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

DOE Project Number DE-FE-0031866

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

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U.S. Department of Energy
National Energy Technology Laboratory
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# Presentation Outline

- Project Overview
- Background and Approach
- Technical Accomplishments
- Summary and Future Work

# Associated Gas Flaring Factsheet: 2018 BAKKEN

| Reporting Agency | Total Annual Flared Volume (MMCF) | Total Annual $CO_2$ Emissions (MM tonne) | Estimated Number of Flared Wells | Estimated Number of Operators |
|---|---|---|---|---|
| **NDIC** | 63,329 | 5.23 | 11,982 | NA |

- Total Annual $CO_2$ Emissions were calculated assuming complete combustion of flared gas volumes at STP conditions (0°C/1 atm) using the average gas composition shown below

*Average Natural Gas Composition by Mol %*

| *Play/Basin* | *C1* | *C2* | *C3* | *C4* | *$H_2S$* | *$CO_2$* | *$N_2$* | *He* | *Other* |
|---|---|---|---|---|---|---|---|---|---|
| **Bakken** | **52.7%** | **24.6%** | **12.9%** | **1.3%** | **3.8%** | **2.8%** | **0.0%** | **0.4%** | **1.6%** |

- Data for the average gas composition of a flare was acquired from an Eagle Ford Shale Oil Report[1] and is calculated from an unknown number of samples

## Average Flaring Volume Per Flare (MCFD)

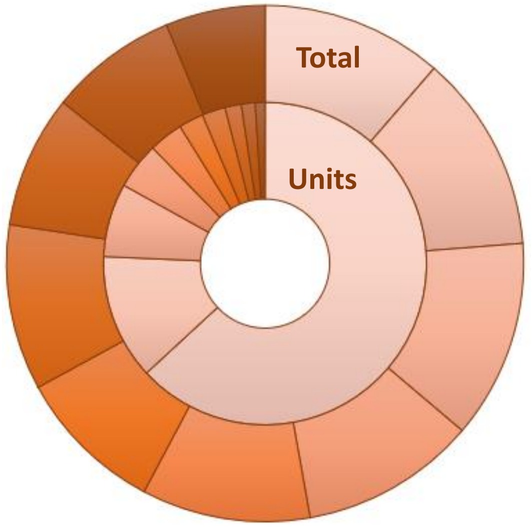
| 2018 Yearly | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **27.4** | | | | | | | | | | | |
| 1st Half | | | | | | 2nd Half | | | | | |
| **25.6** | | | | | | **29.2** | | | | | |
| Q1 | | | Q2 | | | Q3 | | | Q4 | | |
| **23.9** | | | **27.3** | | | **27.9** | | | **30.5** | | |
| January | February | March | April | May | June | July | August | September | October | November | December |
| **24.5** | **24.9** | **22.4** | **26.8** | **29.8** | **25.2** | **26.3** | **27.3** | **30.1** | **31.4** | **30.7** | **29.3** |

- Flaring values are reported on a monthly basis per well and include operational flaring days
  - Values were totaled and then averaged per month, per quarter, bi-annually, and yearly

- Data was acquired from the North Dakota Industrial Commission and then characterized for flaring volume calculations[2]
  - Daily flaring volumes were calculated using provided reporting information and then averaged based on a chronological period.

## 2018 Bakken Flaring Report Results

| Flare Size (MCFD) | Flare Units | Total Volume (MCFD) |
|---|---|---|
| **<=100** | 3,781 | 99,761 |
| **100-200** | 753 | 109,036 |
| **200-300** | 442 | 109,508 |
| **300-400** | 280 | 96,755 |
| **400-500** | 206 | 92,716 |
| **500-600** | 149 | 81,686 |
| **600-700** | 140 | 91,261 |
| **700-800** | 98 | 73,091 |
| **800-900** | 83 | 70,739 |
| **900-1,000** | 58 | 54,669 |




- Monthly reports include flared volume in MCF (1000 $ft^3$), operational days, location, and producing field information for each **individual flare**.
- Daily flaring volumes were calculated by dividing the reported monthly flared volume in MCF by the number of operational days to estimate MCFD
- Flare Units represent the number of flaring reports in the year 2018 that fell into the respective bin value.
- The Total Volume represents the total volume of flared gas for all units within each size category.



1: Ghandi, A., et. al, Institute of Transportation Studies, UC Davis, Prepared for Argonne National Laboratory, September 2015, Energy Intensity and Greenhouse Gas Emissions from Crude Oil Production in the Eagle Ford Region: Input Data and Analysis Methods
2: North Dakota Industrial Commission, Oil and Gas Division, General Statistics https://www.dmr.nd.gov/oilgas/stats/statisticsvw.asp

# Background-The Need

The Issue of Flaring Gas

Shale Gas Exploration

Wellhead Equipment

(Bakken, ND)

Natural gas flaring, venting up in Texas

# Project Overview

## Goals and Objectives

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.

# Project Overview

## Outcomes and 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.

# Benefit to the Program

***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***

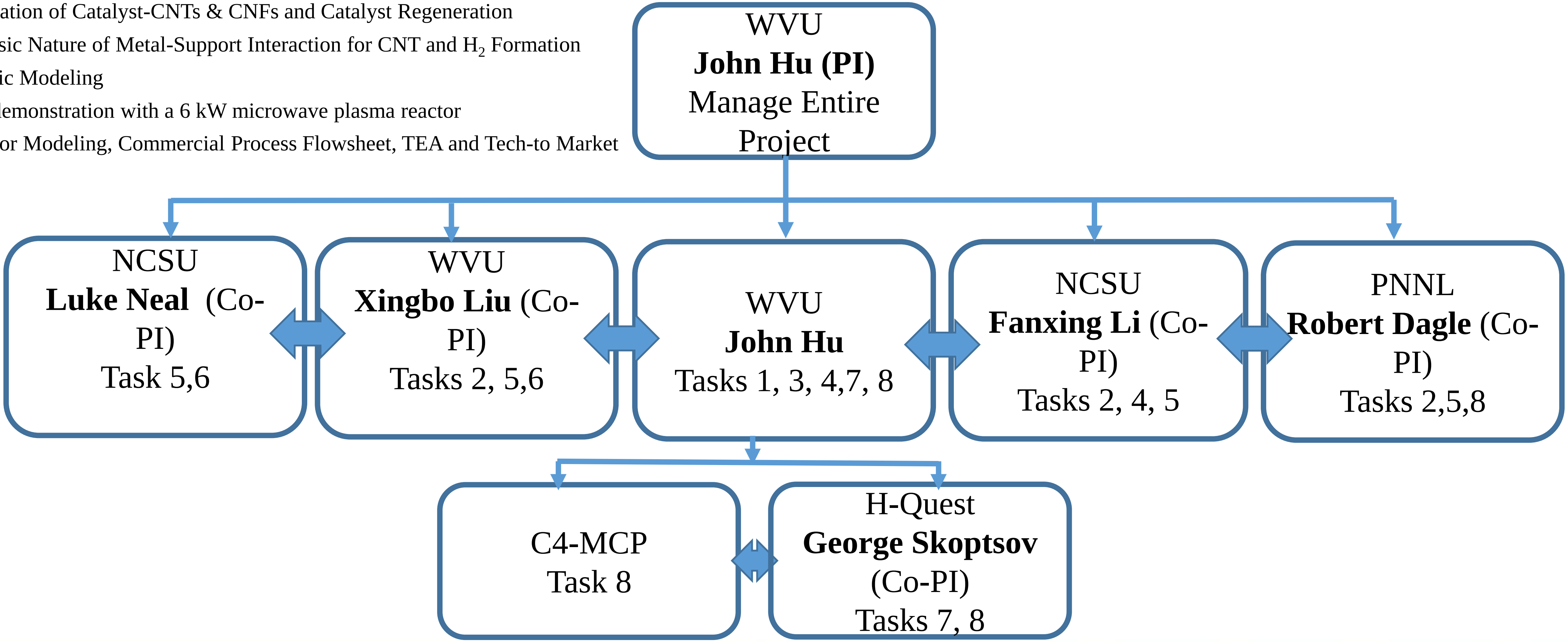
In the stranded gas location where pipeline is not available, distributed production and shipping solid carbon by truck and rail are an economically feasible. CNTs/CNFs are high-value products used as composite,  fibers, electrode for electric arc steelmaking (needle coke replacement), polymers, plastics,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

# Organization Chart

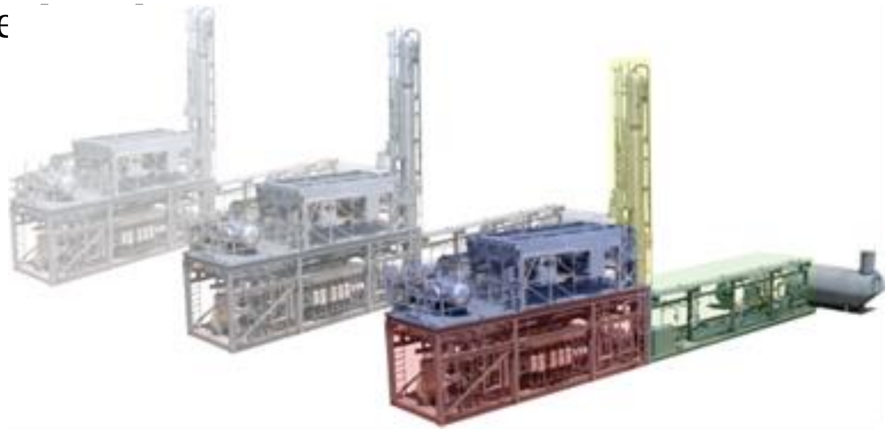
Task 1.0 - Project Management and Planning
Task 2. Catalyst Design, Synthesis and Characterization
Task 3. Variable Frequency Microwave Reactor Test
Task 4: Separation of Catalyst-CNTs & CNFs and Catalyst Regeneration
Task 5. Intrinsic Nature of Metal-Support Interaction for CNT and $H_2$ Formation
Task 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



