# Production of hydrogen and carbon from catalytic natural gas pyrolysis

*FWP-1022467*


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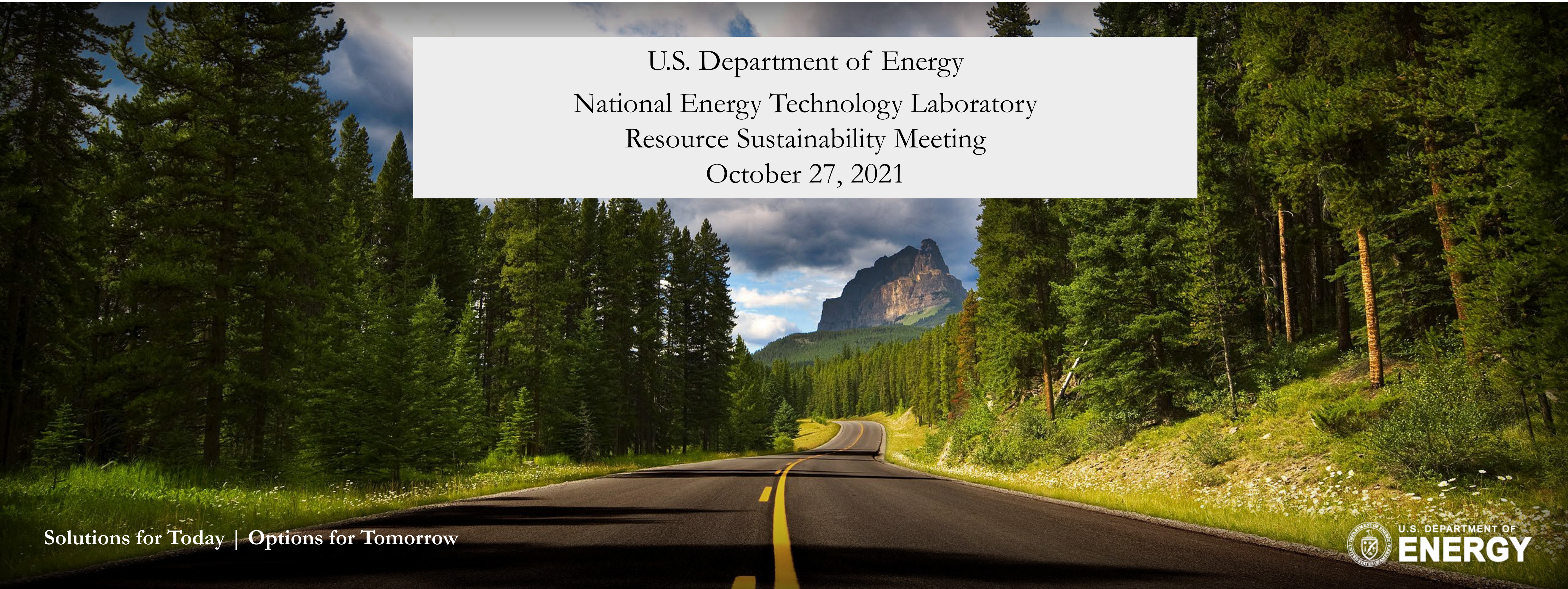

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Meeting
October 27, 2021

Solutions for Today | Options for Tomorrow

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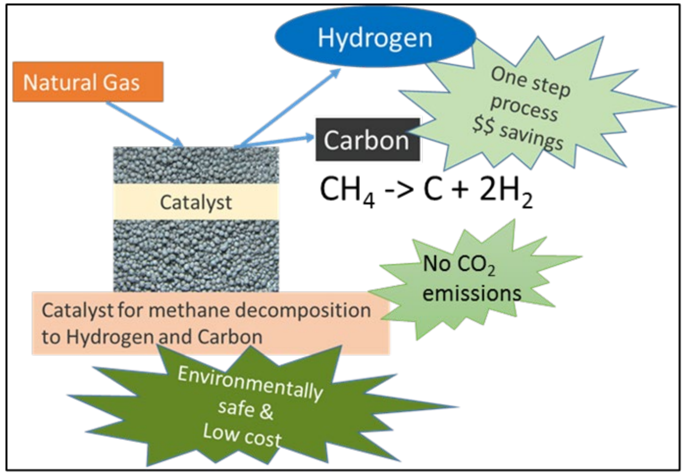
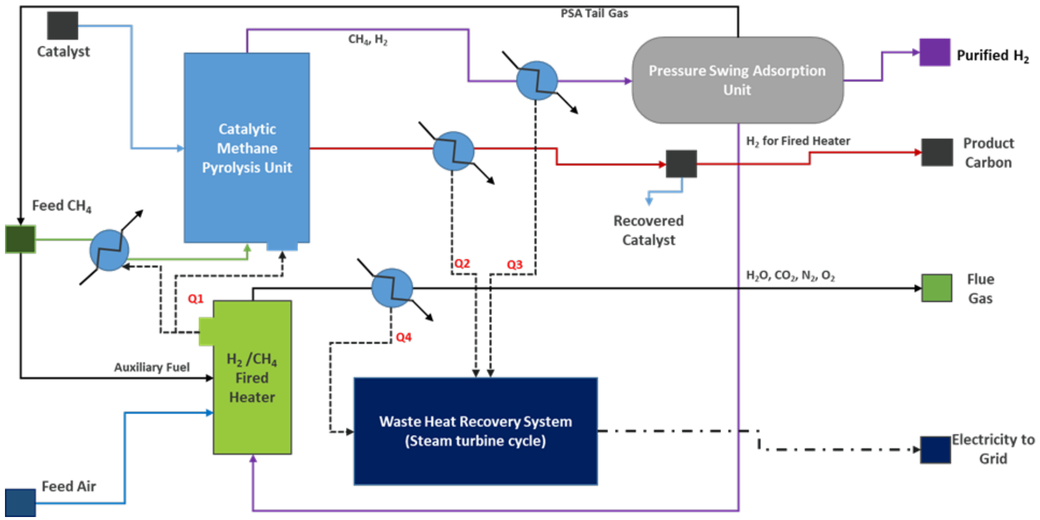
# Funding and Project participants

- **Current Funding – Natural Gas Decarbonization and Hydrogen Technologies - NETL FWP** *1022467*
- **Overall project performance dates - EY21 to EY22**
- **Project participants at NETL – Ranjani Siriwardane (PI), Jarret Riley (Lead Che. Eng.), Chris Atallah (Chem. Eng.), Michael Bobek (Mech. Eng.), Engineering technicians**
- **Industry contacts**
  - One industry partner– NDA finalized and negotiating licensing applications for a specific application
  - Second industry partner has expressed interest for demonstration tests for different application – NDA finalized & discussions continuing
  - Discussion with external research institute on reactor scale up and demonstrations
- **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)




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



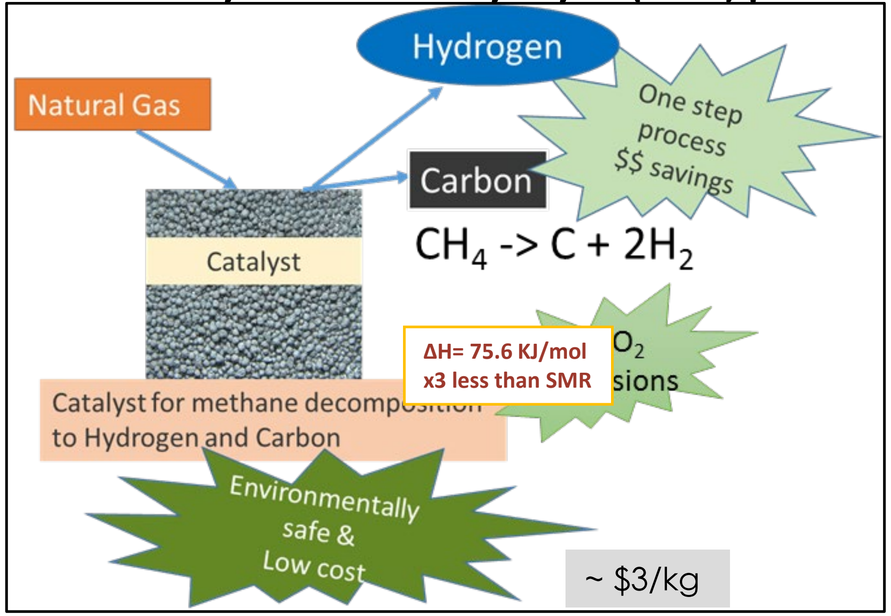

- Catalyst decomposes methane (and other components of NG) to H2 and carbon in CMP Unit
- CxHy → xC + 0.5yH2
- CMP Unit Operates at 650-750°C
- Desirable pressures: 2-15 atm (dependent upon H2 delivery pressure)

**Technical Advantages:**

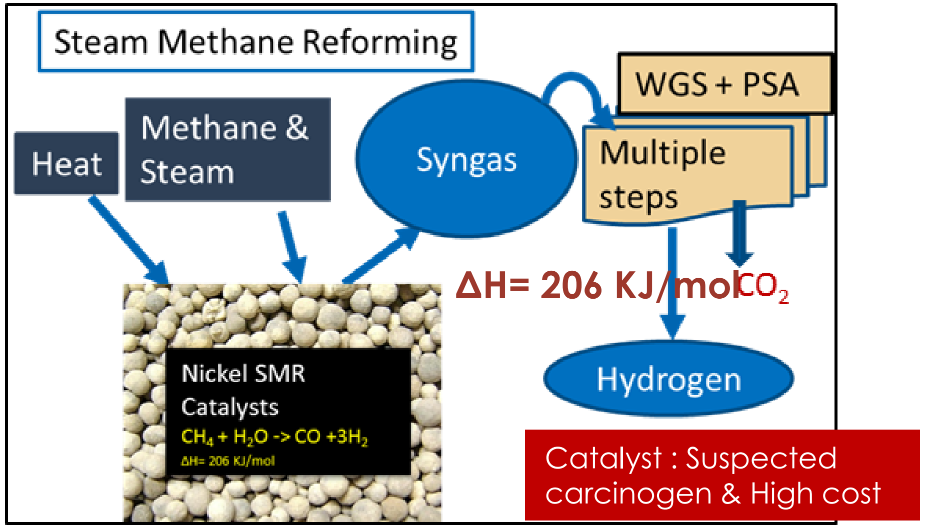
- **One step process to produce two valuable products $H_2$ and carbon from natural gas/flare gas**
- **No $CO_2$ emissions (when heat is supplied via H2 combustion)**
- **Mildly endothermic**
- **Preliminary systems analysis indicated an economical path for converting natural gas into transportable,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

