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

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Partner Institutes:

Pacific Northwest National Laboratory

North Carolina State University

H-Quest Vanguard, Inc.

C4-MCP

SolCalGas

June 8, 2021

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Project Goal

The objective of the project is to develop a novel, low-cost process intensified modular process to directly convert flare gas or stranded gas to carbon nanomaterials and co-product hydrogen (H_2) with high conversion, selectivity, and stability. The proposed project is based on a patented technology for one-step conversion of natural gas to carbon nanotubes (CNTs) and carbon fibers (CNFs) without emitting carbon dioxide:

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

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.

Expected Outcomes/Key Deliverables

- ❑Electromagnetic sensitive catalyst development, synthesis, scale up.
- ❑Microwave pilot reactor design and performance test at capacity of 2-5 kg/day.
- ❑Modular component design, fabrication and pilot test for 100 hours
- ❑Commercial design flowsheet, Technoeconomic analysis.
- ❑Technology-to-market strategy, plan, and commercialization.

Overview

Timeline

Project Stat Date: 03/20/2020
Project End Date: 03/19/2023

Barrier

- ❑ Catalyst stability
- ❑ Control the quality of CNTs/CNFs, crystallinity, metal free
- ❑ Separation of catalyst-CNTs and CNFs
- ❑ Energy efficiency

Budget

Total Project Budget: $3,791,000
Total Recipient Share: $ 791,221
Total DOE Funds: $3,000,000

Partner

Pacific Northwest National Laboratory
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Relevance and Impact

Scientific and Technical Impact

The project advance both basic and applied fossil energy research. Understanding the reaction mechanism at interface of catalyst-methane molecule under microwave irradiation is important for basic fossil energy research.

Economic Impact

In the stranded gas location where pipeline is not available, distributed production and shipping solid carbon by truck and rail are an economically feasible. CNTs/CNFs are high-value products used as composite, fibers, electrode for electric arc steelmaking (needle coke replacement), polymers, plastics, and batteries.

Environmental Impact

Different from gas combustion for electricity generation, microwave pyrolysis creates much less CO_2 and pollutants by converting carbon in the natural gas into solid carbons. It reduces the volume of flared gas.

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 deployed and transported to remote locations.

Natural gas flaring, venting up in Texas

Advantages of using MW heating

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

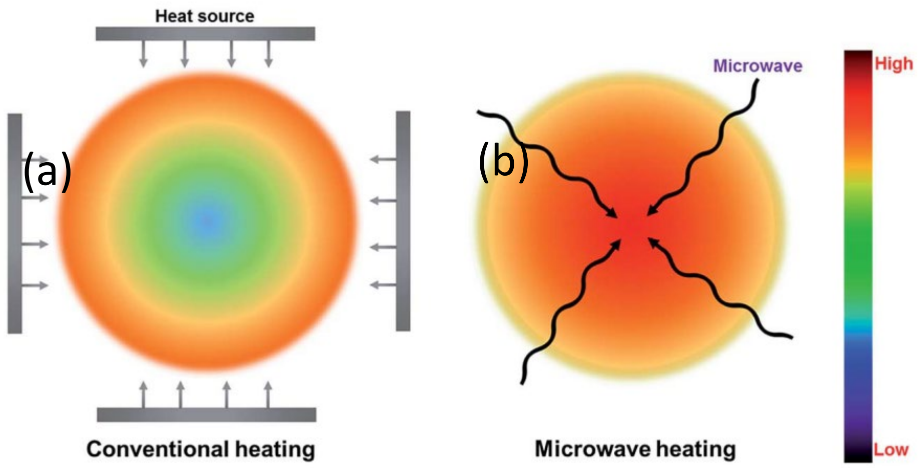


Fig 1. Schematic diagram of (a) conventional heating;
(b) microwave heating

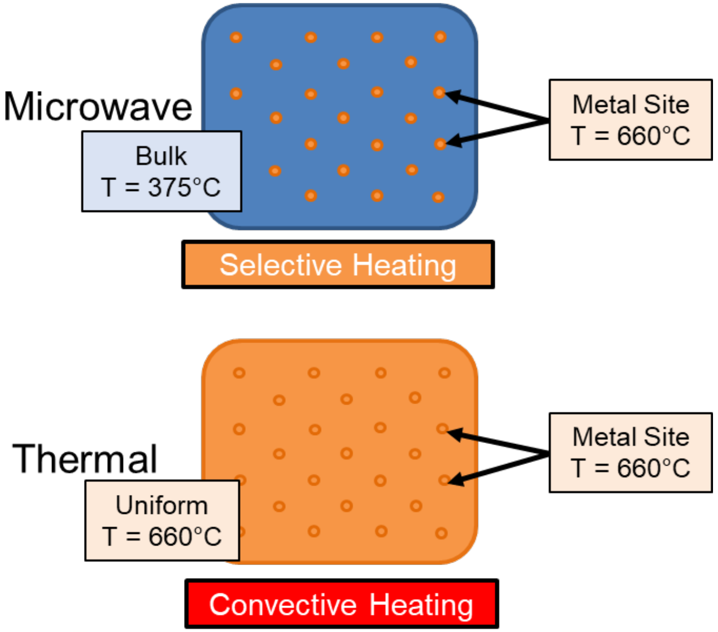
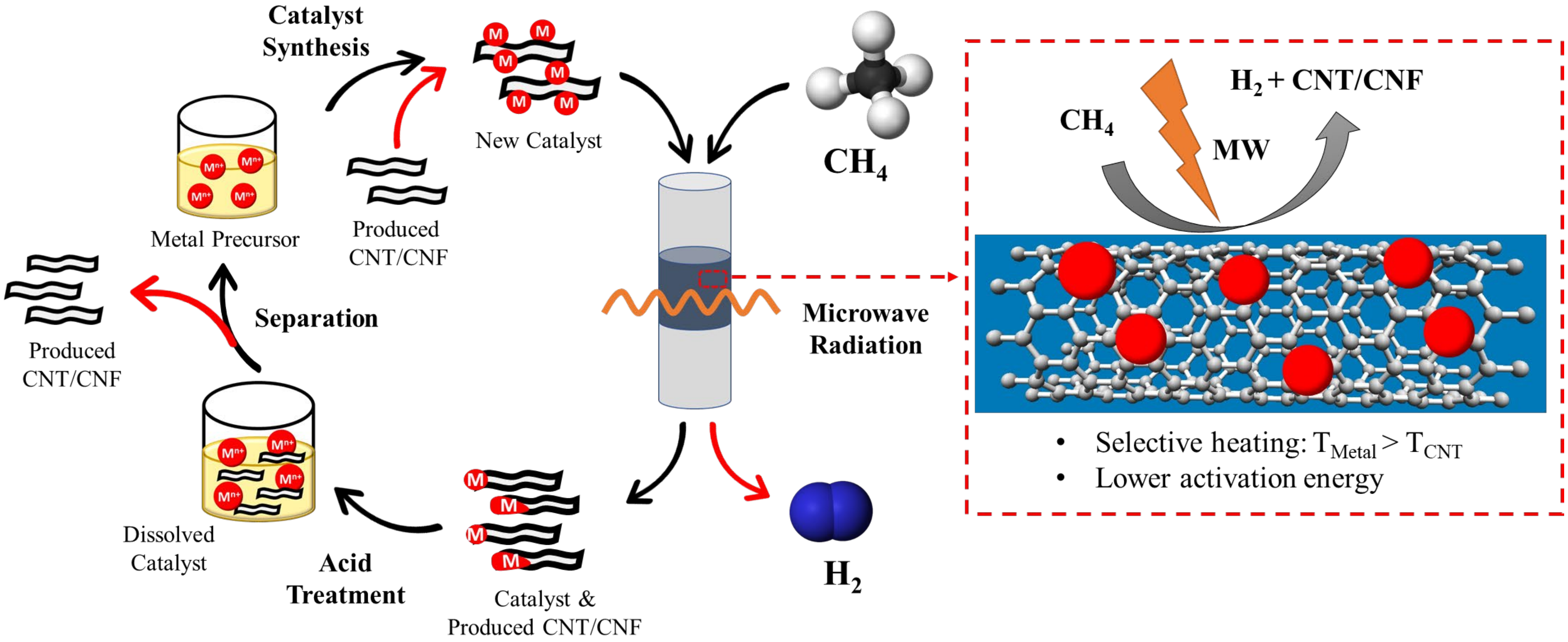