# Technical Status

# 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.



Modular Unit

*Advantages of using MW heating*

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

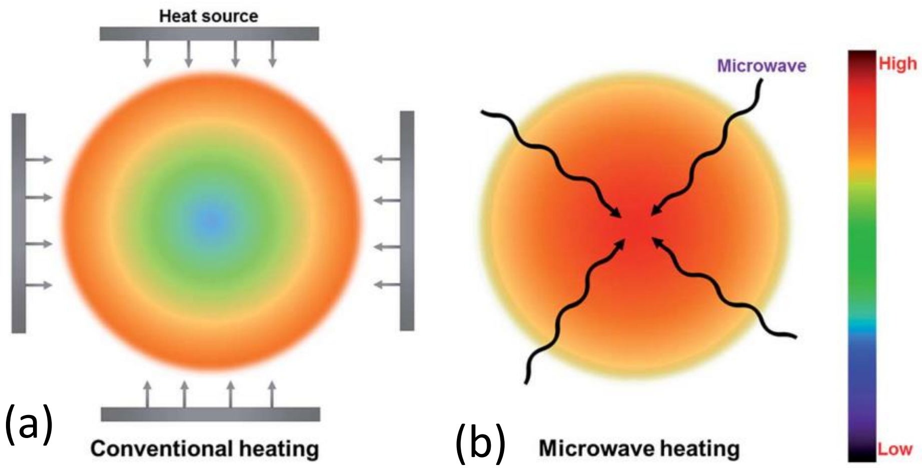



Fig 1. Schematic diagram of (a) conventional heating;
(b) microwave heating

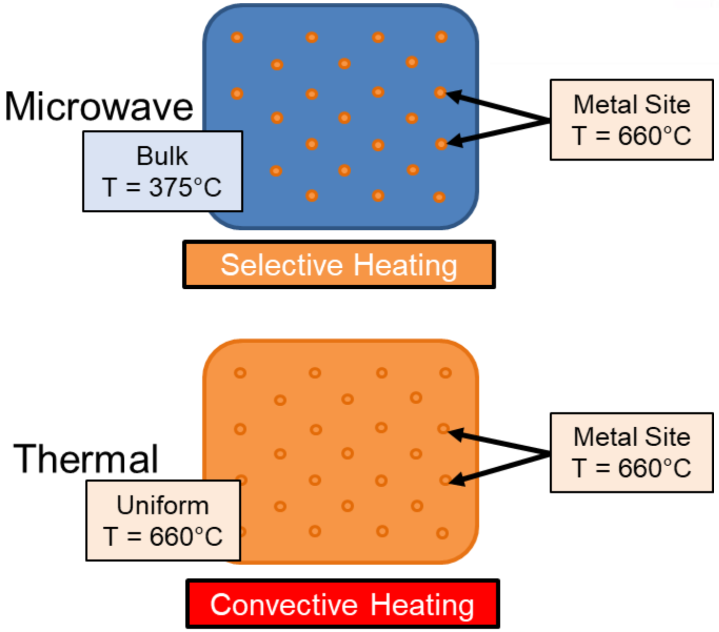


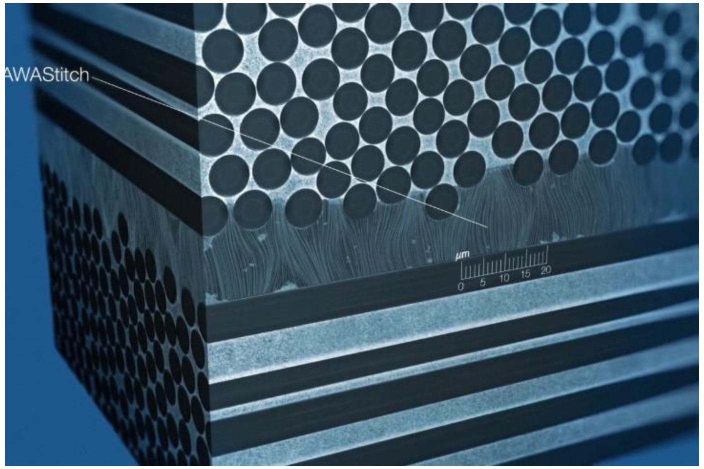

Fig 2. Selective material heating and reduce the bulk temperature

# Zero-Carbon Dioxide Emission Hydrogen Production

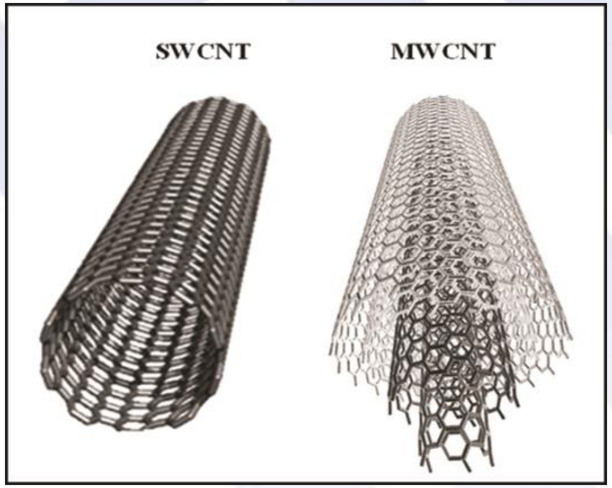
- **WVU patented technology turns natural gas into hydrogen and high value carbon without carbon dioxide:**