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

**Catalytic Methane Pyrolysis (CMP) process**




**Current commercial SMR process**







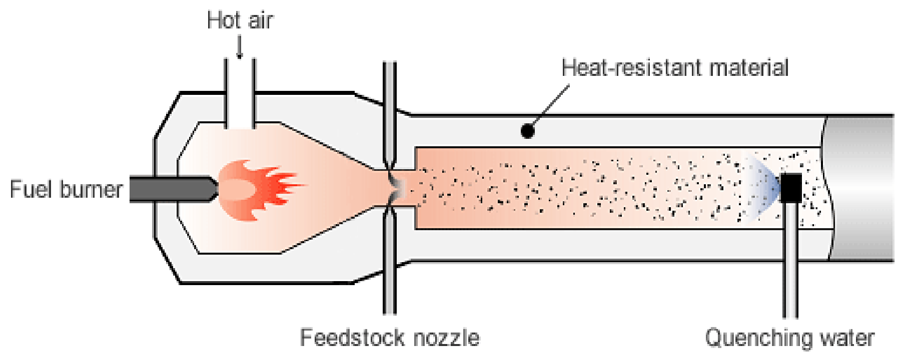
- **SMR - current commercial technology being used for $H_2$ generation from NG**
- **CMP is inherently competitive to this process with some minor trade offs**
  - **Advantages:**
    - **Less processing steps to create H2**
    - **3x less endothermic**
    - **Additional carbon product with $CO_2$ emission mitigated**
    - **Low cost catalyst materials**
  - **Trade-offs:**
    - **Lower $H_2$ yield – ~30%less/mol CH4**

Ranjani Siriwardan

# Technical Background

## Pros cons & costs associated with conventional approaches for carbon production

Current commercial carbon production- furnace black method 1300 $^0$C *(ASAHI Carbon co. ltd.)*




Catalytic methane decomposition will have minimal CO2 and pollutant gas emissions

- **Carbon (>95% ) is produced by furnace black method**
  - Partial combustion of fuel (coal tar, natural gas, oil)
- **Generate a substantial amount of pollutant emissions in addition to CO2 emissions**
- ***As regulations for reducing emissions continue to become stricter, industry will need to invest significant capital in cleaner, more efficient methods of carbon production.***

- Current carbon nano fibers and nano tube production methods are expensive, energy intensive and contribute to CO2 emissions

# Research focus areas to address major challenges

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- **Catalyst development**
  - Demonstrating 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 tests**

- **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
  - Industry contact expressed interest

# 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 and assess the economic viability using TEA to enable scale up

## Specific project goals and milestones

Year 1:

- Catalyst material development and performance testing.
- Process screening assessment based on methane

Year 2:

- Evaluate effect of major components in natural gas (e.g., ethane, propane) on the performance
- Demonstrate long-term cycle (30 hours) stability on bench scale tests with natural gas components to meet the net hydrogen yield target of > 25% defined by EERE
- Obtain TGA data with all natural gas components to develop rate expressions to obtain kinetic rate parameters required for TEA

Year 3:

- Obtain performance data in a prototype sub-pilot scale reactor system to be used in conjunction with systems analysis
- Conduct system TEA assessment for Go/No-Go.

Year 4:

- Demonstrate technology in a pilot scale reactor (> 25 hours continuous operation).

# Accomplishments - Technical Approach & Status
# Benefits based on preliminary screening analysis with methane

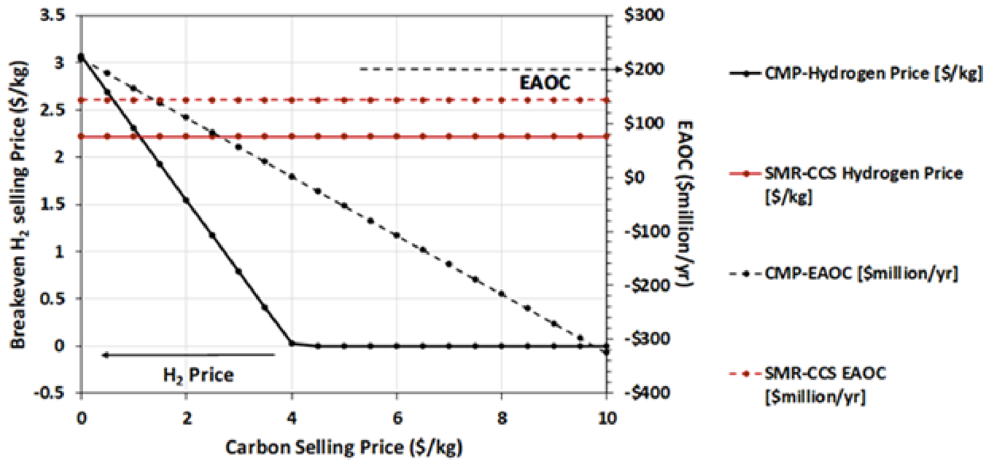
- Heat for the process can be produced by combusting less than 20% H2 – no CO2 emissions for heat production
- Net energy, thermal input are lower, and efficiency is higher with CMP than commercial SMR
- H2 selling price is sensitive to C price. When C price is > $2/kg the process is more competitive than SMR
    - Nano carbons from our process >> $10/kg and has a great potential for success
- Catalyst recycle is not necessary when catalyst price is < $8/kg
    - Catalyst price for Fe based catalyst in current work is projected to be < $3/kg
    - Promote business opportunities to U.S. iron mining companies

**Table ES.1.** Market Analysis for Potential Carbon Products (K = thousand, M = million, MT = metric ton) (Dagle et al. ANL -17-11/PNNL-26726. EERE report, Nov. 2017)

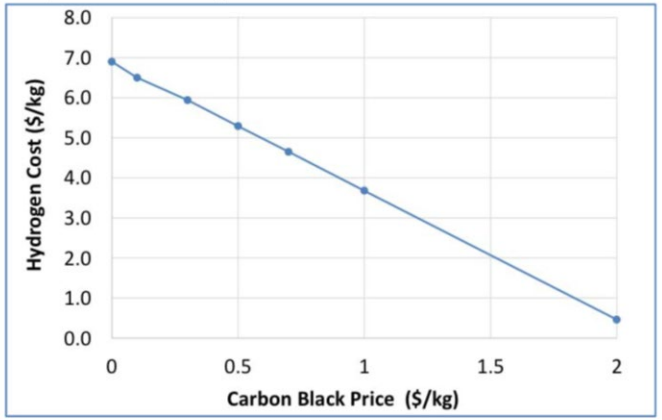
| Type of Carbon | Types of Applications | Expected Price for Carbon | Size of the Market (current/ projected) | Corresponding Hydrogen Production[(a)] |
|---|---|---|---|---|
| Carbon black [1] [2] [3] | Tires, printing inks, high-performance coatings and plastics | $0.4–2+ /kg depending on product requirements | U.S. market<br>• ~ 2M MT (2017)<br><br>Global market<br>• 12M MT (2014)<br>• 16.4M MT (2022) | U.S. market<br>• 0.67M MT<br><br>Global market<br>• 4M MT (2014)<br>• 5.4M MT (2022) |
| Graphite [4] | Lithium-ion batteries | $10+/kg | Global market<br>• 80K MT (2015)<br>• 250K MT (2020) | Global market<br>• 27K MT (2015)<br>• 83K MT (2020) |
| Carbon fiber [5] [6] [7] | Aerospace, automobiles, sports and leisure, construction, wind turbines, carbon-reinforced composite materials, and textiles | $25–113/kg depending on product requirements | Global market<br>• 70K MT (2016)<br>• 100K MT (2020) | Global market<br>• 23.3K MT (2016)<br>• 33.3K MT (2020) |
| Carbon nanotubes [8] [9] | Polymers, plastics, electronics, lithium-ion batteries | $0.10–600.00 per gram depending on application requirements | Global market<br>• 5K MT (2014)<br>• 20K MT (2022) | Global market<br>• 1.7K MT (2014)<br>• 6.7K MT (2022) |
| Needle coke [10] | Graphite electrodes for electric arc steel furnaces | ~$1.5/kg | Global market<br>• ~1.5M MT (2014) | Global market<br>• ~0.50M MT (2014) |

(a) Based on stoichiometric ratio of carbon to hydrogen present in methane. Does not take into account process efficiency or use of hydrogen to provide process heat or loss of hydrogen during hydrogen recovery.

***Sensitivity of carbon selling price on H2 selling price and equivalent annual operating costs (EOAC). Comparison of NETL CMP with SMR based on preliminary systems analysis.***

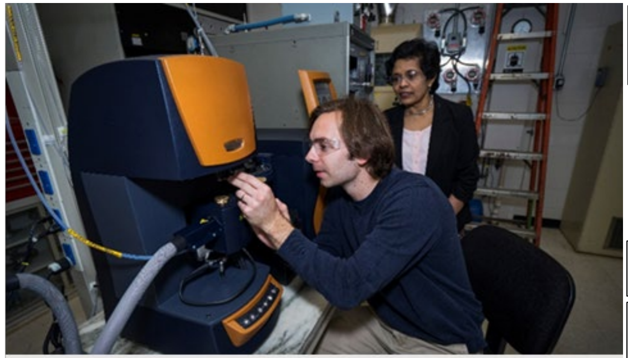



**Sensitivity of carbon selling price on net hydrogen cost for the small-scale plasma case study** (Dagle et al. ANL -17-11/PNNL-26726. EERE report, Nov. 2017)

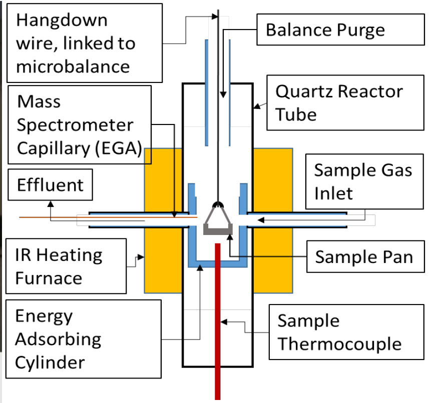


# Facilities used for experimental evaluation

**Catalyst preparation facility**
**- Prepares <10 Kg quantities**

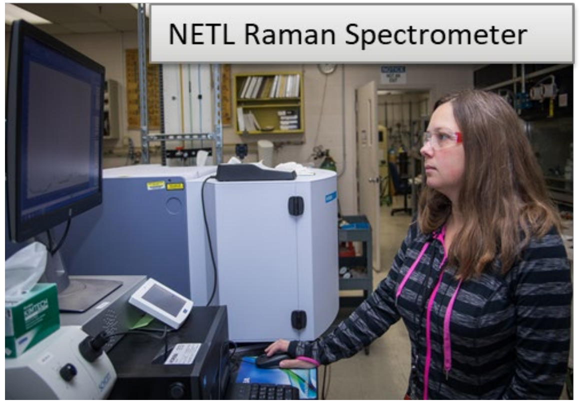



Thermogravimetric Analyzer



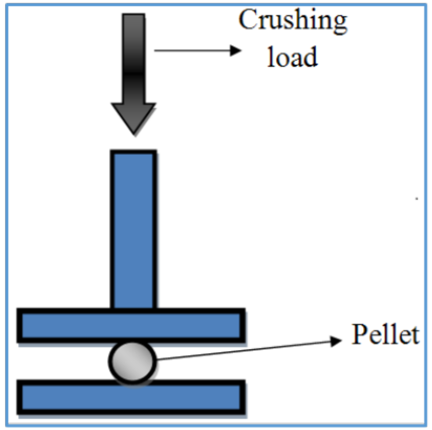

- Use mg level quantities
- Introduce methane
- Weight gain to determine carbon formation rates