Fig 2. Selective material heating and reduce the bulk temperature

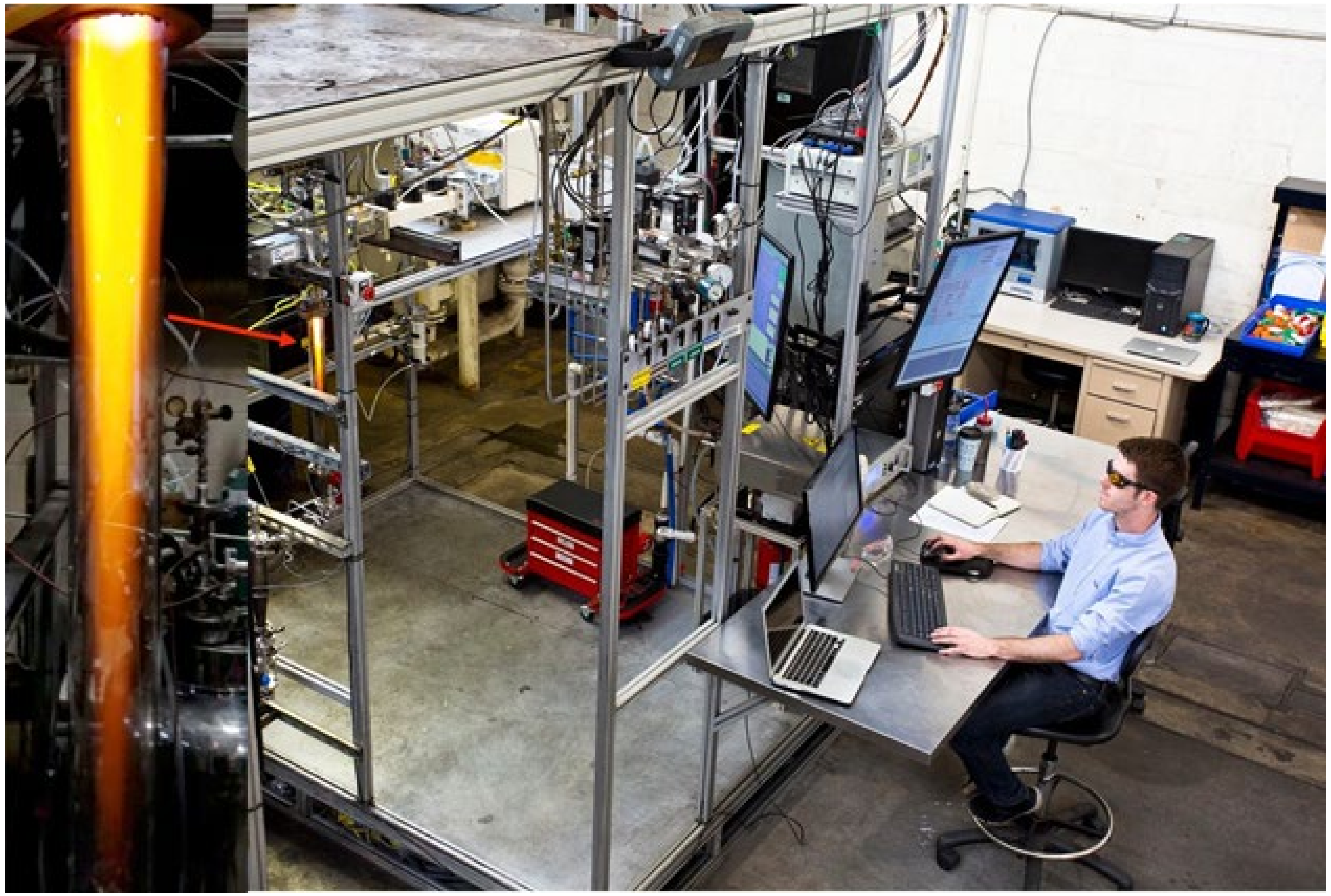
Approach: Overcome the Challenges

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



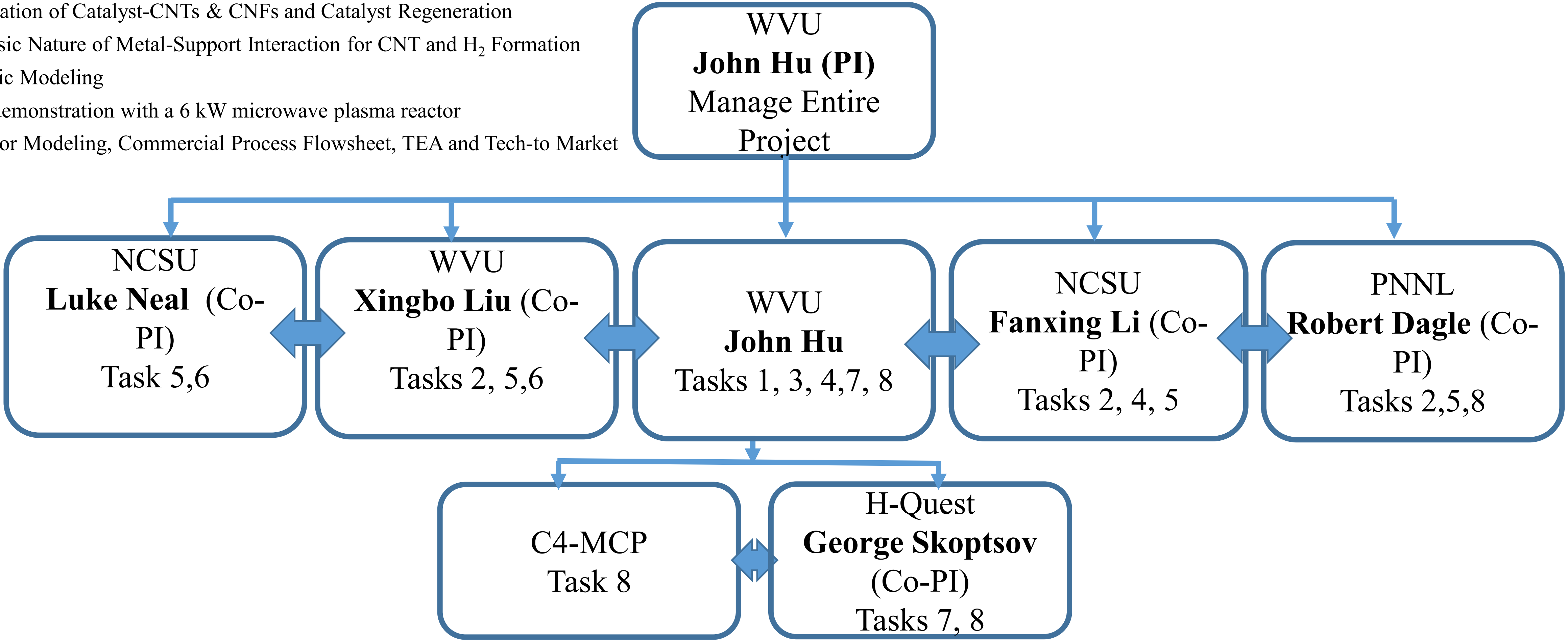
- Selective heating: $T_{Metal} > T_{CNT}$
- Lower activation energy

Approach-Demonstration at Microwave Plasma Fluidized Pilot Unit (6 kW)



Collaboration and Coordination

Task 1.0 - Project Management and Planning
Task 2. Catalyst Design, Synthesis and Characterization
Task 3. Variable Frequency Microwave Reactor Test
Task 4: Separation of Catalyst-CNTs & CNFs and Catalyst Regeneration
Task 5. Intrinsic Nature of Metal-Support Interaction for CNT and H_2 Formation
Task 6. Kinetic Modeling
Task 7 Pilot demonstration with a 6 kW microwave plasma reactor
Task 8. Reactor Modeling, Commercial Process Flowsheet, TEA and Tech-to Market



