Production of hydrogen and carbon from catalytic natural gas pyrolysis

FWP-1022467

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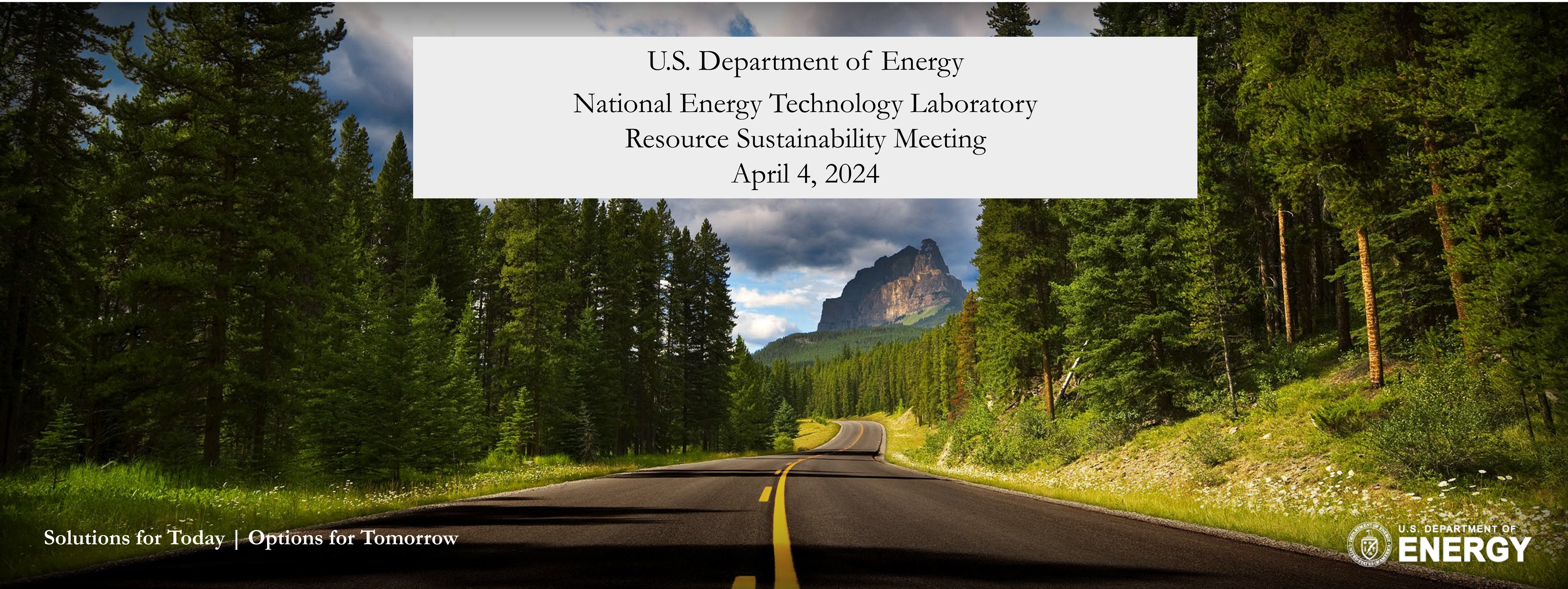
U.S. Department of Energy/National Energy Technology Laboratory



U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Meeting
April 4, 2024

Solutions for Today | Options for Tomorrow

Funding and Project participants

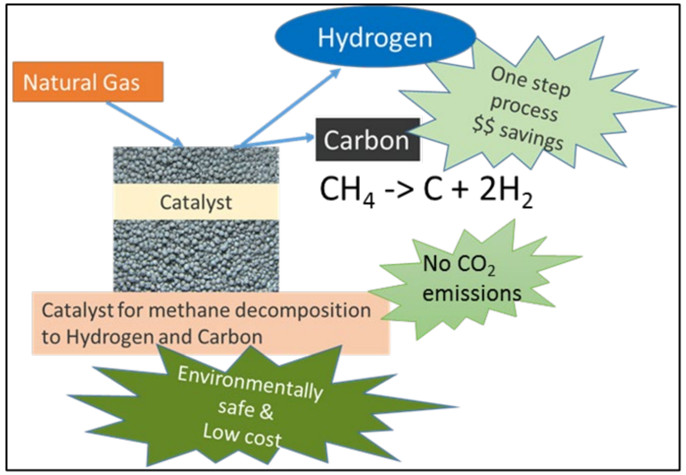
- **Current Funding – Natural Gas Decarbonization and Hydrogen Technologies - NETL FWP** *1022467*
- **Overall project performance dates - EY22 to EY23**
- **Project participants at NETL – Ranjani Siriwardane (PI, Ph.D. Physical Chemistry), Jarret Riley (Ph.D. Chem. Eng.), Hayat Adawi(Ph.D., Chem. Eng.), Michael Bobek (Ph.D. Mech. Eng.), Chris Atallah (Chem. Eng.), Donald Jeffries (Engineering technician)**

Industry contacts – FastForward

  - Initial CRADA was signed and is currently seeking investor funds to finalize the CRADA by August 2024

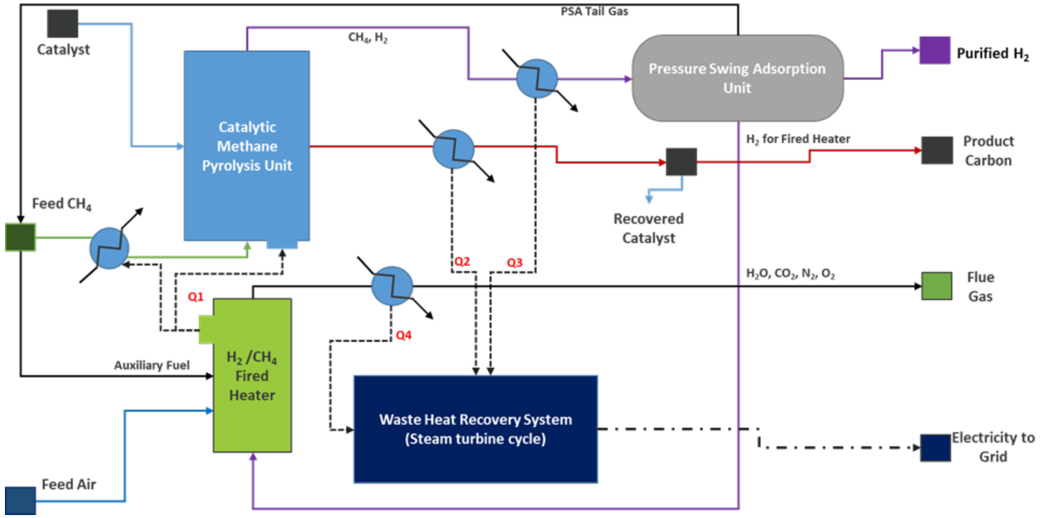
- **Future support**
  - NETL systems analysis group- in technoeconomic analysis
  - NETL CFD team for future reactor design and scaleup

Technology Background
Concept - Catalytic methane pyrolysis (CMP)



- Catalyst decomposes methane (and other components of NG) to H2 and carbon in CMP Unit
- CxHy → xC + 0.5yH2
- CMP Unit Operates at 650-750°C
- Desirable pressures: 2-15 atm (dependent upon H2 delivery pressure)

BFD of Catalytic NG Pyrolysis Process for the co-production of H_2 and C



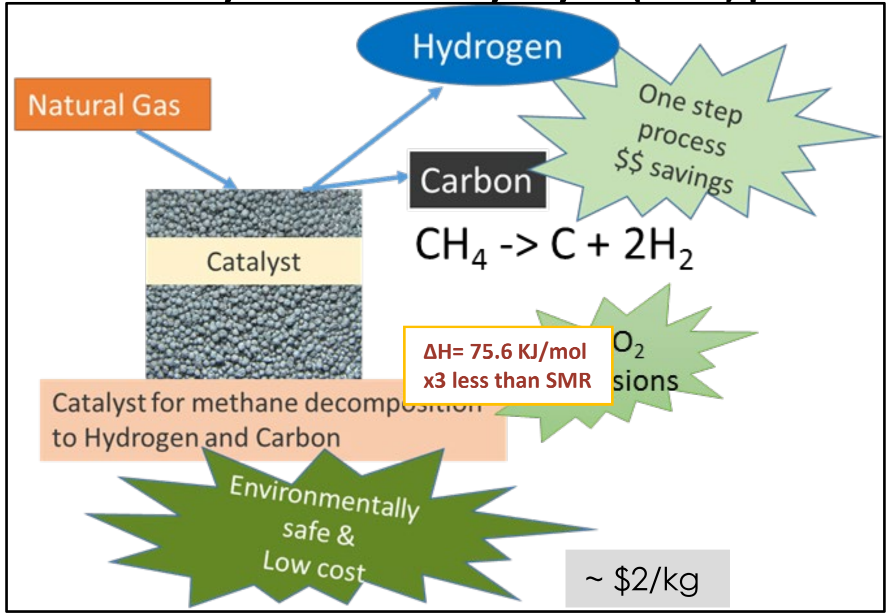
Technical Advantages:

- **One step process to produce two valuable products H_2 and carbon from natural gas/flare gas**
- **No CO_2 emissions (when heat is supplied via H2 combustion)**
- **Mildly endothermic**
- **Preliminary systems analysis indicated an economical path for converting natural gas into transportable, value-added products.**

Technology Background

Advantages of H_2 production from catalytic methane pyrolysis (CMP) vs. steam methane reforming (SMR)

Catalytic Methane Pyrolysis (CMP) process



Hydrogen

Natural Gas

One step process $$ savings

Carbon

Catalyst

$CH_4 \rightarrow C + 2H_2$

ΔH= 75.6 KJ/mol
x3 less than SMR

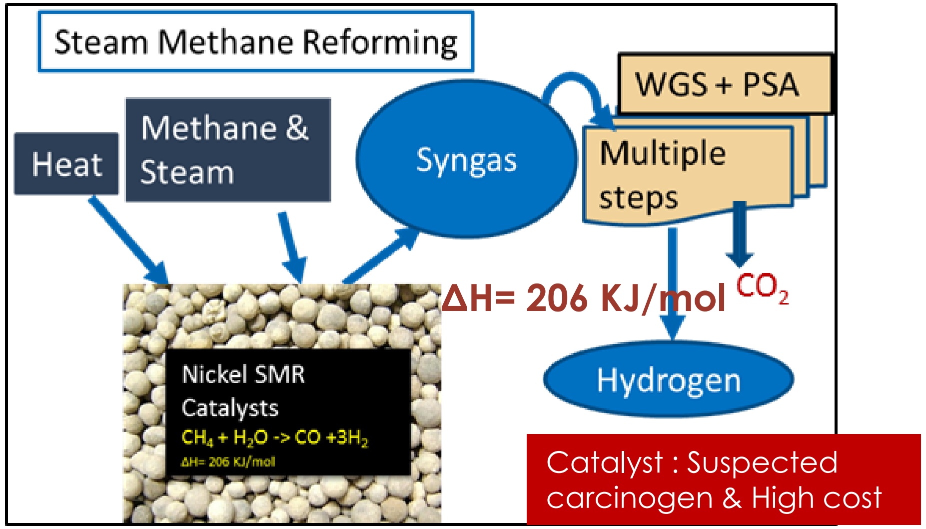
O_2
sions

Catalyst for methane decomposition
to Hydrogen and Carbon

Environmentally safe & Low cost

~ $2/kg

Current commercial SMR process



Steam Methane Reforming

Heat

Methane & Steam

Syngas

WGS + PSA

Multiple steps

ΔH= 206 KJ/mol

CO_2

Hydrogen

Nickel SMR Catalysts
$CH_4 + H_2O \rightarrow CO + 3H_2$
ΔH= 206 KJ/mol

Catalyst : Suspected carcinogen & High cost

- **SMR - current commercial technology being used for H_2 generation from NG**
- **CMP is inherently competitive to this process with some minor trade offs**
  - **Advantages:**
    - **Less processing steps to create H2**
    - **3x less endothermic**
    - **Valuable carbon product with CO_2 emission mitigated**
    - **Low cost catalyst materials**
    - **No steam required**
  - **Trade-offs: Lower H_2 yield – ~30%less/mol CH4**

Identified challenges

- Process scale up strategies to obtain an economical H2 production process

- Carbon purity and separation for various applications
  - Initial screening suggests a mixed allotrope
  - Develop techniques to better quantify carbon product to aid in purity refinement

- Heat integration for a commercial process with no CO2 emissions
  - Strategies to be explored and implemented in system studies

Research focus areas to address major challenges

- **Catalyst development**
  - Improvement of catalyst formulation to obtain high rates of H2 production
  - Effective with all species in NG (e.g., ethane, propane etc.)
  - Long term performance for an economical process

- **Demonstration of continuous H2 production with catalyst in bench scale, sub pilot and pilot scale tests**

- **Improve the value of carbon to lower the H2 production costs**
  - Develop identification methods for various carbon allotropes
  - Develop methods to separate various carbon allotropes.

