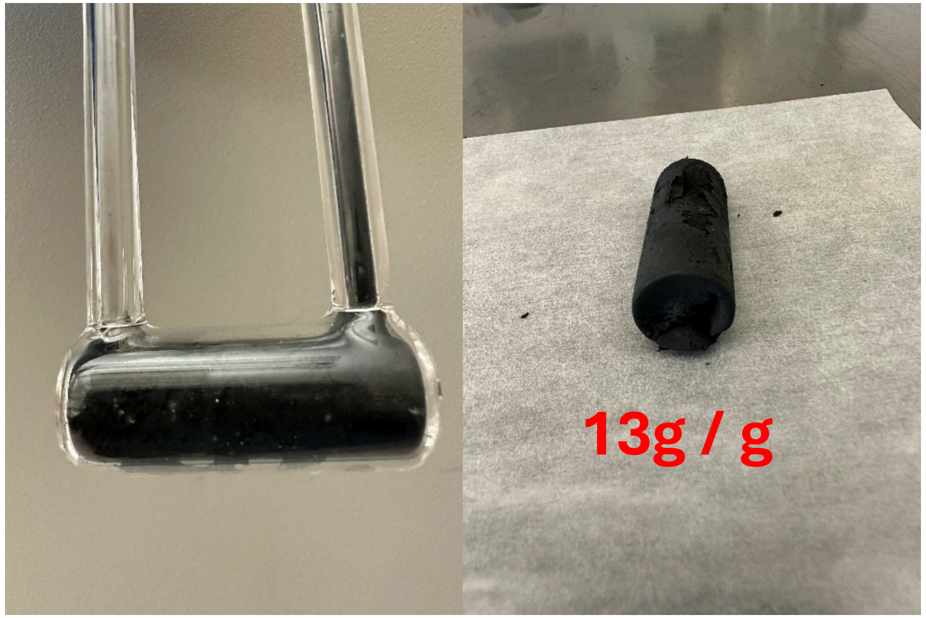
Key Findings:

- By inducing non-stoichiometry on the A-site of the perovskite facilitates Ni exsolution, promoting favorable conditions for the CDM reaction.
- Exceptional carbon yield of approximately 13 grams per gram of catalyst.
- Extended injections are anticipated to further elevate carbon yields.

Methane Pyrolysis Over Perovskite Type Mixed Oxides: Fresh and Post CDM samples

Fresh

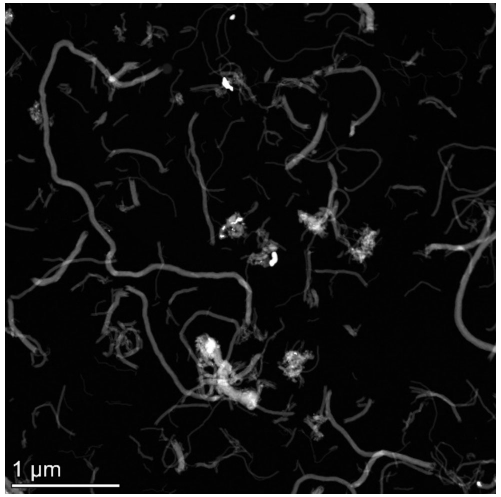
Post CDM



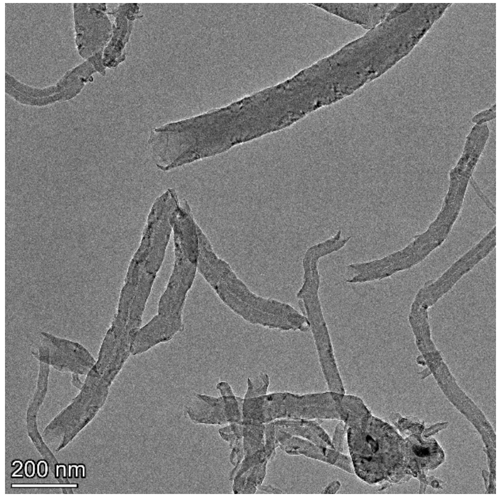
More CNTs might be grown and the CH_4 conversion might be stable for more then 10 hours by reloading the grounded form of the spent catalyst.