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Equipment and Facilities

The team is equipped

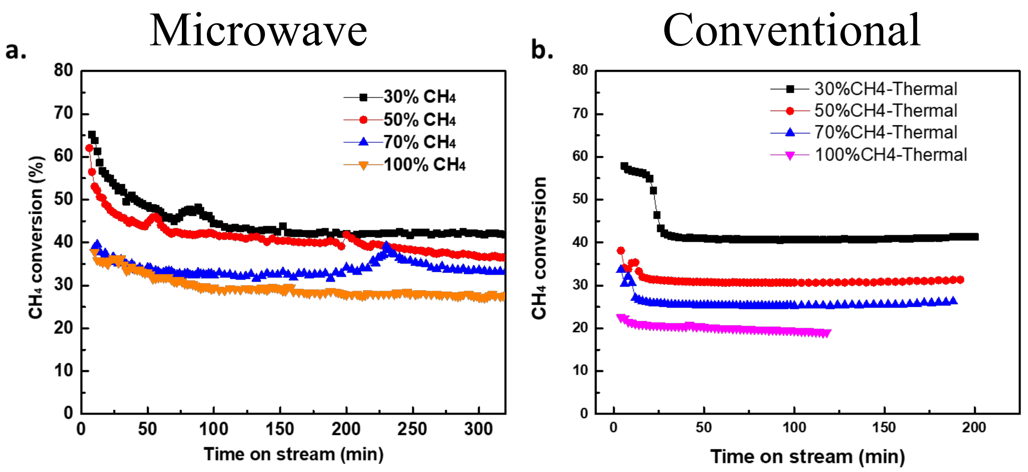
- Two variable frequency (5.85-6.65 GHz, 200W), solid sate microwave reactors
- One fixed frequency (2.45 GHz, 950W), solid state microwave reactor
- One fixed frequency (2.45 GHz, 3kW), magnetron microwave reactor
- Network analyzer

- PNNL-In-situ and ex-situ characterization
- NCSU- Catalytic reactors and analytical instrumentations for material science and surface chemistry
- H-Quest-pilot scale microwave reactor (6 kW)

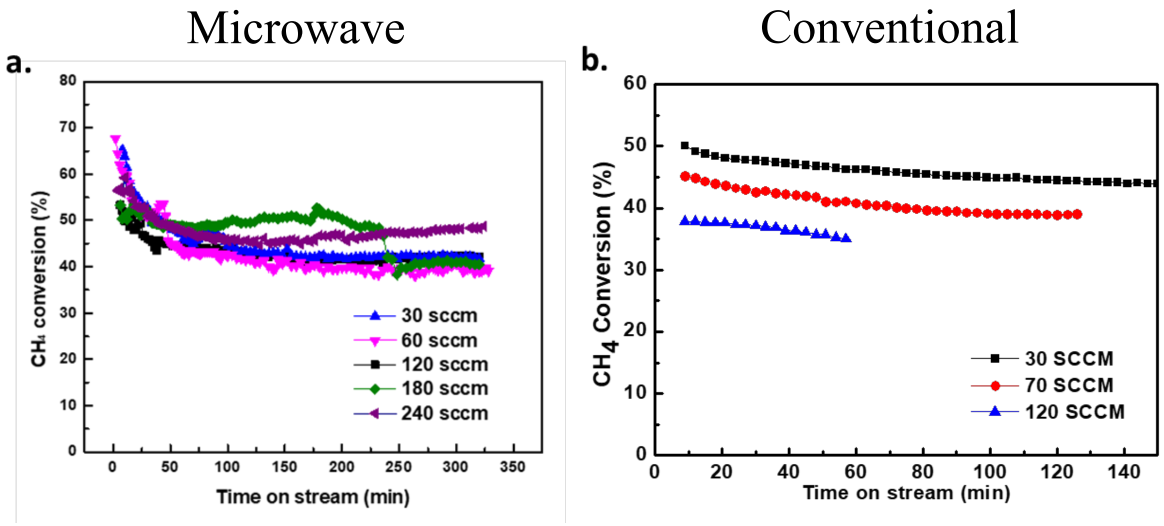
Accomplishments and Progress

Catalyst for Dielectric Heating: Ni-Pd supported by CNT

- 10Ni-1Pd/CNT Catalyst under MW heating showed a great performance on methane pyrolysis.
- The methane conversion decreased as the methane partial pressures increased under MW. It was consistent with the trend observed under conventional heating.
- The study of flow rate showed that faster flow did not necessarily lead to a decreased conversion that was observed under conventional heating.



Partial Pressure



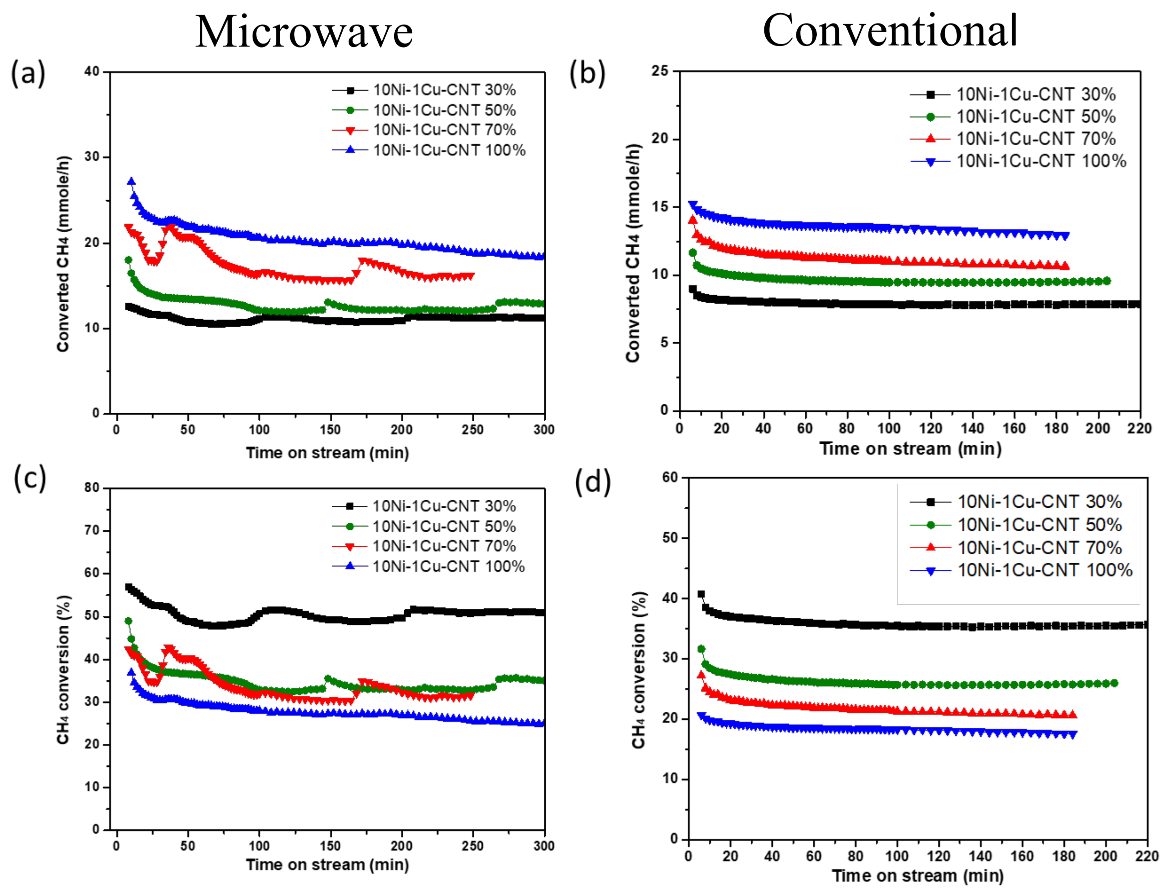
Flow rate

Catalyst Reduction conditions:
- Temperature: 400 C
- Flow rate = 70 sccm
- Concentration = 10% H2
- Time: 4 h

Testing conditions:
- Temp.=550 °C
- Amount of catalyst = 0.2 g
- Frequency = 5850 MHz

Catalyst for Dielectric Heating: Ni-Cu supported by CNT

- 10Ni-1Cu/CNT Catalyst under MW heating demonstrates obviously better performance than that under traditional heating at the same setting temperature.
- The results showed the good activity for around 6 hours under 30%-100% methane partial pressures.
- Although conversion decreased with CH_4 partial pressure, the amount of converted CH_4 increased with CH_4 partial pressure.

