Catalytic Conversion of Natural Gas to Form Hydrogen and Solid Carbon

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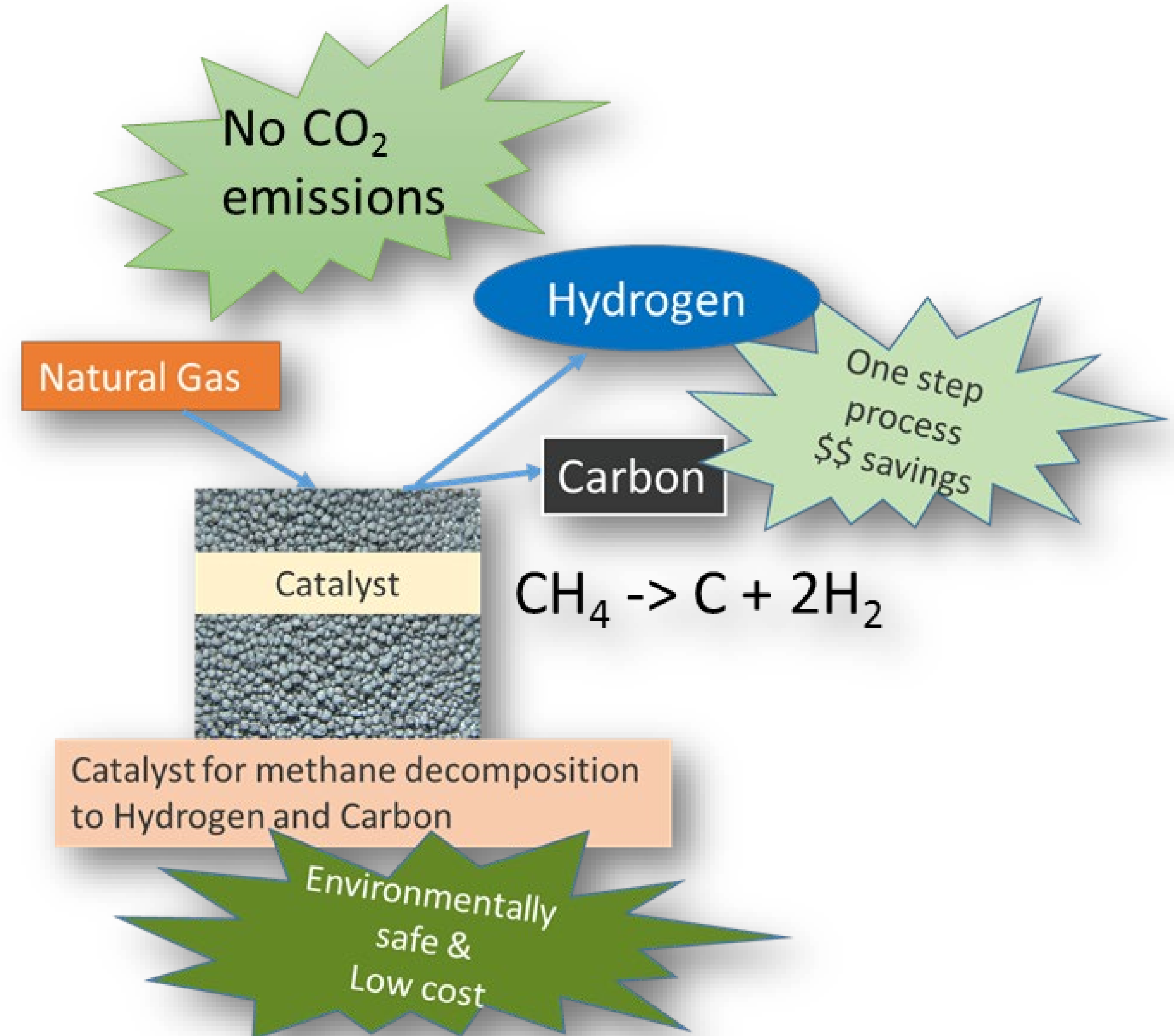

U.S. DOE Hydrogen and Fuel Cells Program
Annual Merit Review and Peer Evaluation Meeting

April 29- May 1, 2019

Project Overview

Timeline

- Project Start Date: Oct. 2017
- Project End Date: July 2020

Budget

- Overall: $2,1000,000
  - EERE: $1,500,000
  - NETL/FE Cost Share: $600,000

Technical Barriers[1]

- Increasing H_2 yields at lower temperatures to improve process costs
- Controlling quality/grade of solid carbon to favor high value product streams
- Separating solid carbon and catalyst materials

Technical Targets[1]

Breakeven analysis[1] estimates:

- H_2 sell price of $4/Kg requires:
  - NG price: $1.50-$4.00/MBtu
  - Carbon price: $4-12/Kg
  - NG Price @ ~40% of process costs

Partners

- NETL's University Consortium for Fossil Energy Research (**NETL-UCFER**)
- 2018 DOE Technology Commercialization Fund Award

[1] "An Overview of Natural Gas Co-Production of Hydrogen and Value Added Solid Carbon Products", Nov 2017, DOE-EERE/FCTO Commissioned Reports: ANL-17/11; PNNL-26726

Motivation

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Thermal Decomposition is a Competitive Process for Hydrogen Production

Table 7 – Comparison of hydrogen production costs for different processes ([85], with permission from the International Journal of Hydrogen Energy).

Process	Total hydrogen production cost in U.S. $ for 10^3 SCF	By-product	By-product credit (U.S.$)	Net cost for 10^6 Btu (U.S. $)
Methane cracking	2.29	Carbon	0.65	5.1
Hydrocarb process	5.82	Carbon	4.04	5.52
Steam reforming	2.06	Steam	0.16	5.9
Coal gasification with electricity chemical shift (Westinghouse)	4.51	Steam	1.8	8.4
Partial oxidation	3.12	Sulphur	0.03	9.6
Steam iron	4.75	Power	1.14	11.21
High temperature steam electrolysis	5.06	Oxygen	0.84	13.12
Texaco gasification	4.35	Sulphur	0.08	13.26
Coal gasification with high temperature electrolysis	4.43	None	0	13.76
K-T gasification	5.12	Sulphur	0.02	15.84
Water electrolysis	6.57	Oxygen	0.83	17.83

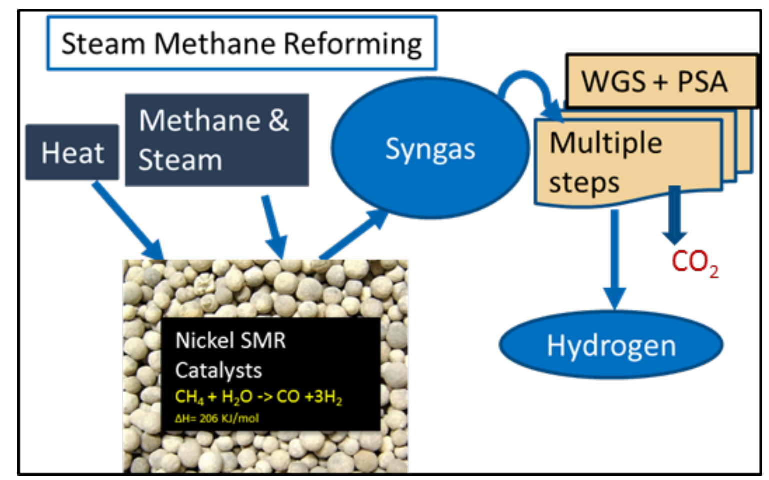
Ref- Steinberg M, Cheng HC. Modern and prospective technologies for hydrogen production from fossil fuels. Int J Hydrogen Energy 1989;14:797-820. (cited in "Review of methane catalytic cracking for hydrogen production" by Ashraf M. Amin , Eric Croiset , William Epling, International Journal of Hydrogen Energy, Volume 36, Issue 4, Feb. 2011, 2904-2935

Motivation

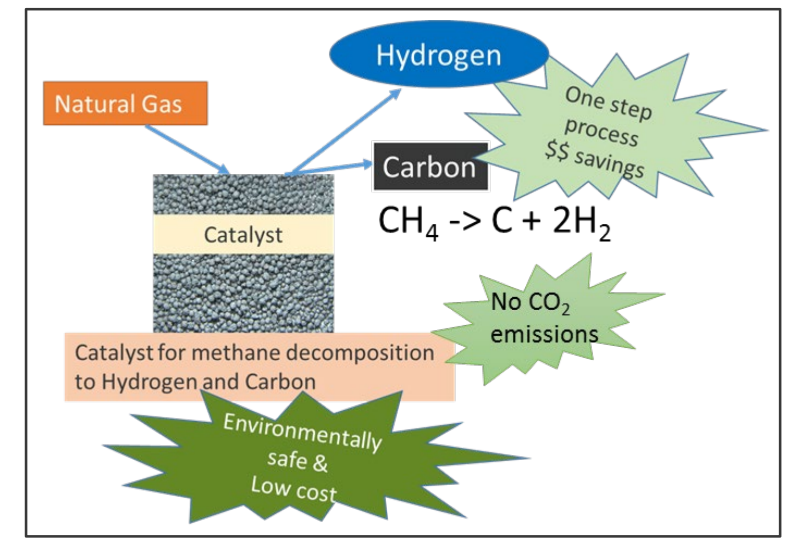
Advantages of Catalytic Methane Decomposition Versus Commercial Steam Methane Reforming