- **Process simulation - TEA/LCA to determine economic viability**
  - Identify and acquire necessary data

- **Scale up de-risking**
  - Integrating data with CFD would enable scale up de-risking of CMP unit
  - Working with industry partner for commercialization

Project Objective/Technical Approach

Research Objective: Demonstration the process in a pilot system for commercialization

Determine the feasibility of the process using bench scale/sub-pilot scale experimental data, improve value of carbons and assess the economic viability using TEA to enable scale up

Specific project goals and milestones

Phase 1 – Scale up initiation of catalytic process – large scale preparation, optimizing performance in sub pilot tests and carbon separation method development

- **Synthesis and exploration of advanced catalyst formulations to improve system performance**
- **Carbon generation and carbon separation for product analysis**
- **Complete learning trial test in large fluid bed**

Phase 2 – Scale up bench marking, extensive parametric studies and identify the best method for large scale carbon separations

- **Complete a learning trail in large fluid bed with parametric evaluations**
- **P, T, Catalyst composition effects and improve the value of carbons**

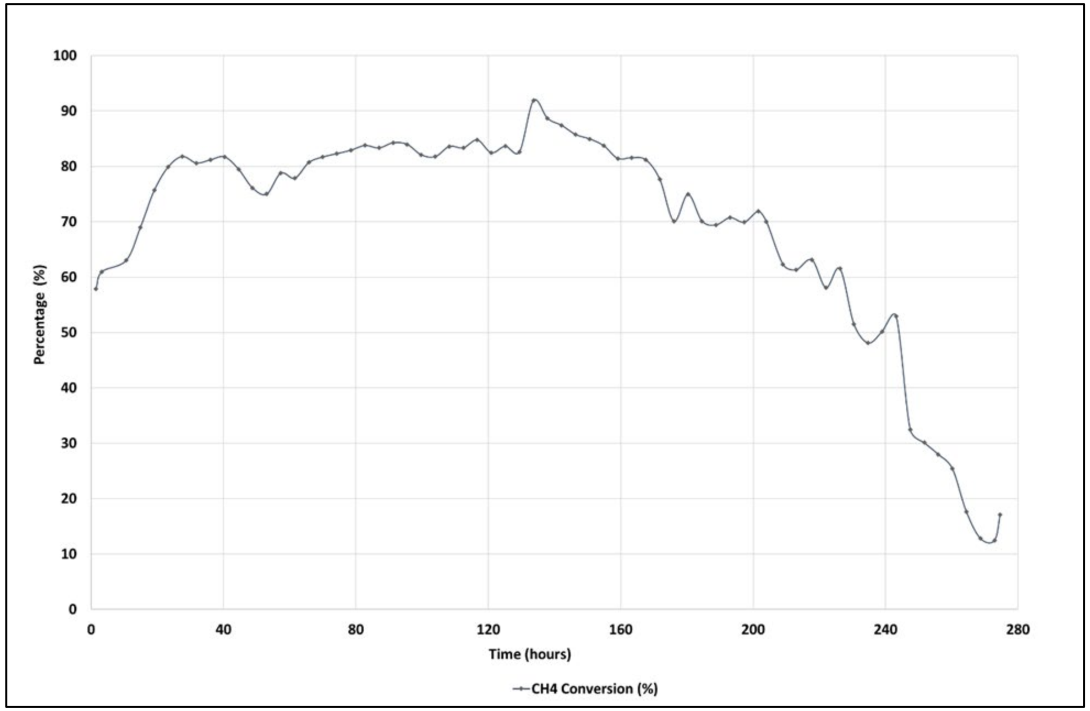
Phase 3 –Concept demonstration to inform commercial scale reactor design and refine TEA

- **Catalyst synthesis and fluid bed analysis support for TEA**
- **Carbon product analysis and provide data for TEA**
- **Carbon formation model validation and provide for TEA**

Research Highlights from last year presentation (EY 22)

Solutions with NETL novel patented catalyst to major issues with prior catalysts

H2 concentrations during fluid bed tests with NETL catalyst

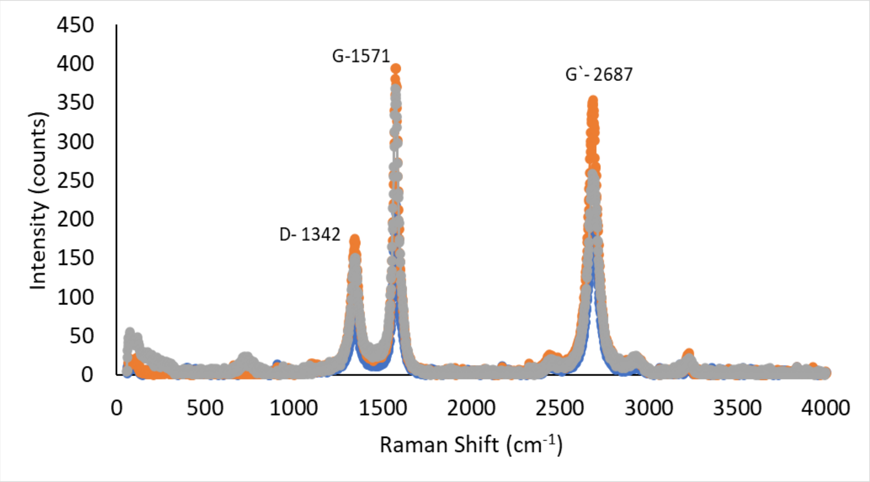


EY22 research highlights

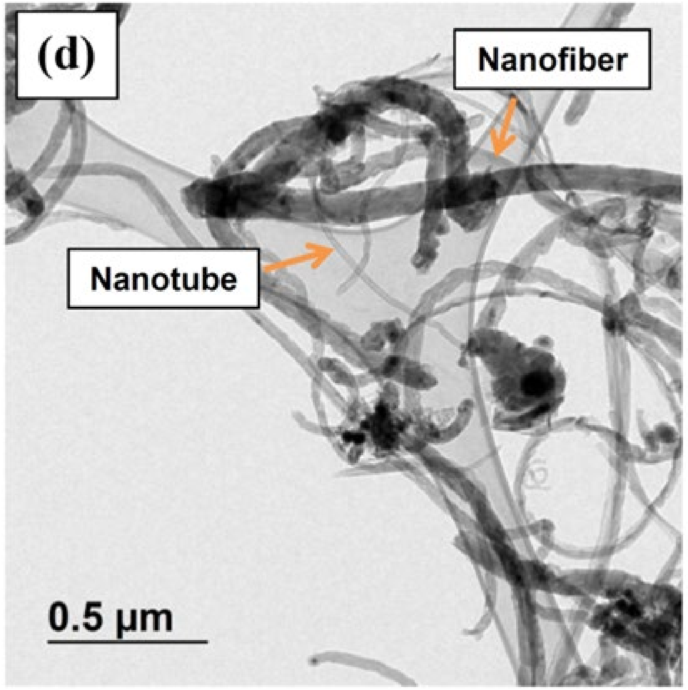
- Fluid bed tests with catalyst (500 g) showed >80% methane conversion to H2 and nano carbons at 700 °C for more than 160 hrs. during the 240 hr. test – **Significant accomplishment not reported before**
- Demonstrated 100% conversion of ethane and propane during fluid bed test
- Catalyst production technique consistent for industrial level preparation. Estimated cost < $2/kg
- Preliminary Systems assessments suggest significant advantages over SMR for H2 production.

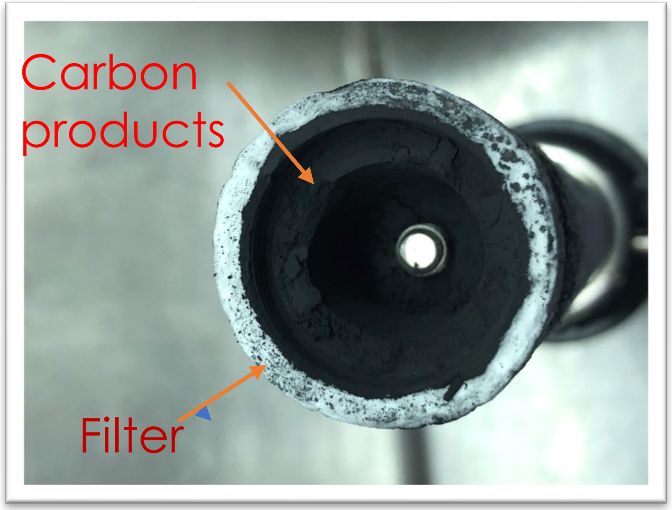
Research highlights from last year EY22 (contd.) Confirmed Valuable Carbon Formation by various spectroscopic analysis

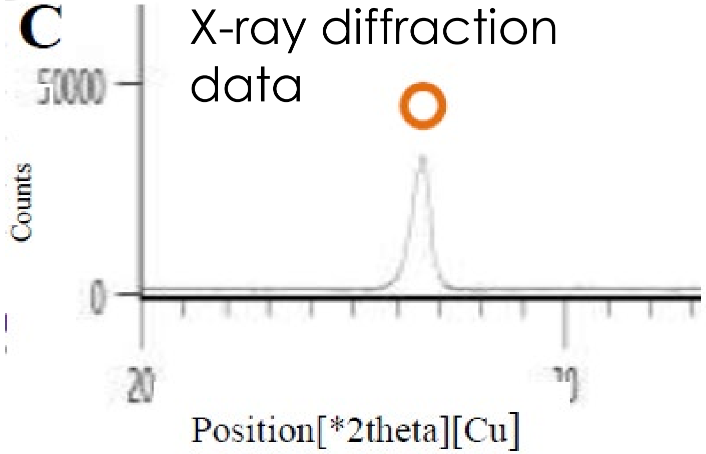
Raman Spectroscopy



Transmission electron micrographs(TEM)