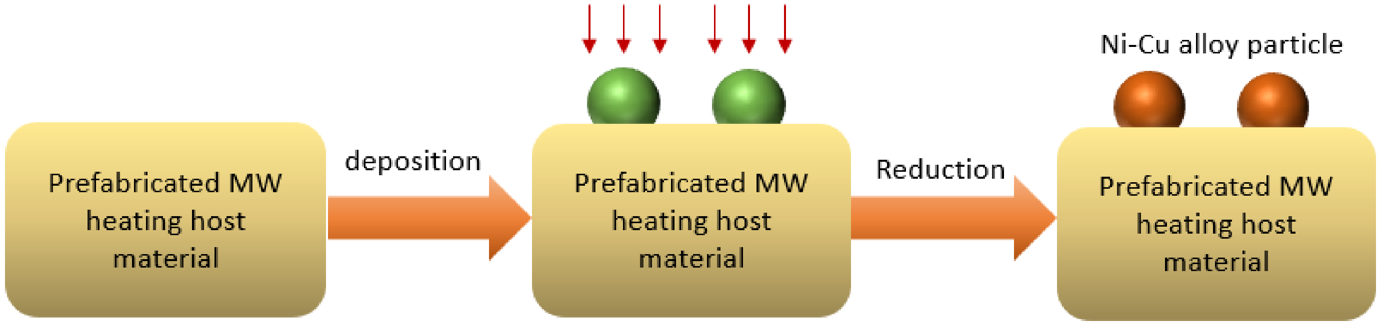


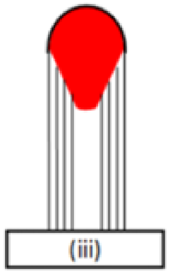
Catalyst Reduction conditions:
•Temperature: 400 C
•Flow rate = 70 sccm
•Concentration = 30% H2
•Time: 4 h

Testing conditions:
•Temp.=550 °C
•Flow rate=30 sccm
•Amount of catalyst = 0.2 g
•Frequency = 5850 MHz

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

Route 1: traditional ex-situ surface deposition

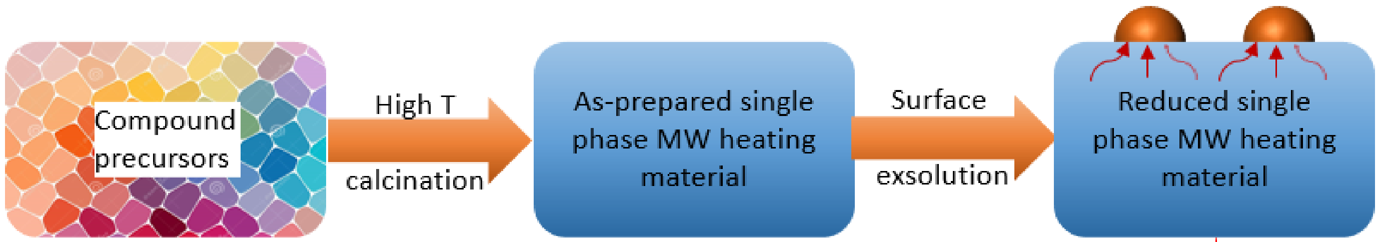


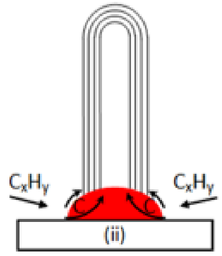


Tip-grown

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

Route 2: new in-situ surface exsolution

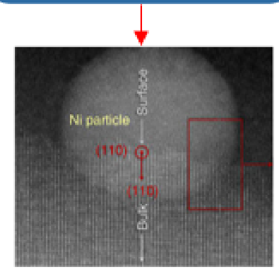




Base-grown

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

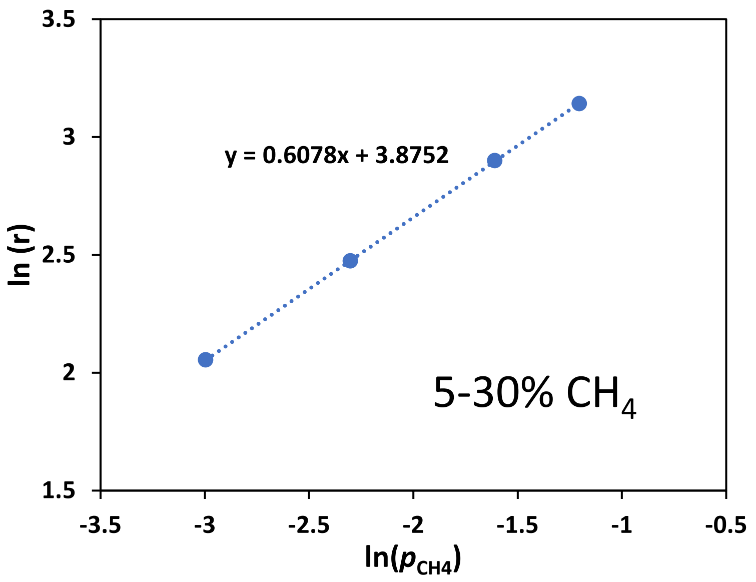


Surface catalyst exsolution control:

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

Kinetic Modeling:
Reaction order of methane pyrolysis over NiPd/CNT



$$\ln(rate) = -\frac{E_a}{R} * \frac{1}{T} + \ln(\, p_{CH4}^{n} * k_{app})$$

- Reaction order of 0.6 for CH_4 at 5-30% concentration
- K_{app} = 86498 ($h^{-1}bar^{-0.6}$)
- Rate equation for CNT formation: rate = 86498 $h^{-1}bar^{-0.6}$ * $p_{CH4}^{0.6}$ * exp(-6167.6/T)

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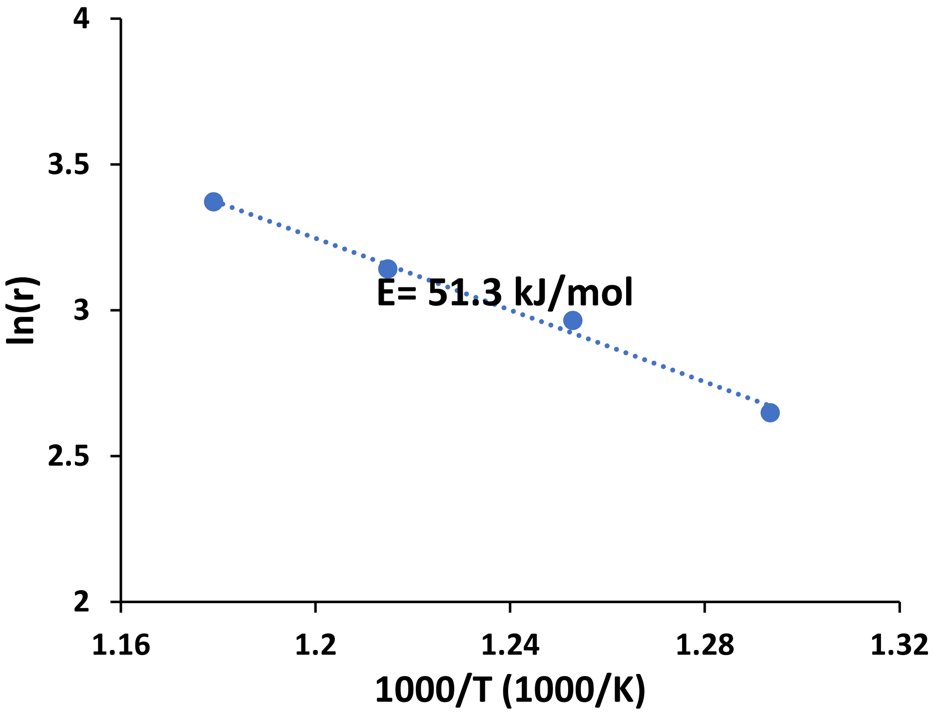
Activation energy for methane pyrolysis over NiPd/CNT



- 3 mg catalyst, reduction in 10%H_2 at 400^{o}C for 1 h, followed by reaction with 250 ml/min of 30%CH_4/Ar at 500-575 ^{o}C for 20 min
- Activation energy of 51.3 kJ/mol for NiPd/CNT catalyst

  86.8-115.8 kJ/mol for CH_4 dissociation over Ni(111)

  58.6-85.7 kJ/mol for Ni-Mg-Al catalyst

Techno-economic Analysis (PNNL)

Microwave-Assisted Catalytic Methane Pyrolysis (MW) versus Thermal Decomposition (TD)

- Process modeling/ cost analysis for two models:
  - **Microwave-assisted catalytic methane pyrolysis (MW)** – process under development
  - **Commercial carbon black via thermal decomposition (TD)** – baseline process for comparison

- Potential carbon products:

Type	Price ($/kg)	Global Market (MT/yr)
Carbon black	0.4-2	12 M (2014)
Graphite	10+	80 K (2015)
Carbon fiber	25-113	70 K (2016)
CNT	100+	5 K (2014)
Needle coke	1.5	1.5M (2014)

Amorphous carbon, less value (Carbon black)

Crystalline carbon, higher value (Graphite, Carbon fiber, CNT)