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

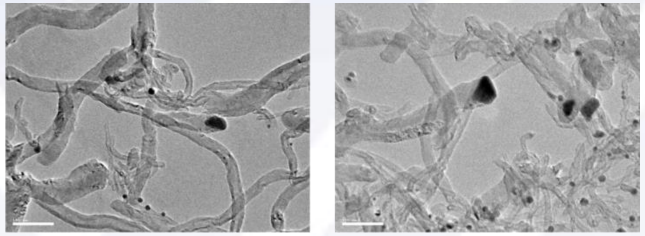
**Turquoise Hydrogen**




Carbon Composite



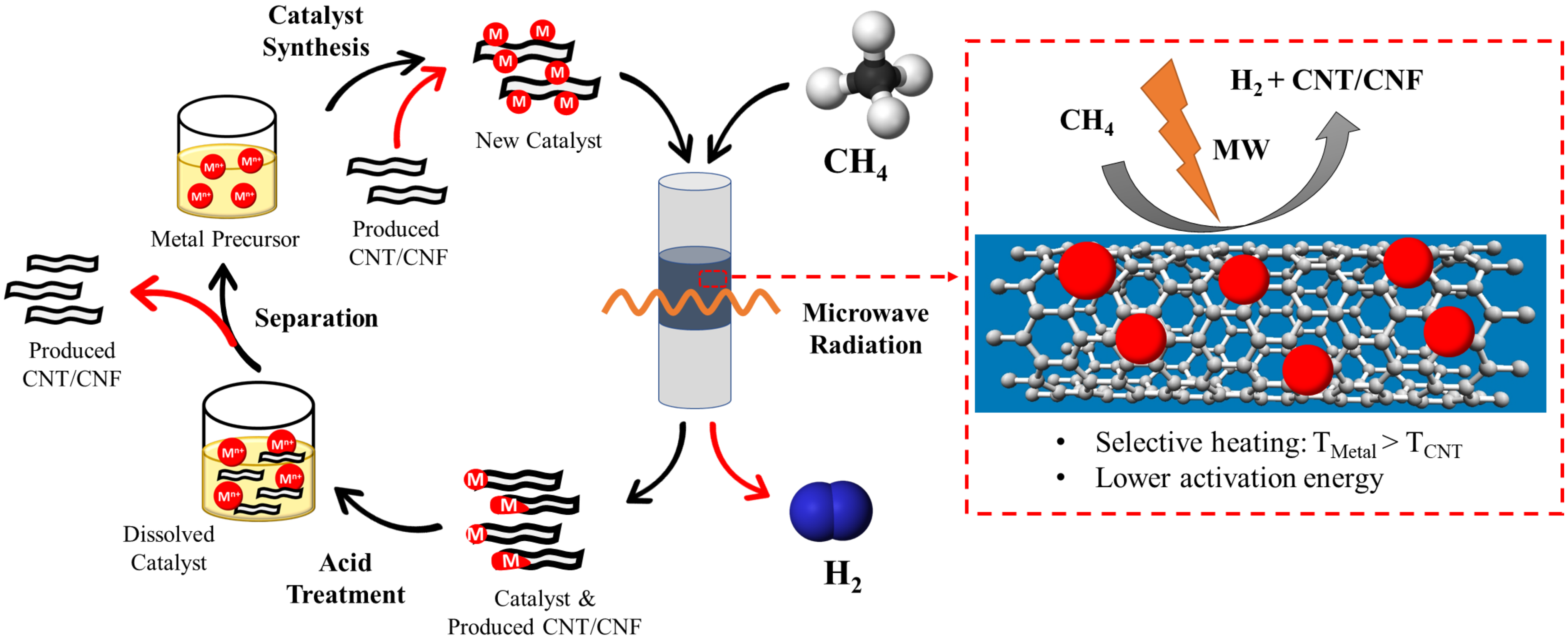

Carbon Nanotubes



*Scale bar = 100 nm*

# 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.

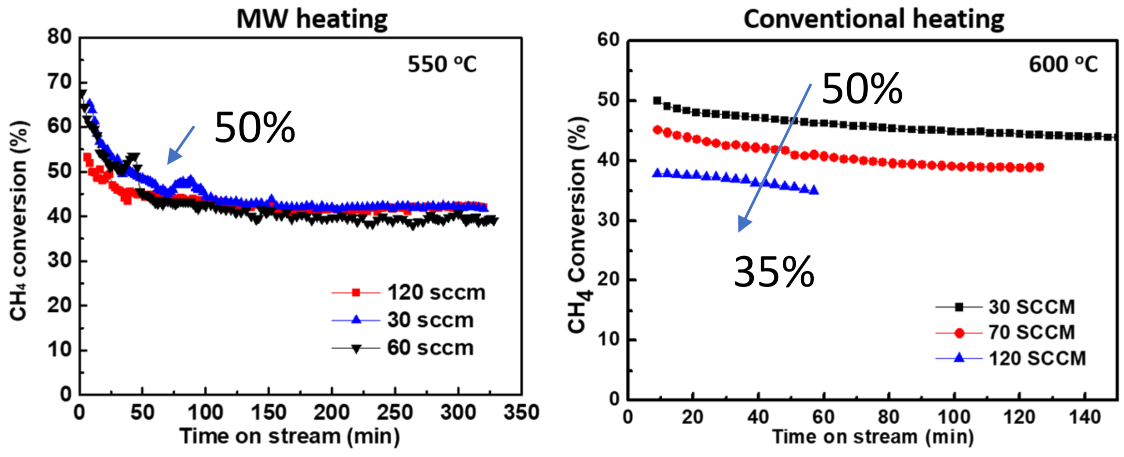



- Selective heating: $T_{Metal} > T_{CNT}$
- Lower activation energy

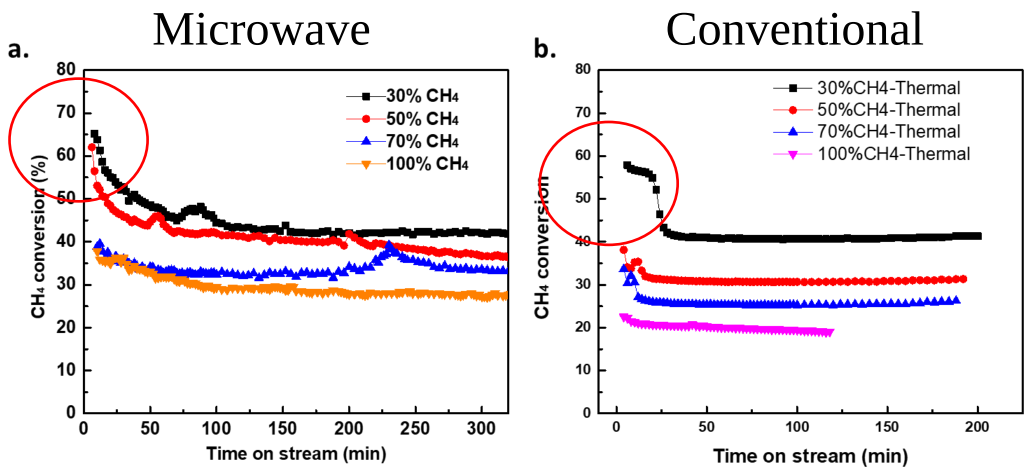
# Accomplishments to Date

- Electromagnetic sensitive catalysts
- Microwave reactor and microwave plasma pilot test
- Catalyst and carbon product characterization
- Kinetic modeling
- Technoeconomic analysis

# Catalyst for Dielectric Heating: Ni-Pd supported by CNT



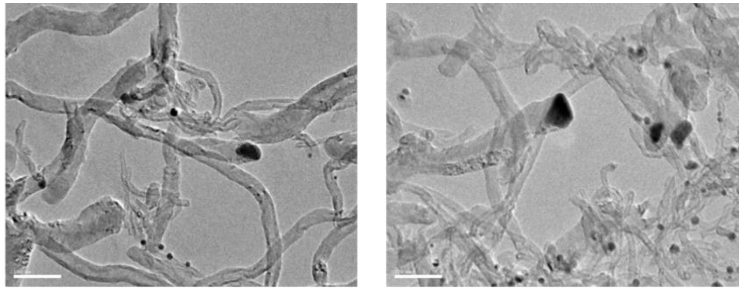

**Effect of Flow Rate**




**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.

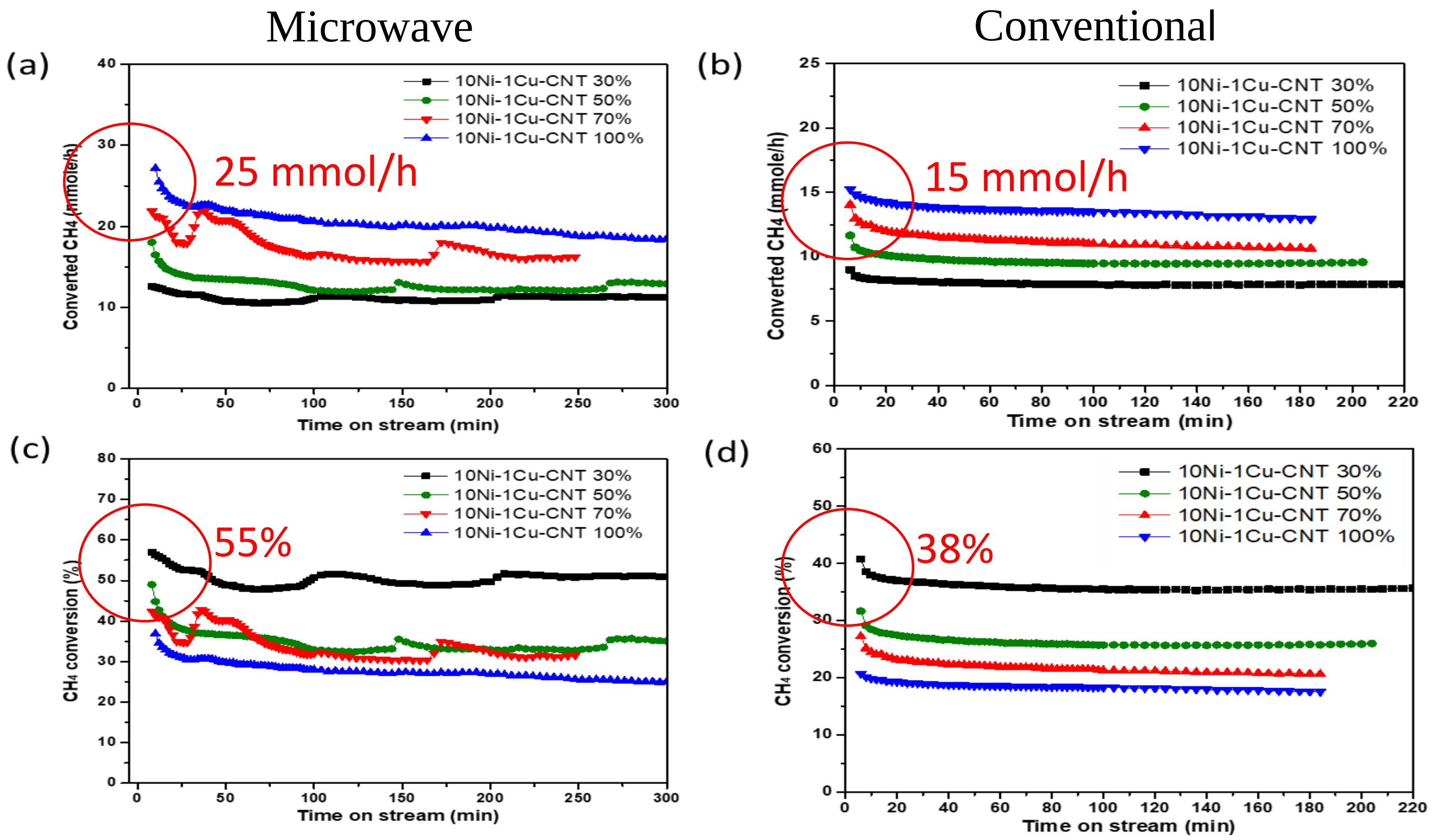
- Under microwave irradiation, $CH_4$ conversion is higher for any concentration of methane.
- Similar trend is observed under MW vs conventional.



*Scale bar = 100 nm*

# Catalyst for Dielectric Heating: Ni-Cu supported by CNT

## We can replace Pd with Cu




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

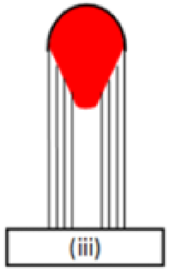
- The amount of $CH_4$ converted increased with increase in $CH_4$ concentration, **25 mmol/h vs 15 mmol/h**
- Catalyst can handle 30%-100% methane concentration (partial pressures), stable for the duration of test
- Under microwave, 10Ni-1Cu/CNT Catalyst demonstrates obviously better performance than conventional heating heating, for example, **55%** methane conversion under microwave vs **38%** under thermal

# 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

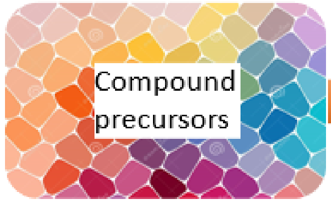
Ni-Cu alloy particle



Tip-grown

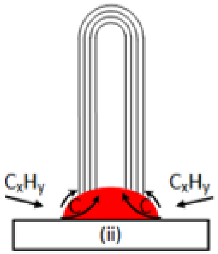
Clean-cut interface between Ni-Cu alloy particle and host materials, tend to break-way

## 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

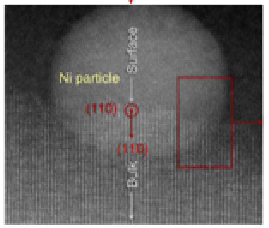
Ni-Cu alloy particle



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

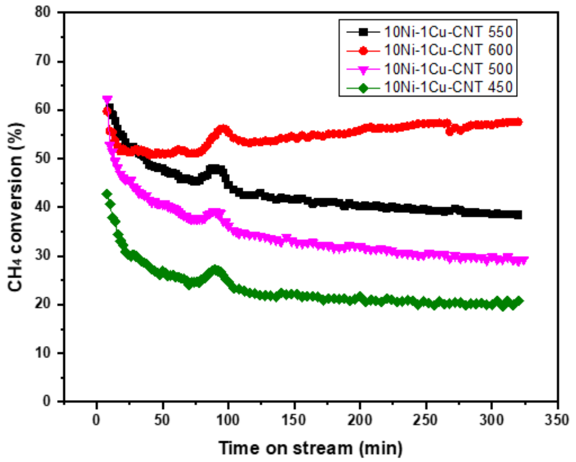


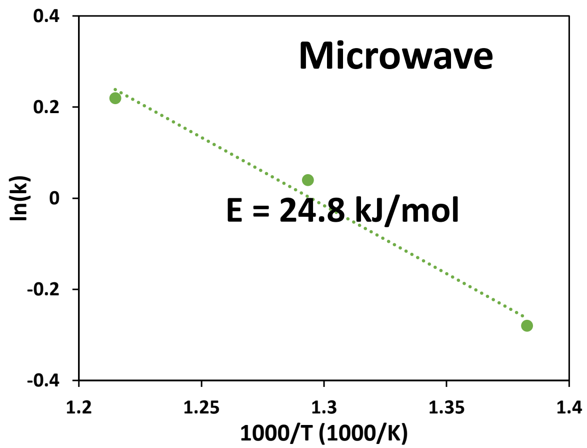

Surface catalyst exsolution control:

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

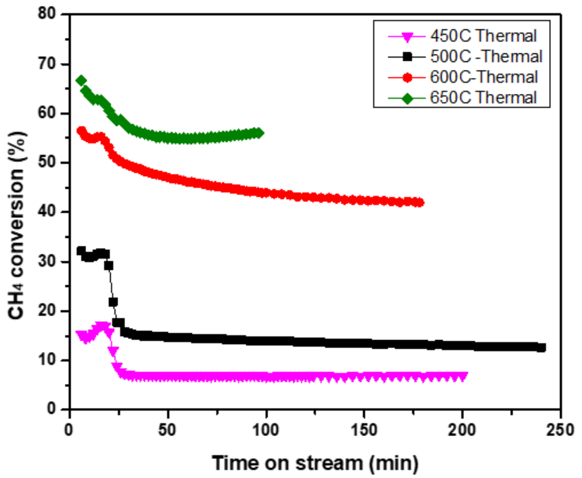
- High entropy compound as host tends to decrease to single oxides at intermediate T
- Higher reducibility of NiCuOx than other elements

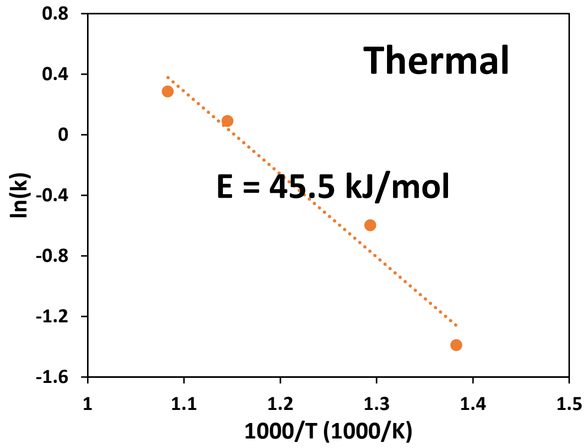
# Kinetic Modeling Results- Microwave vs Thermal, Ni-Cu/CNT Catalyst




$k_{0\_MW}$= 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**

WestVirginiaUniversity

# Techno-economic Analysis (PNNL)

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

Pacific Northwest NATIONAL LABORATORY

- 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) |

Carbon black → **Amorphous carbon, less value**

Graphite, Carbon fiber, CNT → **Crystalline carbon, higher value**

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

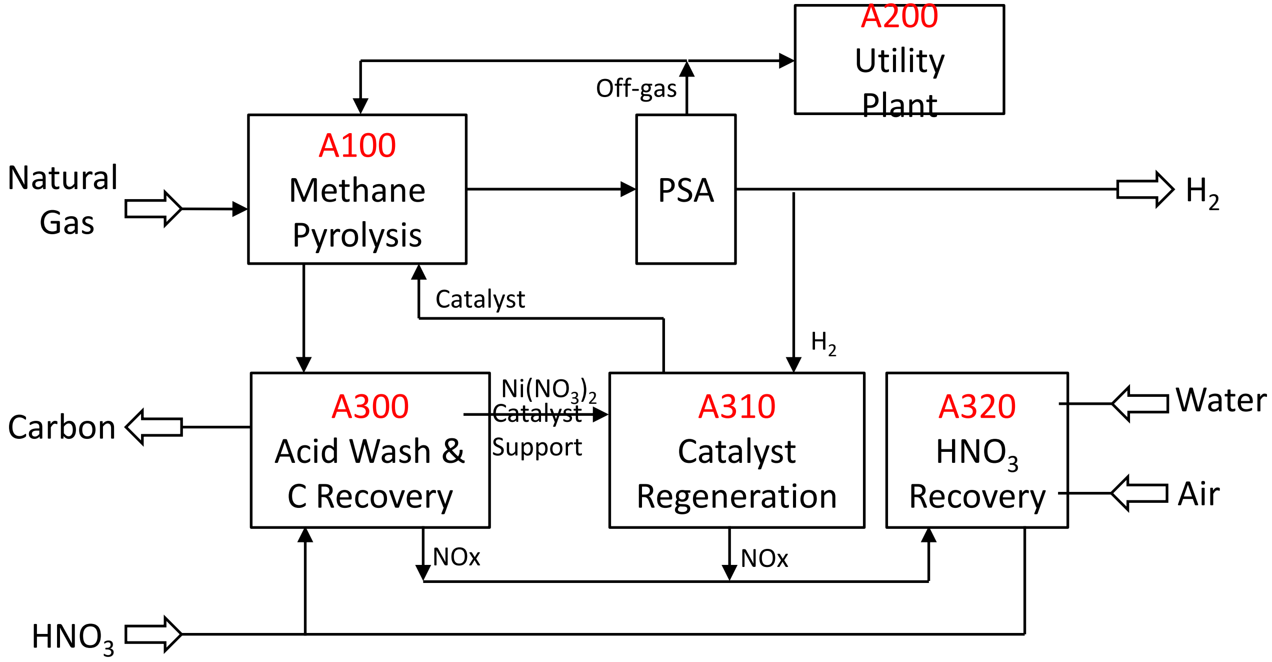
- Key Economic Assumptions

| 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)

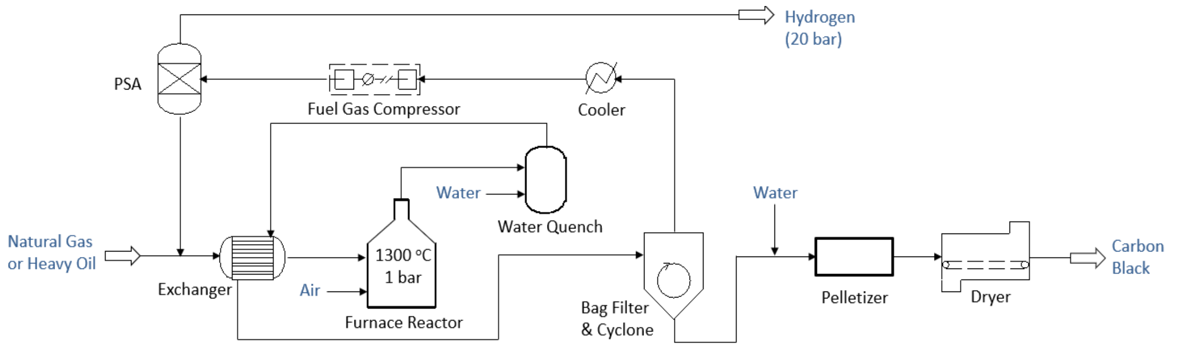
## Microwave (MW) and Thermal Decomposition (TD) Process Models

- 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

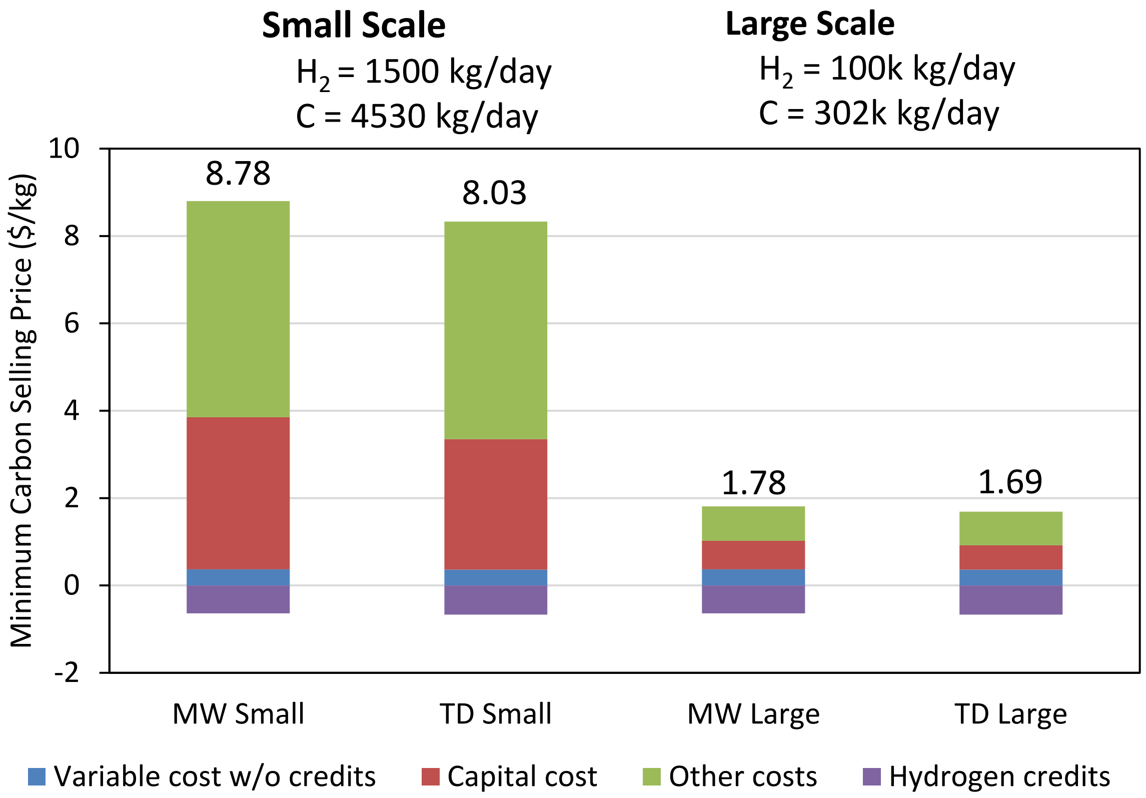
- Process flow diagram for thermal decomposition (TD) - ***baseline commercial process***