	Steam Methane Reforming (SMR)	Catalytic Decomposition
Heat of reaction (KJ/mol)	206	75.6
Catalyst	Ni based-suspected carcinogen- $190/kg	Earth Abundant & Environmentally benign - $0.20/kg
Processing steps after initial reaction	1. Water gas shift reaction (WGS)-convert CO to H2 2. PSA for CO2/H2 separation	1. Methane/H2 separation
CO2	Sequestration necessary	Little to No CO_2 generated
Additional valuable products	None	Solid Carbon
Process Cost	$6.21 /GJ (Lane & Spath, 2001, NREL/TP-S10-31351) 18.8 kcal/mol. H2 (https://www.osti.gov/servlets/purl/40652 Brookhaven National lab)	$5.38/GJ 11.3 Kcal/mol. H2

Current Commercial SMR Process



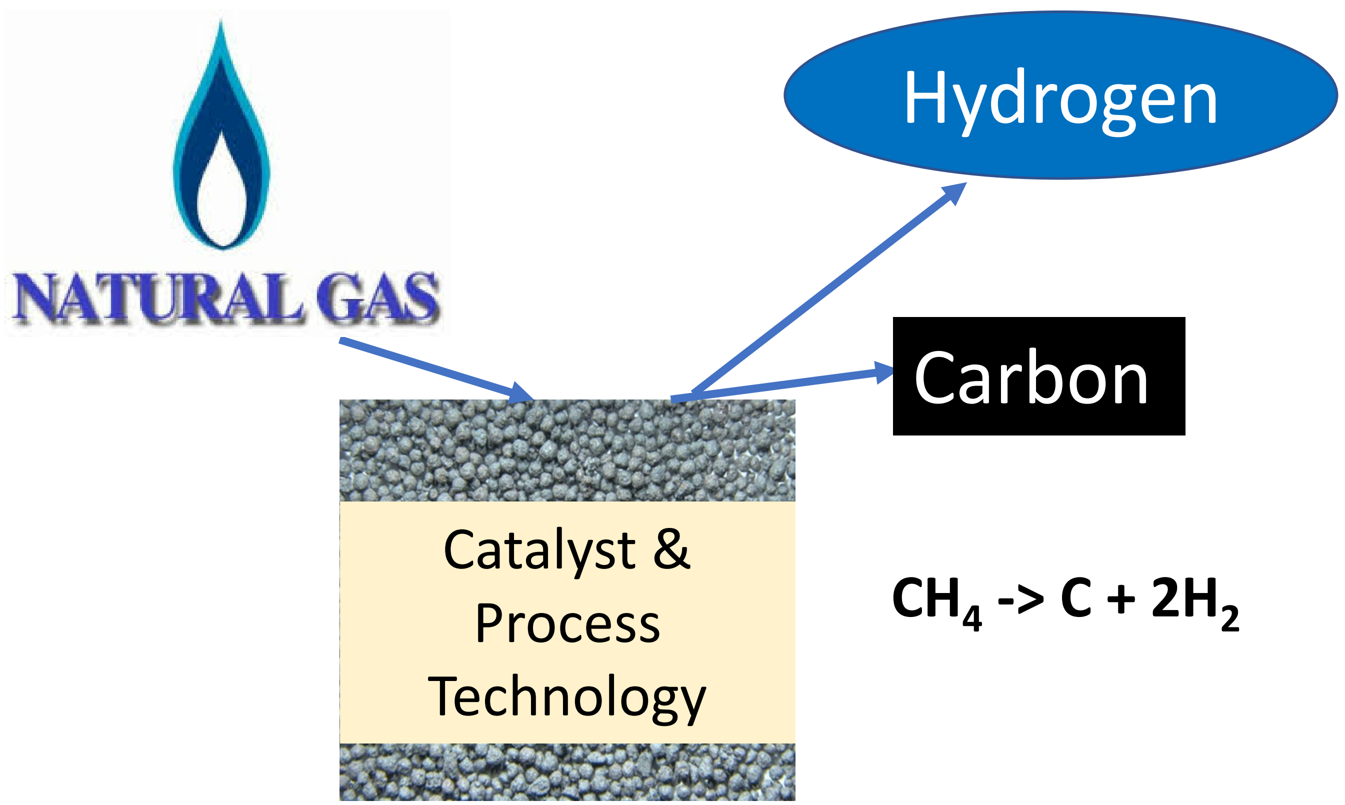
Methane Decomposition Process



Previous Issues with H2/C production with thermo-catalytic methane decomposition

- Catalyst deactivation & lifetime
- Poor methane conversion (16-45%)
- Separating catalyst from carbon

General Technical Approach



$$CH_4 \rightarrow C + 2H_2$$

General Technical Approach:

- Optimize catalyst & chemical process technology for producing H_2 & high value solid carbons

- Consider utilizing all components of NG feedstock: methane & natural gas liquids (ethane, propane, etc)

- Targeted carbons:
  - Carbon nanotubes for structural composites
  - Ultra-long carbon nanotubes (μm to mm length)
  - Graphitic carbon for refractories, batteries etc.

Accomplishments and Progress

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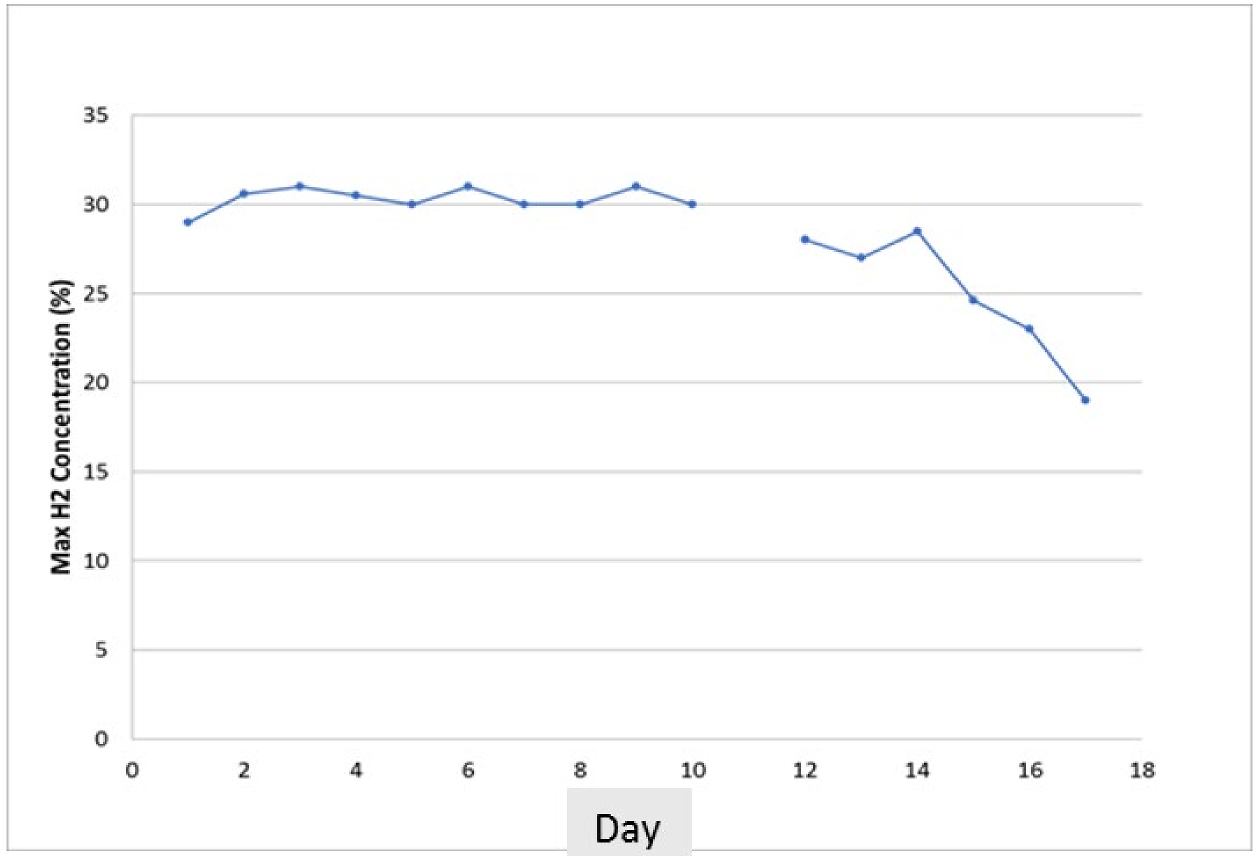
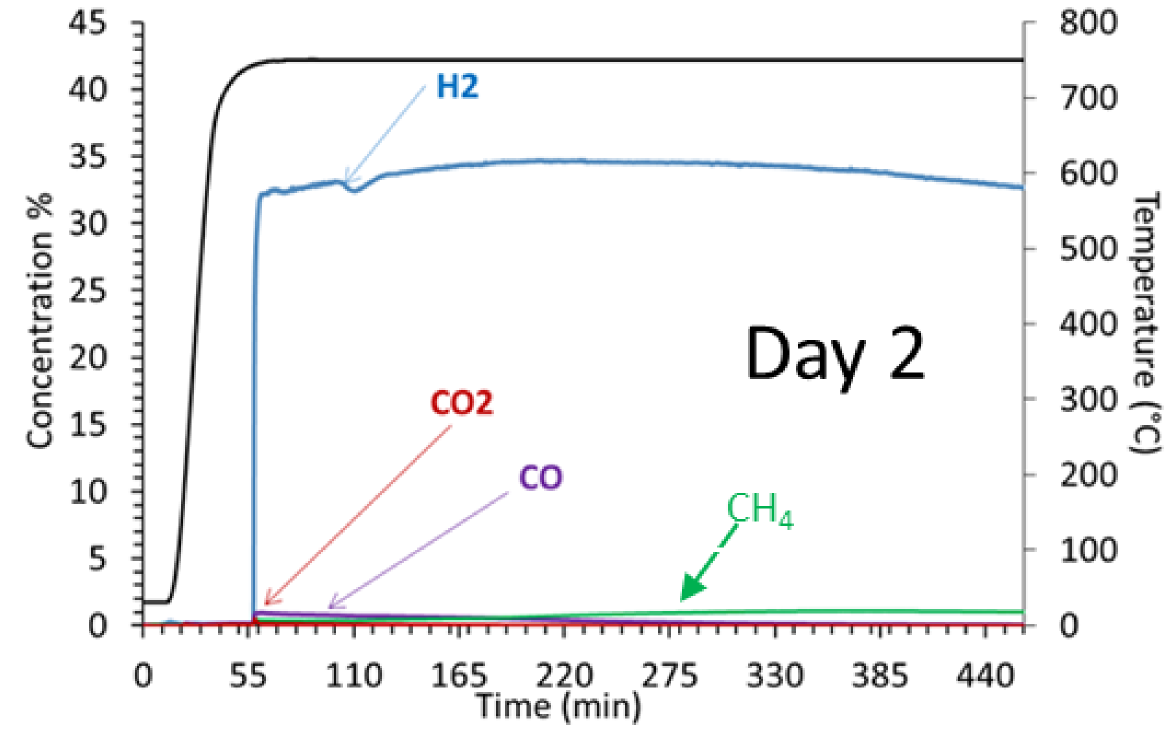
Maximum H_2 concentration during 17-day tests with CH_4 (15-17 vol.%) at 700 ^{0}C