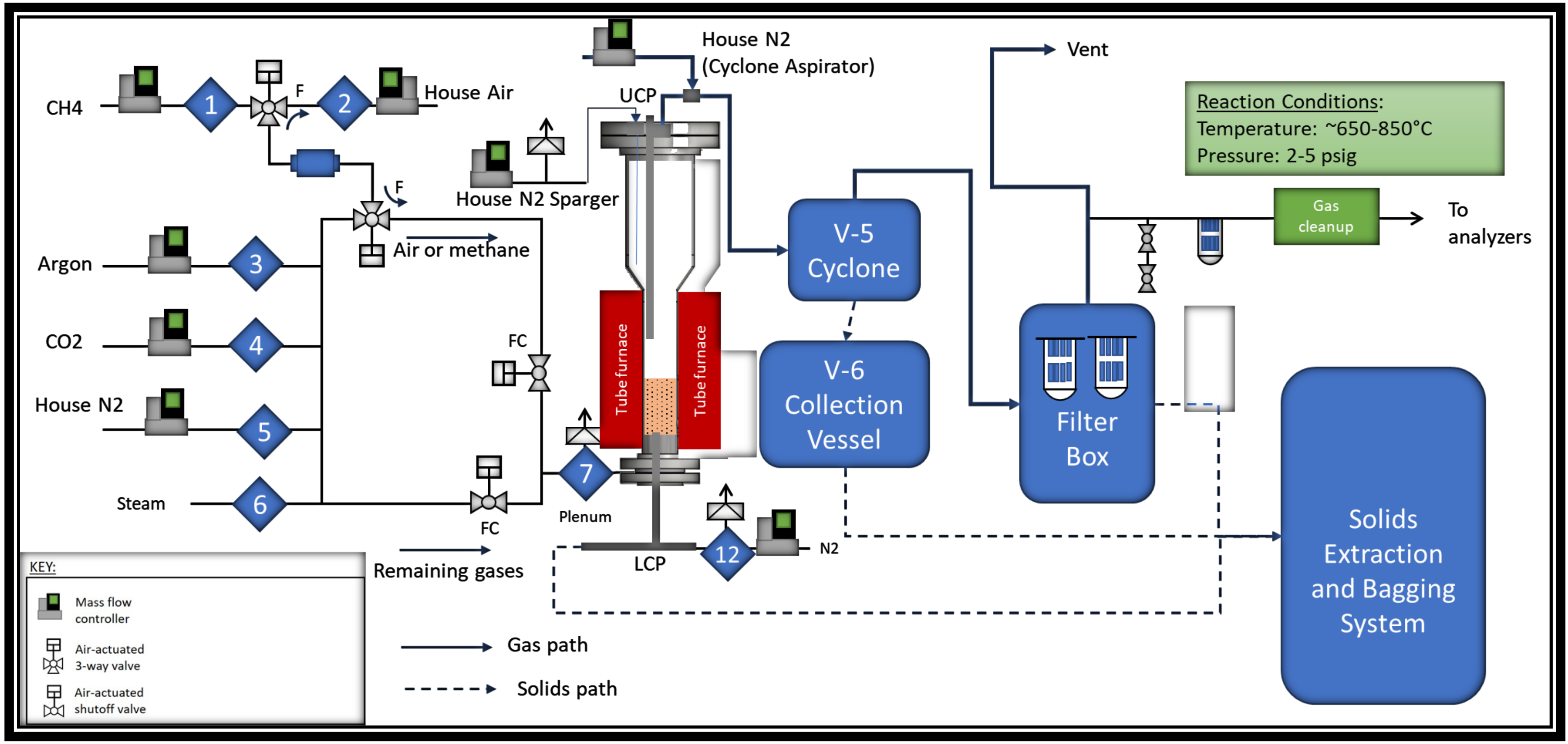






- Carbon containing fines were collected continuously in filters
- XRD - identified graphitic carbon
- Raman spectroscopy and TEM - identified carbon nano fibers/tubes

Research Highlights for EY23
Modification of large fluid bed that can handle up to 5 kg

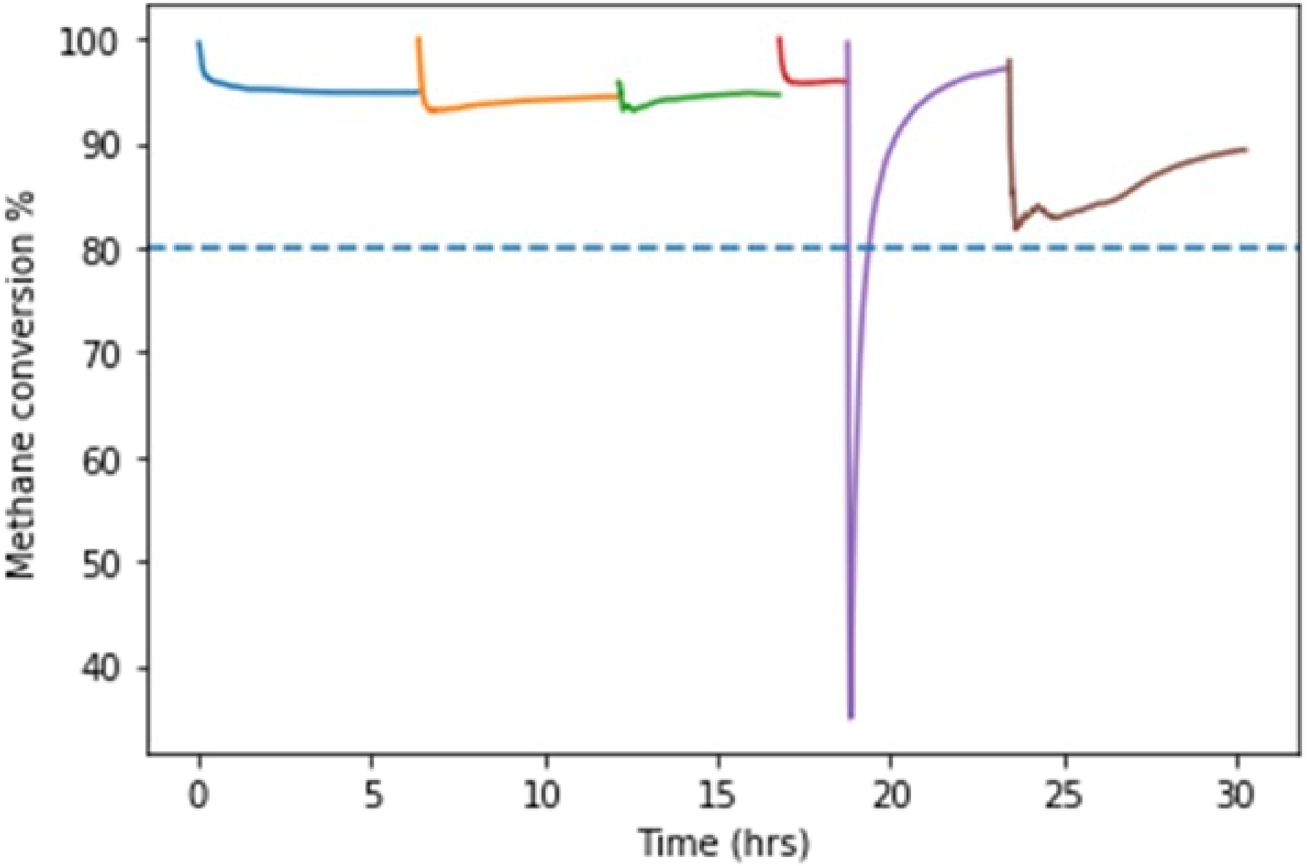


Reaction Conditions:
Temperature: ~650-850°C
Pressure: 2-5 psig

- Modifications which included addition of cyclone, collection vessel, solid extraction unit and filter box are complete
- Started shake down tests

Methane pyrolysis test results with 4.5 kg catalyst in sub-pilot scale fluidized bed unit

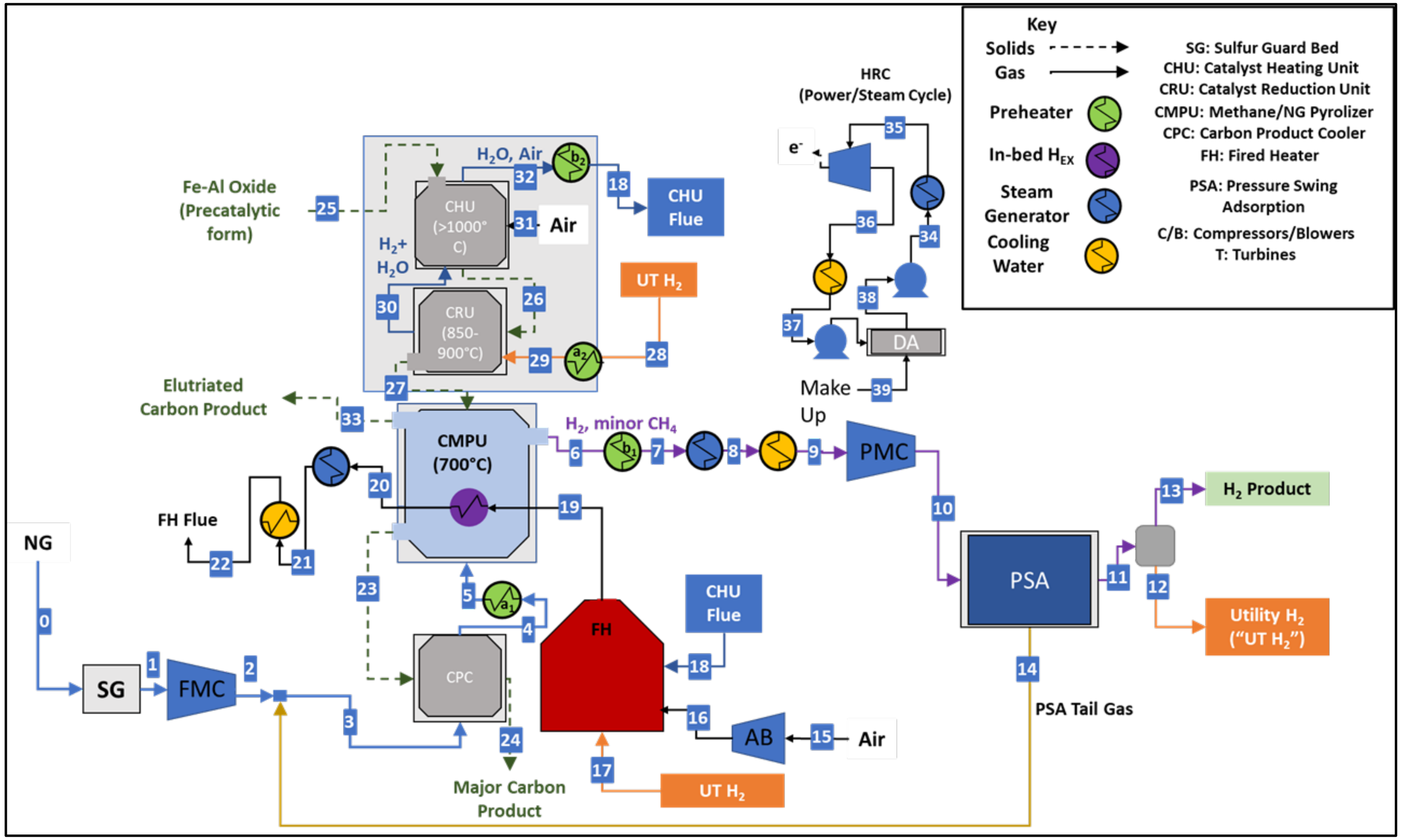
Methane conversion to H2 at 700 C with 4.5 kg of catalyst during the fluidized bed tests



Key accomplishment for scaling the technology
- 10 times more catalyst (4.5 kg) in current tests than in previous tests (500 g)

- **The catalyst was tested with methane at 30 SLPM flow velocity which is 1.75 x minimum fluidization velocity.**
- **5 Kg batch of catalyst was prepared at NETL**
- **Initial scoping tests which lasted for 40 hrs. were conducted varying the methane concentration and the catalyst amount to obtain the methane conversion to H2 >80%.**
- **The tests were conducted at the optimal conditions with 4.5 Kg of catalyst at 700 C**
- **Test time was limited about 6 hrs. for each day. Reactor was cooled overnight due to safety protocols.**
- **It was possible to achieve >80% methane to H2 conversion for 30 hrs. with 4.5 Kg of the catalyst in the sub-pilot scale reactor tests.**

GHG emission free System for the catalytic pyrolysis of hydrocarbons to H2 and carbon –Provisional patent



Novel elements of the reactor train

- **CHU/CRU- Counter Current Bubbling Bed Catalyst Heat treatment and activation unit - Activation of the oxide form, pre-catalyst material (PCM), to create Active Catalyst material (ACM)..**
- **CMPU- fluidized bed that has a form of ACM present to facilitate pyrolysis with In-bed heat exchange**
  - Integration of CMPU with thermal energy that doesn’t generate CO2(FH)
  - Example H2
  - Includes carbon recirculation unit
- **CPC- Counter Current Moving Bed Carbon product cooler/basic Classifier and NG Feed Preheater**
- **HRC – Heat recovery cycle linked to waste heat recovery for process electricity generation**
- **PSA – CMPU H_2 Effluent purification**

GHG emission free System for the catalytic pyrolysis of hydrocarbons to H2 and carbon –Provisional patent application