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

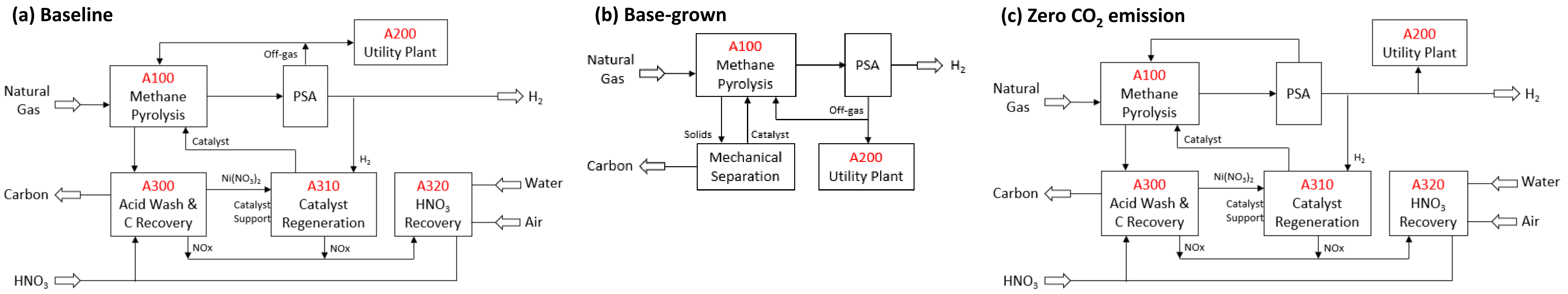
# Techno-economic Comparison – Results & Discussion

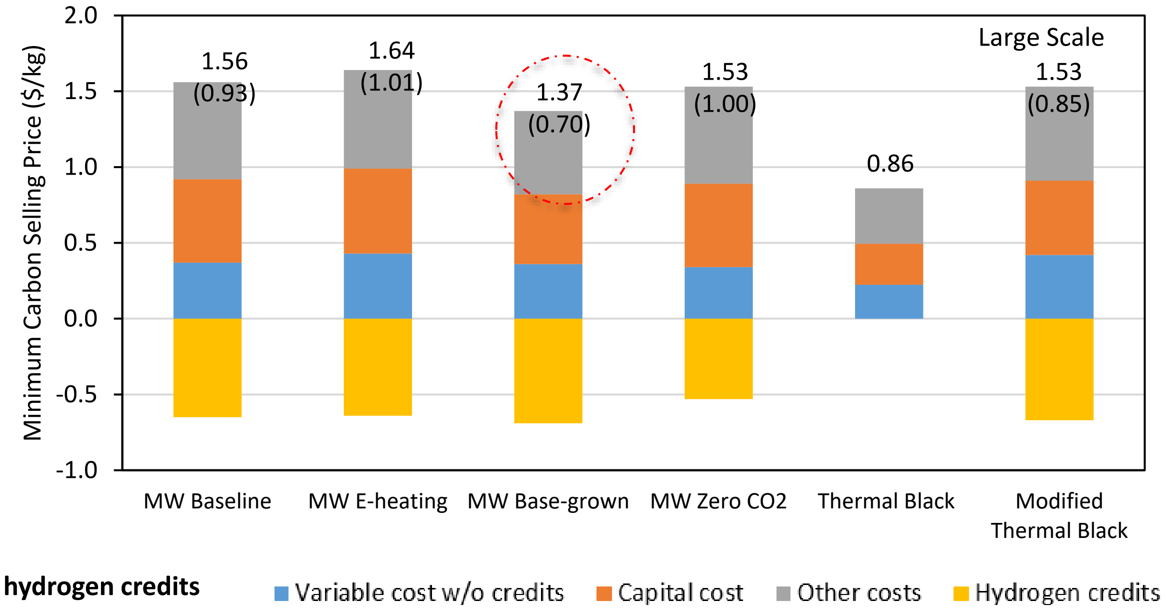
| | Microwave-Assisted Catalytic Pyrolysis (MW) | Carbon Black Process via Thermal Decomp. (TD) |
|---|---|---|
| Configuration | | |
| Reactor Temp (°C) | 550 | 1300 |
| Conversion (%) | 45 | 40 |
| Carbon recovery (%) | 100 (Acid wash) | (Bag filter) |
| Heat source | 80% fuel, 20% power | 100% fuel |
| 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.

# Updated TEA for Different Microwave Pyrolysis Cases




*() MCSP w/ hydrogen credits

- **The crystalline carbons from our technology will need to sell 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 this.**
- **Benefit from $CO_2$ tax is not considered**

Minimum selling price has 15% return built in already

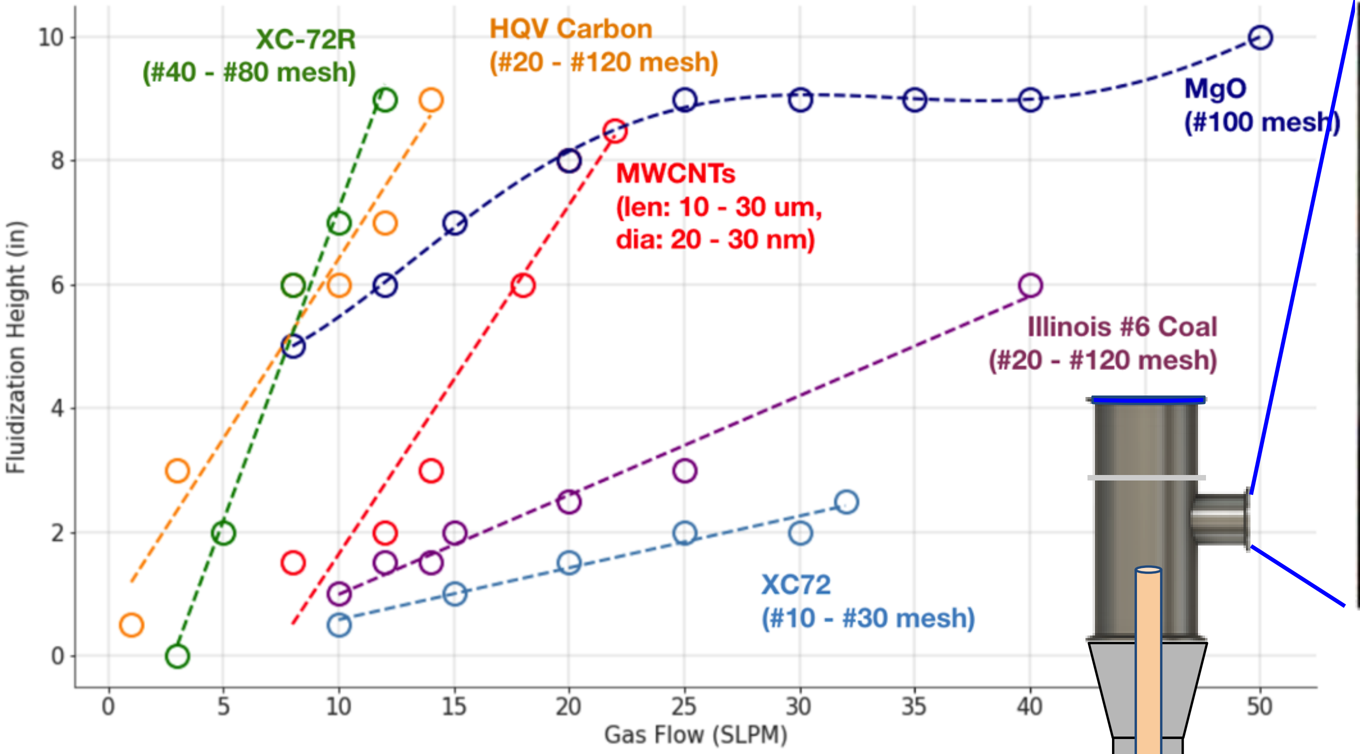
# Overview Pilot Test

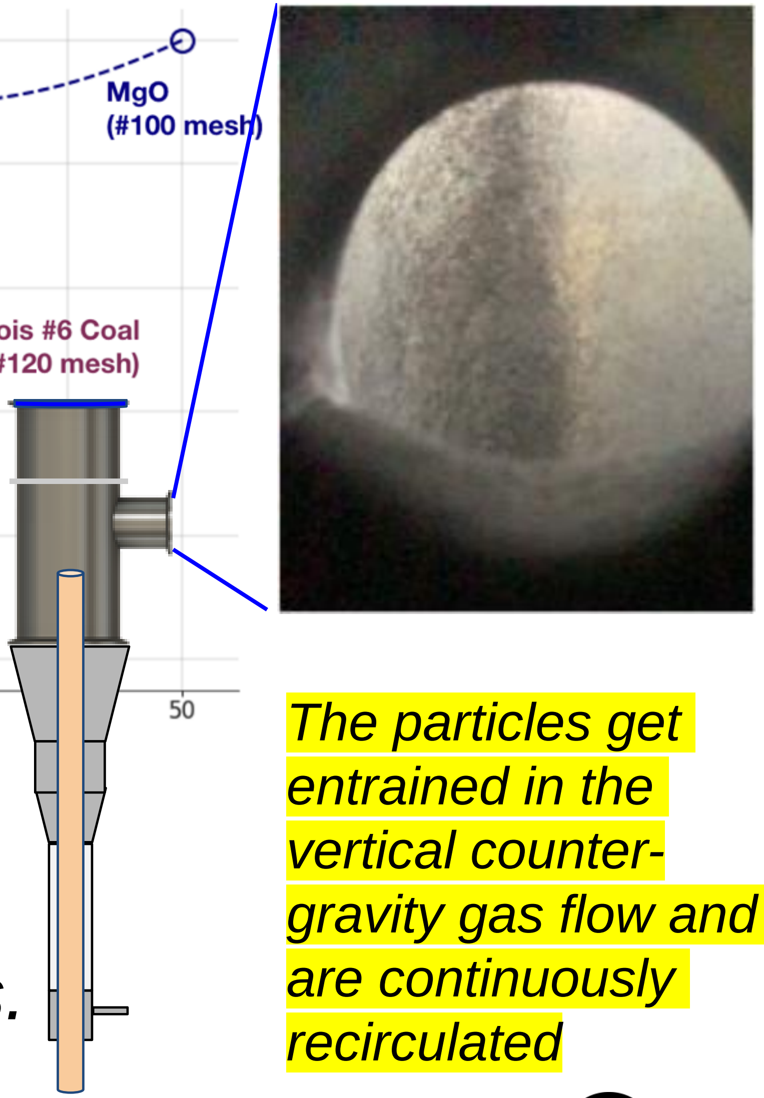
Current status:

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

Quest

# 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*

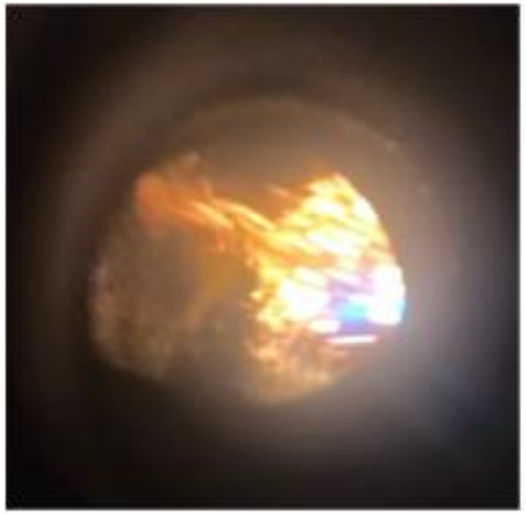
# Reactor configurations iteratively modified to maximize plasma extents and particle interaction

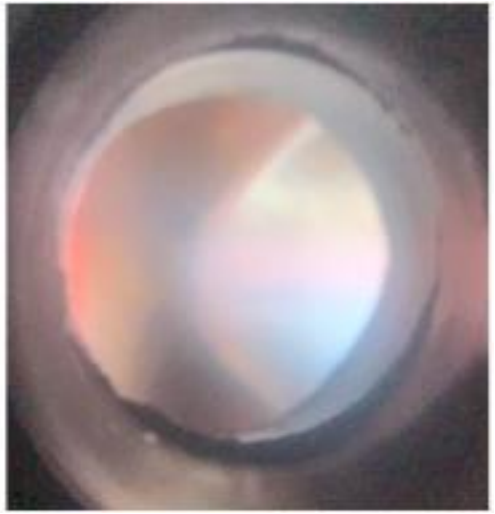
**General description**

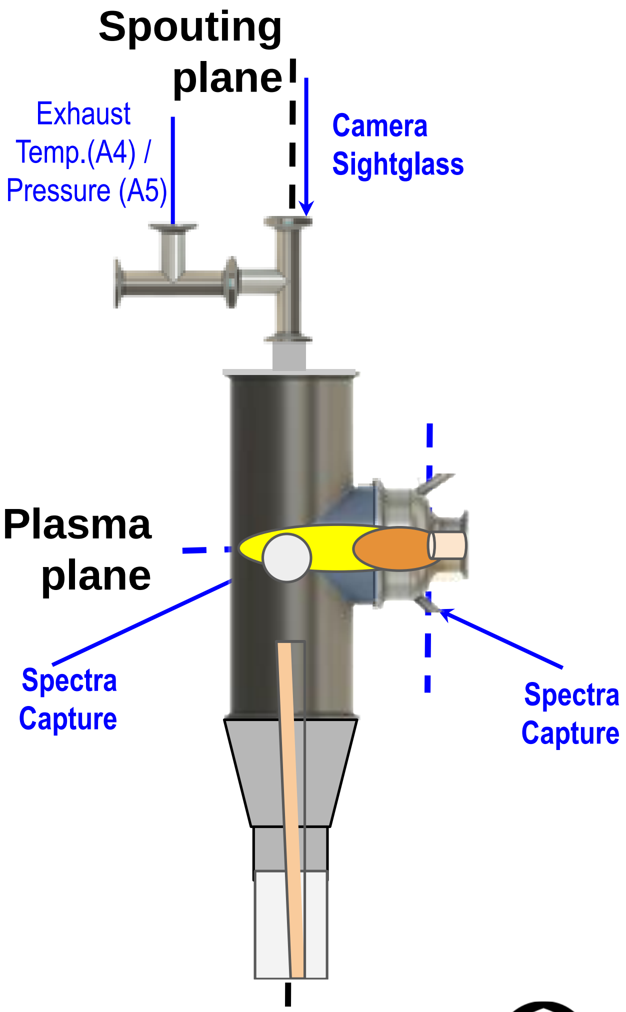
- Feed supplied vertically from below in either spouted or fluidized configuration;
- Ionized gas (plasma) is launched horizontally cross-axis to entrained feed;
- Exhaust entrainment and particle loss controlled by limiting gas velocities.

**Instrumentation:**

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

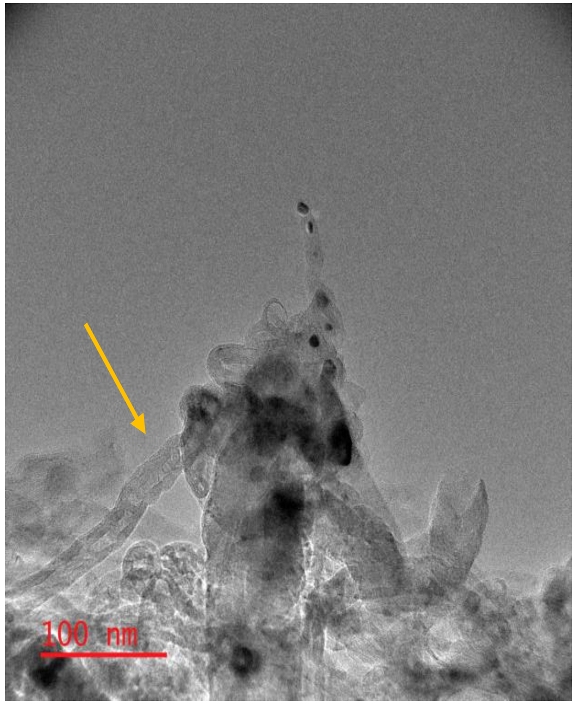


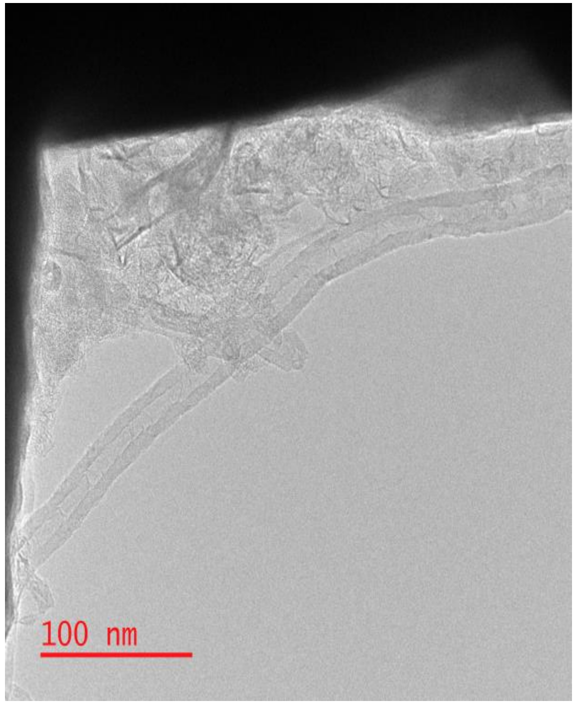


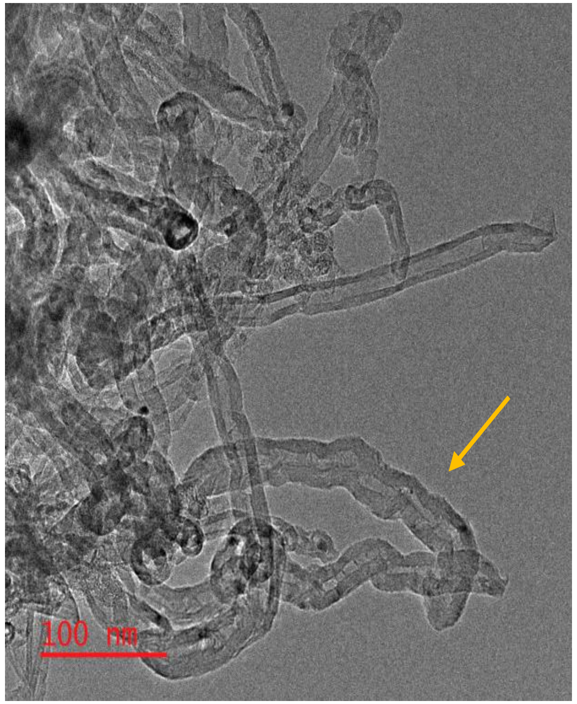



Quest

# TEM indicated growth of CNTs following microwave plasma treatment of methane entrained MWCNTs



# Synergy Opportunities

- $CO_2$-free hydrogen utilization.
- Hydrogen for $CO_2$ conversion
- Simultaneous conversion of natural gas and $CO_2$
- Possible integration of renewable power- intermittent nature

# Project 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 CAPEX and OPEX.
- ❑ 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

# Future Work

- ❑ Develop low-cost catalyst-CNT separation processes
- ❑ Scale-up catalyst synthesis protocol
- ❑ Pilot scale microwave plasma reactor test at H-Quest
- ❑ Post test characterization of spent catalysts and carbon nanomaterials
- ❑ Process simulation and technoeconomic analysis based on pilot test data
- ❑ Market research & development of advanced carbon materials.