**In-Situ XRD-**
***Identification of graphitic carbon***

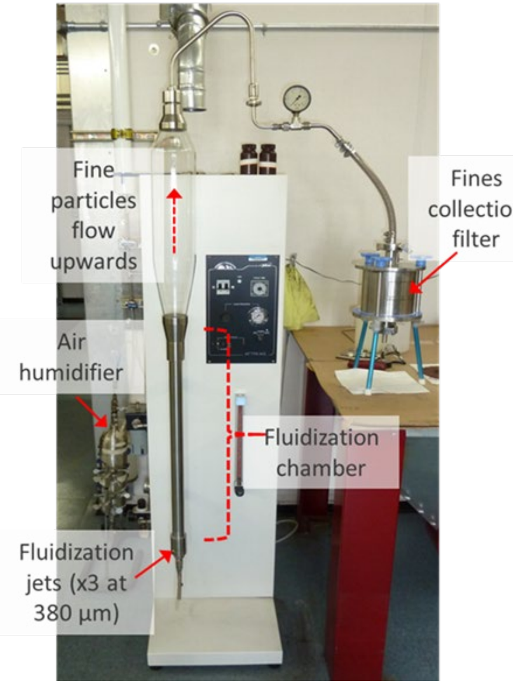



Identify nano carbon structures

**Crush strength measurements**

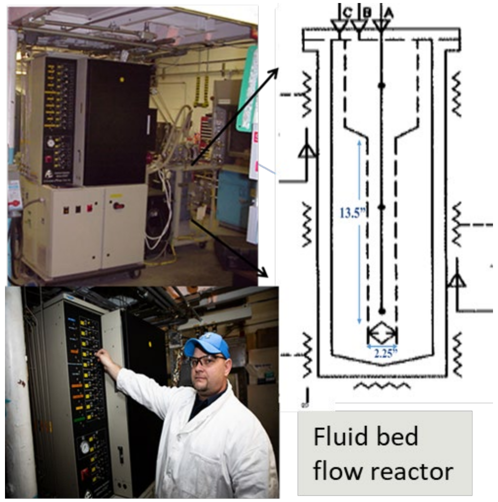



**ASTM 5757-11**
**Attrition Method**

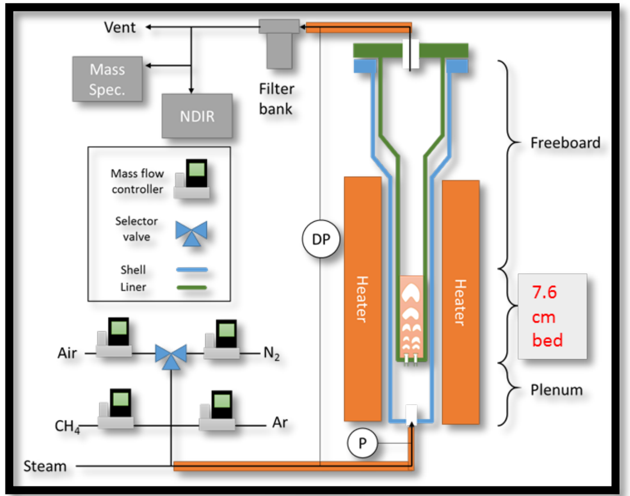


# Facilities used for experimental evaluation

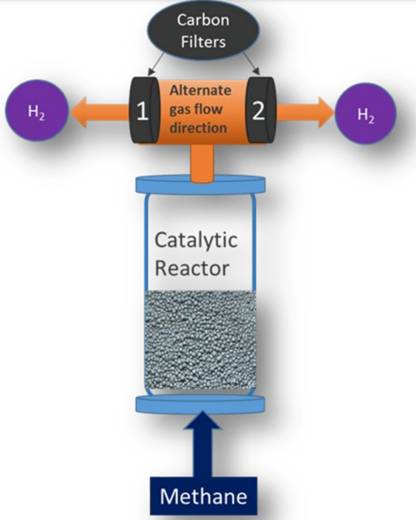
## Fluidized Bed Flow Reactor




Fluid bed flow reactor



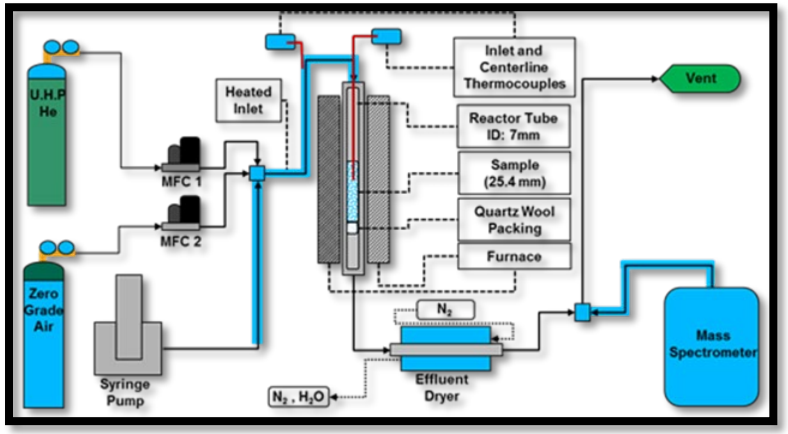

- 300-500 g of catalyst
- Operate at 1.5-3 x Umf
- Continuous operation with collecting carbon in dual filters switching effluent gas flow direction




## 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



# NETL Patent Approved Methane Pyrolysis Catalysts – Solves a Major Barrier Issue Advancing $H_2$ Production with Near Zero $CO_2$ Emissions

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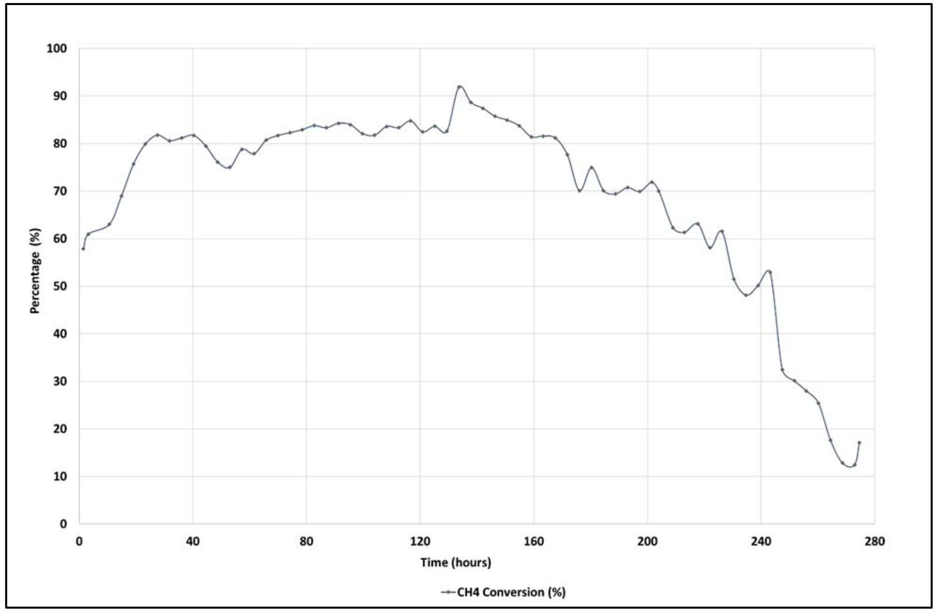
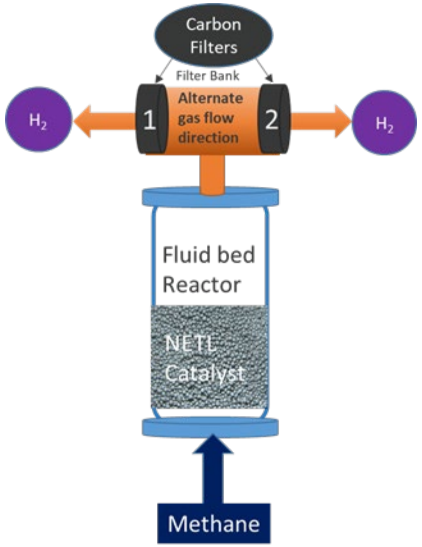
## H2 concentrations during fluid bed tests with NETL catalyst at 700 C




NETL catalyst demonstrated continuous $H_2$ production for 160 hrs. with 80-90% methane to $H_2$ conversion rate

- **Observed activity of NETL catalyst is unprecedented as there are no test results reported in the literature showing similar activity for such a long duration.**
- **All carbon were identified as valuable nano carbon fibers and nano tubes**
- **Testing has validated the remarkable long-term stability and performance of the catalyst technology that is intended to convert natural gas into valuable products (H2 and carbon nanotubes/fibers)**

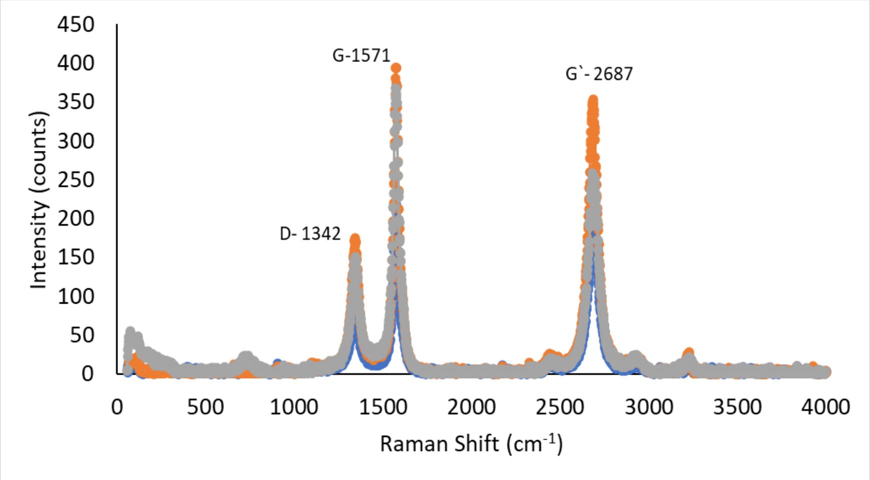
- Industry interest – Patent licensing negotiations for specific applications
- Available for other licensing agreements