NATIONAL ENERGY TECHNOLOGY LABORATORY

Proof of Concept – Functional model through process simulation

Metric	Performance outcomes (Commercial Scale)	Performance outcomes (Demo Scale)
Fuel	Natural Gas (NG)	
H_2 output (kg/hr)	8,100	81
H_2 Yield (kg/kg Fuel)	0.172 (5.809 kg NG/kg H_2)	0.1715 (5.831 kg NG/kg H_2)
Fuel converted to H_2	4.51 kg NG/kg H_2	4.66 kg NG/kg H_2
Fuel required For Heating/prep	0.357 kg H_2/kg H_2	0.4 kg H_2/kg H_2
Industrial Electricity Usage (kWh/kg H_2)	4.82	5.3
Industrial Electricity Generation (kWh/kg H_2)	1.767	1.78
Net Electricity Usage (kWh/kg H_2)	3.053	3.52
CO_2 emissions (kg/kg H_2)	0	0
Carbon Yield (kg/kg NG)	0.716	0.724

Simulation outcomes for processes of 2 different functional Scales:

Demonstrate realistic H_2 yield outcomes for a GHGe free process using Utility H2

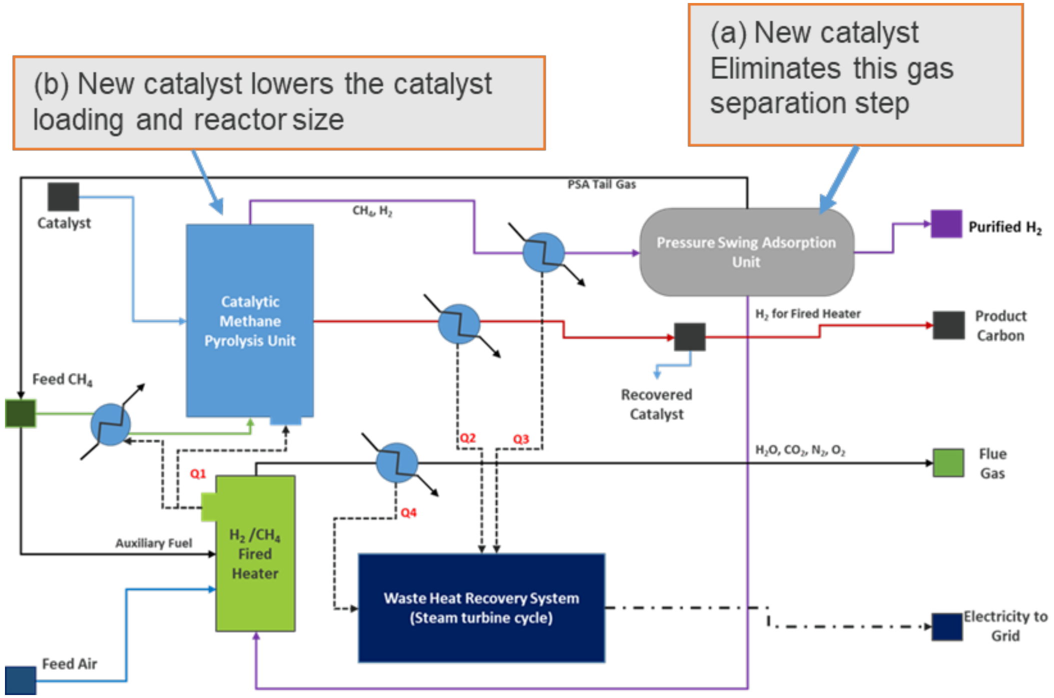
Demonstrate a need for 35-40% H_2 usage for Heating and ACM prep

Scale Efficiency tradeoffs

Improved methane pyrolysis catalysts

Report of invention for patent application was approved by invention review board

Process steps involved in methane pyrolysis


(b) New catalyst lowers the catalyst loading and reactor size

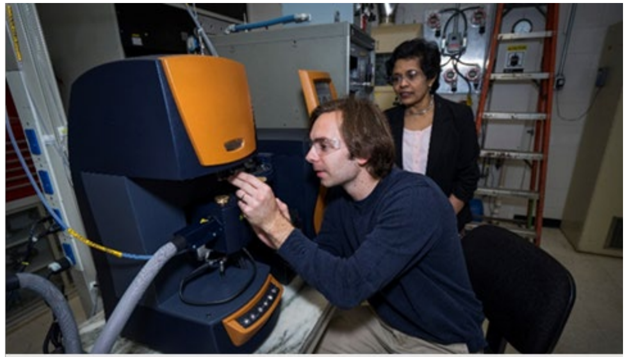
(a) New catalyst Eliminates this gas separation step

Improved methane conversion to H2 addresses an important process issues

- Eliminates the methane/H2 separation unit
- Contribute to use of less catalyst and smaller reaction vessels lowering the cost
- Increase in H2 yield per mole of methane reducing the cost of H2 production.
- Increased kinetics will contribute to cost reduction.

Facilities used for experimental evaluation

Catalyst preparation facility
- Prepares <10 Kg quantities

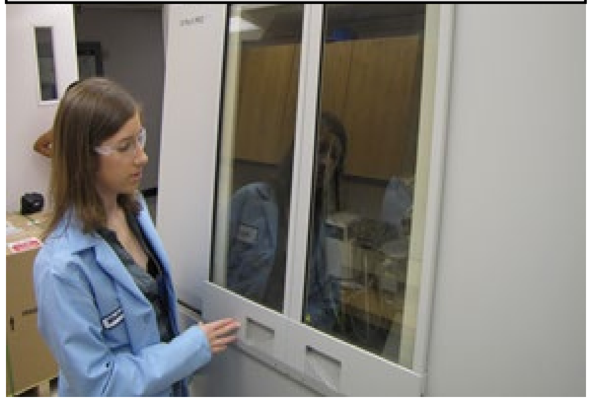


Thermogravimetric Analyzer

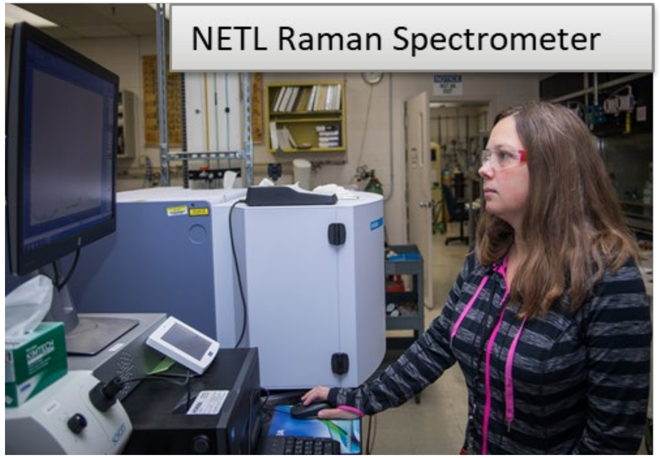
Initial catalyst evaluation method using thermogravimetric analysis

Carbon structure identification methods

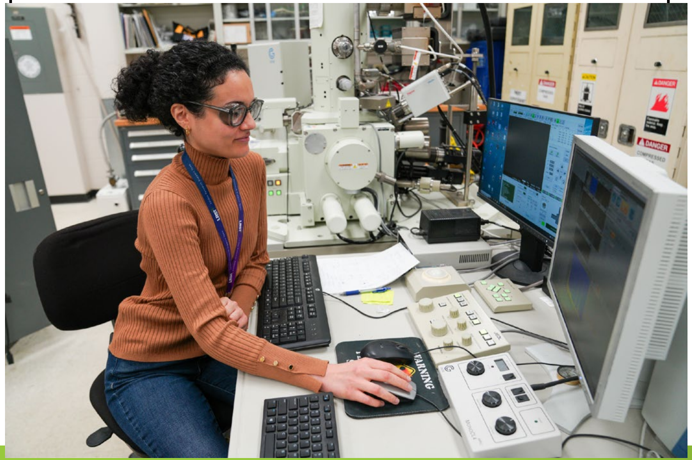
X-Ray Diffraction
Identification of graphitic carbon



NETL Raman Spectrometer



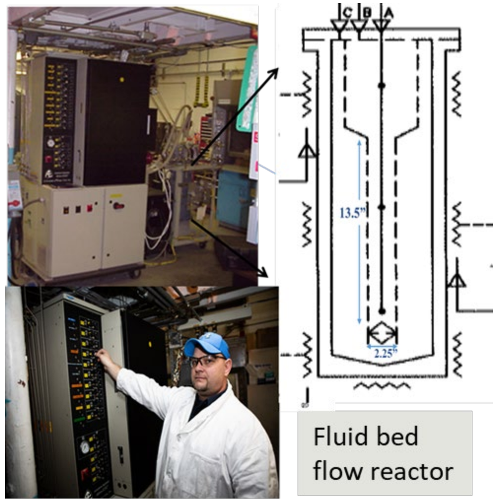
Scanning electron microscopy



Transmission Electron Microscopy
(External facility)

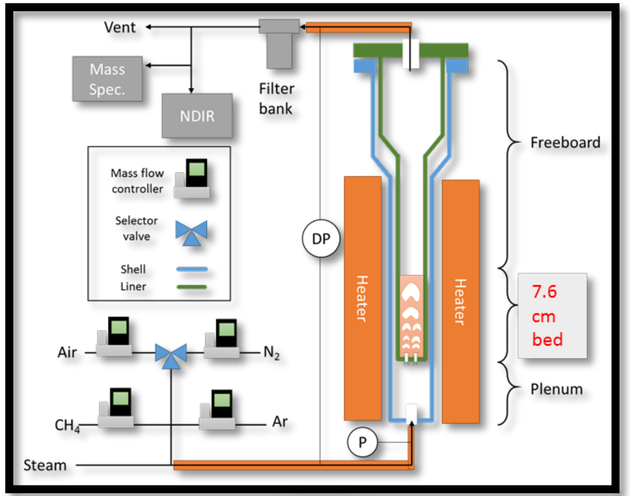
Facilities used for experimental evaluation

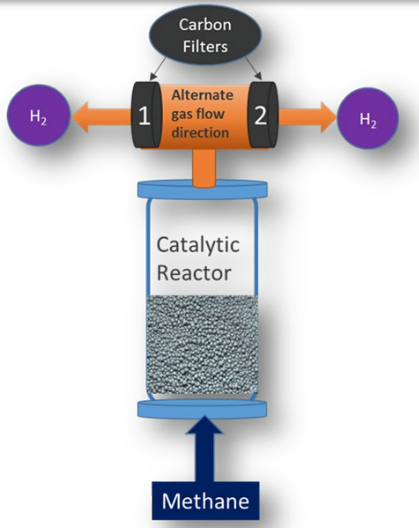
Fluidized Bed Flow Reactor



Fluid bed flow reactor

- 300-500 g of catalyst
- Operate at 1.5-3 x Umf
- Continuous operation with collecting carbon in dual filters switching effluent gas flow direction