M = million; K = thousand; MT = metric ton
Dagle, et al., PNNL-26726, 2017

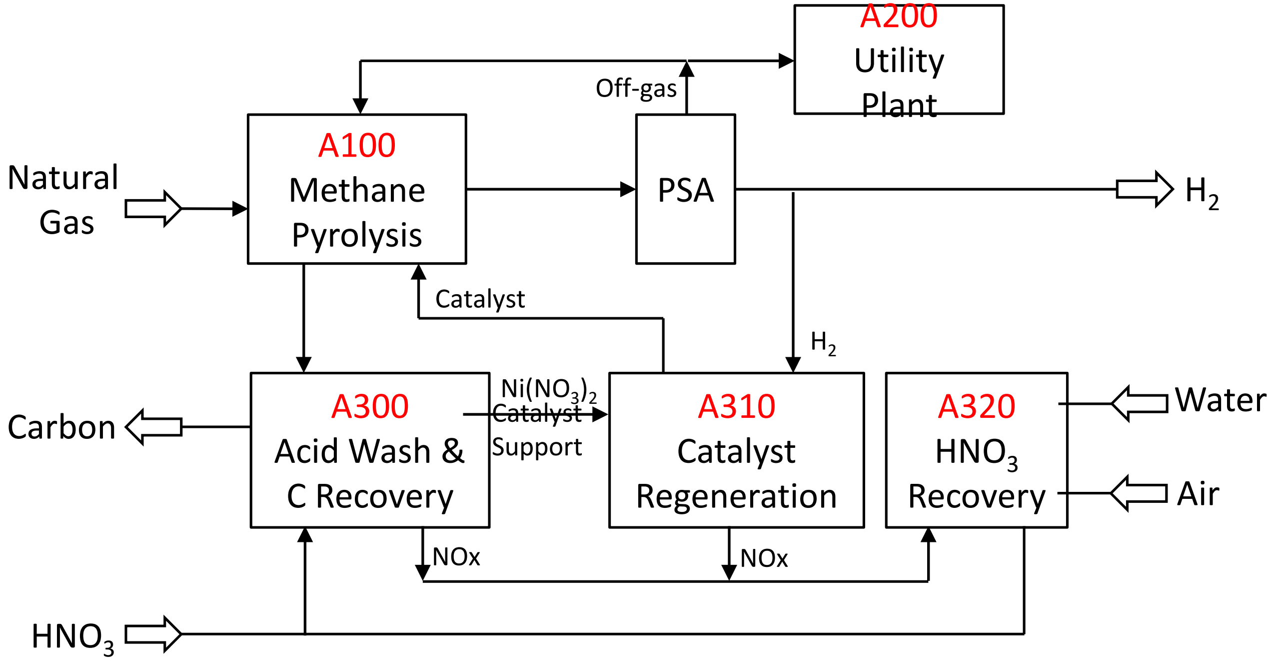
- Key Economic Assumptions

Pricing basis		Other assumptions	
Year	2018	**Plant scale (kg CNT/day)**	**S=4,530; L=302,000**
Catalyst ($/kg)	4.12	**Plant scale (kg H_2/day)**	**S=1500; L=100,000**
Natural gas (¢/kg)	19.5	Project contingency (%)	25
60% nitric acid (¢/kg)	21.2	OSBL cost (% of ISBL cost)	20
H_2 ($/kg)	0-2.0	Capital cost scaling factor	0.6
Cooling water (¢/MGal)	14.7	ROI (%)	15
Electricity (¢/kWh)	5.04	Depreciation (%)	10

Techno-economic Analysis (PNNL)

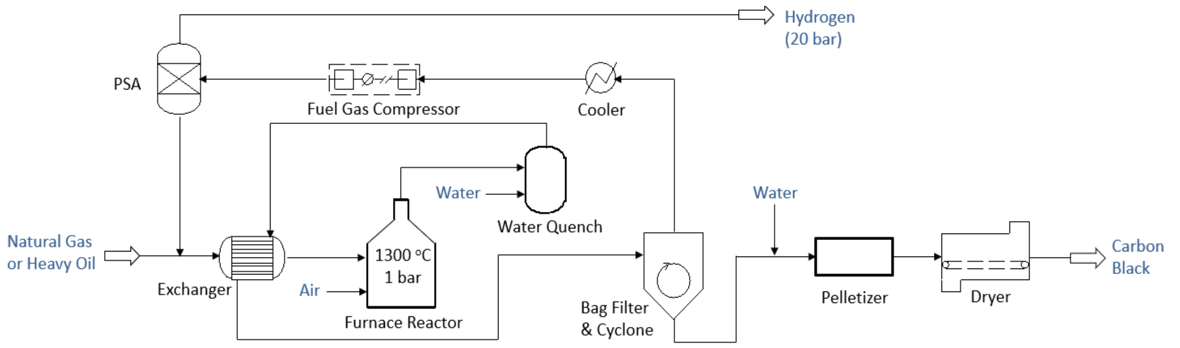
Microwave (MW) and Thermal Decomposition (TD) Process Models

- Process flow diagram for microwave-assisted catalytic methane pyrolysis (MW) – ***under development***



- Lower temperatures required (< 800°C)
- Requires catalyst/ carbon separation & catalyst resynthesis
- Produces valuable carbon nanotube product

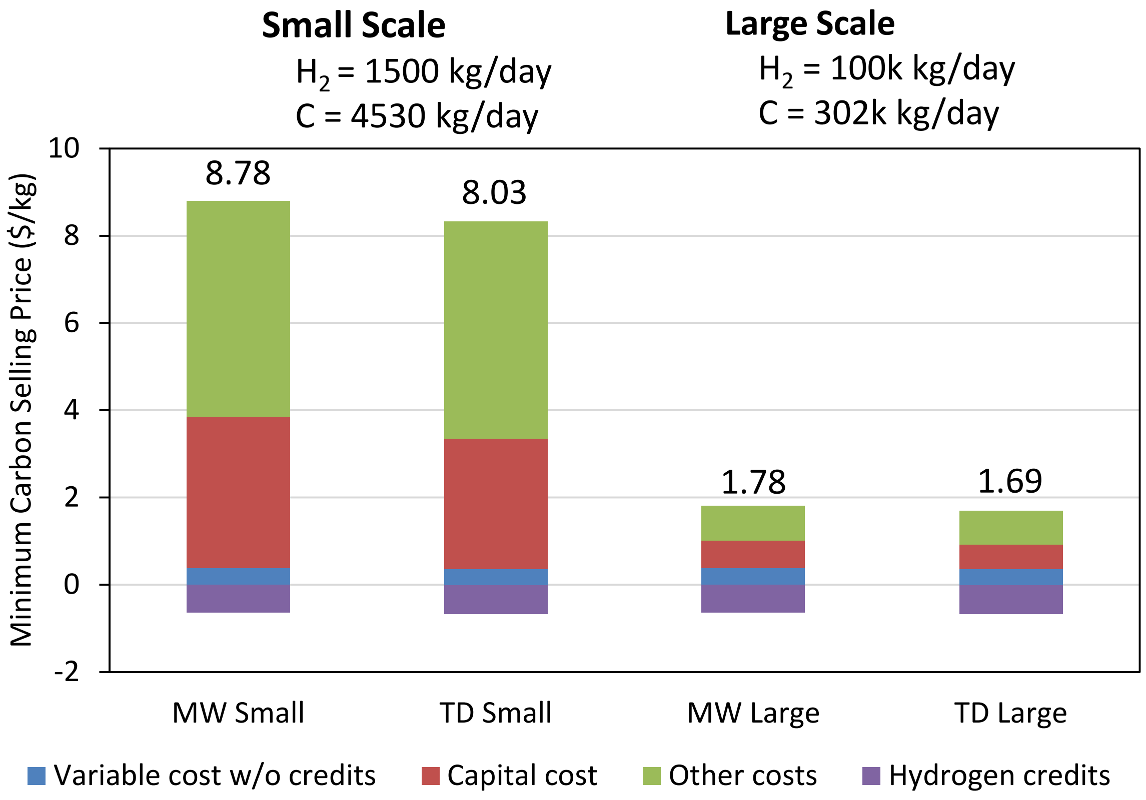
- Process flow diagram for thermal decomposition (TD) - ***baseline commercial process***



- Thermal process, requires high temperatures (>1200°C)
- Relatively simple process
- Produces solid carbon black as main product
- Technically mature, commercially available

Techno-economic Comparison – Results & Discussion

	Microwave-Assisted Catalytic Pyrolysis (MW)	Carbon Black Process via Thermal Decomp. (TD)
Configuration		
Reactor Temp (°C)	550	1300
Conversion (%)	45	40
Carbon recovery (%)	100 (Acid wash)	(Bag filter)
Heat source	80% fuel, 20% power	100% fuel
Hydrogen recovery (%)	90 (PSA)	90 (PSA)
Process Measures		
Energy (%, LHV)	90.2	75.1
Carbon (%)	89.1	72.5
CO_2 emission (kg/kg C)	0.41	1.40