Performance of catalysts reported in the literature

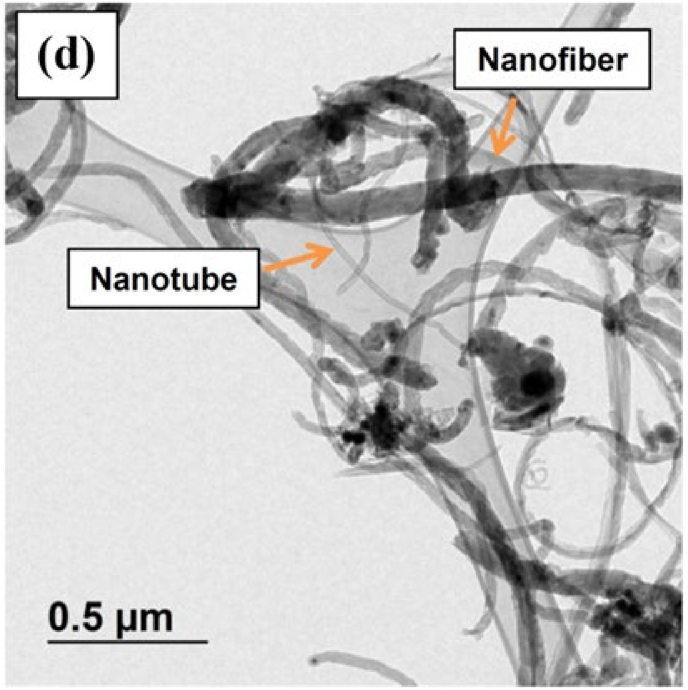
| Catalyst | Preparation | Reactor Bed | Catalyst Lifetime | $CH_4$ Conversion |
|---|---|---|---|---|
| Fe/MgO | Impregnation | Fixed | 150 minutes | 45% |
| 2Ni-1Fe-1Al | Co-precipitation | Fixed | 150 hours | 40% |
| $Fe/SiO_2$ | Impregnation | Fixed | 150 minutes | 95% |
| Fe/MgO | Impregnation | Fixed Bed | 200 minutes | 25% |
| $Fe/Al_2O_3$ | Fusion Nitrates | Fluidized | 6 hours | 18% |
| $Ni\text{-}Fe\text{-}SiO_2$ | Sol-Gel | Fixed | 400 minutes | 16% |
| FeMo/MgO | Fusion Nitrates | Fixed | 200 minutes | 92% |
| $Fe/CeO_2$ | Co-Precipitation | Fixed | 150 minutes | 25% |
| Fe-Cu | Raney-Type | Fixed | 200 minutes | 30% |

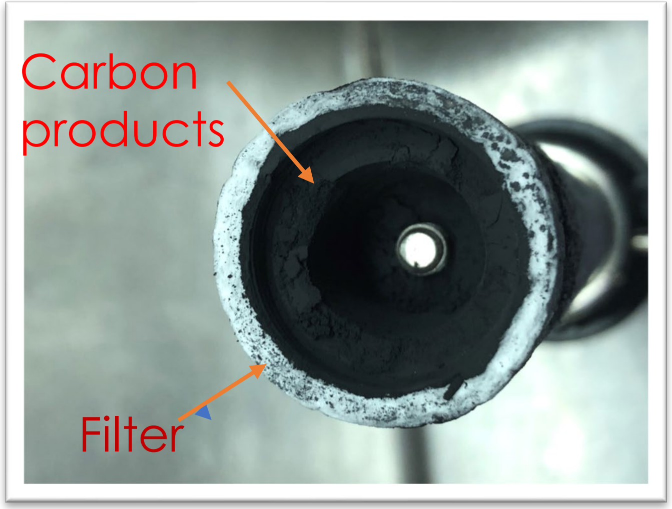
# Confirmed Valuable Carbon Formation by various spectroscopic analysis

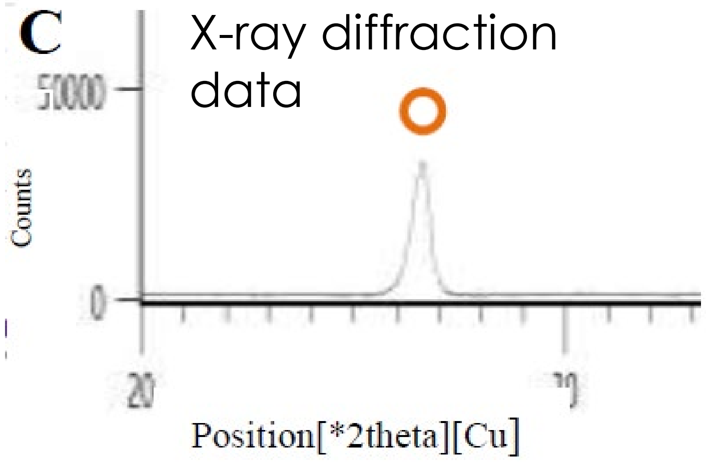
### Raman Spectroscopy




### Transmission electron micrographs(TEM)



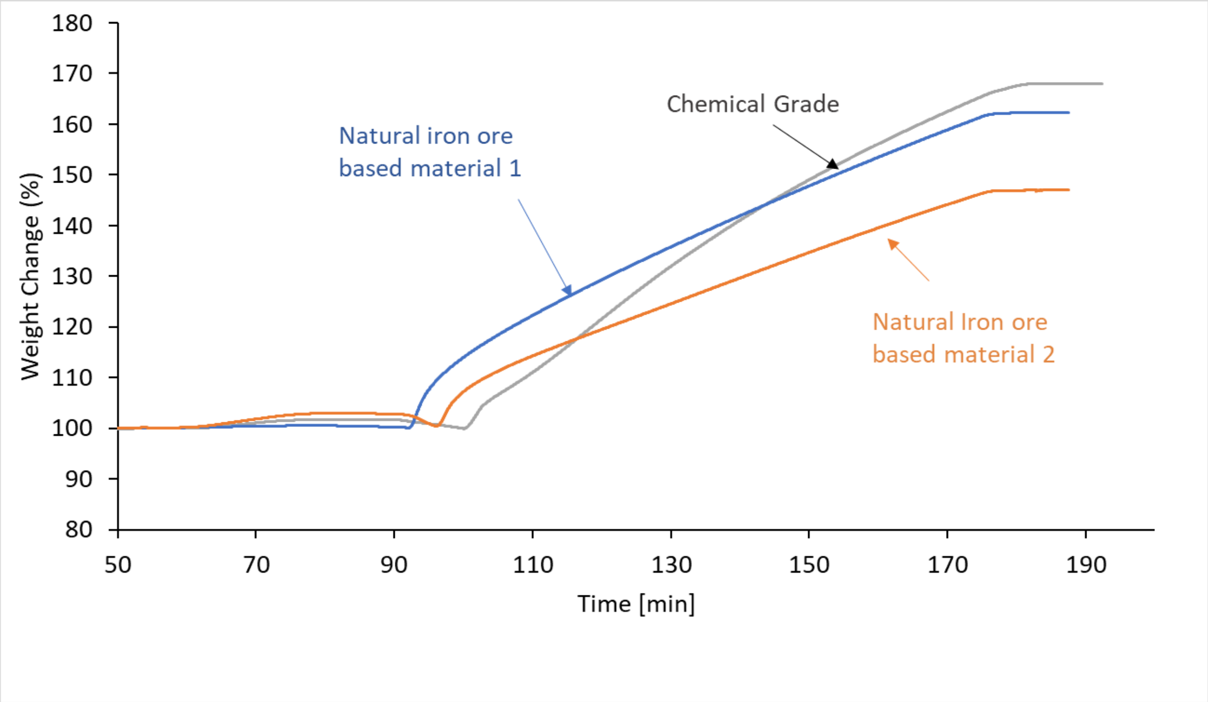




- Carbon containing fines were collected continuously in filters
- XRD - identified graphitic carbon
- Raman spectroscopy and TEM - identified carbon nano fibers/tubes

# Effect of raw material purity on reactivity

TGA reactivity data at 700 C with 10% CH4




- Chemical grade material has >99% purity
- Mineral grade materials
  - Low purity
  - Low cost - ~38 times lower than with chemical grade
- One natural mineral based material had similar performance as chemical grade – Low-cost option
- Some natural grade materials had no activity
- Trace impurities affect the reactivity

# Exploring component of NG: Ethane and methane pyrolysis

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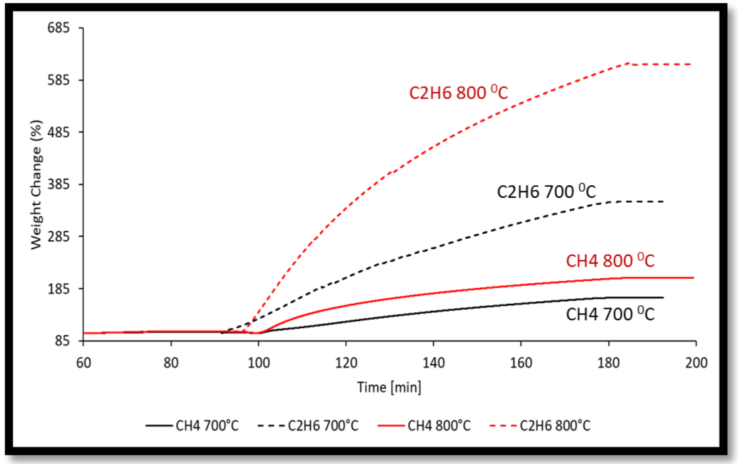
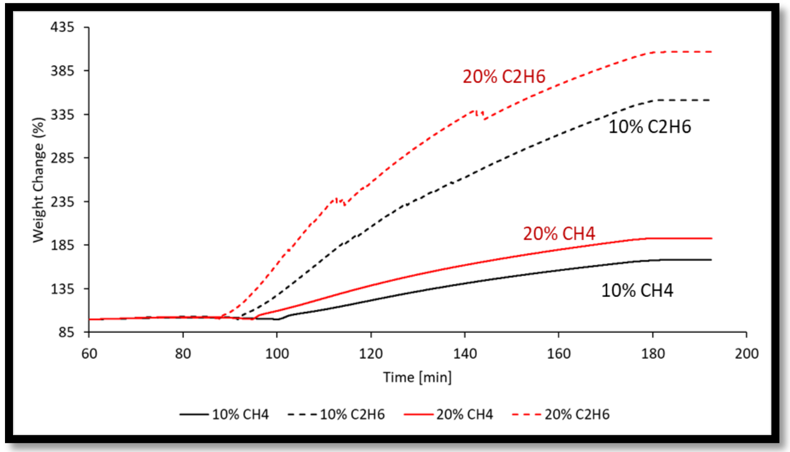
**TGA data -Effect of temperature with 10% gas**




**TGA data- Effect of concentration at 700 $^{0}$C**




TGA

- Ethane decomposition rates are significantly higher than the rates with methane
- Higher temperature has a significant increase in ethane decomposition
- Concentration has some effect but not significant as temperature effect