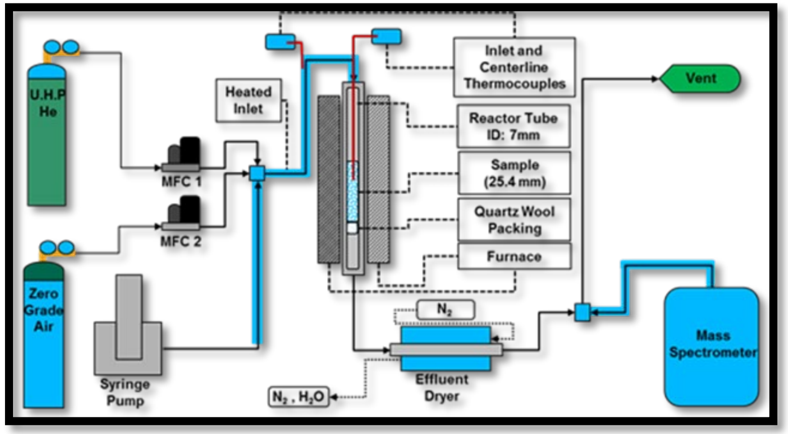




Fixed Bed Flow Reactor

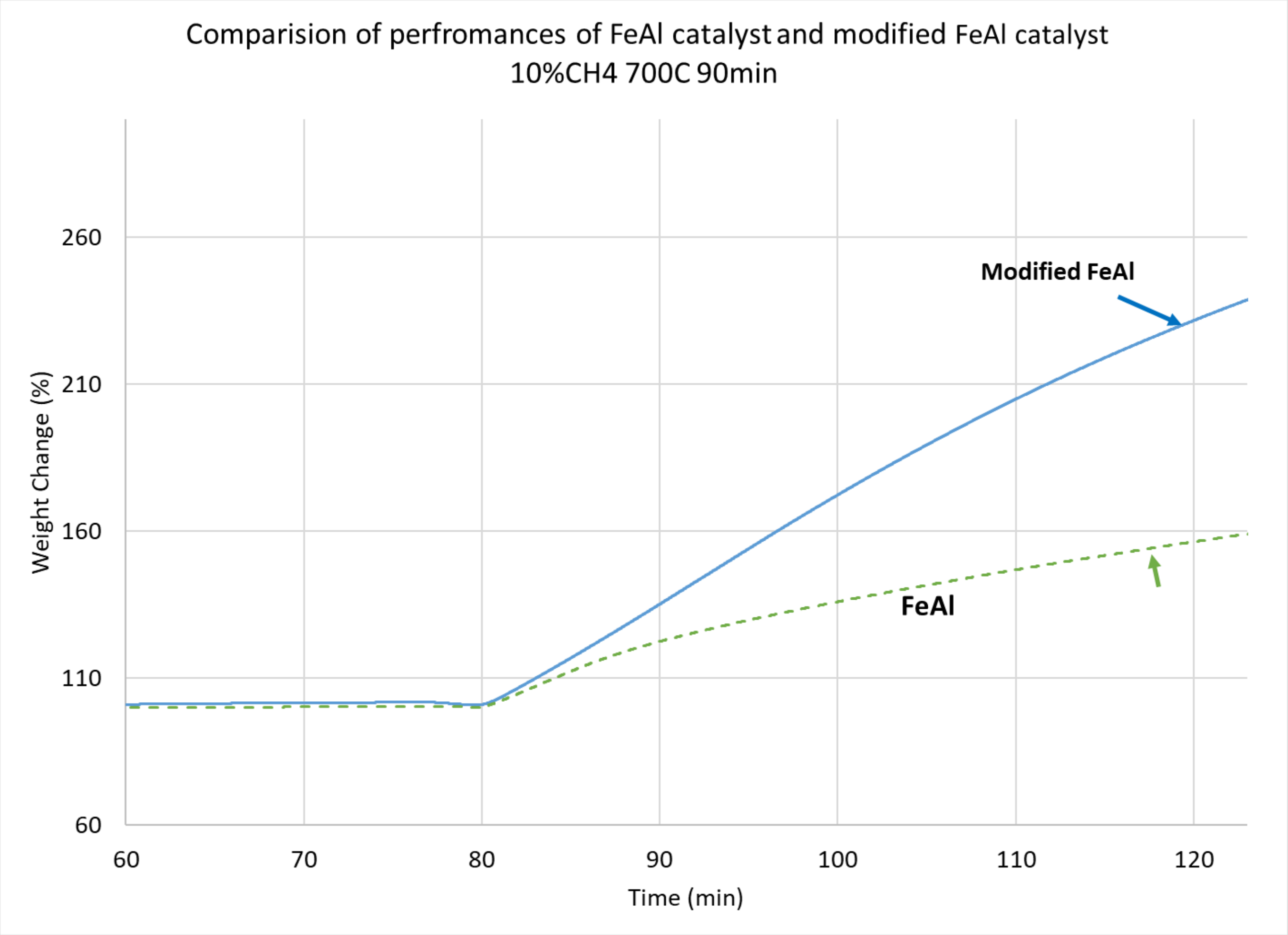
Fixed bed flow reactor

- 8-10 g of catalysts (160-600 μ)
- 100 sccm of ~20 vol.% methane in Helium at 650-750 C
- Measured effluent gas concentrations with mass spectrometer



Improved methane pyrolysis catalysts

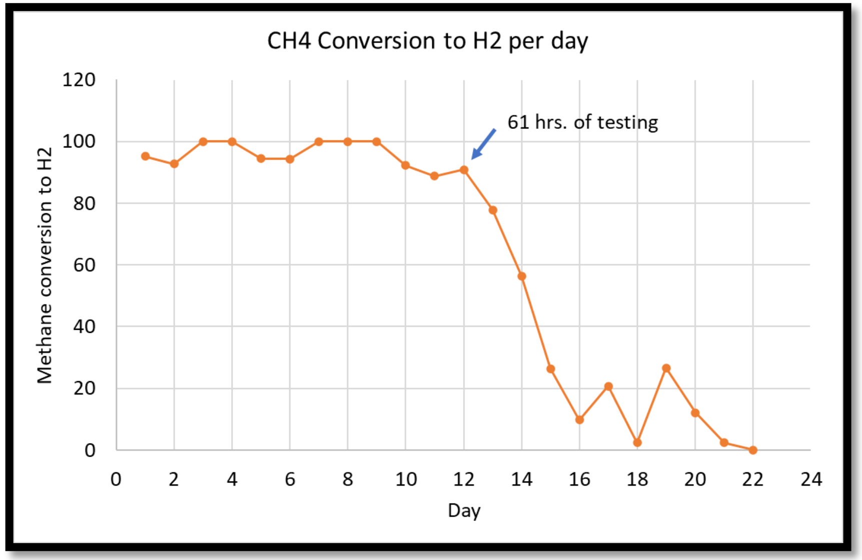
Thermogravimetric analysis (TGA) performance data



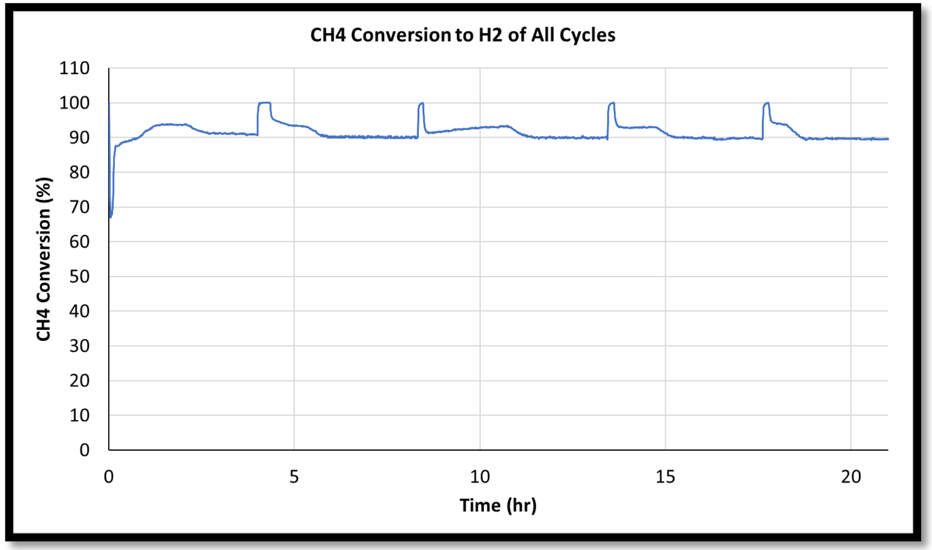
- **TGA – Methane was introduced to 60 mg of catalyst at 700 C and weight changes were analyzed with time**
- **Weight change reflects the carbon production rate from pyrolysis**
- **Modified FeAl catalyst showed higher carbon production rate**

Improved methane pyrolysis catalysts

Fixed bed flow reactor data with modified catalyst at 700 °C

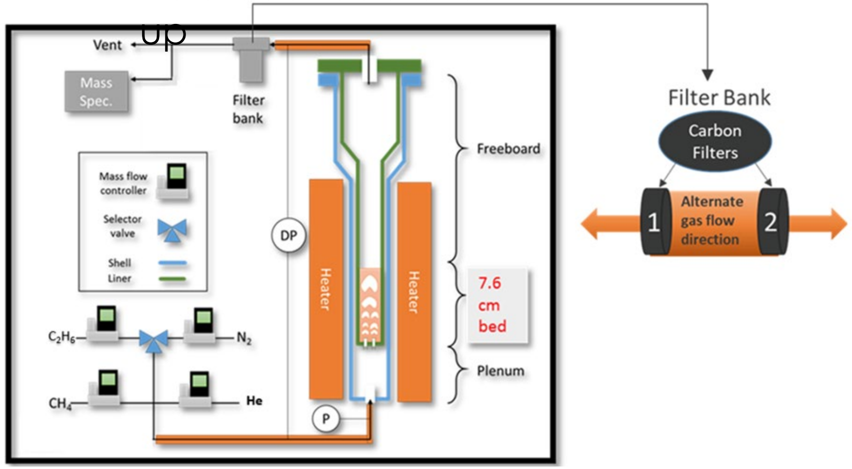


Fluidized bed data with modified catalyst at 700 °C

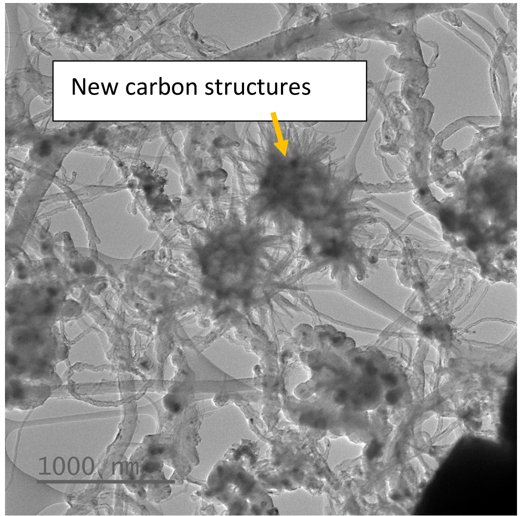


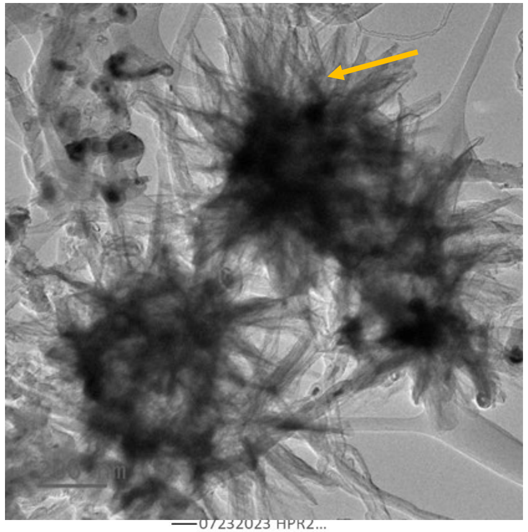
- Fixed bed data
  - Fines removed by sieving when the pressure increased
  - CH4 conversion to H2 was 92-100% for 61 hrs. Previous FeAl it was around 90% for about 28 hrs.
- Fluid bed data
  - Dual filters for carbon collection
  - Conversion was >90% (64 hrs. test still continuing) and previous catalyst it was around 80%

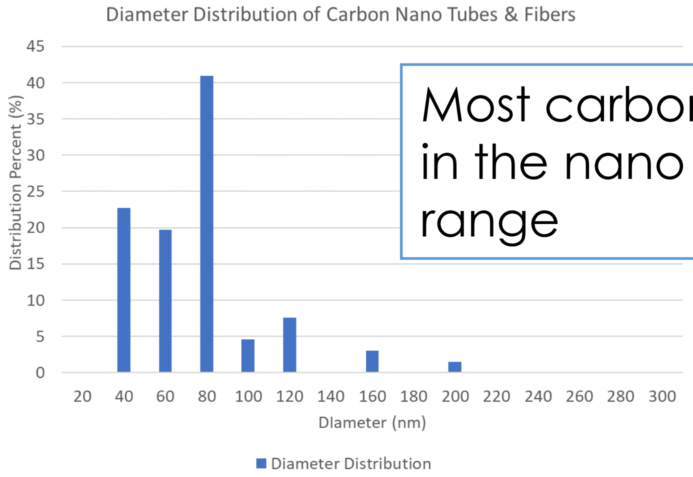
Fluid bed reactor set up



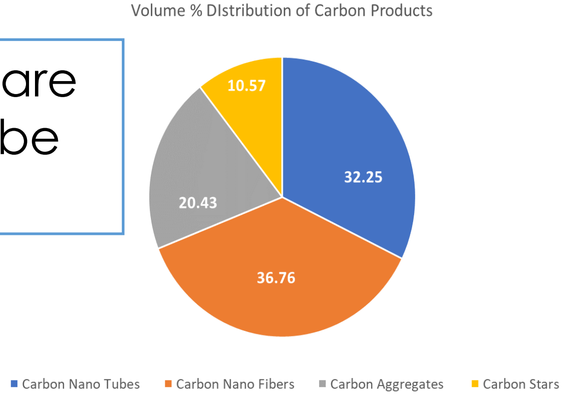
Carbons from improved methane pyrolysis catalysts