Methane Pyrolysis Over Perovskite Type Mixed Oxides: Carbon growth

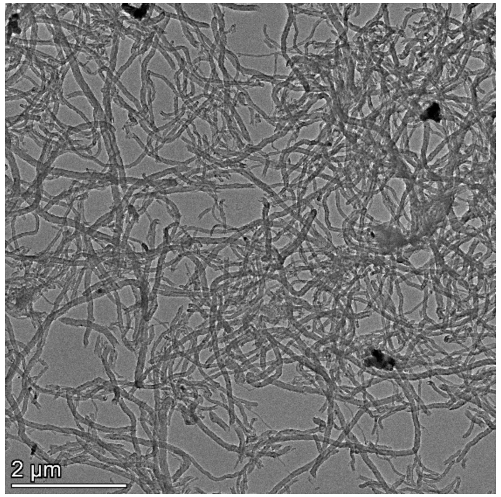
$LaNiO_3$

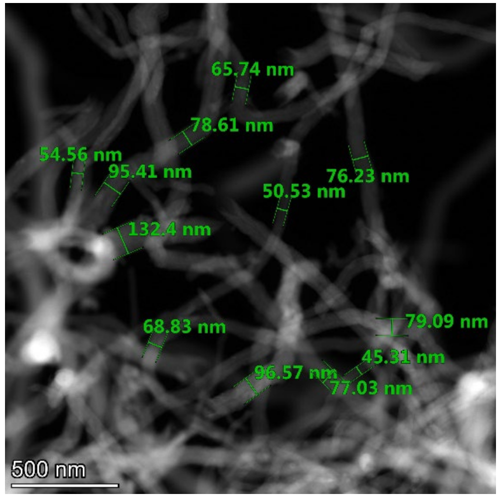


$La_{0.33}Ca_{0.67}Ti_{0.35}Ni_{0.65}O_3$



$La_{0.25}Ca_{0.50}Ti_{0.35}Ni_{0.65}O_3$



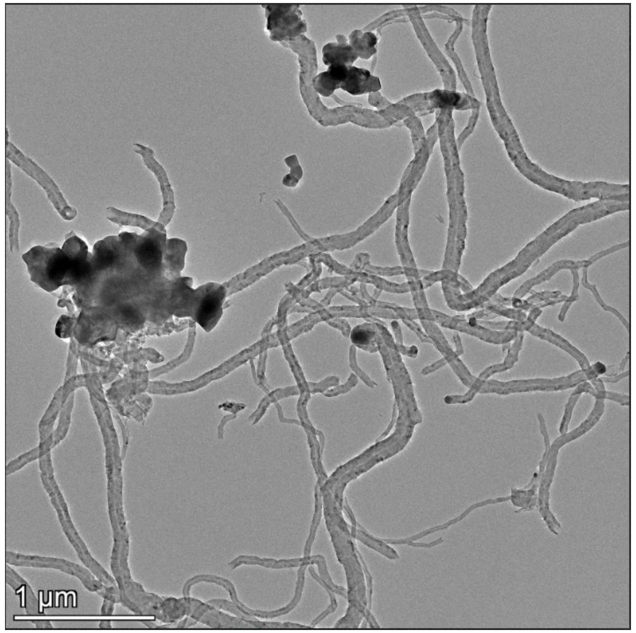


Key Findings:

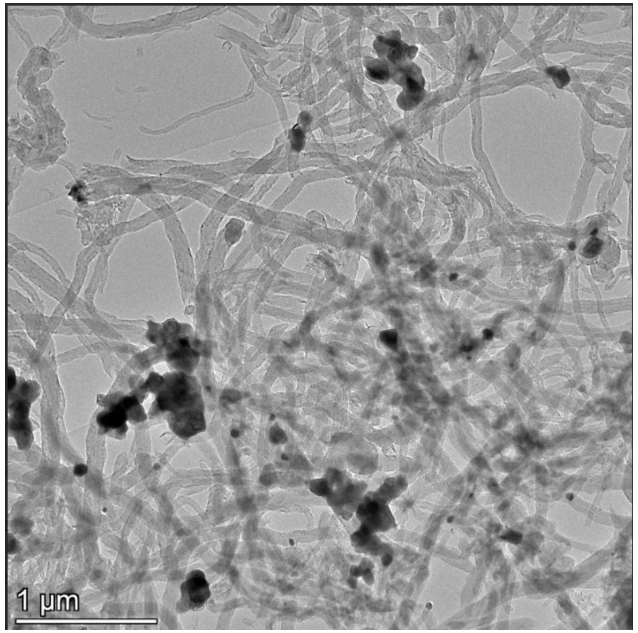
- The best performing perovskite (i.e. non-stoichiometric $La_{0.25}Ca_{0.50}Ti_{0.35}Ni_{0.65}O_3$) shows well defined CNTs.
- The stoichiometric ($La_{0.33}Ca_{0.67}Ti_{0.35}Ni_{0.65}O_3$) and the base perovskite ($LaNiO_3$)show broken CNTs.

Methane Pyrolysis Over Perovskite Type Mixed Oxides: Evolution of Carbon Growth

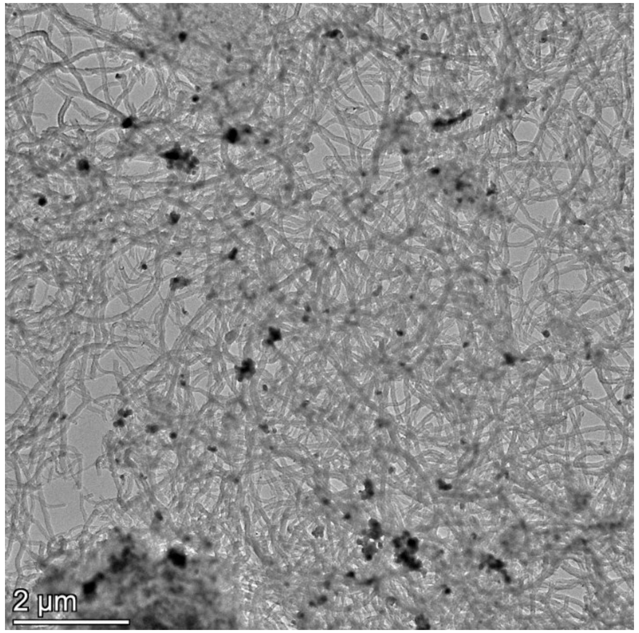
CDM:Post 1 hour



CDM:Post 3 hour



CDM:Post 6 hour



The best performing perovskite (i.e. non-stoichiometric $La_{0.25}Ca_{0.5}Ti_{0.35}Ni_{0.65}O_3$) shows well defined CNTs that continue to grow with near uniform morphology as the reaction proceed.

Fluidized-Bed Microwave Reactor

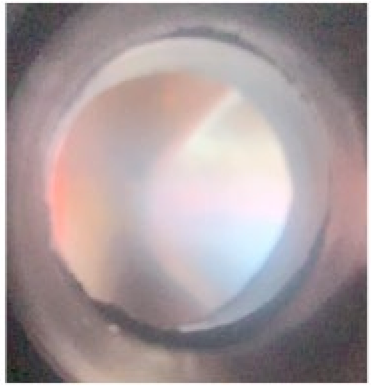
Reactor configurations iteratively modified to maximize plasma extents and particle interaction

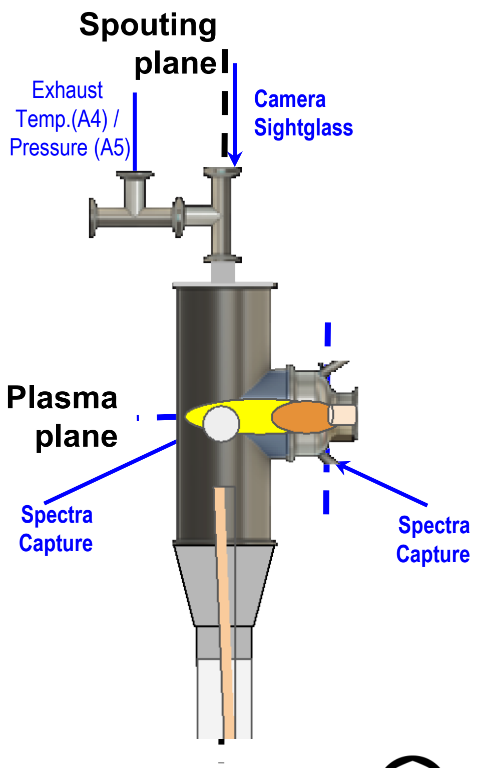
General description

- Feed supplied vertically from below in either spouted or fluidized configuration;
- Ionized gas (plasma) is launched horizontally cross-axis to entrained feed;
- Exhaust entrainment and particle loss controlled by limiting gas velocities.