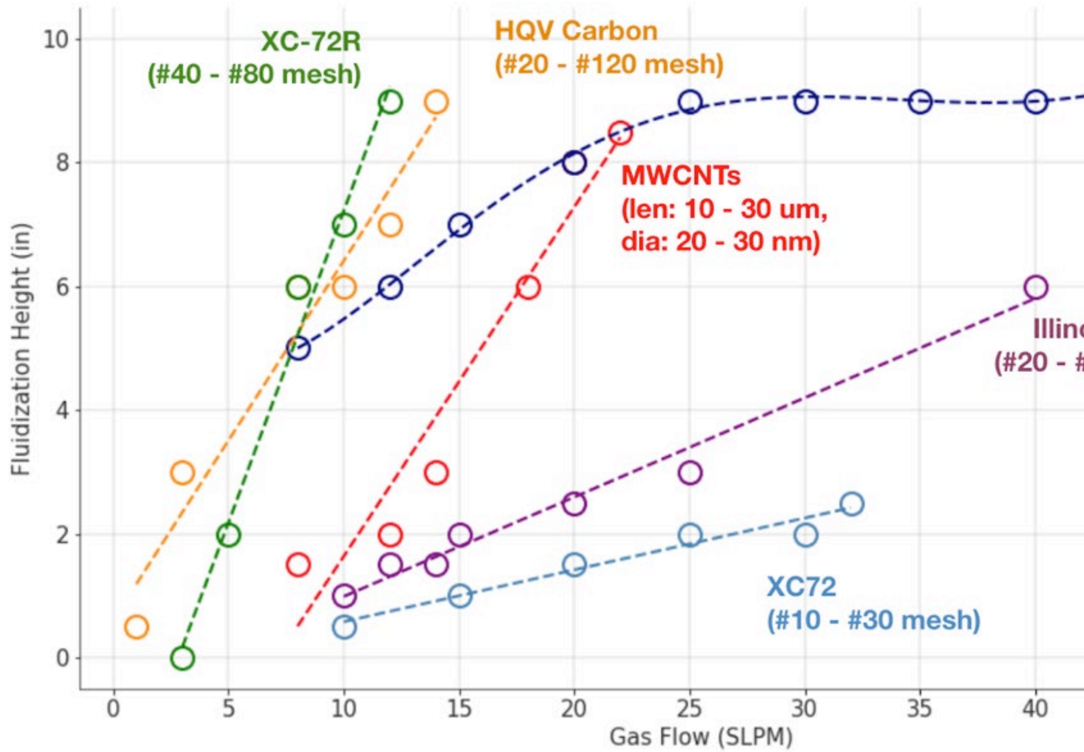
- **Min. carbon selling price (MCSP)** of MW process slightly greater than TD process due to solid separation and catalyst regeneration cost.
- MW process has **higher energy** and **carbon efficiency**, and **lower CO_2 emission,** versus TD process due to lower operating temperature and higher single pass conversion.
  - Note: zero CO_2 emission enabled with process modification, to be evaluated.
- Carbon nanomaterial product from MW process is crystalline, higher value than amorphous carbon produced from TD process.

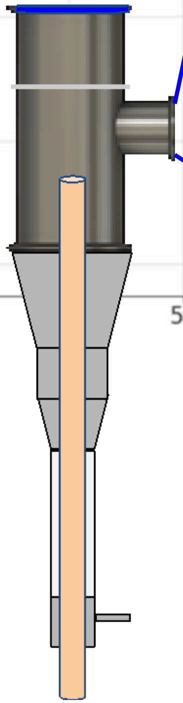
Overview Pilot Test

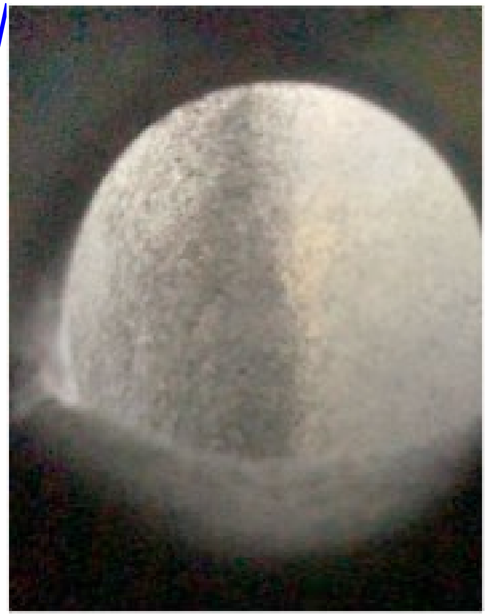
Current status:

(1) tested spouted and fluidized bed reactor prototypes
(2) evaluated fluidization of multiple materials
(3) shown MWCNT microwave plasma entrainment

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

Quest

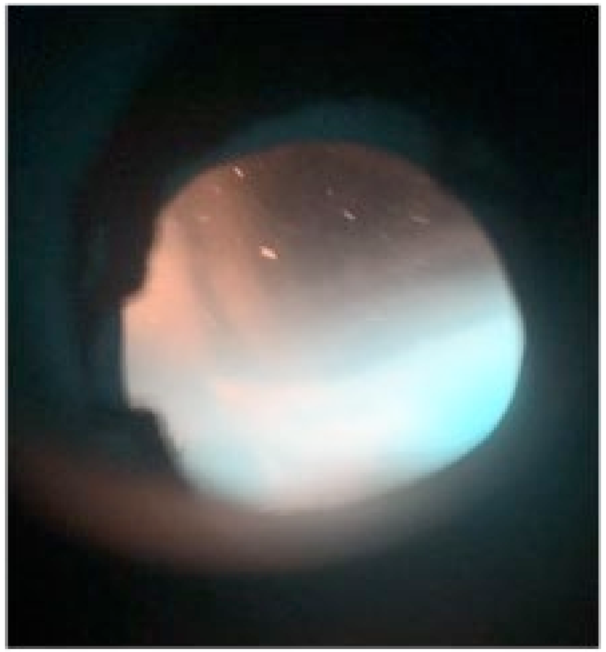
Methane Conversion without Entrained Particles

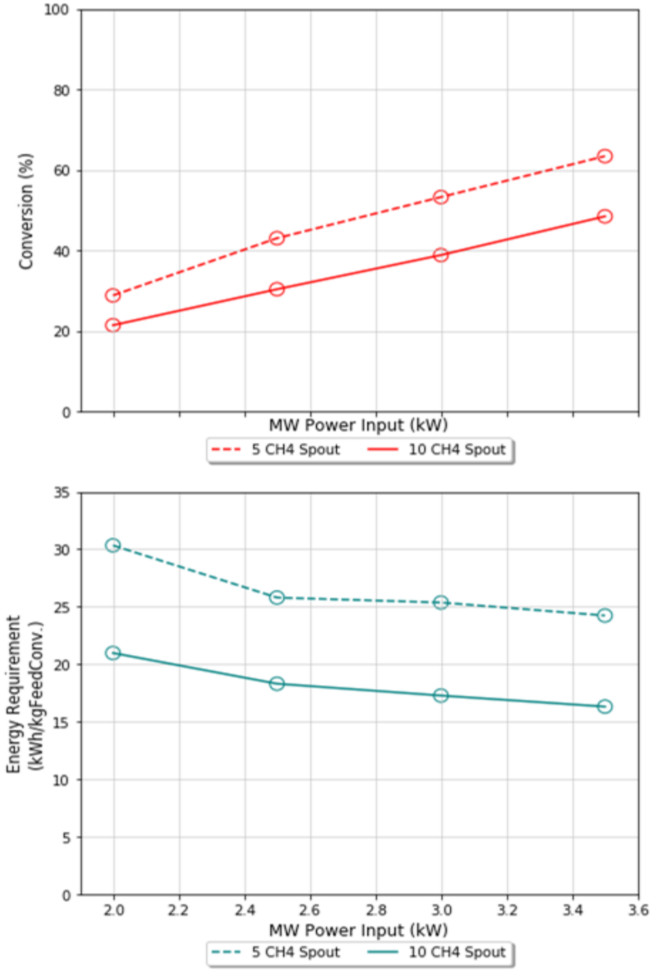
Microwave power: 2-3.5 kW
Entrainment gas: 5-10 slpm CH_4
Entrained particles: None

Methane conversion rate: 20%-60%

High selectivity to C_2H_2: >70%

High SER: >15 kWh/kgCH_4





Promising results for a prototype unoptimized system.
Baseline for catalytically assisted conversion.