# Gantt Chart

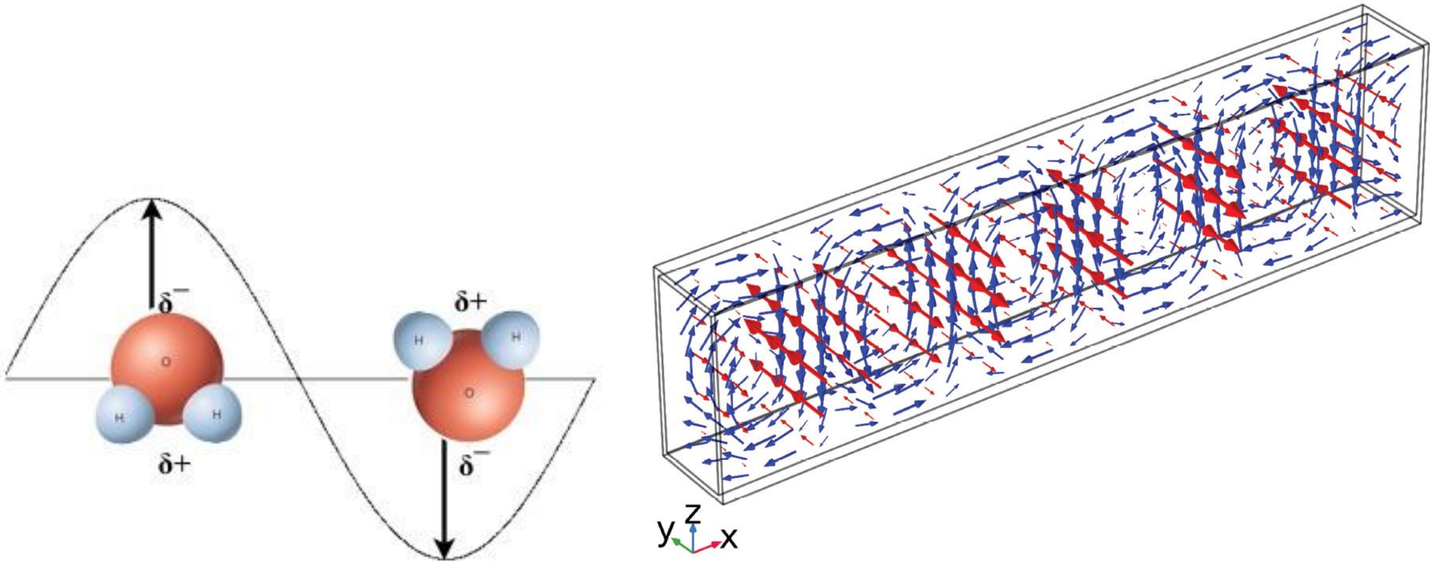
Table 4.1. Updated Project Timeline **Green**=original schedule, **Orange**=task extension into BP-2

| **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 |

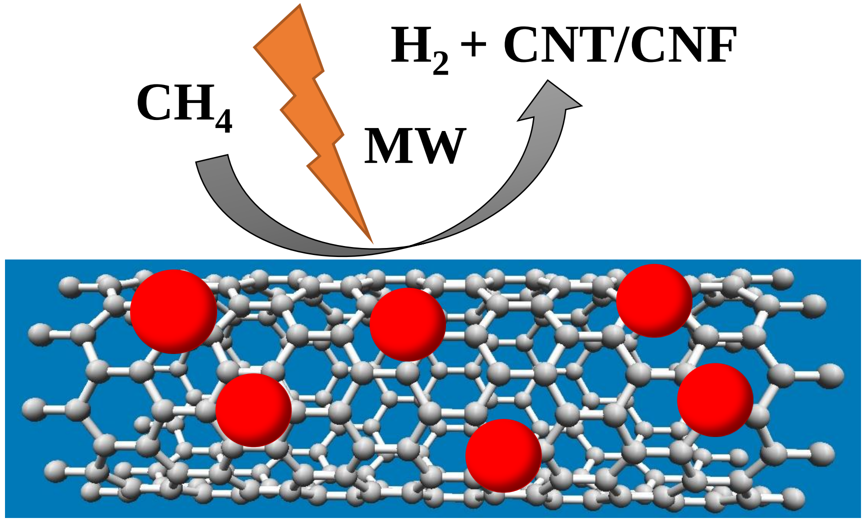
# Appendix

# 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.

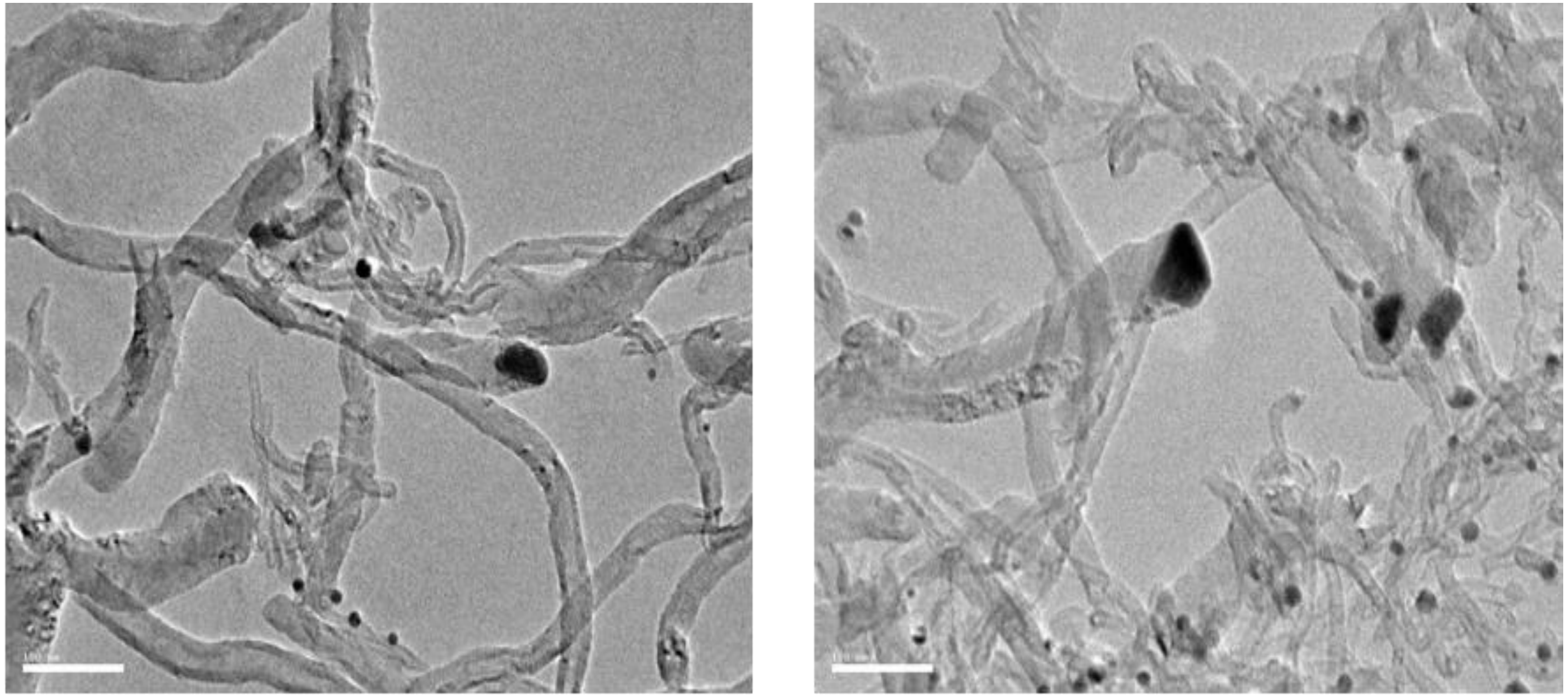



Field distribution of a TE10 waveguide (red arrows: electric field; blue arrows: magnetic field; the direction of wave propagation is −x; a larger arrow indicates a stronger field)[2].