Instrumentation:

- Viewports for camera and spectral capture
- TC and pressure transducers downstream

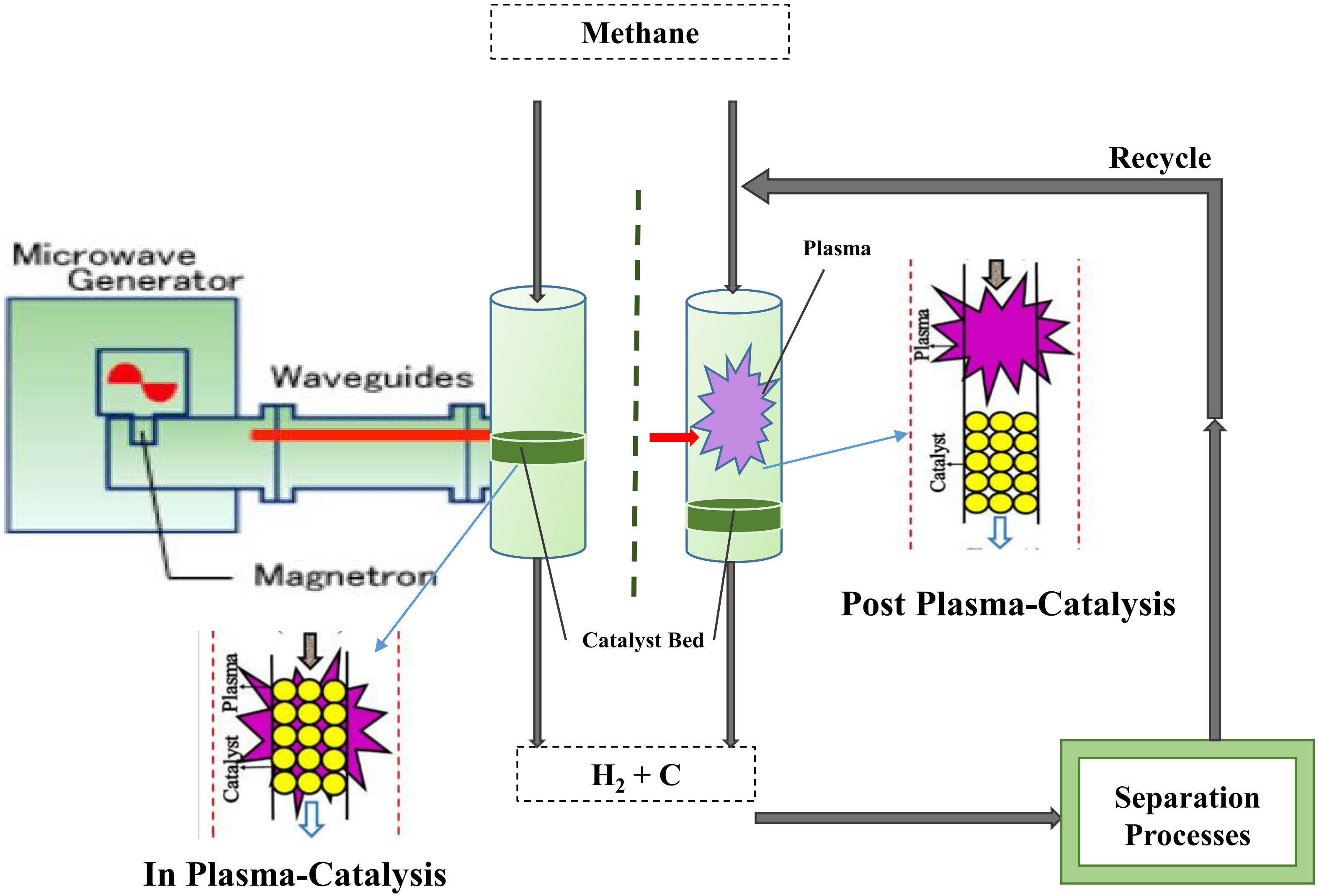




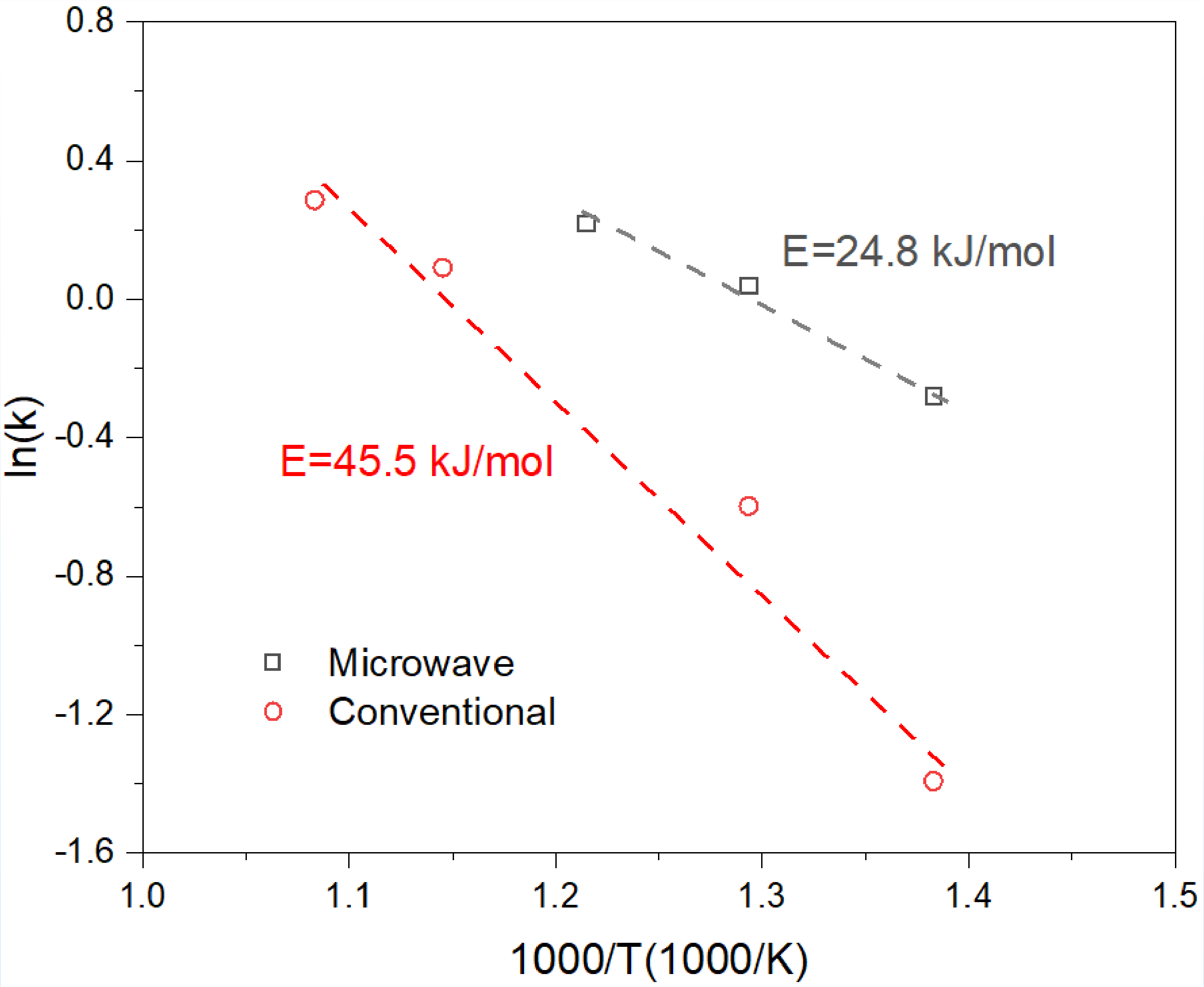
HQuest

Kinetics and Process Improvement
(Supporting Pilot Plant Test)