Effluent gas concentrations during the test on Day 2

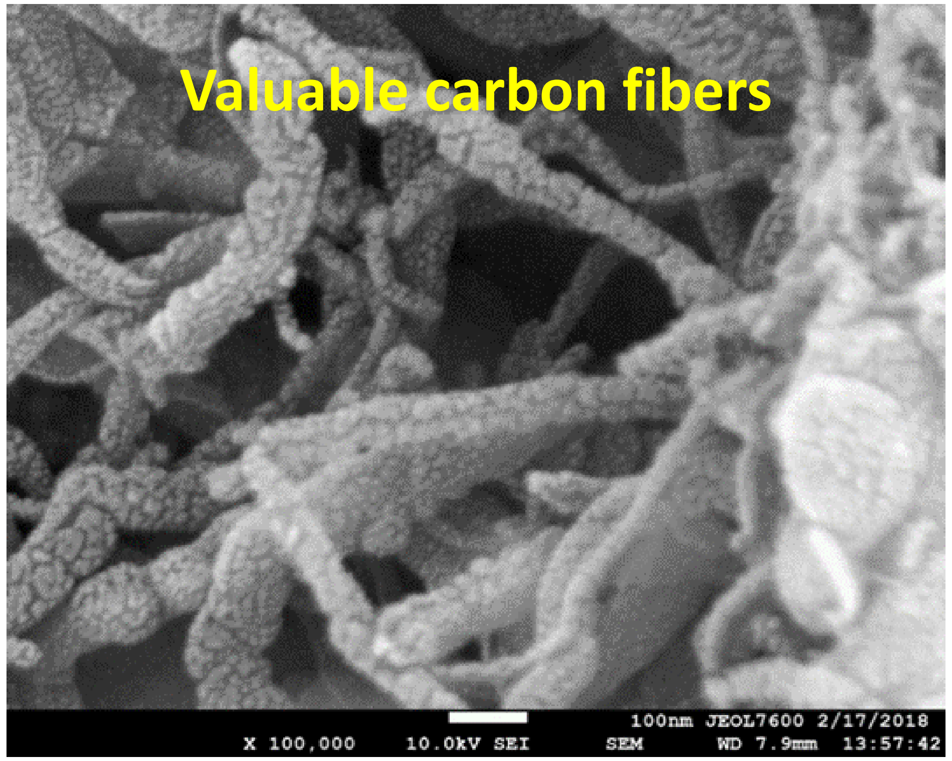


Several Technical Barriers Solved with NETL Catalyst (Patent Pending) Formulation

- **Total test time is about 60 hrs. – Significantly higher than reported in the literature**
- **Methane conversion is about 95-90% for 50 hrs and 70-80 % for rest of the hours -** higher than previous reports of 16-45%
- Carbon separated by physical sifting & catalyst is still active in reactor after sifting (good for at least 17 days of cycles)
- Fluidized tests initiated.