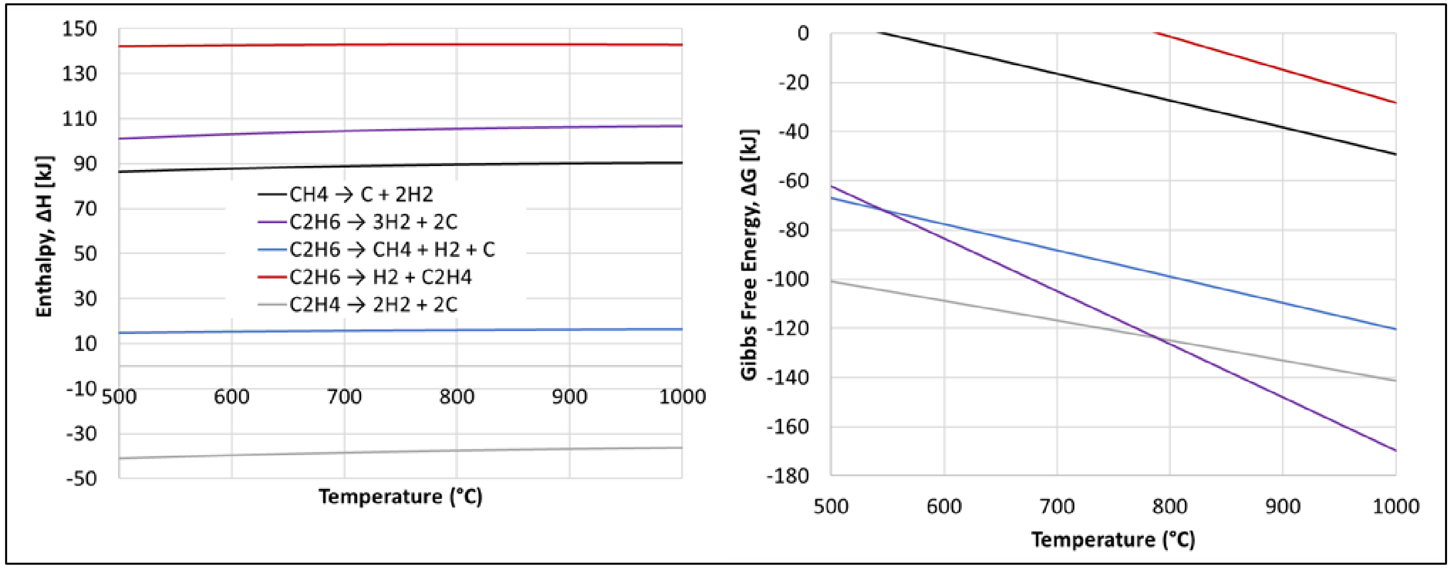
Table: Bond dissociation energies (J. Phys. Chem A 2015, 118,7810-7837)

| Species | Dissociating Bond[a] | 0 K | 298.15 K | Uncert. |
|---|---|---|---|---|
| Methane, $CH_4$ | $H{-}CH_3$ | 432.373 | 438.892 | ± 0.065 |
| Methyl, $CH_3$ | $H{-}CH_2$ (to $^{eq}CH_2$) | 457.21 | 463.14 | ± 0.13 |
| | $H{-}CH_2$ (to $^{3}CH_2$) | 457.21 | 463.14 | ± 0.13 |
| | $H{-}CH_2$ (to $^{1}CH_2$) | 494.87 | 500.66 | ± 0.13 |

| Species | Dissociating Bond[a] | 0 K | 298.15 K | Uncert. |
|---|---|---|---|---|
| Ethane, $CH_3CH_3$ | $H{-}CH_2CH_3$ | 415.25 | 421.77 | ± 0.26 |
| | $CH_3{-}CH_3$ | 367.87 | 376.66 | ± 0.19 |
| Ethyl, $CH_3CH_2$ | $H{-}CH_2CH_2$ | 146.08 | 150.59 | ± 0.27 |
| | $CH_3CH{-}H$ (to $^{eq}CH_3CH$) | 446.57 | 452.61 | ± 0.82 |
| | $CH_3CH{-}H$ (to $^{3}CH_3CH$) | 446.57 | 452.59 | ± 0.82 |
| | $CH_3CH{-}H$ (to $^{1}CH_3CH$) | 459.04 | 464.84 | ± 0.87 |
| | $CH_3{-}CH_2$ (to $^{eq}CH_2$) | 409.83 | 418.03 | ± 0.31 |
| | $CH_3{-}CH_2$ (to $^{3}CH_2$) | 409.83 | 418.03 | ± 0.31 |
| | $CH_3{-}CH_2$ (to $^{1}CH_2$) | 447.49 | 455.55 | ± 0.31 |

# Pyrolysis Reaction Routes with methane and ethane

Enthalpy and Gibbs Free Energy as a function of temperature

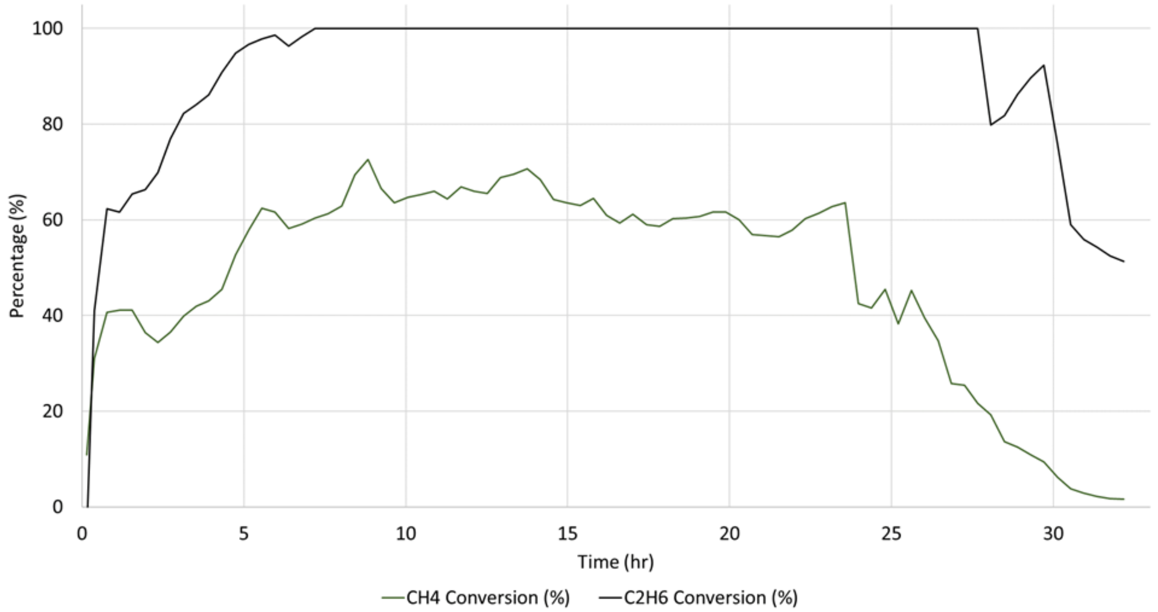



| Reaction | ΔG (kJ/mol 700°C) | ΔH (kJ/mol(@700°C) |
|---|---|---|
| R1-$CH_4 \rightarrow C+2H_2$ | -16.5 | 88.8 |
| R2-$C_2H_6 \rightarrow 2C+3H_2$ | -104.8 | 104.5 |
| R3-$C_2H_6 \rightarrow CH_4+C+H_2$ | -88.2 | 15.7 |
| R4-$C_2H_6 \rightarrow C_2H_4+H_2$ | 12.1 | 142.9 |
| R5-$C_2H_4 \rightarrow 2C+2H_2$ | -116.9 | -38.4 |

- Gibbs free energies for $C_2H_6$ decomposition are more negative, hence easily achieved as compared to $CH_4$;
- Reaction with ethane is more productive in generating carbon with a steeper slope compared to $CH_4$ alone suggesting that the mechanism proceeds mainly through R2 to completion.
- If $C_2H_6$ pyrolysis proceeds only via R3, then the mass change would asymptoticly approach that of R1 and a prevalence of $CH_4$ would be seen in the effluent gases.
- In fluid bed experiments with $C_2H_6$, a small amount of $CH_4$ was also observed indicated that R3 takes place in addition to R2
- Mechanisms that generate ethylene (R4) are not thermodynamically favorable at temperatures below 790 °C.

# Fluid bed data with methane and ethane (4:1 conc. ratio) at 700 C

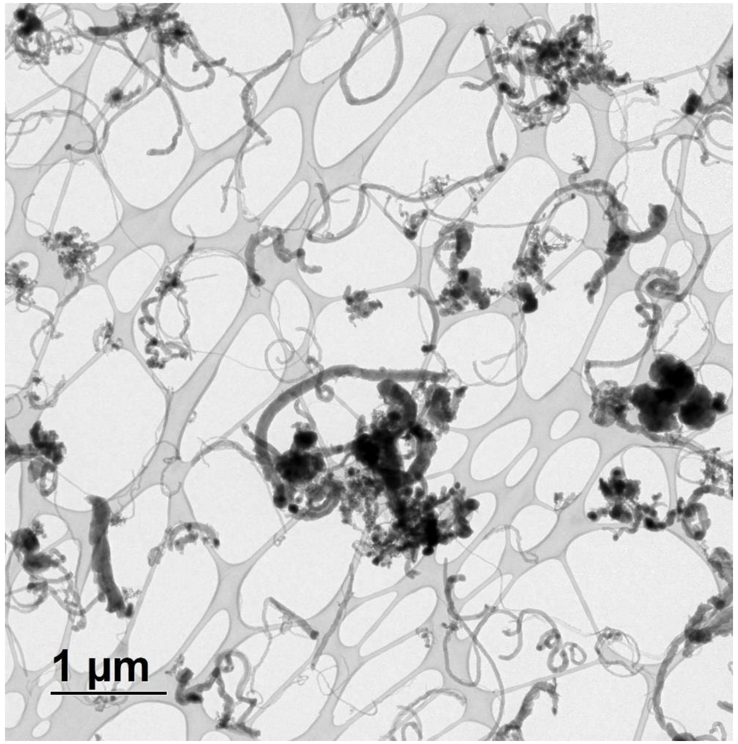
**Percentage of CH4 conversion to H2 during fluid bed methane/ethane pyrolysis test with NETL catalyst at 700 C**




Fluid bed tests

- 100 % conversion of ethane to H2
- Higher conversion of ethane than methane
- Higher H2 effluent concentration
- Fluid bed data consistent with TGA data
- Carbon nano fibers and nano tube formation