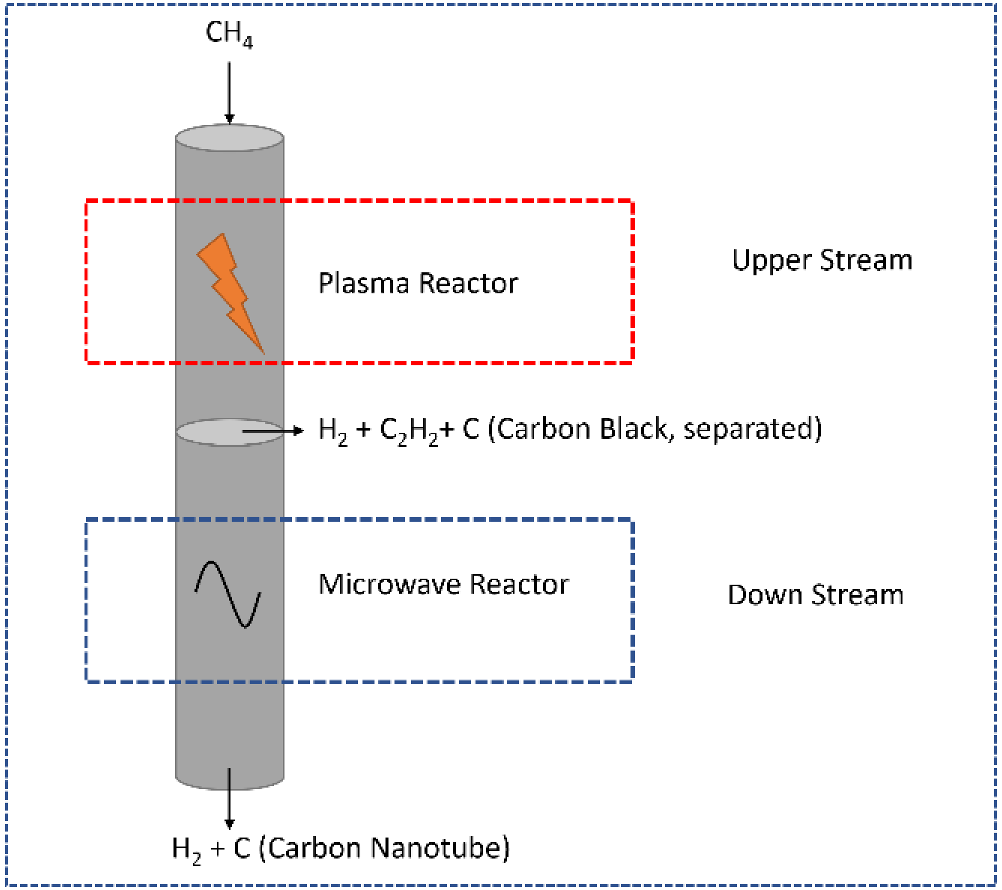
Process Scheme



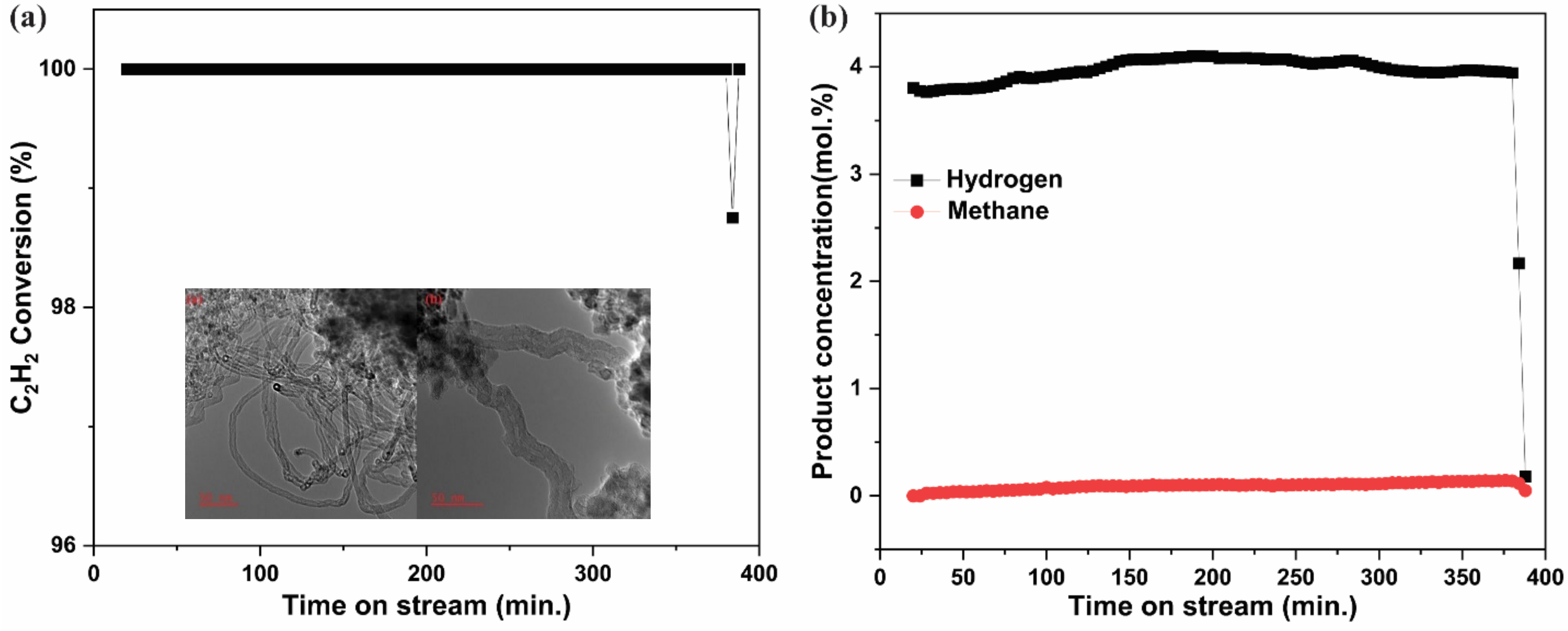
Microwave Irradiation Lowers Activation Energy



Single Reactor Two-Stage Process



Second Stage Reaction-Pyrolysis of Acetylene