HQuest

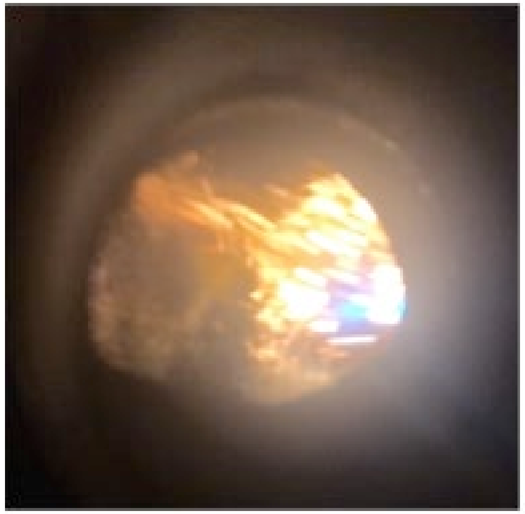
Reactor configurations iteratively modified to maximize plasma extents and particle interaction

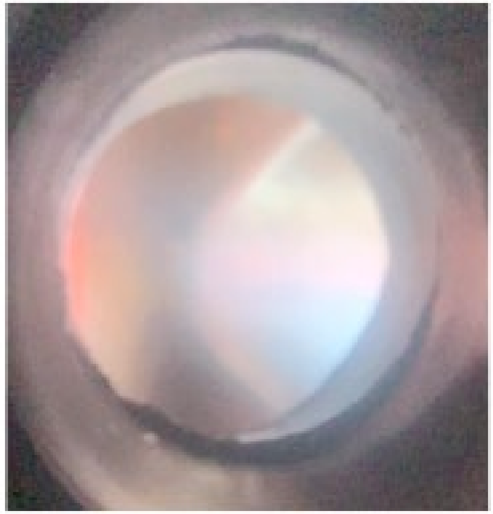
General description

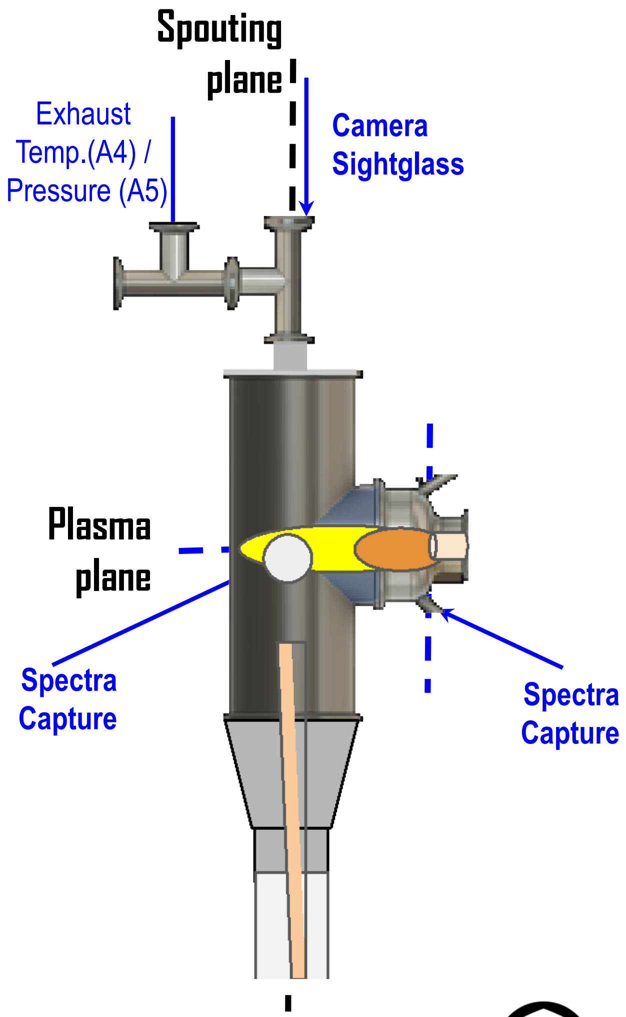
- Feed supplied vertically from below in either spouted or fluidized configuration;
- Ionized gas (plasma) is launched horizontally cross-axis to entrained feed;
- Exhaust entrainment and particle loss controlled by limiting gas velocities.

Instrumentation:

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







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Summary

- Catalyst formulation Ni-Pd and Ni-Cu are developed. Precious metal Pd is replaced by Cu
- The microwave sensitivity are observed. New catalyst formulation “base-growth” is developed which will lower the cost of separation.
- Process simulation and TEA model developed. Kinetics model has been developed.
- Microwave plasma pilot plant commissioning
    - Tested spouted and fluidized bed reactor prototypes
    - Evaluated fluidization of multiple materials
    - Shown MWCNT microwave plasma entrainment

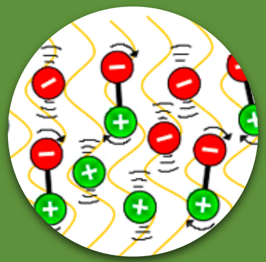
Proposed Future Work

- ❑ Develop low-cost catalyst-CNT separation process
- ❑ Scale-up catalyst synthesis protocol from gram level to 100 grams level
- ❑ Pilot microwave plasma reactor test using Ni-Cu supported and unsupported catalyst
- ❑ Post test characterization of spent catalysts and carbon nanomaterials
- ❑ Process simulation and technoeconomic analysis based on pilot test data

Thank You

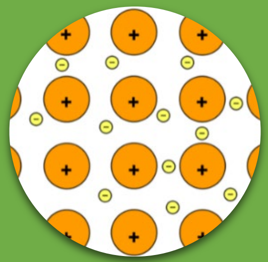
Technical Backup and Additional Information

The Theory: Microwave Sensitive Catalysts



Dielectric loss:

oxide



Conduction loss:

metal

Magnetic loss:

magnetic material

Microwave sensitive material

Thermal energy P per unit volume:

$$P = \pi f \varepsilon_0 \varepsilon_r'' |E|^2 + \frac{1}{2}\sigma |E|^2 + \pi f \mu_0 \mu_r'' |H|^2$$