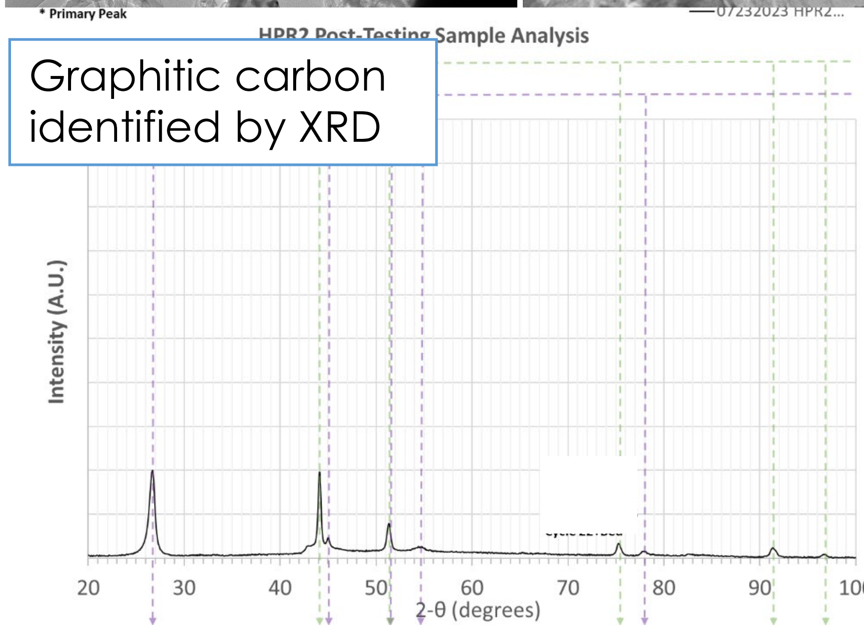






Most carbons are in the nano tube range





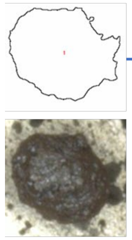
Graphitic carbon identified by XRD

- **XRD data indicated the carbons from Ni-Fe-Al catalyst are graphitic carbons.**
- **TEM data showed a mixture of nano fibers, nano tubes and graphitic carbon clusters.**
- **New carbon structures with nano tubes arranges in a star like formation was observed**
- **Most carbons are in the nano tube range**

Carbon accumulation model development

Mechanism(40% CH4, 60 hrs) based on TGA, OM, SEM, TEM, Raman, particle density and size

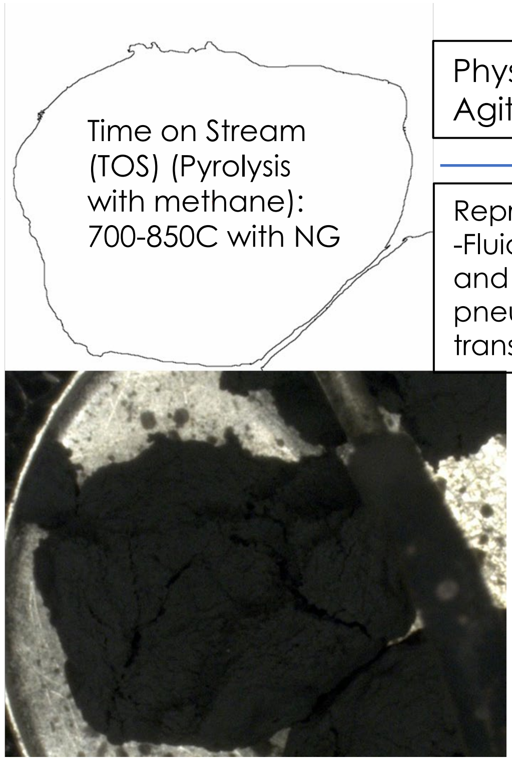
Heat Treated Oxide (Precatalytic)



Densifies pellet & Increase in Grain size

H_2 reduction (Catalytic)

Opens defects and metalizes the catalyst
Grain size is reduced



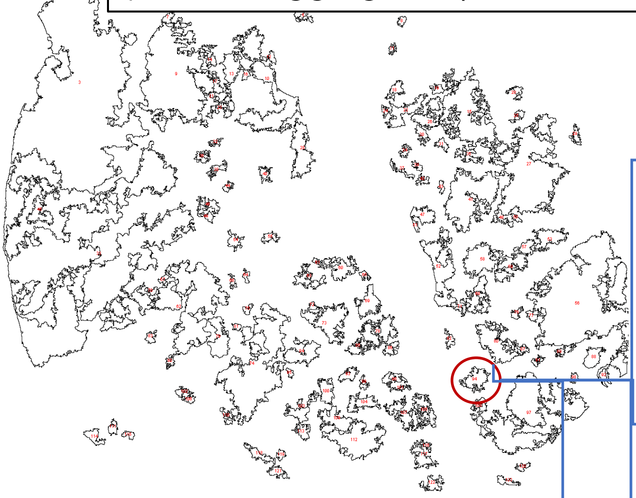
Time on Stream (TOS) (Pyrolysis with methane): 700-850C with NG

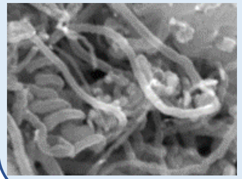
Expansion of particle by carbon accumulation occurs on the grain level to result in ubiquitous expansion
Particle severely weakened by carbon accumulation

Physical Agitation

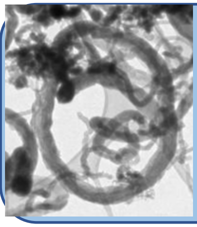
Represents
-Fluidization and pneumatic transport

Fragmentation of Particle to Carbon product Aggregates (mixed Allotrope)



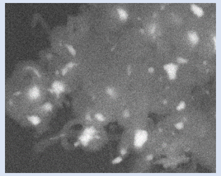


Nanotubes
~63vol%



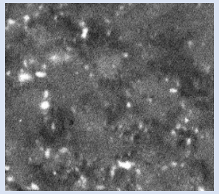
Nanofibers
~4vol%

Graphitic Clusters
~33vol%



Catalyst (White)

Tips, bases, and cores of nano carbons



Intermixed and dispersed. Potentially Separable by chemical means

Next step: Translate particle property data to a particle scale model

Methane Pyrolysis: Particle Scale Modeling

Objective: *Developing a predictive catalyst activity model using a global carbon product accumulation mechanism that accounts for deactivation **during the entire catalyst lifetime**.*

Model Assumptions:

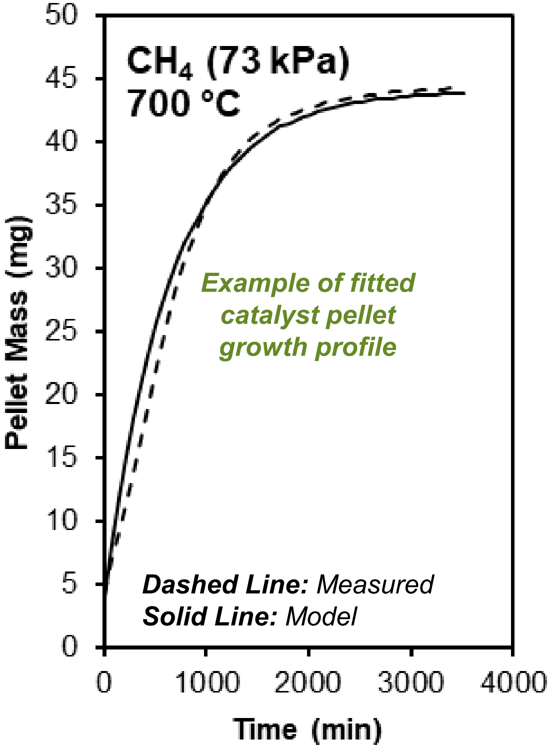
- Steady-state reaction
- Excess alkane concentration
- Spherical catalyst pellet
- Radially uniform Fe site deactivation:

$$C_xH_y(g) + zFe(s) \xrightarrow{k_{Fe}} Fe_zC_x(s) + \frac{y}{2}H_2(g)$$

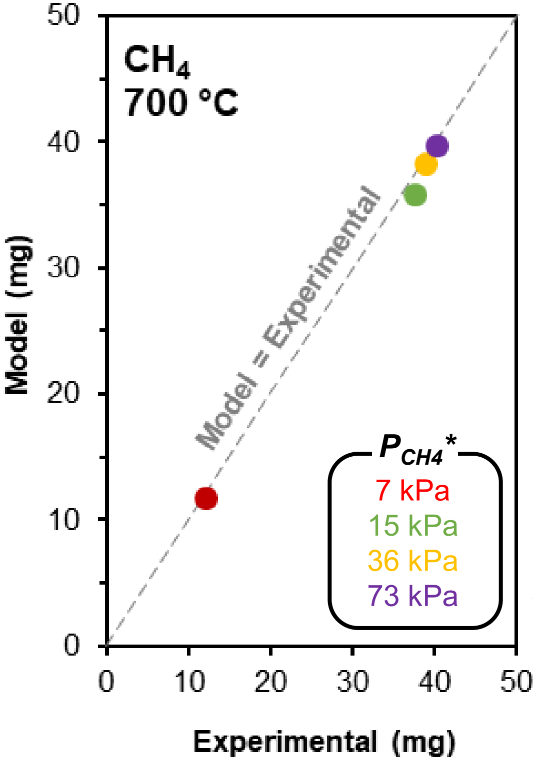
Findings & Further Development:

- Model accurately predicts final carbon product mass at complete pellet saturation
- **Ongoing effort:** Improving model accuracy at sub-saturation reaction times
- **Ongoing effort:** Extracting pellet properties (bulk density and diameter) from particle scale model

Particle Scale Model
Various Temps/Pressures



Total Carbon Product
at Pellet Saturation (Parity Plot)



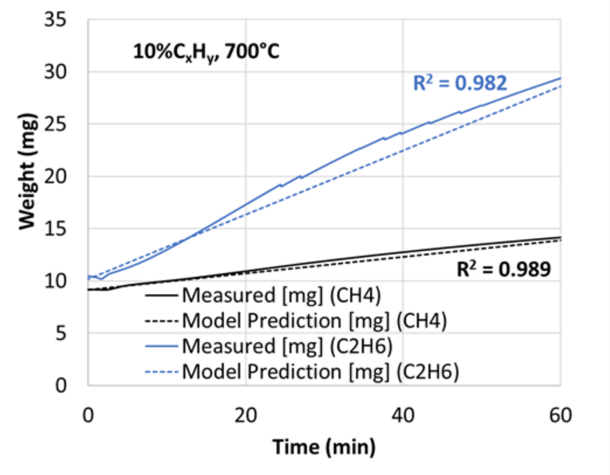
* 100 kPa total reactor pressure

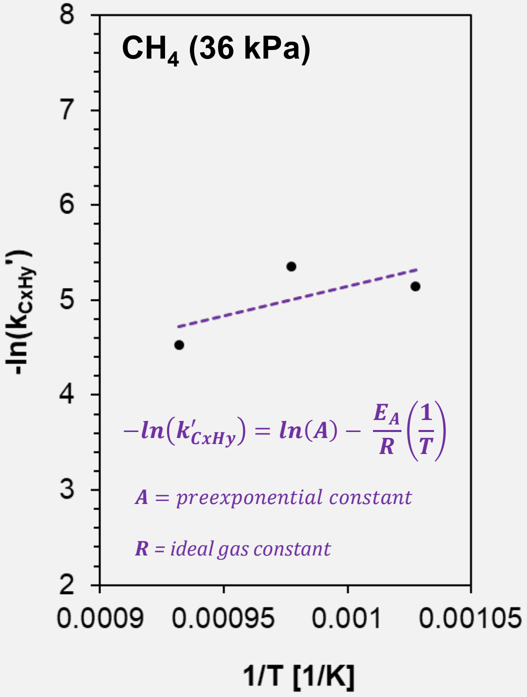
Methane Pyrolysis: Particle Scale Modeling (contd.)