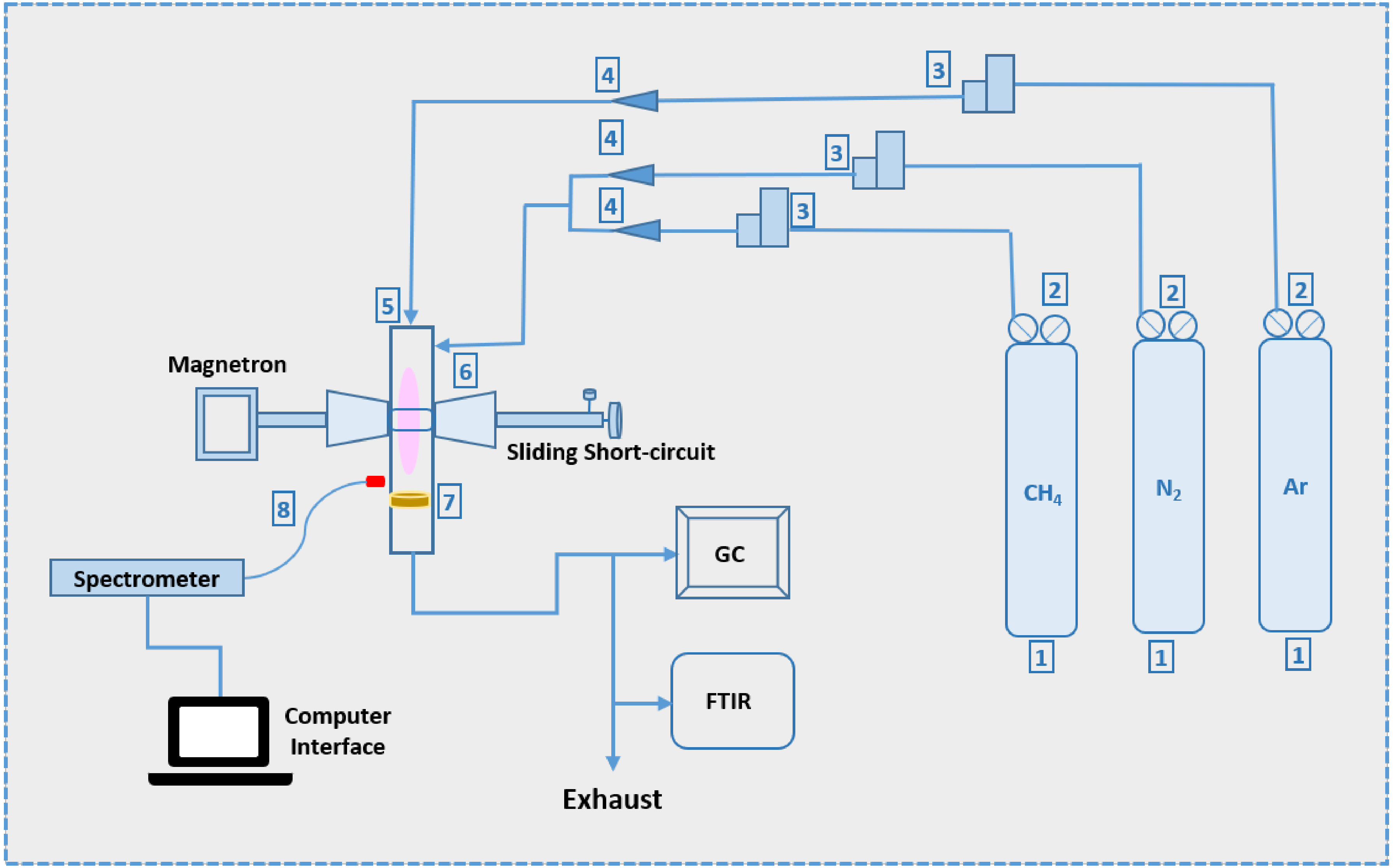
(a) Acetylene conversion and (b) product concentration over 10Ni-1Pd-CNT at 500 °C

Chemical Engineering Journal, 454 (2023), 140115
Applied Catalysis B: Environmental 340(2024),123255