**Transmission electron micrographs(TEM)**



# Carbon Characterization

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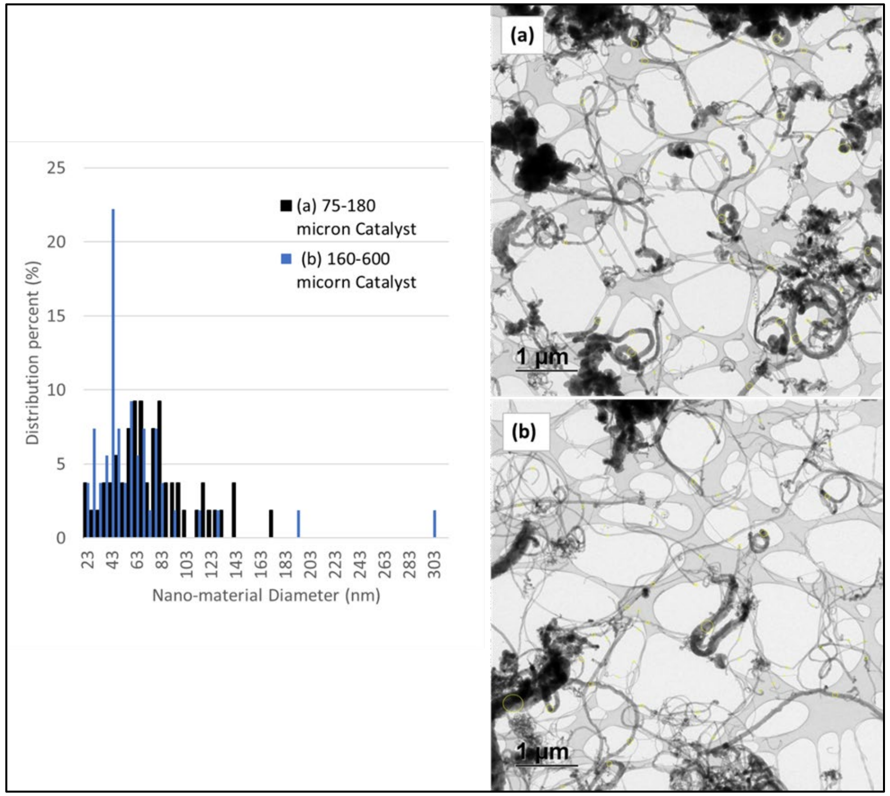
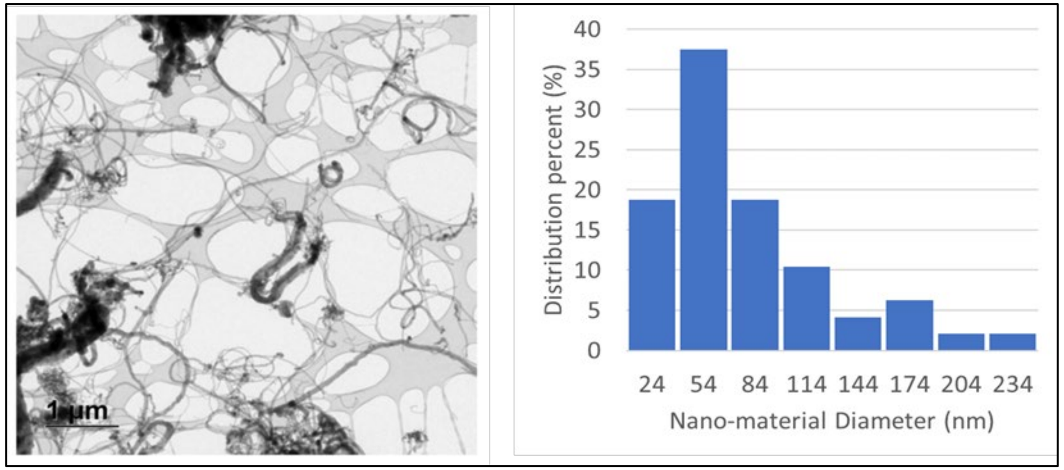
**TEM and size distributions of C produced by fluidized bed methane pyrolysis with different catalyst particle sizes**

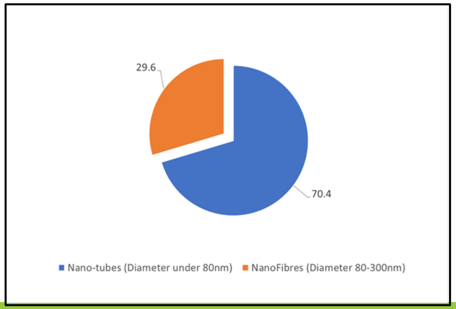



- Nanomaterials favoring diameters of 20-140 nm with a mean of ~50-60 nm and some fibers conglomerating to 200-300 nm in diameter
- These are consequential of the sampling, time on-stream and a more comprehensive data set would be needed to form a quantitative conclusion.

**TEM and size distributions of C produced by fluidized bed methane and ethane pyrolysis**




- **More nano tubes than nano fibers**
- **~35% of the tubes generated were ~50 nm in diameter with larger materials (fibers) approaching 300 nm in diameter.**
- **Quantifying the nanomaterial lengths was challenging**



# Comparison of propane, ethane and methane pyrolysis rates in Thermogravimetric Analysis (TGA)

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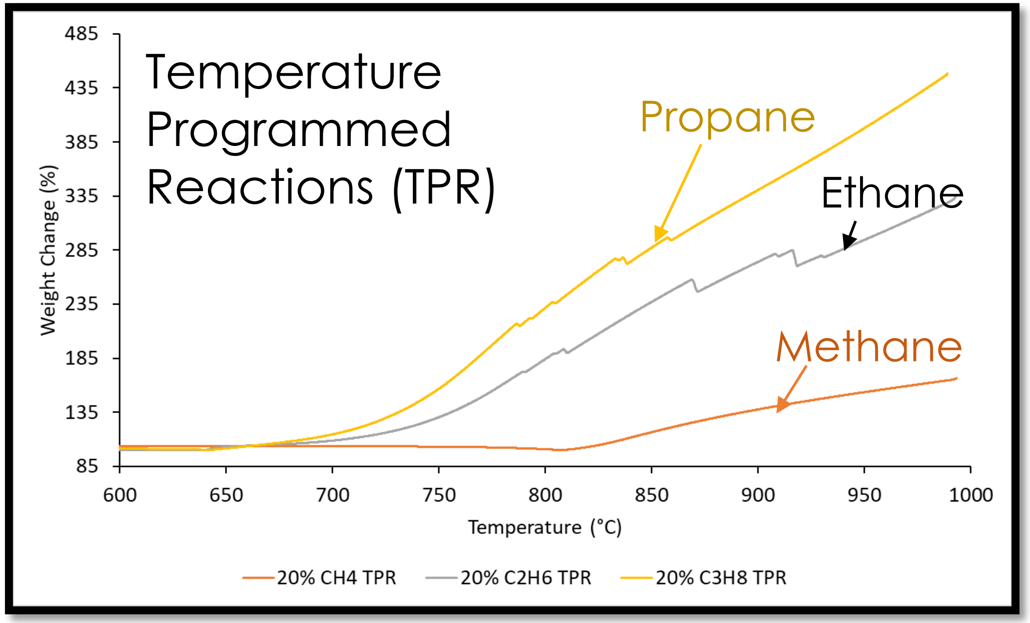
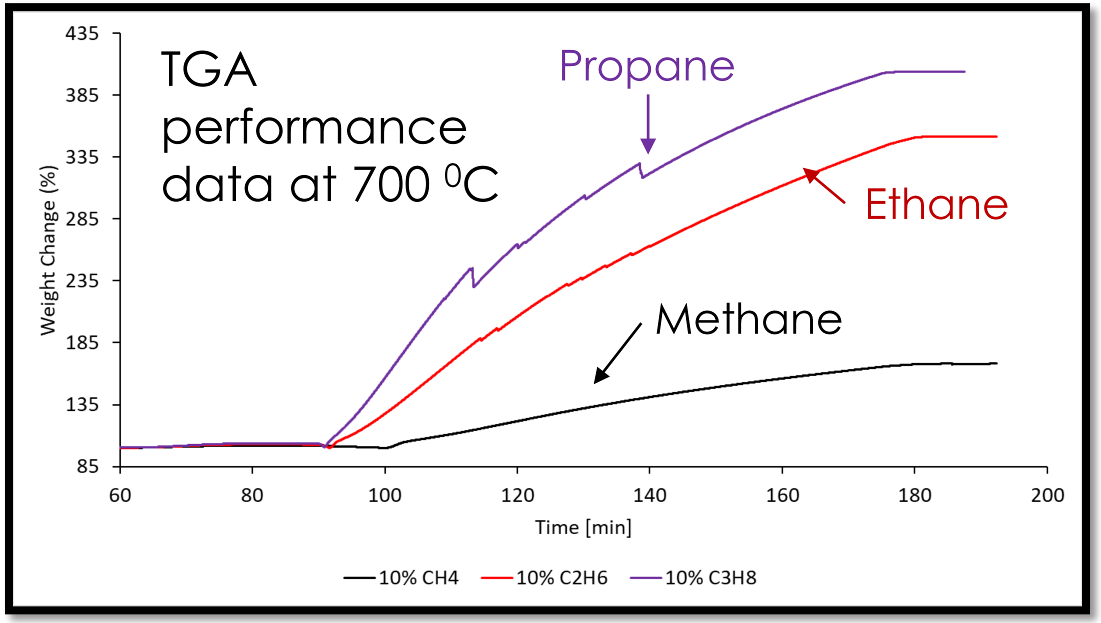
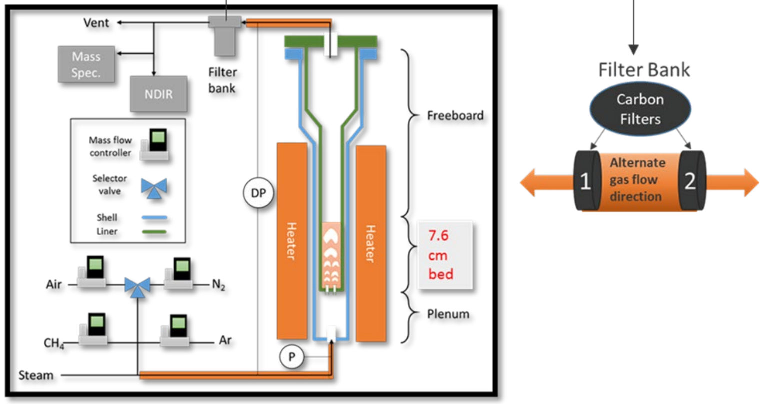


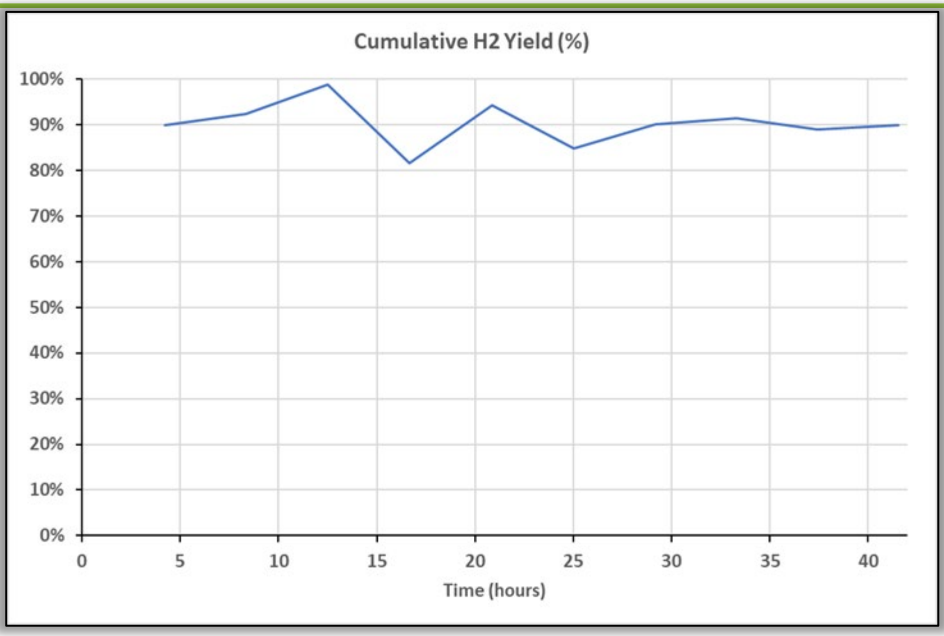




- **TGA weight gain represents the weight gain due to carbon formation from pyrolysis of alkanes**
- **Temperature programmed reactions (TPR) were performed by ramping the temperature from ambient to 1000 C in alkanes**
- **TPR data indicated propane had the highest carbon formation rate and methane had the lowest**
- **TGA isothermal data at 700 C also indicated propane has the highest pyrolysis rate and methane had the lowest**