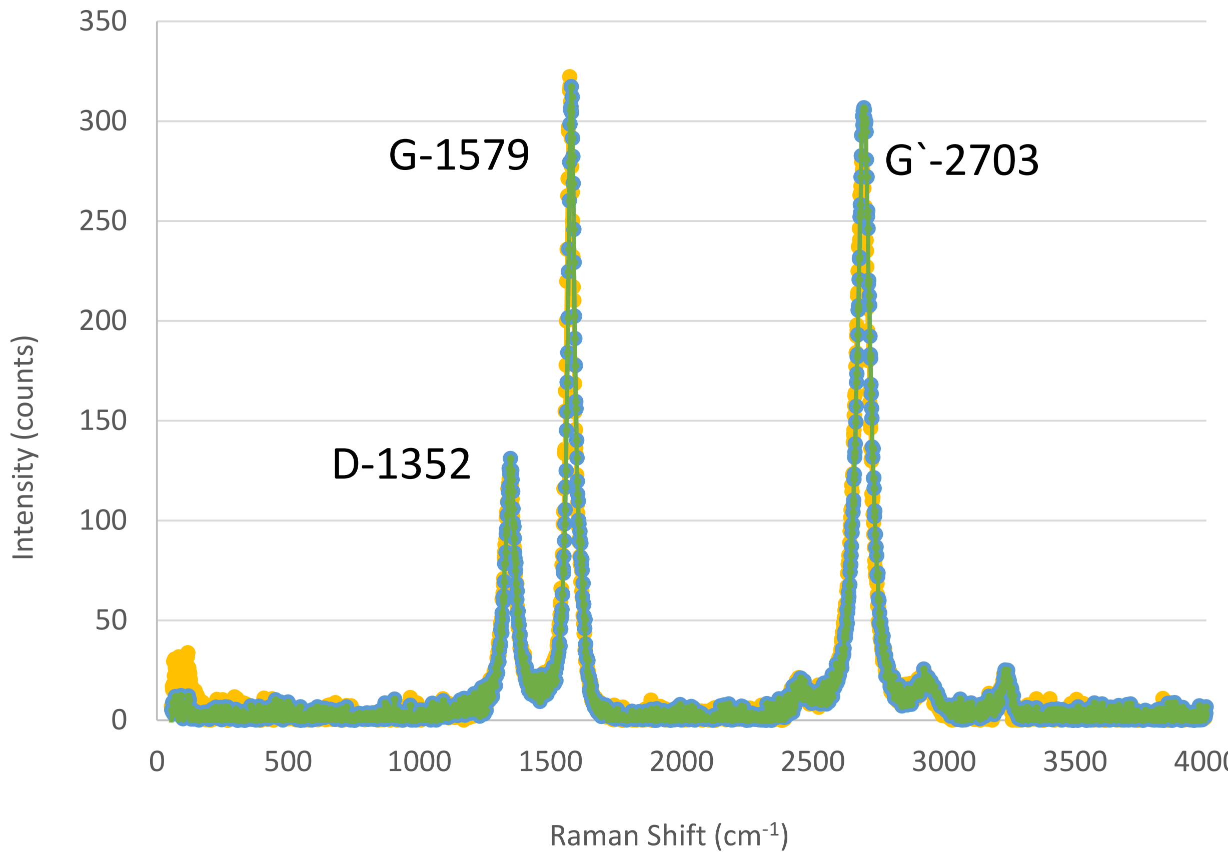
Accomplishments and Progress

SEM Analysis of Carbon



- Carbon fibers observed

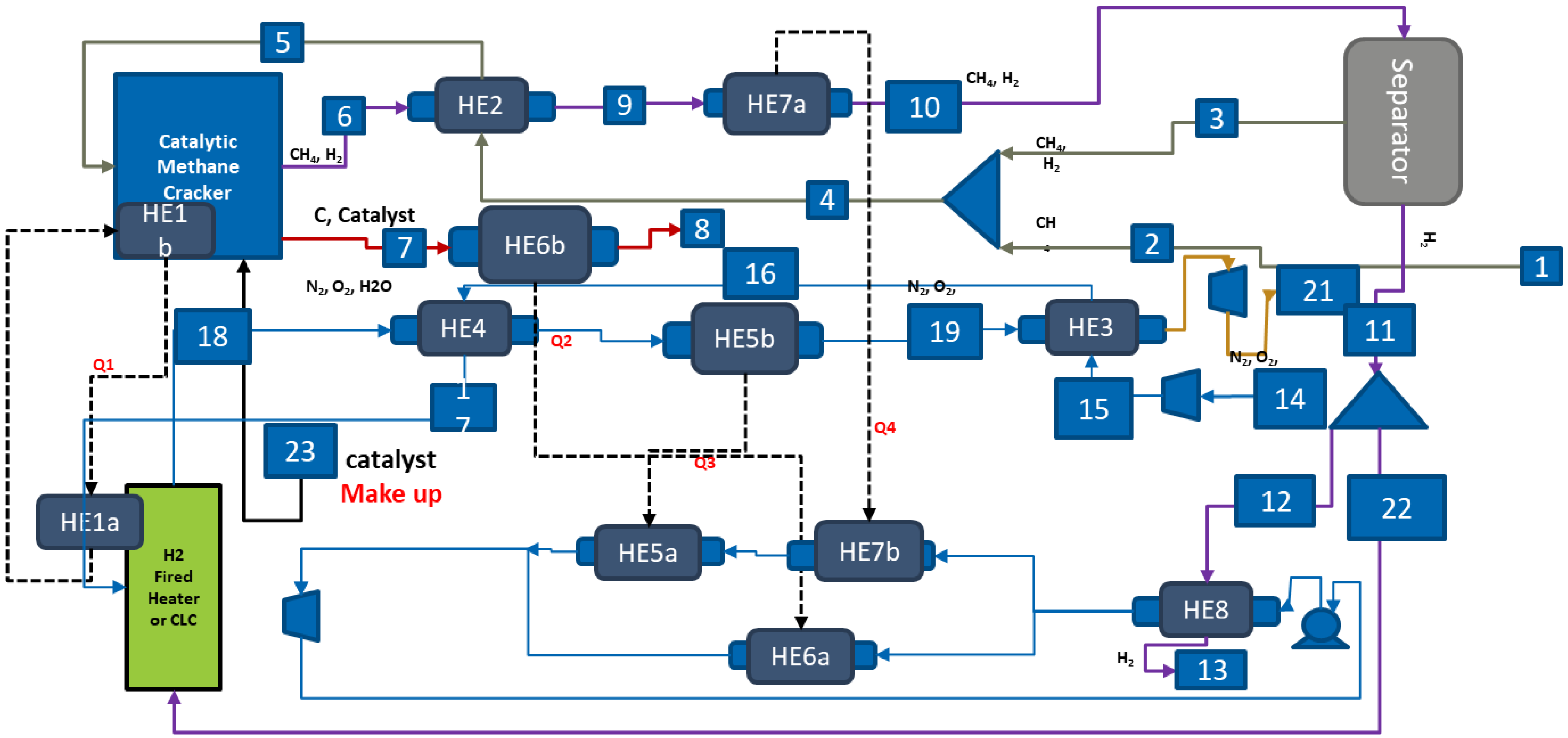
Raman Spectroscopy of Carbon Product



- Sharp D, G and G` bands indicative of graphitic carbon fibers with well ordered structure
- Resemble spectra of multi wall nano-fibers mixed with single wall nano-fibers

Initiated Systems Analysis- Carbon plant production configuration

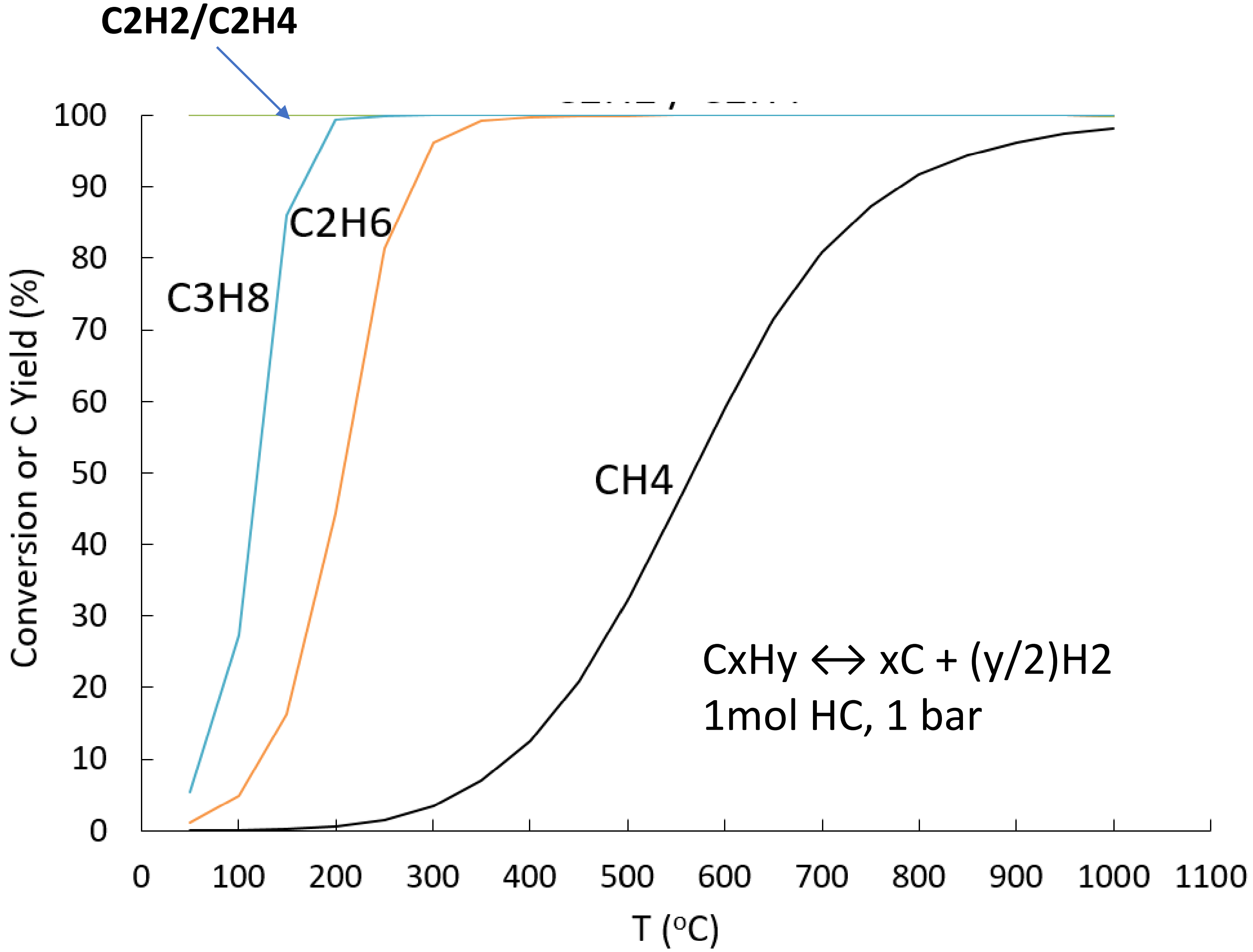
-Aspen simulations



- Two possible heating sources: H2 or CLC
- Capital cost , net energy requirements & include waste heat streams for energy recovery
- Examine the impact of catalyst loss rate on plant economics and feasibility
- Examine effect of carbon sale price and carbon recovery on H2 production cost.
- Results comparisons with H2 costs from conventional SMR plant (Industrial standard)

Accomplishments and Progress

Thermodynamic Calculations Indicate Natural Gas Liquids are Useful Hydrogen & Carbon Feedstocks



- Natural gas contains: methane, ethane, propane, butane, isobutane, & C_5^+ fractions
- Natural gas liquids (C_2 - C_5^+), prevalent in Appalachia, are transforming chemical manufacturing & NGL exports
- Ethylene crackers (ethylene from ethane) & underground storage facilities are being built for manufacturing in Appalachia region
- Natural Gas Liquids are already transforming chemical manufacturing industry[1] (see refs below).

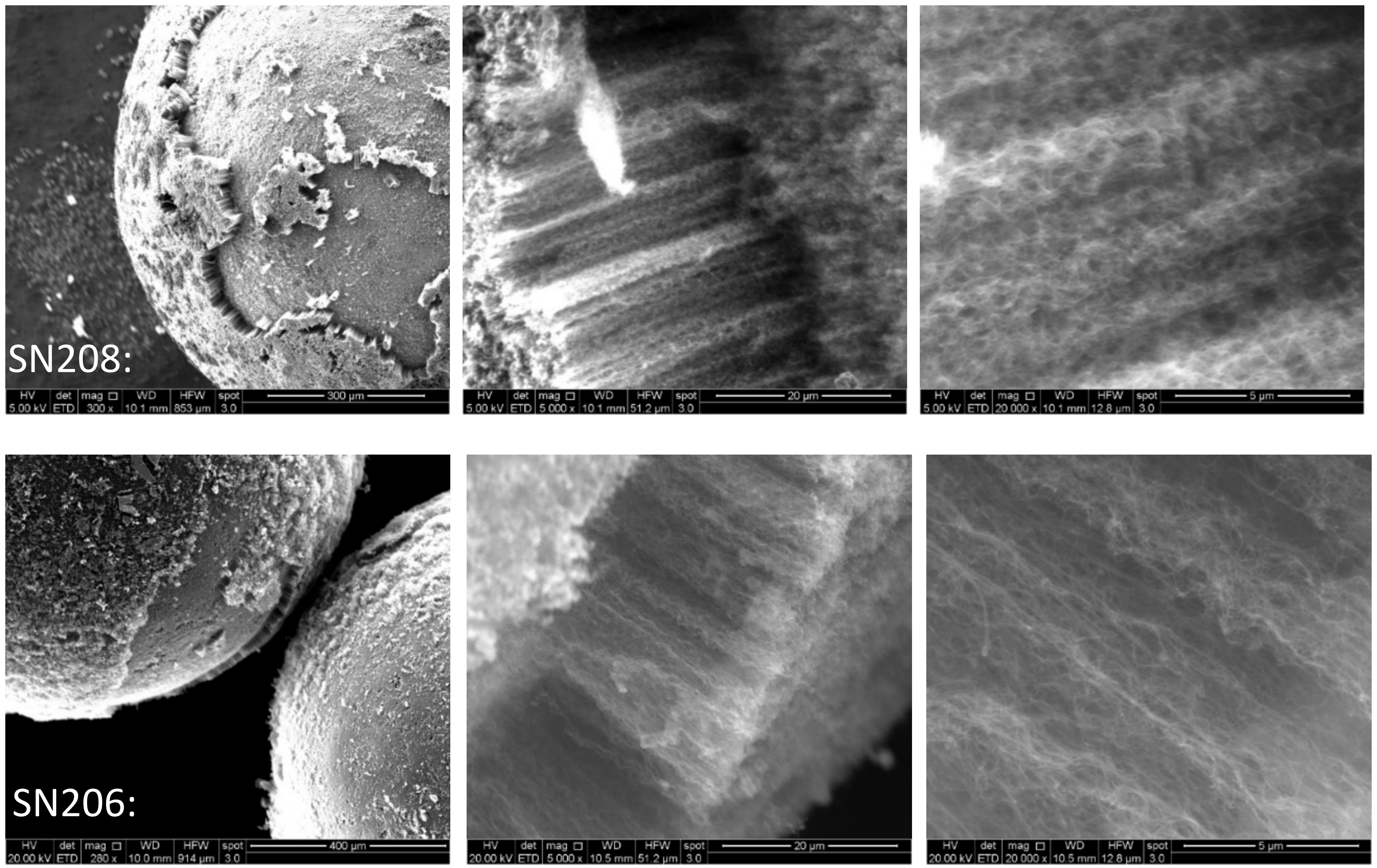
Image: "The great gas gold rush", Nature, pgs 26-28 Oct 5 2017