WestVirginiaUniversity

Pilot Plant Demonstration

Reactor configuration



1. Gas cylinder,
2. Regulator
3. Mass flow controller
4. Valves
5. Quartz tube
6. Microwave generator,
7. Heated catalyst bed,
8. OES

H Quest **decarbonizes natural gas** at the point of use

Natural Gas

Electricity

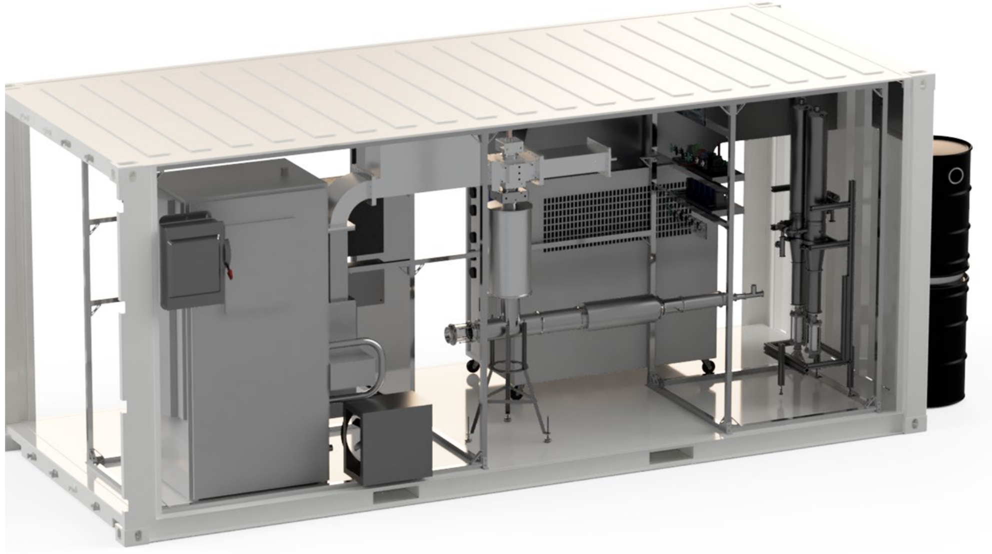
Clean Hydrogen

Engineered Carbon:

- Graphene
- Carbon black
- **Carbon nanotubes**
- Synthetic graphite, and more…

A single **1 ton-H_2/day** plant **eliminates emissions of ~5,000 ton-CO_2/year**

System built and demonstrated in the lab; pilot deployed in the field



Footprint 20’ ISO container

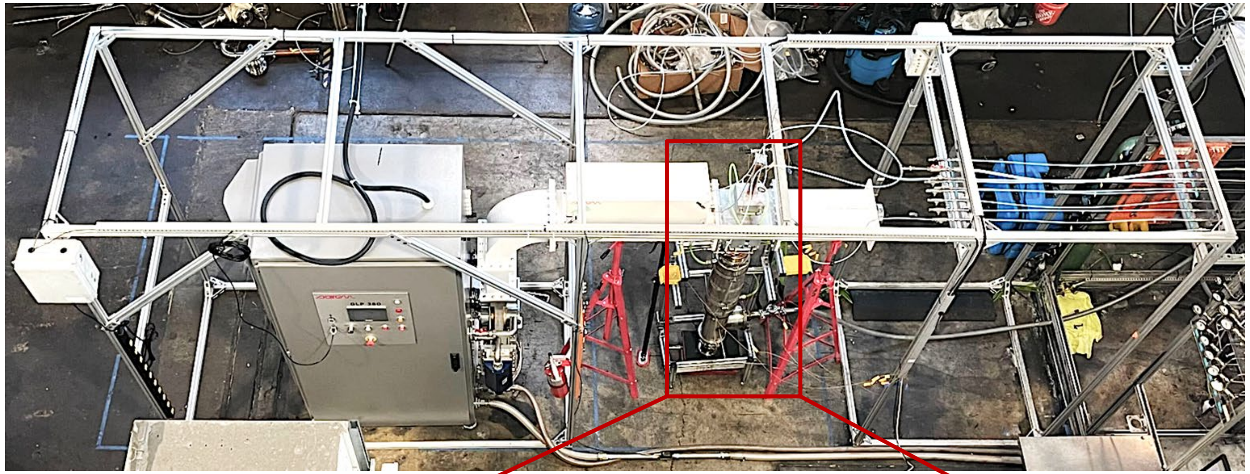
Equipment 36 kW 915 MHz microwave generator