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

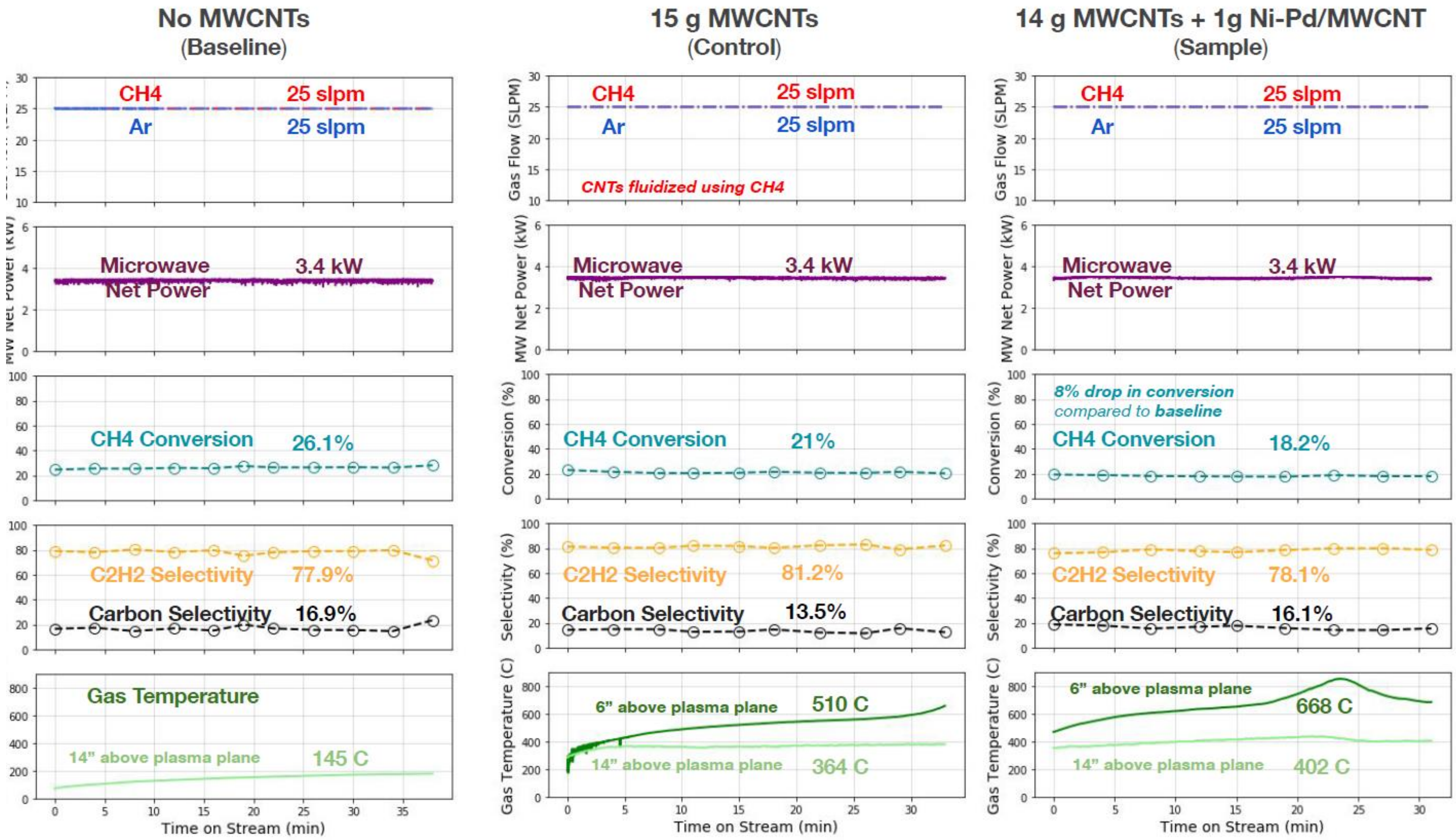
# TEM images of produced carbon nanomaterials and spent catalyst



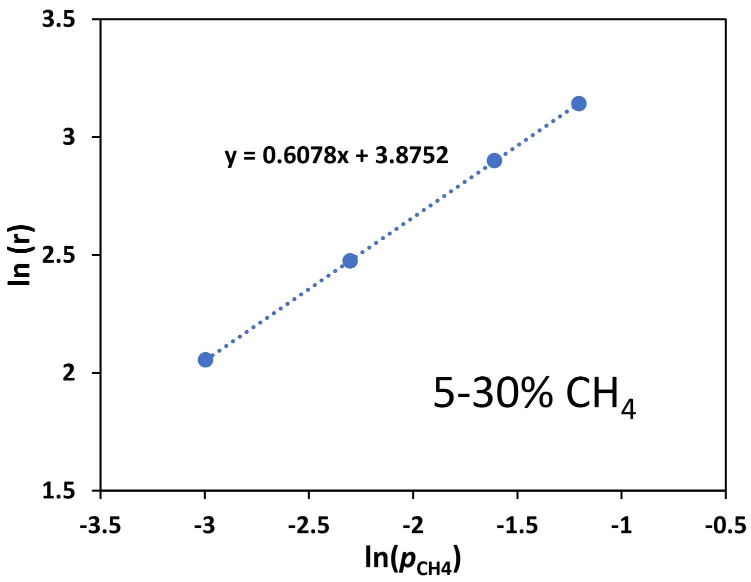
*Scale bar = 100 nm*

**These crystalline carbons will be used as carbon composite, electrode for steel and aluminum industries, polymer additives. They will not be just sold as CNTs**

# Update-Pilot Test



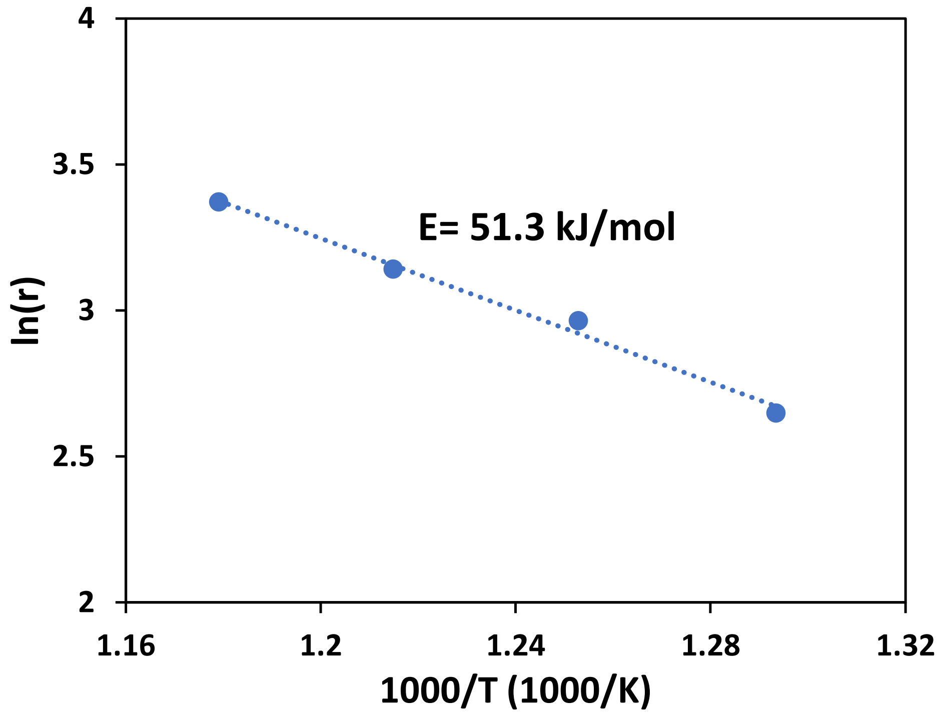
# Kinetic Modeling: Reaction order of methane pyrolysis over NiPd/CNT




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

- 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)

# Activation energy for methane pyrolysis over NiPd/CNT




- 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
- 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

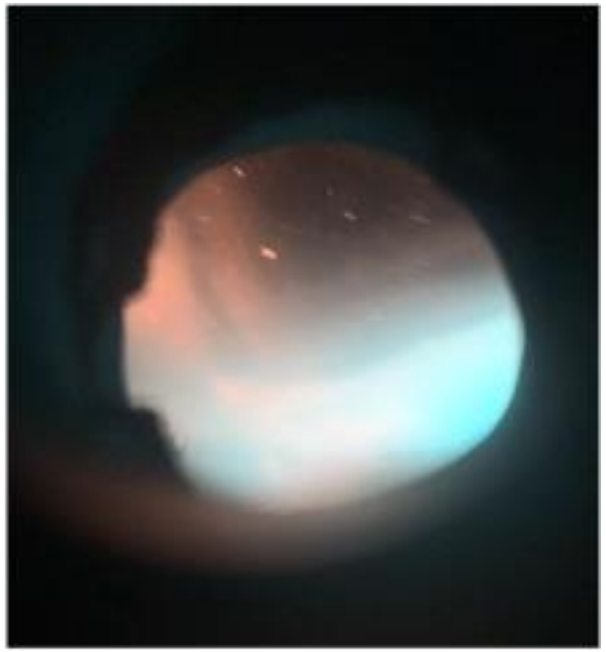
# Methane Conversion without Entrained Particles

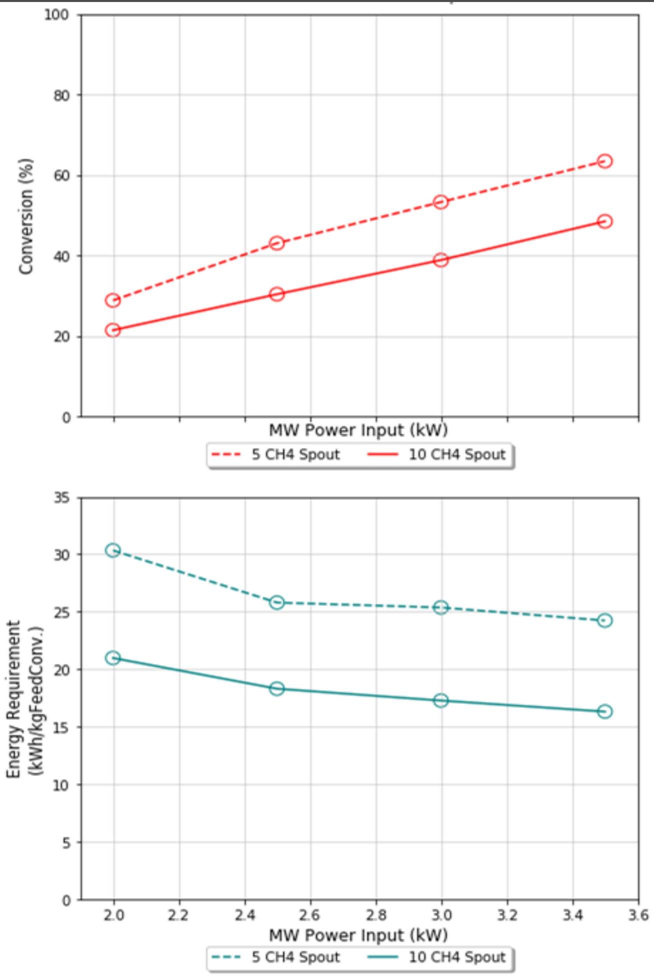
| | |
|---|---|
| *Microwave power:* | 2-3.5 kW |
| *Entrainment gas:* | 5-10 slpm $CH_4$ |
| *Entrained particles:* | None |

*Methane conversion rate: 20%-60%*

*High selectivity to $C_2H_2$: >70%*

*High SER:* >15 kWh/kg$CH_4$






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

HQuest