U.S. DEPARTMENT OF ENERGY

[1] "The Great Gas Gold Rush" Nature, pgs 26-28 Oct 5 2017

Producing Hydrogen and Carbon Nanotubes from Natural Gas

Vertically Aligned Carbon Nanotubes from Ethylene Feedstocks & Fe Catalysts



- Fe catalyst
- Ethylene is efficient feedstock
- Shale derived ethylene is growing market in Appalachia
- Catalysts: proprietary Fe-based system on ceramic support
- 15-25 nm diameter + 50 um length

Producing Hydrogen and Carbon Nanotubes from Natural Gas

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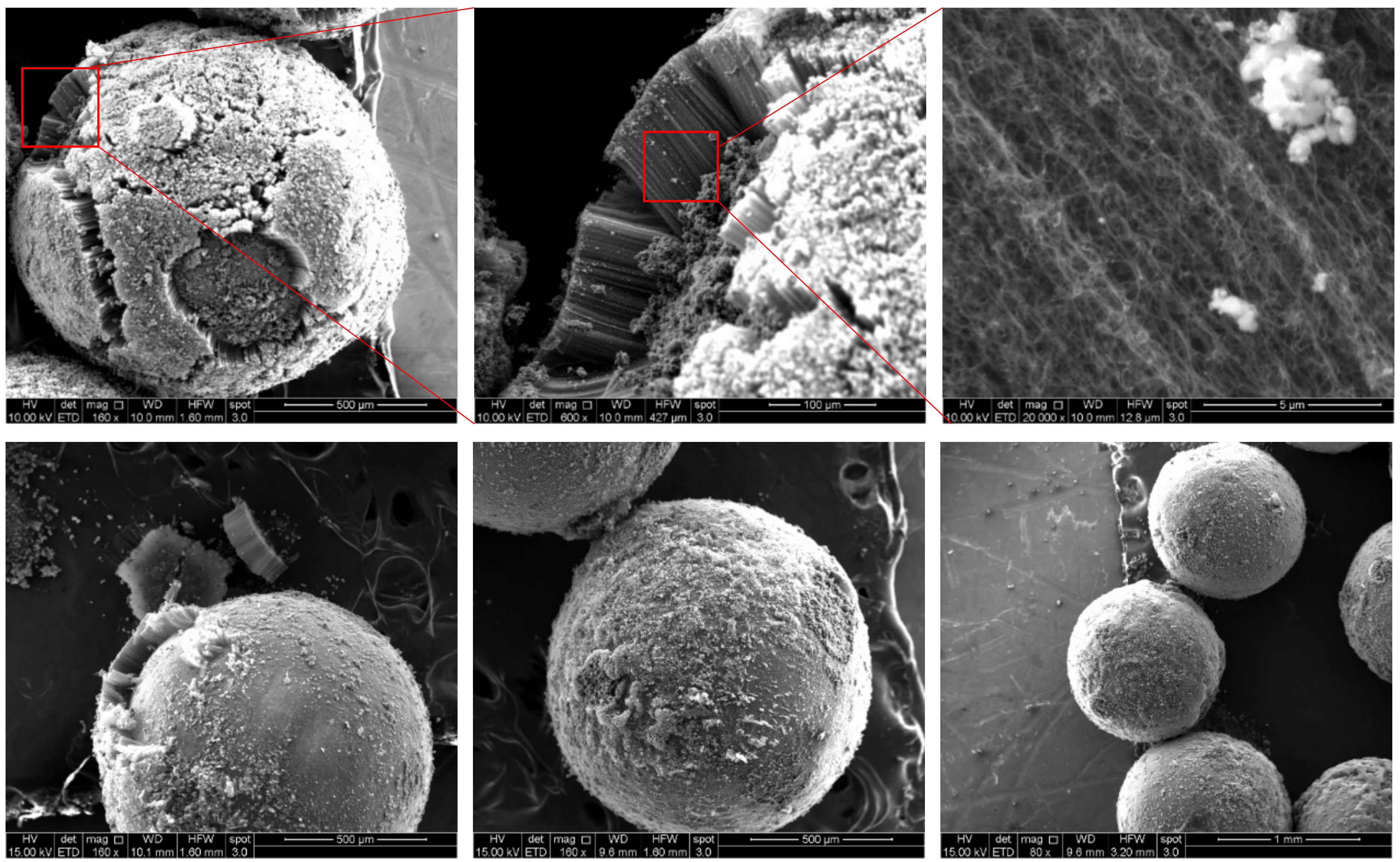
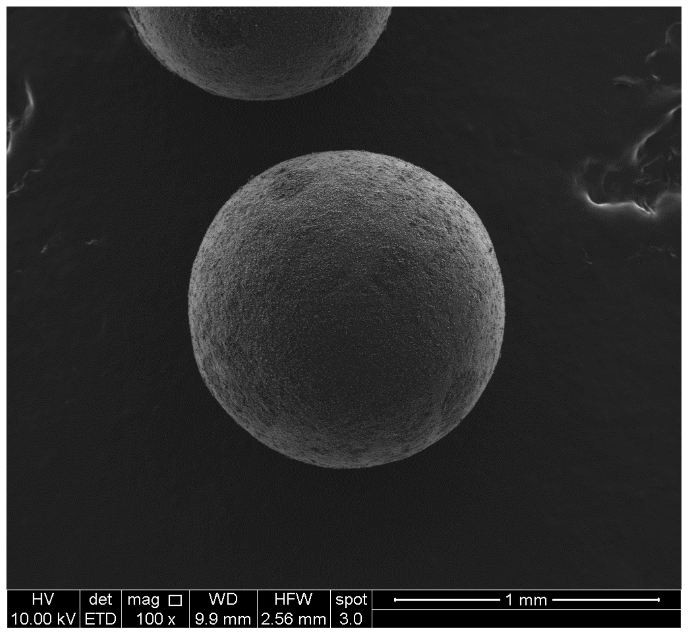
Vertically Aligned Carbon Nanotubes from Fe-Co Catalysts & Ethylene Feedstock

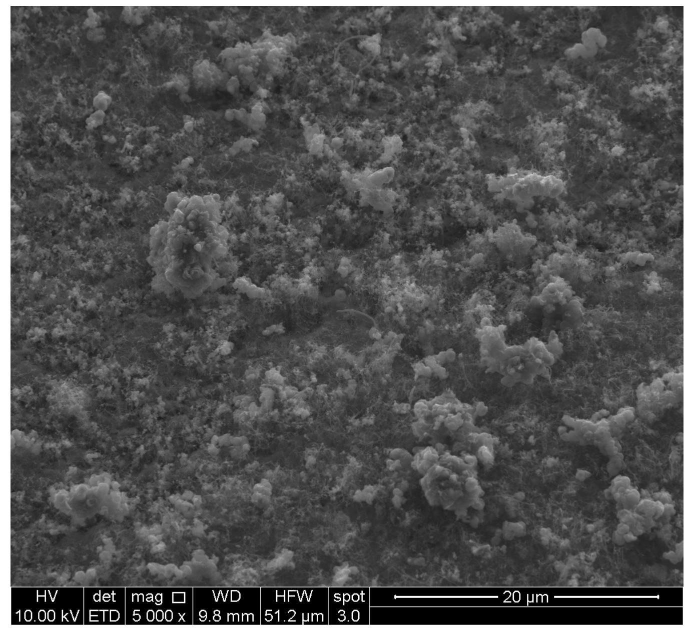


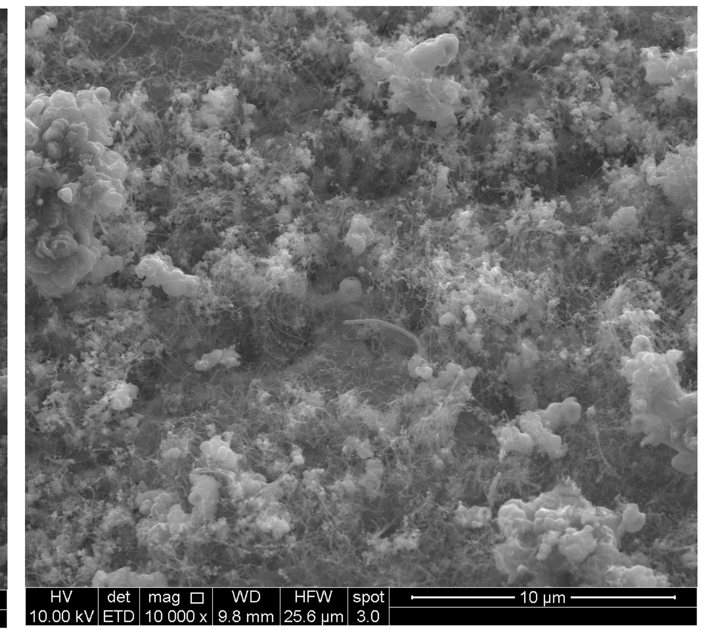
- Fe-Co catalyst
- Ethylene feedstock
- Well aligned growth
- 20-40 nm diameter + 30-120 um length