Throughput 50 - 200 cubic feet/hour of natural gas

TRL 6

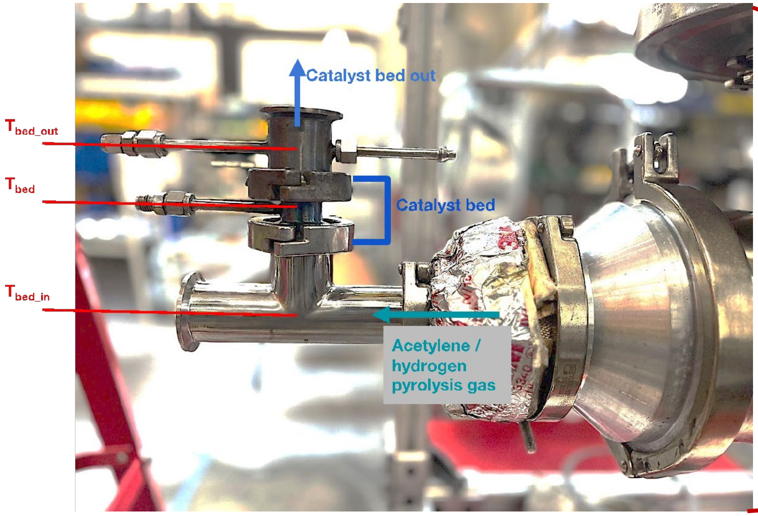
Commercial-scale microwave system

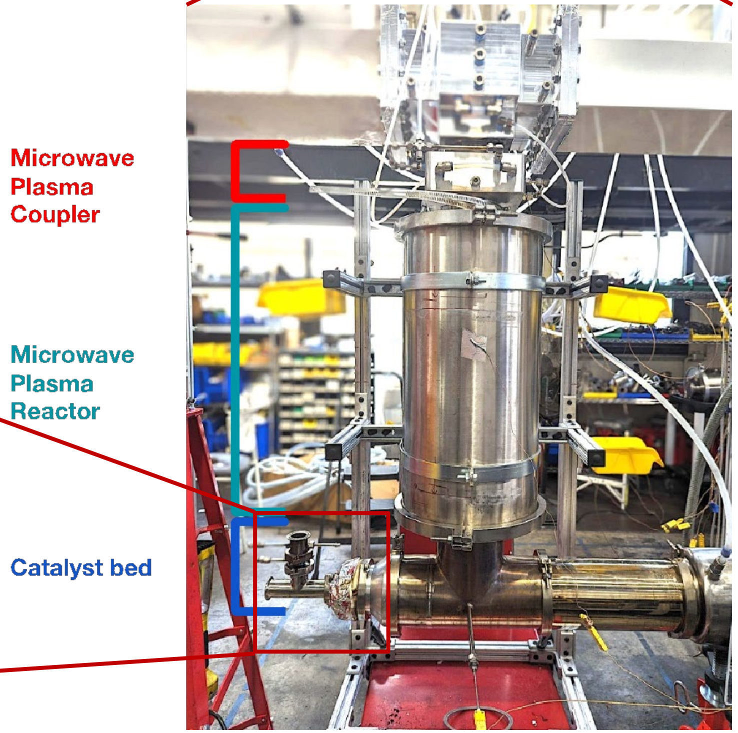
- 36 kW / 915 MHz system demonstrated in 2022
- 36 kW pilot system deployed in the field in 2023
- 100 kW system under test in the lab 2023-2024



CNT catalyst bed

Fluidized bed set up downstream of pyrolysis reactor
Acetylene/hydrogen pyrolysis gas supplied to fluidized bed





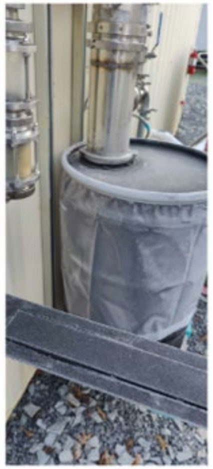
Peoples Gas Pilot

36 kW / 915 MHz system containerized and deployed at a customer facility

H Quest demonstrated:

- Rapid installation (1-2 hours) with minimal infrastructure
- Remotely monitored operation at customer facility
- Conversion of pipeline-grade methane
- Production and collection of carbon materials

PEOPLES



HQuest

Microwave plasma process development since 2014

Strong IP position and technology background

>12 granted patents in US and Canada

$3.6M in R&D projects with DOE and NSF

Start-up company on a steep commercialization trajectory

15 employees | 5,000 sq ft R&D facility in Pittsburgh, PA

Natural gas conversion pilots in the field

Microwave plasma pyrolysis of natural gas

Rapid, direct energy input

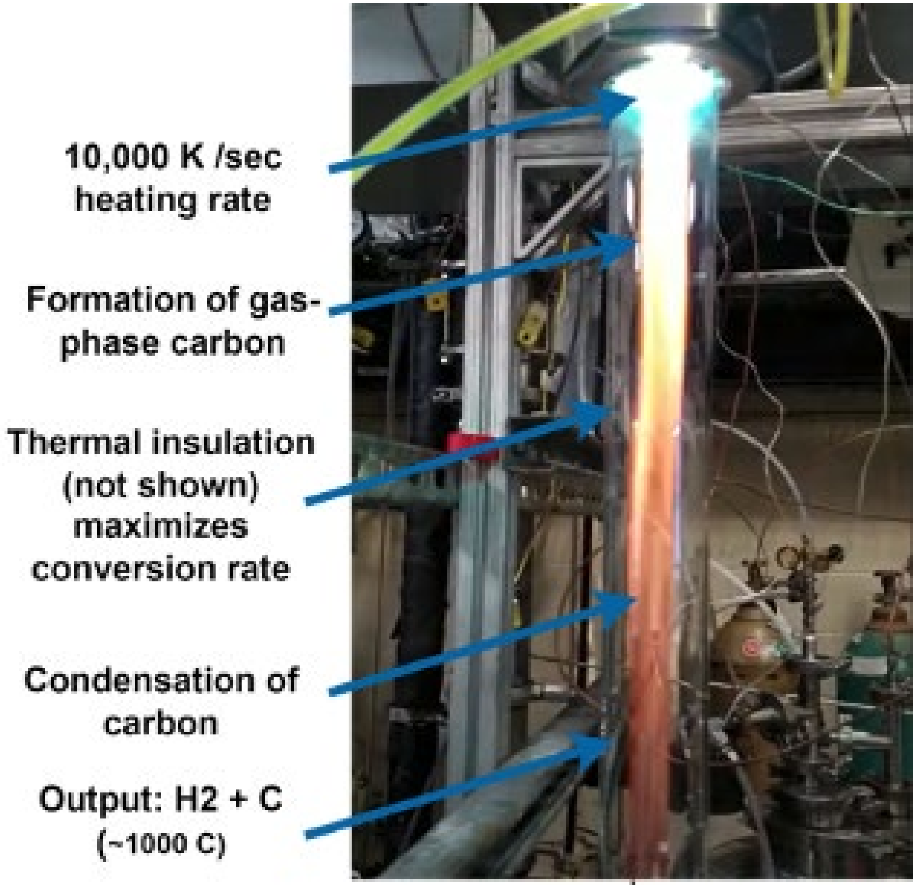
Microwave energy coupling directly into the gas stream
10,000 deg/sec heating rates in small volumes