# Fluidized bed tests of the catalyst with a mixture of gases containing methane, ethane and propane (2:1:0.6 ratio) at 700 C

Fluid bed reactor with dual filter bank



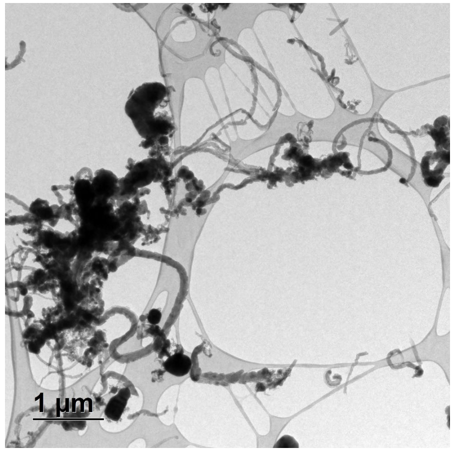

$CH_4 \rightarrow 2H_2 + C$ (R1)

$C_2H_6 \rightarrow 3H_2 + 2C$ (R2)

$C_3H_8 \rightarrow 4H_2 + 3C$ (R4)

**H2 % Yield = H2 conc. x 100 /[(2 x CH4 inlet CH4 conc.) + (3 x C2H6 inlet ethane conc.)+(4 x C3H8 inlet propane conc.)]**

Valuable nano carbon fibers and tubes

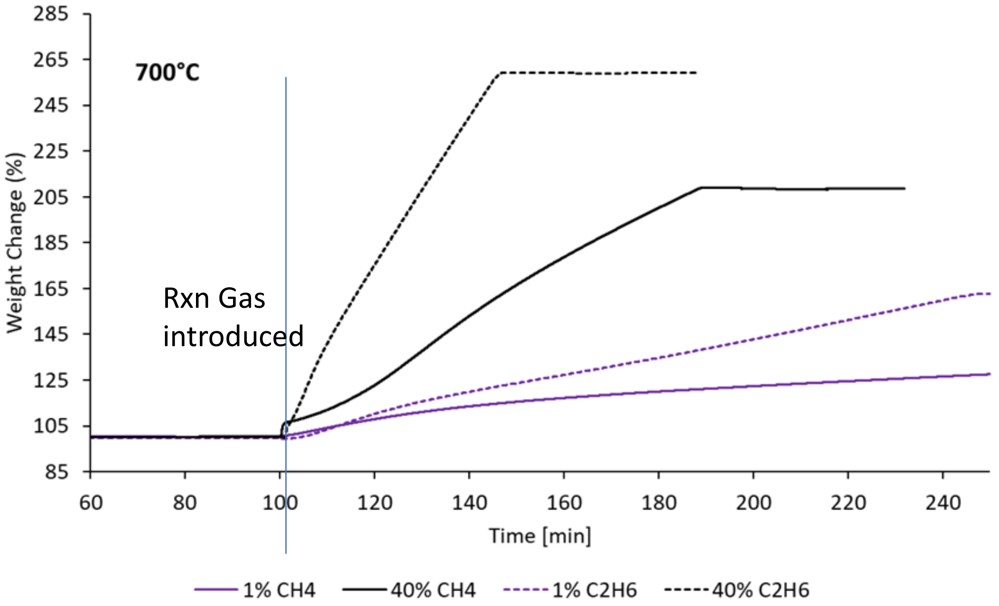



- **Conversion of ethane and propane were 100% and methane conversion was 70% - 40%**
  - Consistent with the TGA data in which propane and ethane decomposition rates were higher than methane.
- **Cumulative H2 % yield during the 40h test remained around 90%, significantly higher than the H2 yield of 25% defined by EERE indicating the high effectiveness of the catalyst.**
- **Experiments conducted with individual gases, ethane and propane indicated that a small amount of methane is also produced from pyrolysis of ethane and propane**
- **Observed valuable nano carbon fibers/tubes**

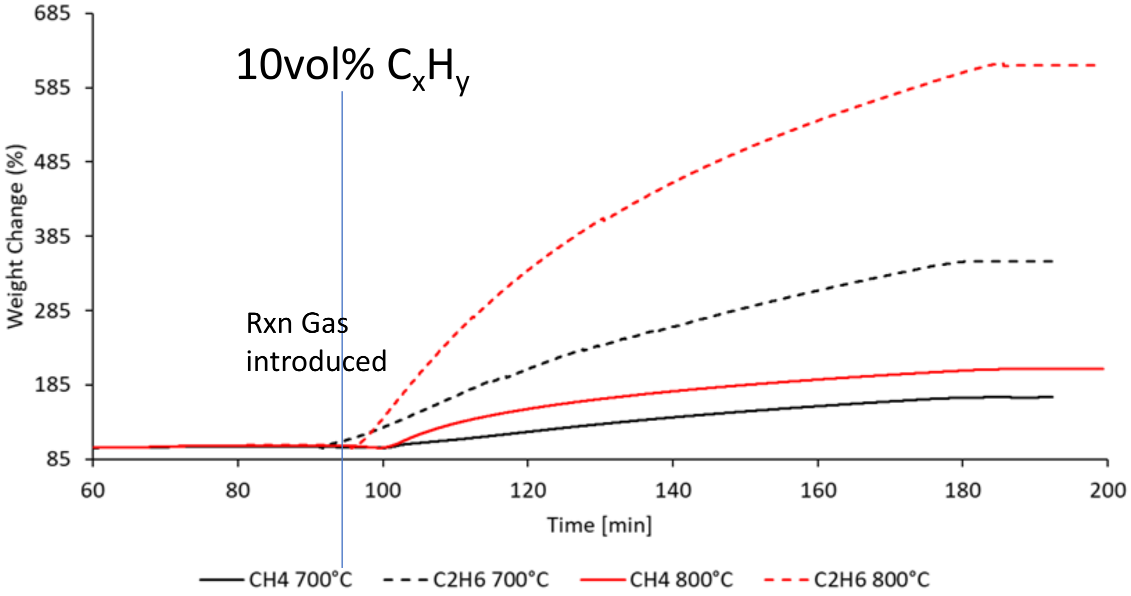
# Kinetic analysis – TGA Data collection

NATIONAL ENERGY TECHNOLOGY LABORATORY

Concentration (Partial Pressure) Effects




Temperature Effects




- **Directly use carbon accumulation TGA weight data to determine pyrolysis reaction parameters**
- **Acquired data to create representative operational parameter matrix for parametric regressions for rate expressions and kinetics**
- **Targeted temperature ranging from 600-900 C**
- **Concentrations ranging from 1-40vol% at atmospheric pressure**

# Kinetic analysis with components of NG: $CH_4$ & $C_2H_6$

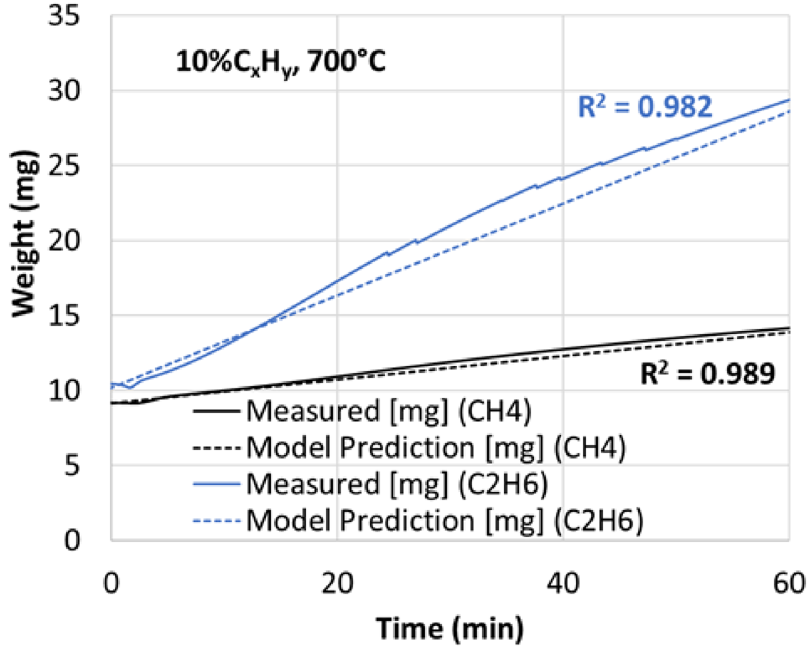
NATIONAL ENERGY TECHNOLOGY LABORATORY

| | |
|---|---|
| Power Law R1 | $R_{c,i} = k_{c,i} P_{g-reactant}{}^{n_i}$ |
| Arrhenius form | $k_{c,i} = A_i e^{\left(-E_{A,i}/RT\right)}, i = 1,2$ |
| Parameter Targets for the regression analysis | $A_i, E_{A,i}, n_i$ |

**Determined Reaction Rate Parameters for the Complete Pyrolysis of Methane and Ethane**

| | | Regressed Rate Parameters and Other Pertinent Properties | | | | | Comparative Rate Calculation (@700 °C, $C_xH_y$ [N/m²] = 20265 ) | |
|---|---|---|---|---|---|---|---|---|
| Gas Reactant | Relevant Conditions | Catalyst Bulk Density, $\rho_b$ [kg/m³] | $E_{A,i}$ Activation Energy [kJ/mol] | $A_i$ (vol. basis) [kmol/m³-sec]/[N/m2]ⁿ | $A_i$ (Catalyst mass basis) [kmol/kgcat-sec]/[N/m2]ⁿ | $n_i$ | $k_{c,i}$ [kmol/kgcat-sec]/[N/m2]ⁿ | $R_{c,i}$ ($g_C/g_{catalyst}$ sec) |
| Methane | 700-850 °C, 1-~40 vol% $CH_4$, 1 atm | 2900 | 43.18 | 0.03 | 1.037E-05 | 0.6 | 4.98E-08 | 0.00023 |
| Ethane | 700-850 °C, 1-~40 vol% $C_2H_6$, 1 atm | 2900 | 62.23 | 0.73 | 0.00025 | 0.6 | 1.15E-07 | 0.00053 |