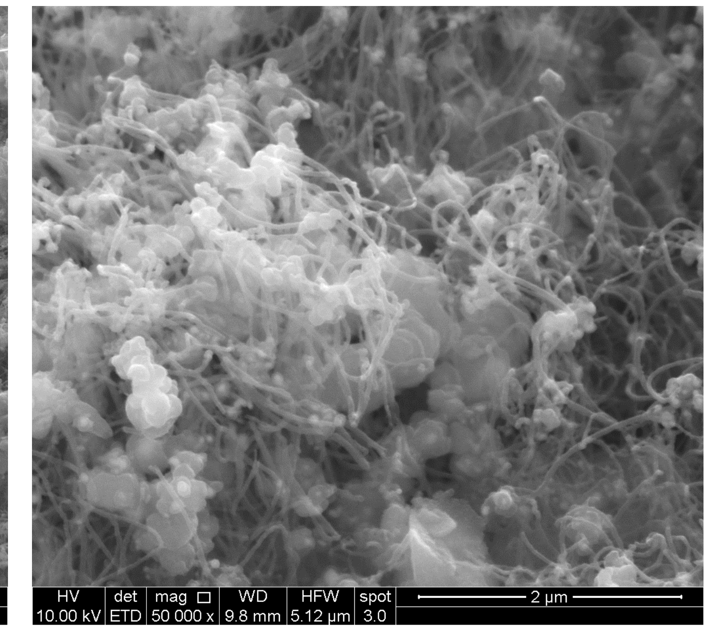
Water Vapor is Critical for CNT Growth

Sample **without** 500 ppm H2O

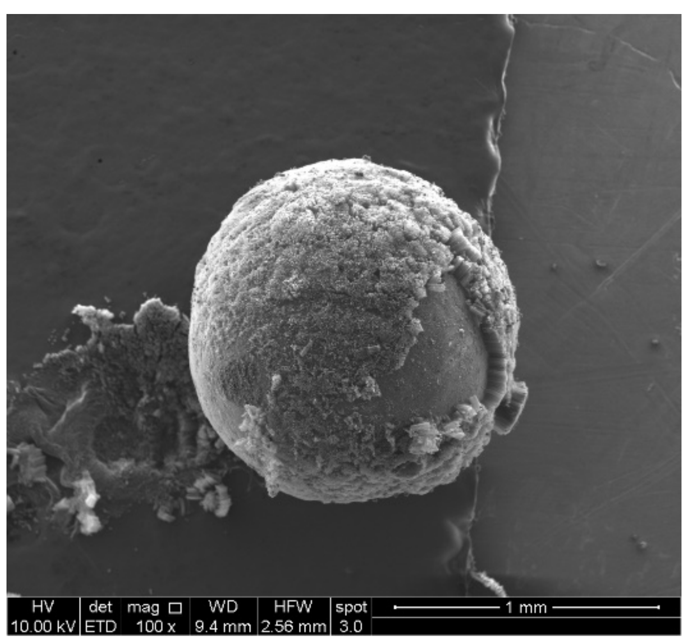


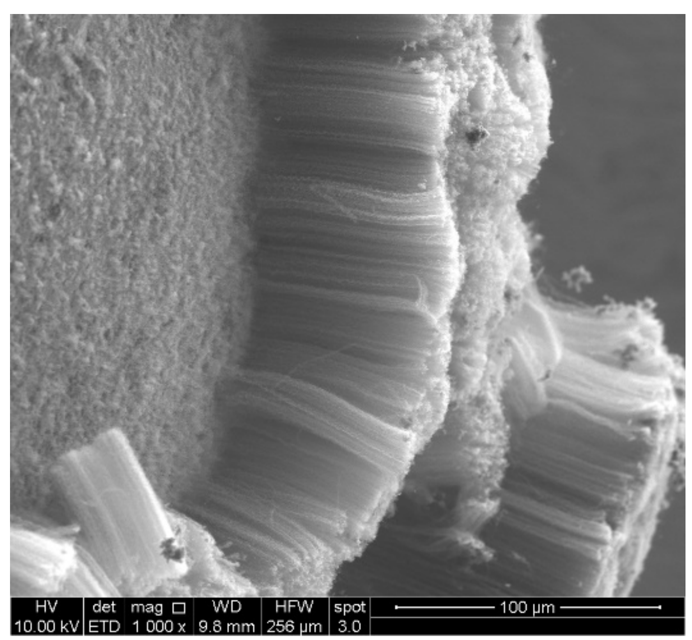


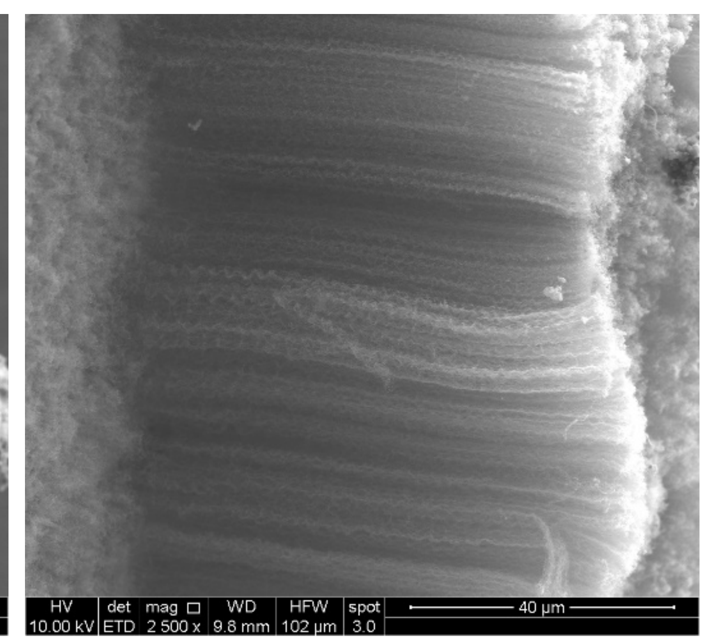


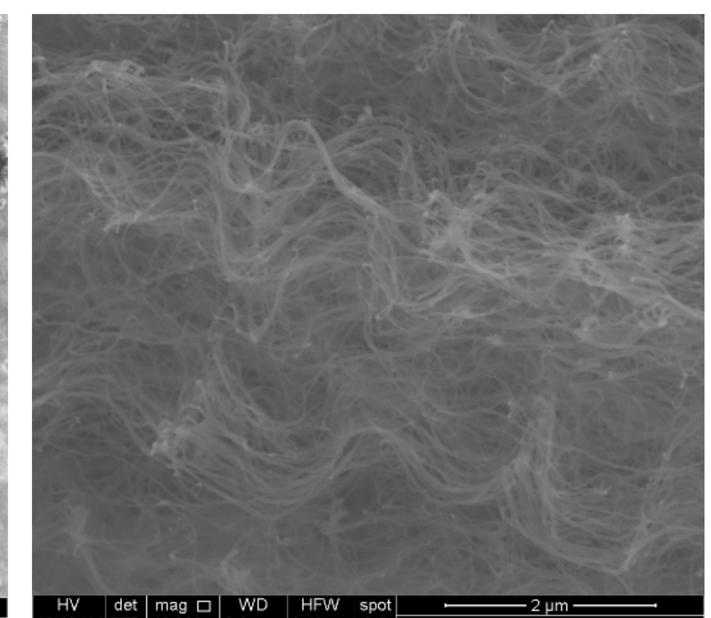


Sample **with** 500 ppm H2O

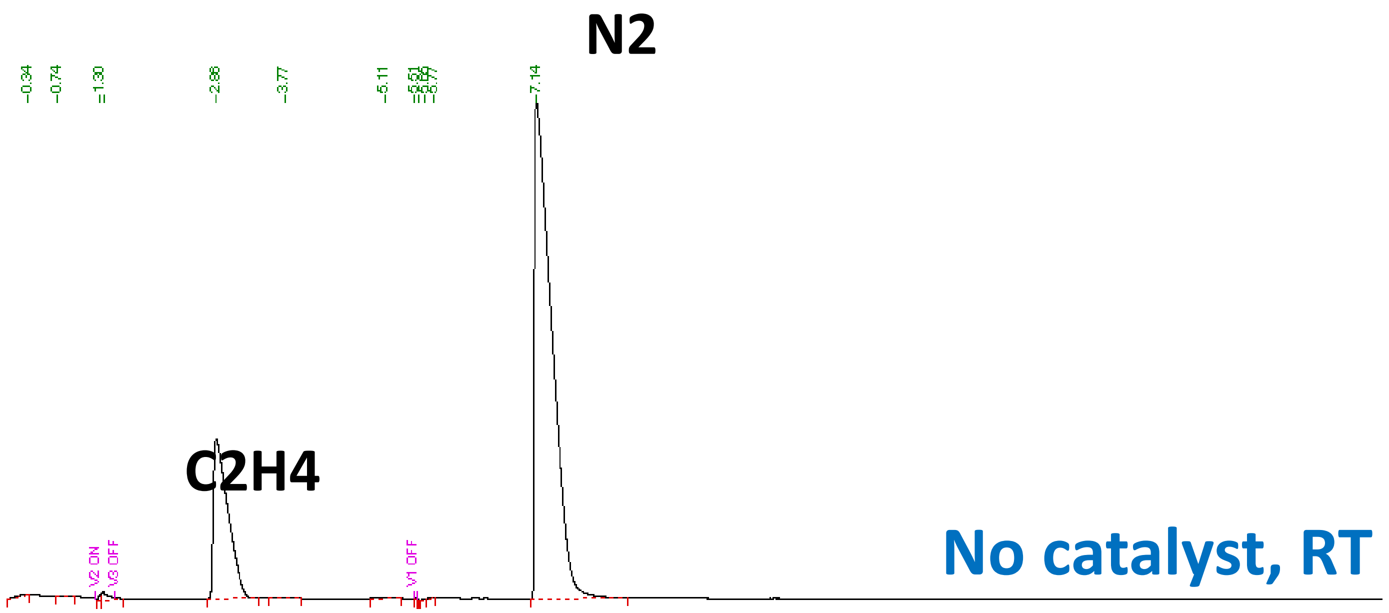


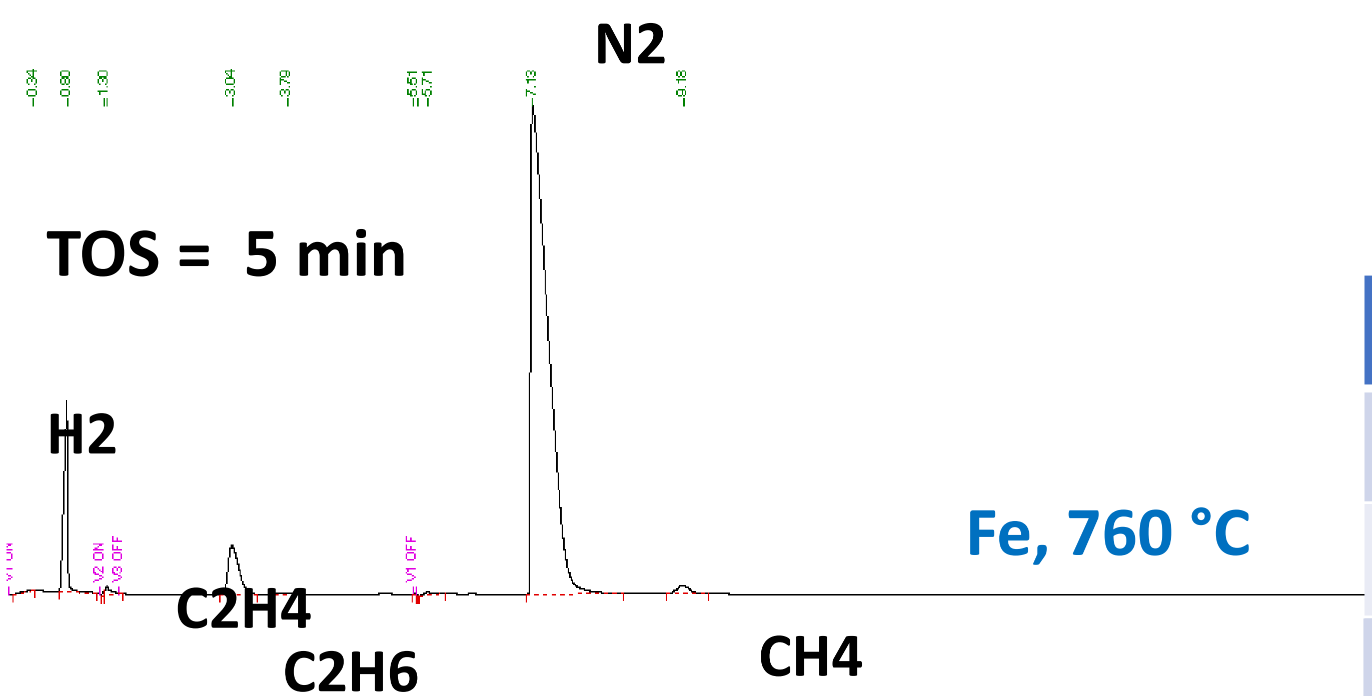


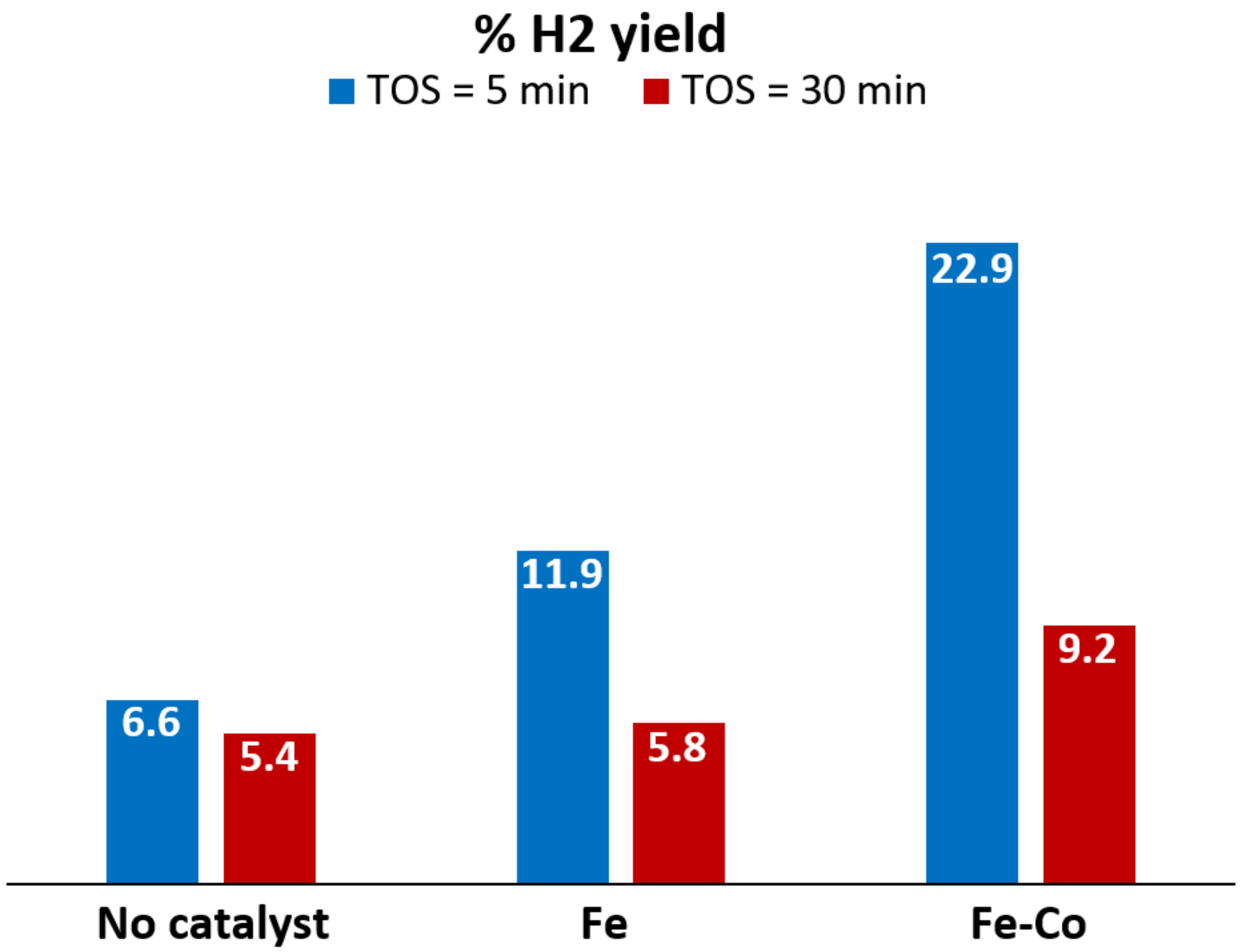




Hydrogen Production During Ethylene Decomposition

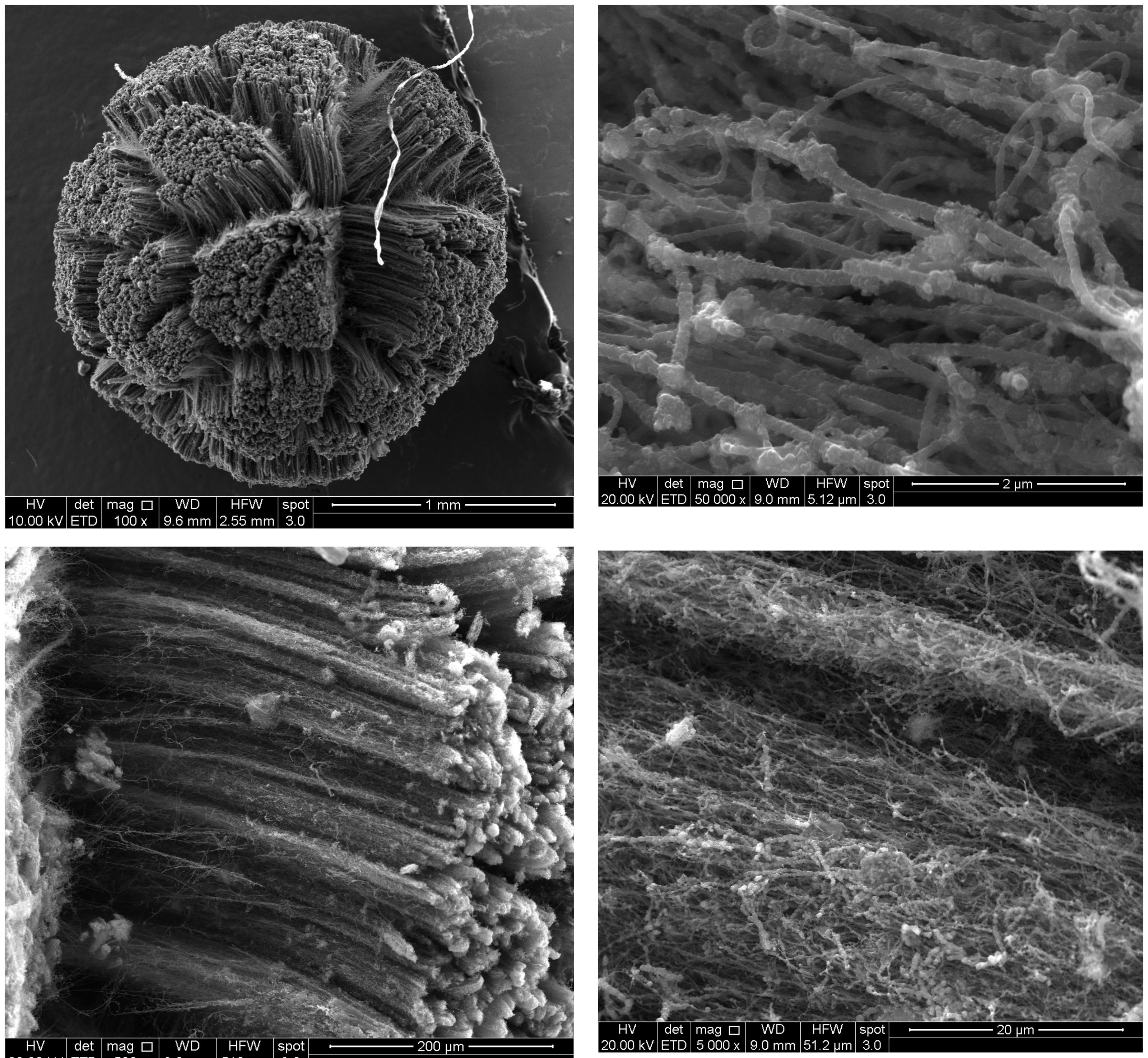






Catalyst	H2 formation rate (μmol/gcat/h)	
	TOS = 5 min	TOS = 30 min
Fe	2643	1283
Fe-Co	5178	2086

Ultralong CNTs from Natural Gas & Ferrocene feedstocks



- Ferrocene is well known feedstock for ultralong CNT growth
- Co feeds of Ethylene & Ferrocene attempted to increase length of CNTs
- Length improves to : ~500 micron
- Hydrogen production is poor during these runs, so approach was abandoned

Accomplishments and Progress

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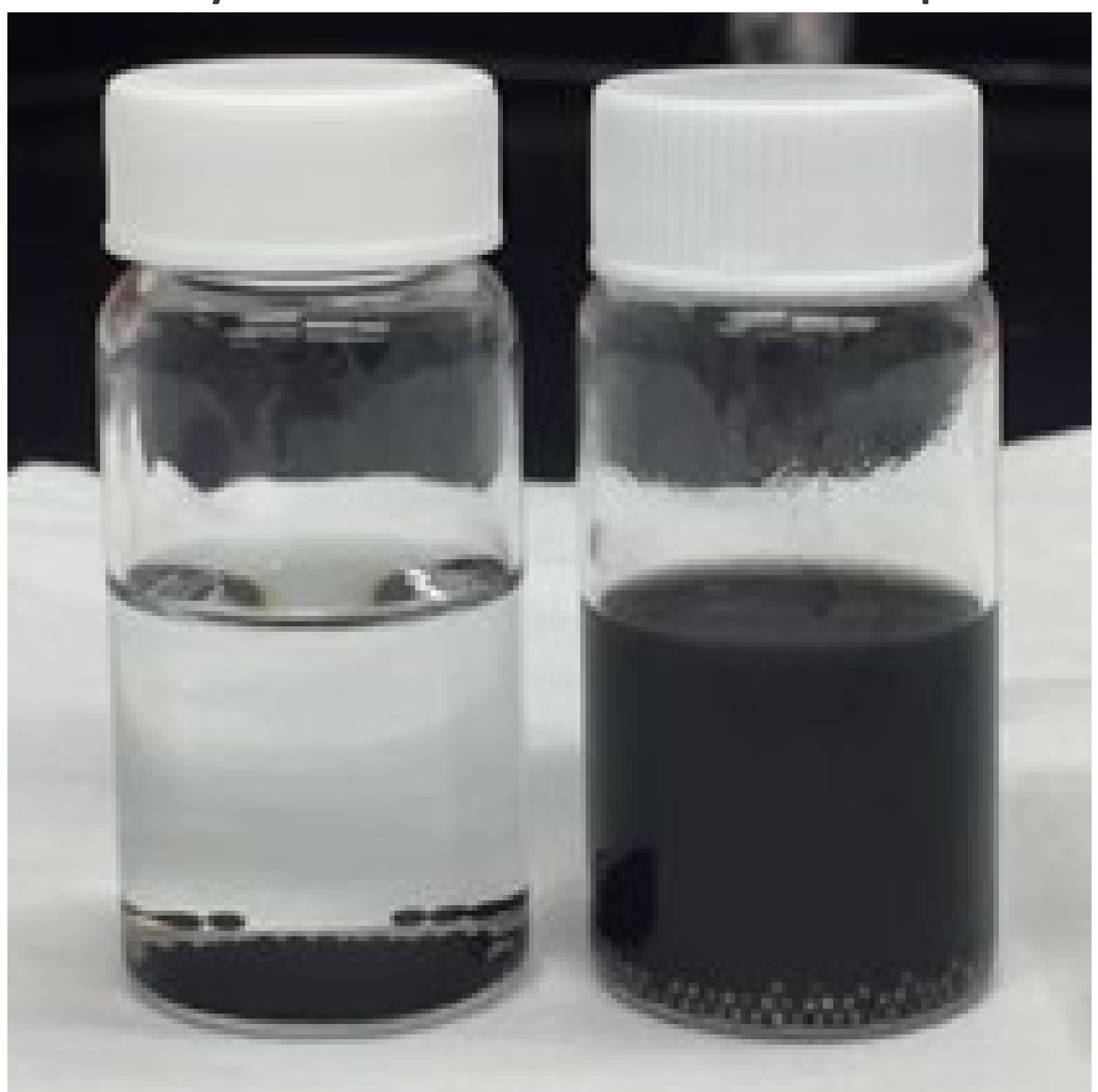
Separation of Vertically Aligned Carbon Nanotubes from Catalyst & Support