Industrial robustness

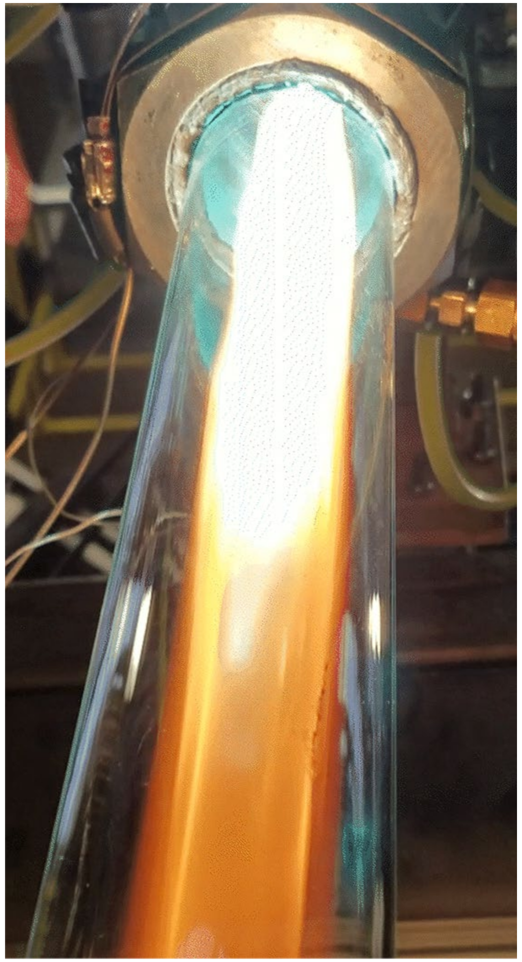
36 kW system piloted in the field
100 kW system under test in the lab

Product control and flexibility

Demonstrated selectivity control and production of carbon black, graphene, acetylene, and aromatics.



H Quest technology offers:



Decarbonization of industrial processes
Electrification of heat and production of hydrogen

Immediate gains for CB sustainability
via blending methane-derived carbon black

Novel, zero-CO_2 pathways to carbon materials
natural gas as a feedstock for a wide range of products

Processing of virgin and recycled CB
plasma upgrading through heat treatment of materials

Project Summary

- Gen 1 catalyst formulation Ni-Pd and Ni-Cu are developed and tested. Precious metal Pd is replaced by Cu.
- Gen 2 catalyst formulation featured "base-growth" is developed which will lower the CAPEX and OPEX.
- Demonstrate the potential of meeting DOE Hydrogen Shot goal of "1-1-1"
- Two U.S. patents, four per-reviewed journal articles and several conference papers.
- Process simulation and TEA model updated. Kinetics model has been completed.
- Microwave plasma pilot plant commissioning and testing are making progress.

Plans for future testing/development/ commercialization

- ❑ Pilot scale microwave plasma reactor test at H-Quest
- ❑ Carbon characterization as electrode for electric arc steel making, additives to concrete and polymers.

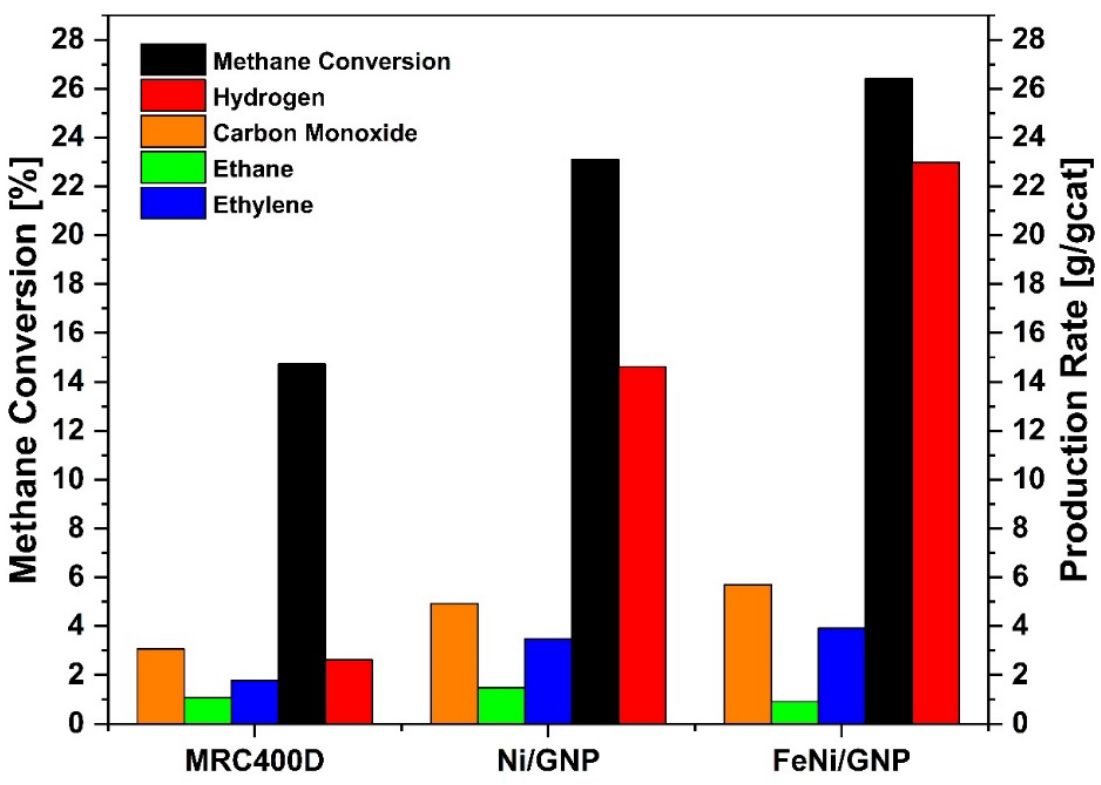
a. **After this project**:
   - ❑ Industrial partners
   - ❑ H_2 Hub

b. **Scale-up potential:** modular approach , wellhead or stranded gas field deployment.

Outreach and Workforce Development Efforts and Achievements

- ❑ Connection with Hydrogen Hubs in WV State.
- ❑ First generation college students in West Virginia.
- ❑ Women, minority Chemical Engineering undergraduate students are trained to operate microwave reactors.

Microwave-assisted methane pyrolysis using shale rock and promoters as catalysts (700^{o}C, 1 atm)



(1) MRC 400D=shale rock
(2) 10% Ni/GNP promoters + 90% shale rock
(3) 10% FeNi/GNP promoters + 90% shale rock
(4) GNP=graphene nanoplatelets

1. The rock sample obtained from shale gas drilling process has catalytic function to produce hydrogen
2. Adding promoters (Fe and Ni) to the rock can boost methane conversion and hydrogen productivity. Promoters are cheap and can be injected to the subsurface during drilling process.
3. High value by-product ethylene was produced, which is "co-benefit" of in-situ hydrogen production.


Thank You