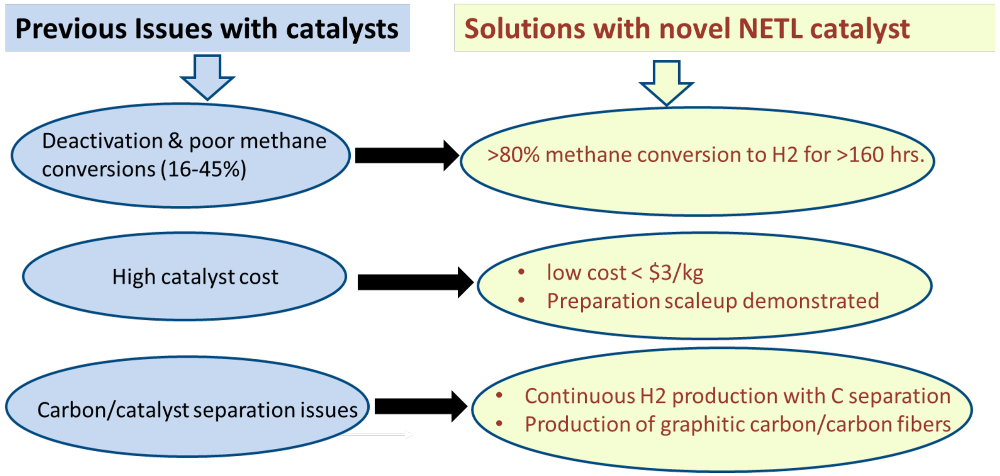
*Depiction of model predictive behavior when compared to experimental data for reactions at 700 °C.*




## Able to conservatively predict pyrolysis reaction behavior with model

- Ethane exhibits a faster rate compared to Methane (consistent with what is observed experimentally)
  - Ethane has a higher pre-exponential factor coupled with a higher activation energy. The rate of pyrolysis with ethane is more sensitive to temperature
- Both have similar partial pressure order dependence ~0.6
- Collected data for C3H8, C2H4, C3H6 and working through rate parameter regressions

# Research Highlights- Solutions with NETL developed novel patented catalyst to major issues with prior catalysts




- Preliminary screening assessment suggested significant advantages over SMR for H2 production and identified some areas of targeted research
- Catalyst optimization – completed w. r. t. particle size and raw materials
  - Small particle size has better performance
  - Raw material – One natural mineral-based material(cost 38 times lower) had good performance
- Demonstrated exceptional performance of catalyst material using lab and bench scale reactor setups
  - Fluid bed test with catalyst with continuously collecting fines in filters
  - Showed >80% methane conversion to H2 and C at 700 °C for 160 hrs.
    - ***Significant accomplishment not reported before***
- Evaluated effect of ethane and propane pyrolysis rates
  - TGA data- highest rates with propane followed by ethane
  - Fluid bed data - 100% ethane and propane conversions
  - Explored cofeeding modes ($C_2H_6$+$CH_4$) which suggest independent reaction behavior
- Collected TGA reactivity data for major components in NG (C1-C3)
  - Developed rate models and kinetic parameters for C1, C2
  - Ongoing work for C2=, C3=, C3

# Bibliography


- R.V. Siriwardane, W. Benincosa, J. Riley, "Novel iron based catalysts for production of carbon and hydrogen from decomposition of methane, Approved by U.S. patent office, 2022
- Riley, J., Atallah, C. , Siriwardane, R. and Stevens, R., 2021, Technoeconomic analysis for hydrogen and carbon Co-Production via catalytic pyrolysis of methane, International Journal of Hydrogen Energy, v. 46, issue 39, p 20338-20358, available at https://doi.org/10.1016/j.ijhydene.2021.03.151
- 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 (under review)
- Invited presentation at ARPA E meeting
- Invited panel member – H2 shot summit

# Identified challenges

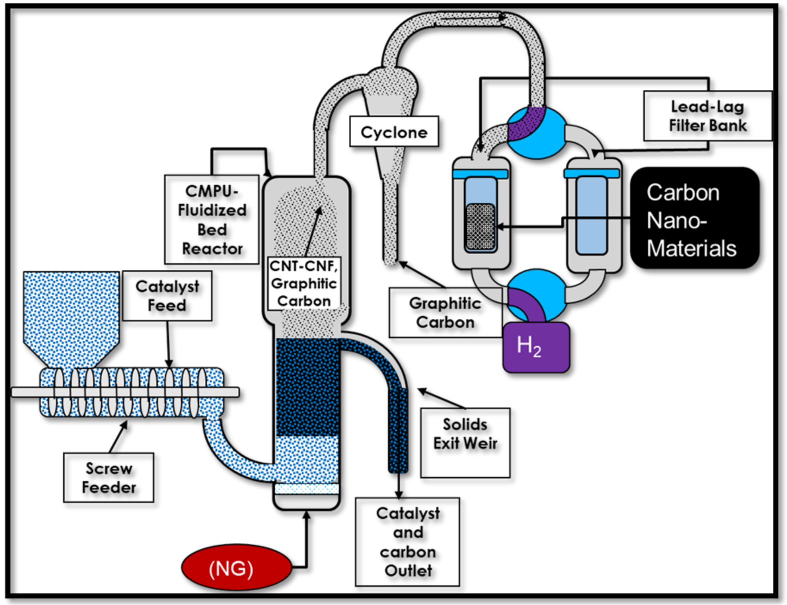
- Carbon purity and type for various applications
    - Initial screening suggests a mixed allotrope
    - Developing techniques to better quantify carbon product to aid in purity refinement
- Identify purity of H2 necessary for applications and define purification strategies
- Heat integration for a commercial process
    - Strategies to be explored and implemented in system studies

# Next Steps

- Complete TGA experimental work and reaction modelling with all components to determine kinetic rate parameters required for system economic assessment
- Assess carbon purification procedures
- Retrofit of an existing larger fluid bed unit (sub pilot scale) at NETL to accommodate batch and continuous operation
- Demonstrate long-term bench scale fluid bed tests in a sub-pilot scale unit and obtain necessary data for TEA analysis
- Complete system assessment incorporating experimentally verified rate expressions and kinetic parameters.
- Larger scale reactor to demonstrate the performance with continuous H2 production and carbon collection
  - Discussions initiated with an industrial partner for scale up
- Reactor scaleup using CFD models and pilot scale operation with an industrial partner for commercialization

## Prototype reactor at NETL

Retrofitting an existing fluid bed - Aim to run for at least 25hrs




- Reactor shell electric heating
- 5kg catalyst with ~0.6 kg/hr catalyst feed rate.
- Methane inlet flowrate: 30-50 L/min balanced with inert

**Estimated Throughput**

- 8 g $H_2$/min → 12kg $H_2$/day
- 24g C/min → 35kg C/day

# Project Summary

- **Novel NETL methane pyrolysis catalysts showed very promising results**
- **Catalyst Preparation**
  - Low-cost raw materials and low-cost preparation method – scaling up easy
  - Projected catalyst cost less than \$3/kg
  - Excellent reproducibility and easy scale up
- **Fluid bed tests with catalyst showed >80% methane conversion to $H_2$ and carbon at 700 °C for more than 160 hrs. and continuing – *Significant accomplishment not reported before***
- **High quality graphitic carbon/carbon fibers were obtained**
  - Continuous carbon containing material collection and $H_2$ production in a fluid bed reactor tests
- **Ethane and propane (components in natural gas) had a positive effect on the catalytic decomposition performance**
  - TGA propane and ethane decomposition rates were faster than that with methane
  - Fluidized bed test conducted with a mixture of propane, ethane and methane showed 100% ethane and propane conversions and 60% methane conversion indicating preference of the catalyst for ethane and propane decomposition.
- **Rate parameters were determined for methane and ethane pyrolysis reactions**
- **Preliminary Systems assessments suggest significant advantages over SMR for $H_2$ production.**
- **Catalyst production technique consistent for industrial level preparations**

# 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. Jarret Riley (Che. Eng.) – Reaction model development and systems analysis
- Chris Atallah (Chem. Eng.) – Material preparation and Aspen modeling
- Michael Bobek (Mech. Eng.) – TGA data operations, reaction modeling
- Donald Jeffries - Engineering technician who operate the fluid bed and fixed bed reactors
- New industrial partner with a specific application – NDA finalized and negotiating licensing applications
- Second industrial partner for demonstrations for a specific application – NDA finalized and discussions continuing
- NETL systems analysis group- future support in technoeconomic analysis
- NETL CFD team for future reactor design and scaleup
- Discussion with external research institute on reactor scale up and demonstrations

# Gantt Chart

## Natural Gas Decarbonization and Hydrogen Technologies: Task 2

*Select a period to highlight at right. A legend describing the charting follows.*

**Period Highlight:** 8

Plan Duration | Actual Start | % Complete | Actual (Flexibility) | Milestone | Go/No Go

| Task | ACTIVITY | PS | PD | AS | AD | PERCENT COMPLETE |
|---|---|---|---|---|---|---|
| 2.1 | Baseline System Study | 1 | 1 | 1 | 1 | 100% |
| 2.2 | Effect of Flare gas components on CMP Performance | 1 | 6 | 1 | 7 | 100% |
| 2.2.1 | Reactor Performance Evaluations | 1 | 9 | 1 | 9 | 80% |
| 2.2.1m | Milestone (EY21.2.A) | 7 | 1 | 7 | 1 | 100% |
| 2.2.2 | TGA Kinetic Studies | 1 | 7 | 1 | 9 | 90% |
| 2.2.2m | Rate Parameters of relevant flare gas/natural components | 9 | 1 | 9 | 1 | 90% |
| 2.3 | Catalyst Optimization | 1 | 7 | 1 | 8 | 85% |
| 2.4 | Carbon product characterization and property determination | 7 | 5 | 7 | 5 | 10% |
| 2.5 | Prerequisite Data collection for SA | 9 | 2 | 9 | 2 | 0% |
| 2.6 | System Assessment (SA) TEA/LCA | 11 | 3 | 11 | 3 | 0% |
| 2.6m | Go/No Go (EY22.2.B) | 13 | 1 | 13 | 1 | 0% |
| 2.7 | Reactor Prototyping (Conversion of SFFBR to sub-pilot rig includes projected time for WO completion) | 8 | 5 | 8 | 5 | 5% |
| 2.7m | Shakedown and batch operation of Sub-Pilot rig (EY23.2.C) | 12 | 2 | 12 | 2 | 0% |
| 2.8.1 | 50-100kg catalyst batch creation | 12 | 2 | 12 | 2 | 0% |
| 2.8.2 | Protoype Continuos Operations, performance assessment, and product characterization | 13 | 5 | 13 | 5 | 0% |
| 2.8m | Go/No Go (EY24.2.D) | 17 | 1 | 17 | 1 | 0% |