Carbon Coated Catalysts In Ethanol

After Sonication Step



Close Up After Sonication

Collaboration & Coordination

Technology Transfer Activities

- DOE Technology commercialization fund Level 1 Proposal awarded for 2018 (Siriwardane)
- Goal: To commercialize the NETL developed technology for production of carbon and hydrogen from natural gas with near-zero air pollutants
    - NETL has submitted two U.S. patent applications for catalyst development for methane decomposition to obtain H2 and carbon
- Status: Collaborative work progressing successfully

Collaboration & Coordination

NETL's University Coalition for Fossil Energy Research (UCFER)

NETL - Penn State

University Coalition for Fossil Energy Research

NETL's UCFER facilitates basic & applied research thru direct collaboration with NETL researchers

Two Project Starts, Dec 2018:

- "Optimization of Microwave-Driven, Plasma-Assisted Conversion of Methane to Hydrogen and Graphene" Prof. Randy Vander Wal, Penn State Univ.
- "Autothermal Methane Decomposition for Large-scale Co-production of CO2-free H2 and Self-aligned Carbon Nanotubes" Prof Hanjing Tian West Virginia Univ.

Two Additional Projects Expected in FY 2019

UCFER Director:

Dr. Chunshan Song, PennState
ucfer-director@ems.psu.edu

DOE Contacts:

Omer Bakshi, NETL
Dr. Madhava Syamlal, NETL

Future Work

- Long term performance testing durability of catalysts in fluidized beds

- Optimize the H_2 product stream
  - Trace methane/NG is present in the product gas stream
  - By-products can be minimized in catalysts step & removed downstream, but will add process costs

- Systems analysis and scaling up the technology (paper study) to obtain a commercial level process

Summary

- NETL developed catalysts & chemical process technologies efficiently decompose natural gas to form H_2 and Solid Carbon.
- Catalyst use low cost, earth abundant, materials and a low cost preparation method for easy scaling
- High NG conversion and high H_2 yields observed for 60 hours of testing
- Carbon product easily removed from catalyst supports by sifting and/or sonication
- Production of valuable carbon products - graphitic carbon, carbon fibers and carbon nanotubes