Dielectric loss	Conduction loss	Magnetic loss

Microwave sensitivity

- Material with high loss tangent

tan δ = ε″/ ε′

ε: dielectric constant

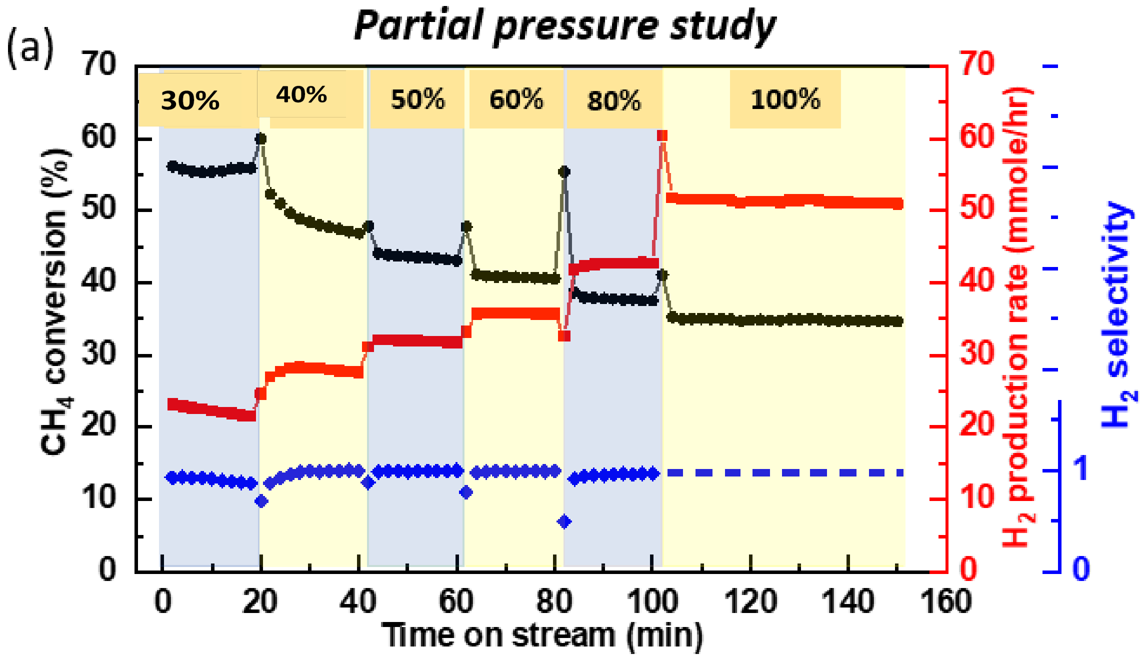
Methane Pyrolysis activity

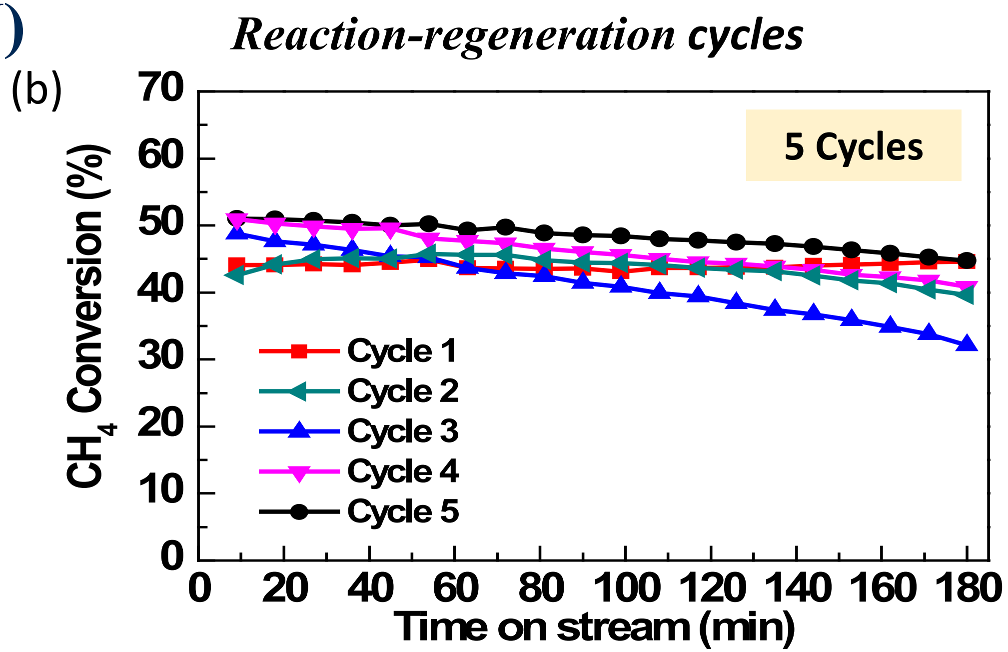
- Methane activation
- Selectivity towards oligomerization

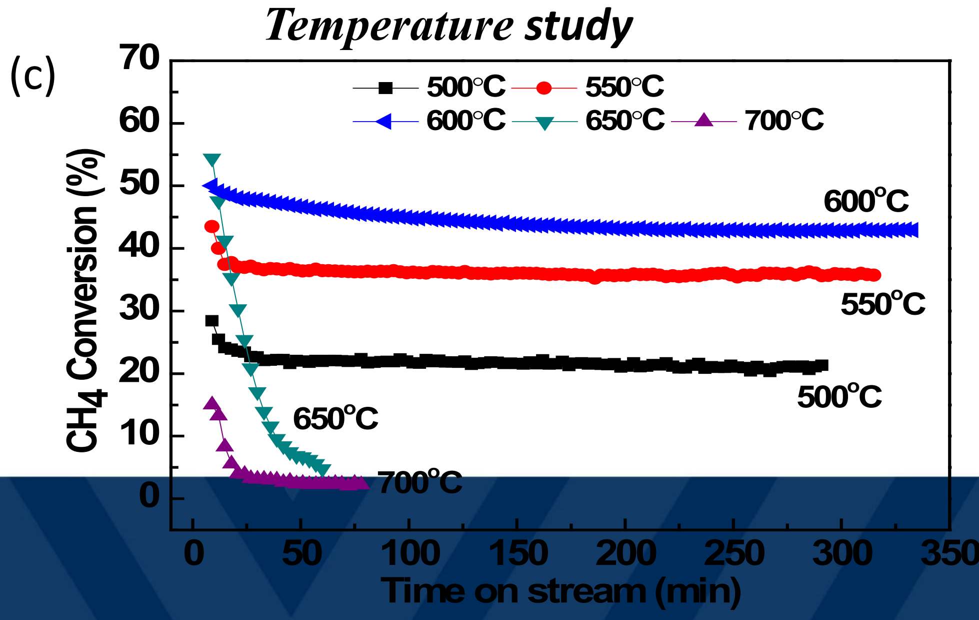
metal/support

Metals: Fe/Ni/Cu/Pd/Co	Supports: Zeolite/SiC/ Carbon/no support

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°C to 700°C, and 600°C is an ideal reaction temperature.

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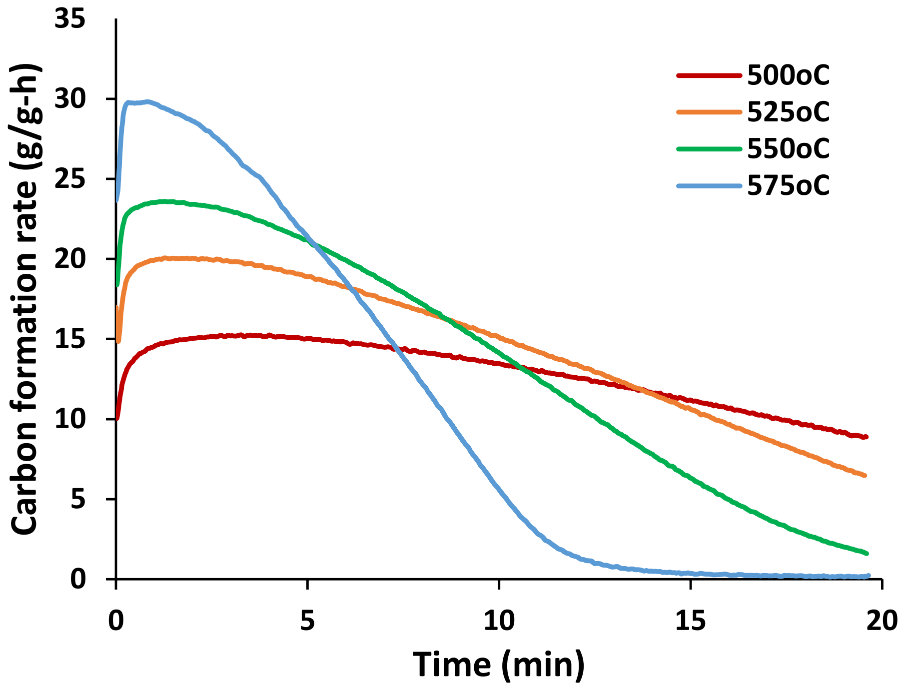
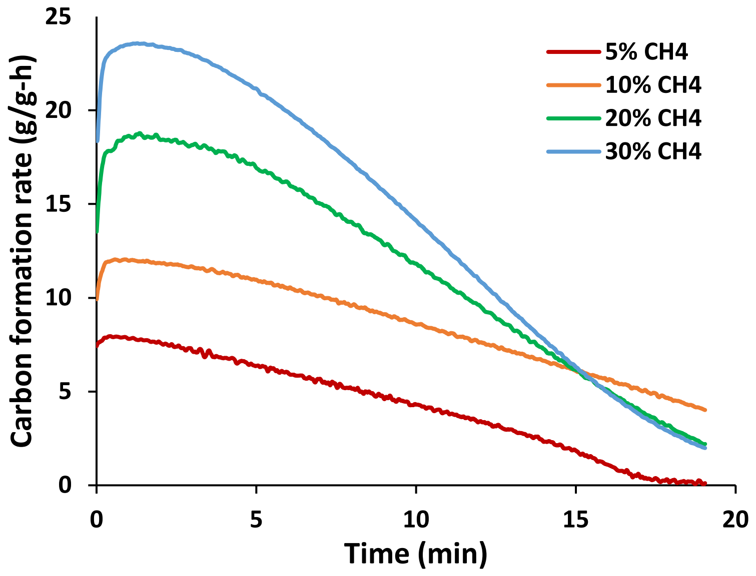
Effect of temperature on carbon formation rate



- 3 mg catalyst, reduction in 10%H_2 at 400°C for 1 h, followed by reaction with 250 ml/min of 30%CH_4/Ar at 500-575 °C for 20 min
- Up to 30 g/g-h carbon formation rate at 575 °C

Effect of methane concentration on carbon formation rate



- 3 mg catalyst, reduction in 10%H_2 at 400^oC for 1 h, followed by reaction with 250 ml/min of 5-30%CH_4/Ar at 550 ^oC for 20 min
- Up to 23 g/g-h carbon formation rate with 30% CH_4