Objective: *Developing a predictive catalyst activity model using a global carbon product accumulation mechanism that accounts for deactivation **during the entire catalyst lifetime**… Previous modeling efforts extracted initial rate kinetics when deactivation effects were negligible.*

Previous Model: Initial Rates --------→ **Current Model:** Captures entire catalyst lifetime while agreeing with previous results.

Depiction of previous model's predictive behavior when compared to experimental data for reactions at 700 °C





$$-ln(k'_{CxHy}) = ln(A) - \frac{E_A}{R}\left(\frac{1}{T}\right)$$

A = preexponential constant

R = ideal gas constant

$$\frac{dM_c}{dt} = \xi_{Fe}\left(k'_{CxHy} P_{CxHy}{}^{n}\right)$$

M_c = Carbon Product mass

ξ_{Fe} = Ratio of available Fe sites

k'_{CxHy} = Alkane consumption rate constant

	Previous Model	Current Model
Reaction Order (n) *in CH_4*	0.6	0.57
Activation Energy (E_A) *(kJ/mol)*	43	52

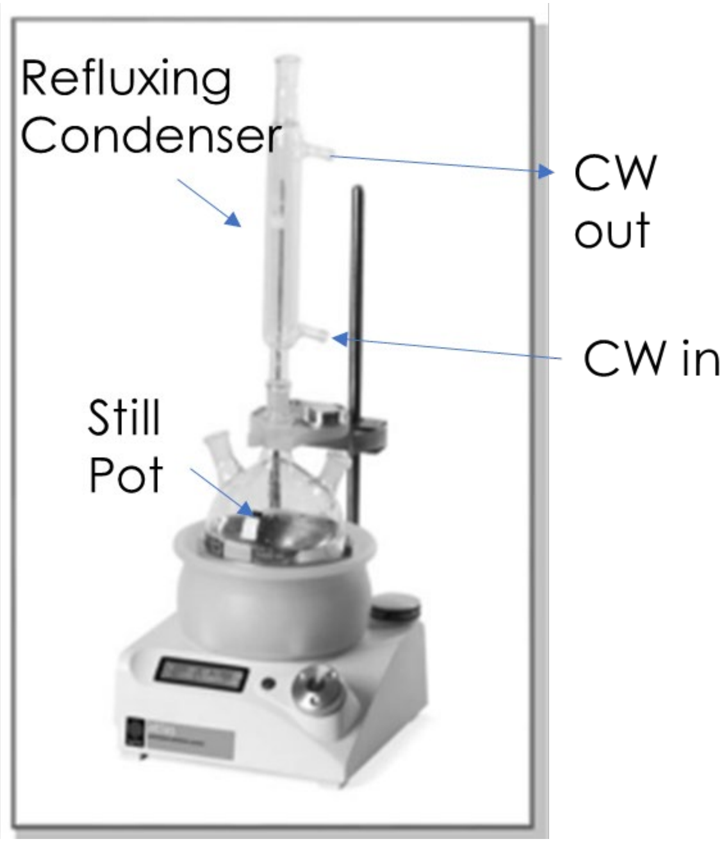
Carbon purification for improving the value
- *Acid Etching for purification of Carbon after fluidized bed tests*

- Carbon samples are contaminated with some catalyst particles
- Introduced 3 M HNO_3 solution at 120 °C under continuous magnetic stirring for 24 and 48 h.
- Residue was filtered and washed with deionized water until the pH was neutral.
- Acid solution contains dissolved metal particles and support of spent catalysts.
- The solid carbon left behind was then dried overnight (16 h) at 120 °C and was characterized using TGA for proximate analysis

	As received	Acid Etched CS1 HNO3 3M
Summary	%	%
Volitiles (moisture)	0.135	0.397
Carbon	73.472	96.122
Residual Inorganic Solids	26.392	3.482
Total	100.000	100.000

Able to greatly purify the carbon product to ~96.5wt% on a dry basis

Syrris Atlas Batch Reactor System



Method Adapted from J. Mater. Chem., 2006, 16, 141–154 and Y. Wang et al. / Chemical Physics Letters 432 (2006) 205–208

Carbon Product Analysis

Objective: *Differentiate carbon allotropes from methane pyrolysis to identify products for separation*

Carbon Product Analysis

Surfactant-Mediated Separation

facilitates allotrope characterization using charge repulsions to stabilize dispersions

Characterization

carbon allotrope differentiation

X-ray Diffraction (XRD)

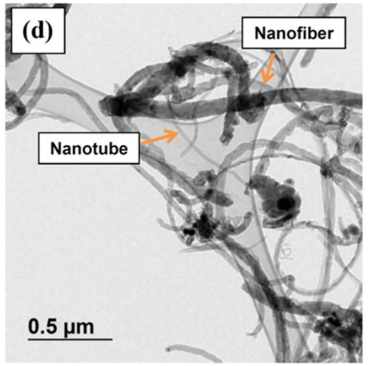
gauge graphitic ordering of products

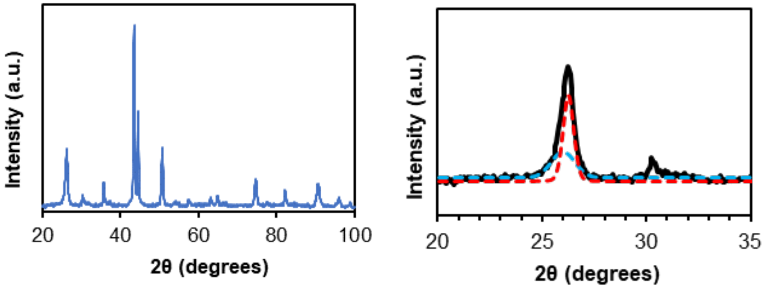
Electron Microscopy (SEM/TEM)

nanoscale imaging of individual carbons

Temperature-Programmed Oxidation (TPO)

deconvolution from combustion profiles





Deconvolution of graphite reflection (hkl 200) enables deduction of CNT content.

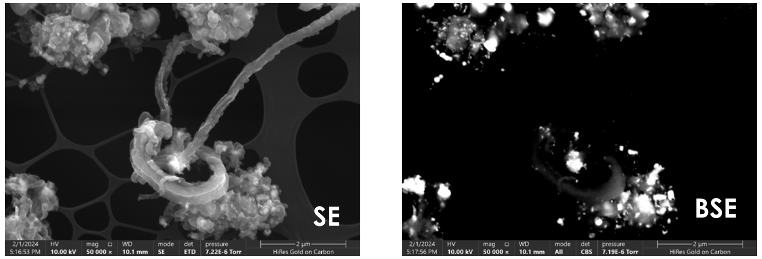
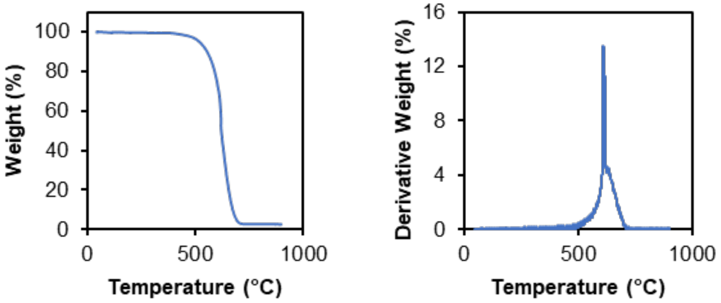


Image analysis yields carbon allotrope size distribution (length v. diameter).



Thermogravmetric analysis (TGA) of combusted carbon standards used to deconvolute combustion profiles of fluidized bed products.

Carbon Product Analysis using temperature programmed oxidation (TPO)

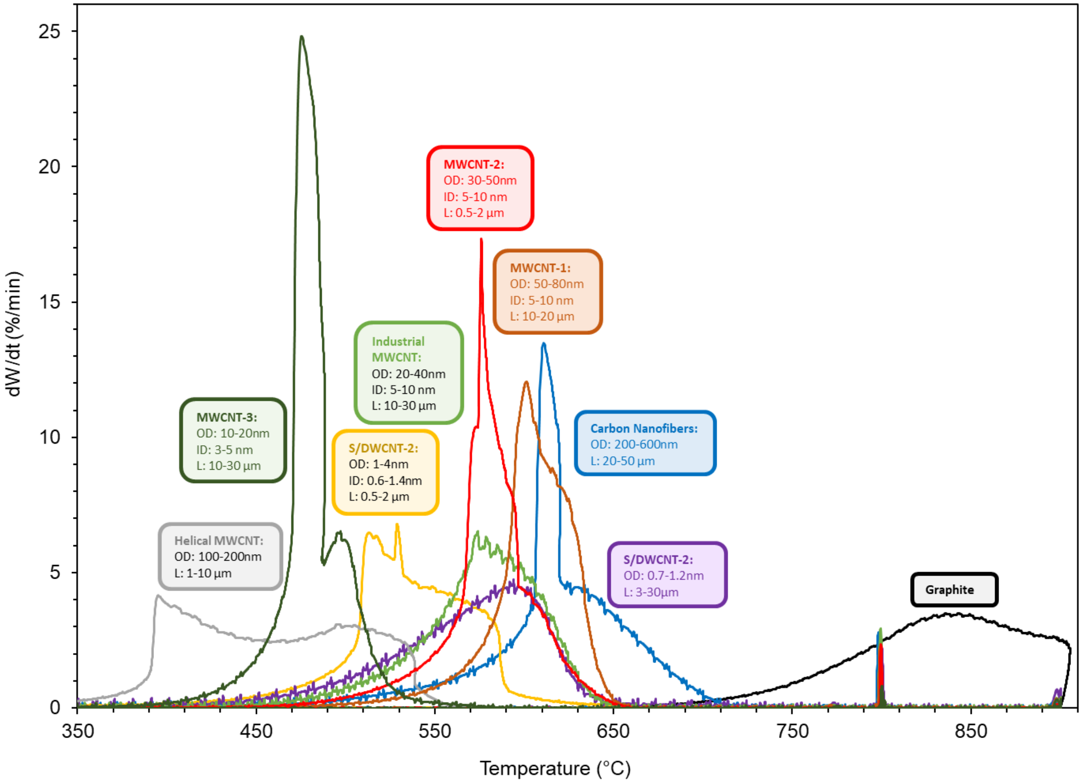
Objective: *Differentiate carbon allotropes from methane pyrolysis to identify products for separation*

Method: Differential temperature-programmed oxidation (TPO) profile of combusted methane pyrolysis fluidized bed product was **deconvoluted as a weighted linear combination of TPO profiles from carbon standards:**

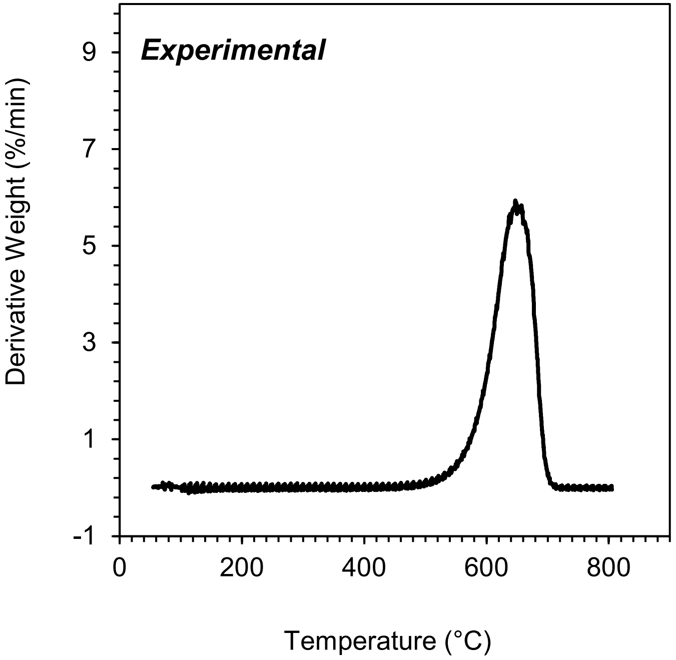
$$\left(\frac{dW}{dt}\right)_{Sample} = \sum_{i=1}^{n} x_i \left(\frac{dW}{dt}\right)_i$$

x_i = wt% of Carbon Standard

Differential TPO Profiles of Carbon Standards



Differential TPO of carbon from fluid bed catalytic methane pyrolysis

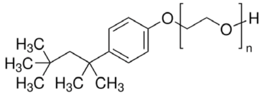


- TPO profiles of carbon from methane pyrolysis with NETL catalyst appear to be closer to the TPO profiles of MWCNT and carbon nano fibers
- Ongoing work to refine deconvolution by growing the suite of carbon standards.

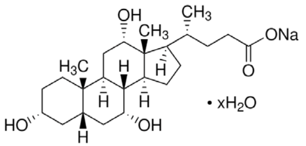
Carbon Product Analysis: Surfactant-Mediated Dispersion and Separation

Objective: *Generate stable dispersions of carbon product that allow for separation of carbon allotropes and imaging of individual carbon allotropes in SEM/TEM.*

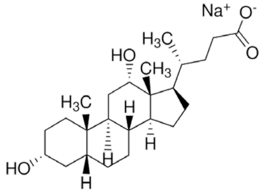
Triton X
nonionic surfactant



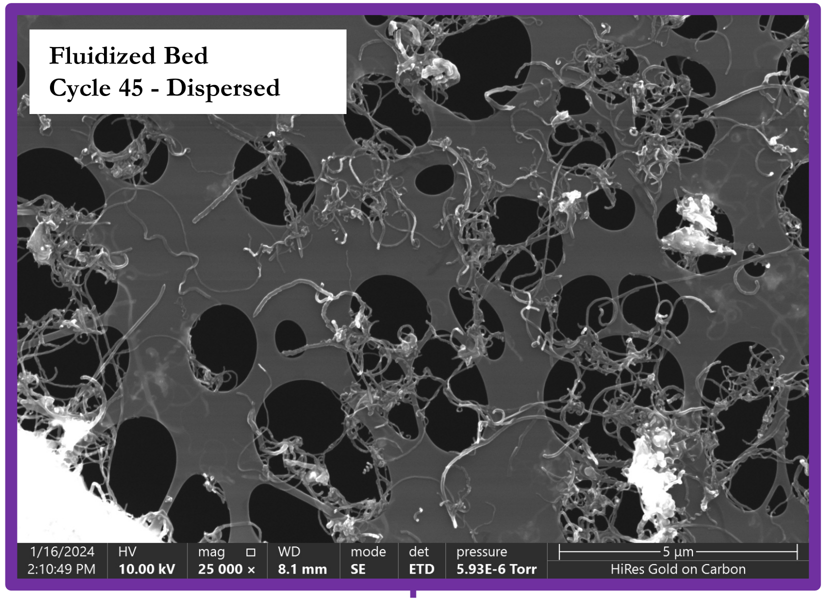
Na-Cholate
anionic surfactant

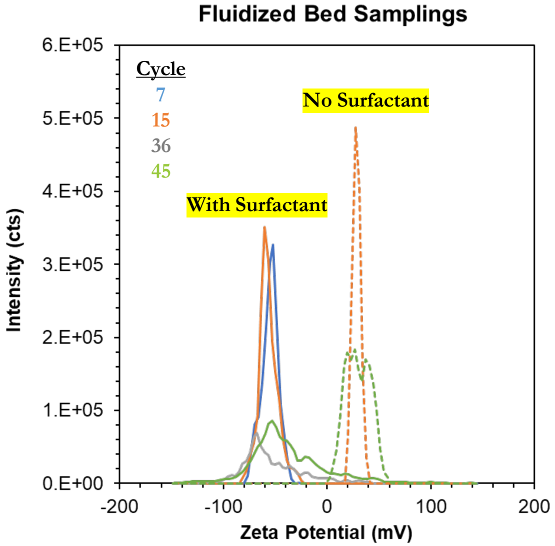


Na-Deoxycholate
anionic surfactant



Best dispersion achieved by ultrasonication in aqueous solution of Na-Deoxycholate (anionic) surfactant





Findings:

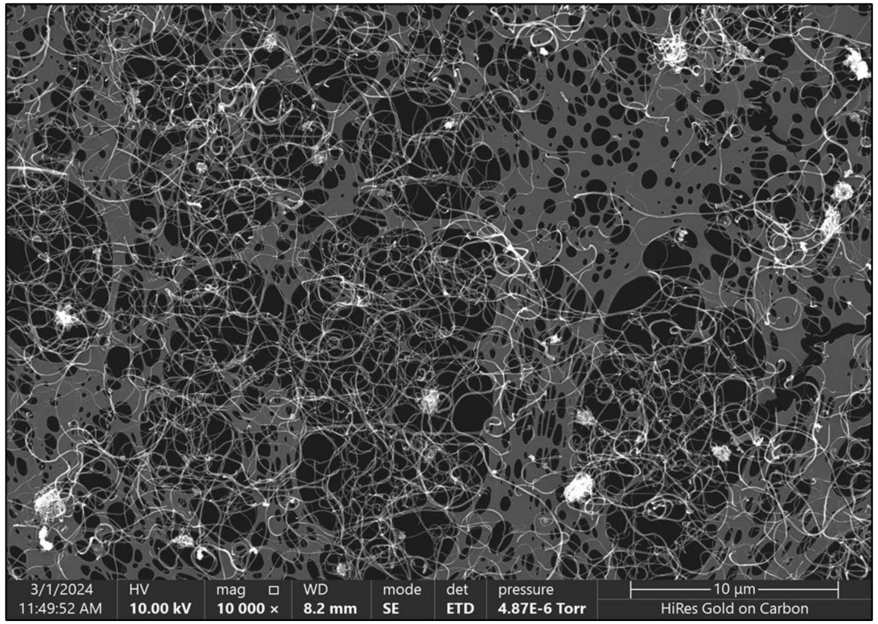
- High negative zeta potential (< -30 mV) of dispersed carbon allotropes indicated stable dispersions.
- Hydrophobic groups interact with carbon materials and ionic heads generate charged surfaces that repel particles of similar charge.

Further Development:

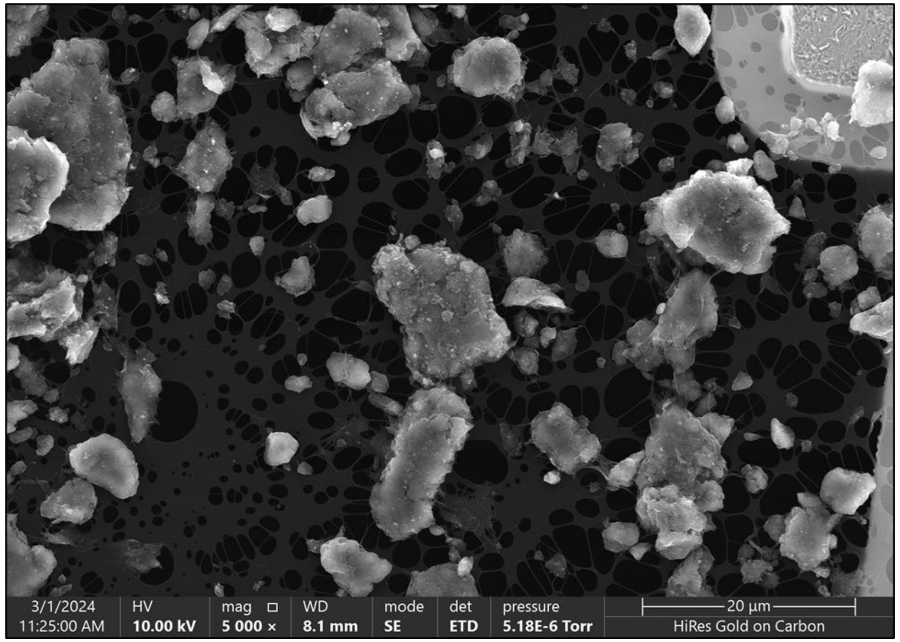
- **Ongoing work:** Dispersions of carbon standards (nano fibers, tubes etc.) enable deconvolution of zeta potential distributions for fluidized bed samplings to deduce relative carbon allotrope content.

Carbon allotrope separation using surfactants

MWCNT/ Na-Deoxycholate



SWCNT/ Na-Deoxycholate



- **MWCNT disperses well in Na-Deoxycholate**
- **SWCNT disperses poorly in Na-Deoxycholate**
- **Carbon allotrope separations can be achieved by selecting the right surfactant for selective dispersion of one type of carbon**

Accomplishments EY23- project summary

- Modification of the sub pilot scale fluid bed that can handle up to 5 kg of the catalyst was completed to satisfy the safety requirements
- Demonstrated >80% methane to H2 conversion for 30 hrs. in the sub pilot scale tests (tests continuing).
- Heat integrated system design was developed. Provisional patent application submitted on “GHG emission free System for the catalytic pyrolysis of hydrocarbons to H2 and carbon”
- Improved catalysts with higher methane to H2 conversion were developed. Report of invention on “Improved methane pyrolysis catalysts for H2 and carbon production” was approved by the NETL invention review board
- Carbon formation model development initiated
- Carbon separation work and quantification of different carbons initiated.

Next steps

- Improve carbon separation methods
- Continue optimization of the formulation
- Parametric studies in 5kg sub-pilot reactor with Fe-based catalyst
- Reactor design based on the fluid bed data and provide data for a TEA
- 25-50 Kg tests (if CRADA partner raises investor funds)
- Demonstrate the reduction of H2 cost through improved system performance and selectivity to valuable carbons.

NETL large scale reactor

- 25-50 kg Catalyst
- Install heaters and safety features

Bibliography

- R.V. Siriwardane, W. Benincosa, J. Riley, "Novel iron-based catalysts for production of carbon and hydrogen from decomposition of methane, patent issued by U.S. patent office
- R. Siriwardane, J. Riley, C. Atallah and M. Bobek, "Effect of ethane on methane pyrolysis with iron-based catalysts to produce carbon and hydrogen", International Journal of Hydrogen Energy 48(2023) 14210-14225
- R.V. Siriwardane and J. Riley, Catalysts with high performance for methane pyrolysis to produce H2 and carbon, ROI approved 1/2024 for a patent application
- J. Riley and R.V. Siriwardane, GHG emission free system for the catalytic pyrolysis of hydrocarbons to H2 and carbon, Provisional patent application 23N-15 submitted 12/27/2023

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.).
- Organization : National Energy technology center/U.S. Department of Energy
- Project participants at NETL
- Dr. Ranjani Siriwardane – Principal Investigator of the project
- Dr. Hayat Adawi (Che.Eng.) – Carbon separations & identifications, Reaction modellling
- Dr. Jarret Riley (Che. Eng.) – Systems analysis and reactor scaling
- Chris Atallah (Chem. Eng.) – Material preparation and Aspen modeling
- Dr. Michael Bobek (Mech. Eng.) – Sub pilot scale reactor operations and data processing
- Donald Jeffries - Engineering technician who operate the fluid bed and fixed bed reactors
- Industry partner – NDA finalized and initial CRADA signed for potential commercialization (currently seeking investor funds)
- NETL systems analysis group- future support in technoeconomic analysis
- NETL CFD team for future reactor design and scaleup

Project Goals

EY 24 - G2.0: Phase 1 Scale Up Initiation of Catalytic Pyrolysis

EY25 - G2.1: Phase 1 Scale up Benchmarking and Parametric Studies

EY 26 - G2.2: Phase 2 Parametric Studies and Concept Demonstration to inform scale up and refine TEA