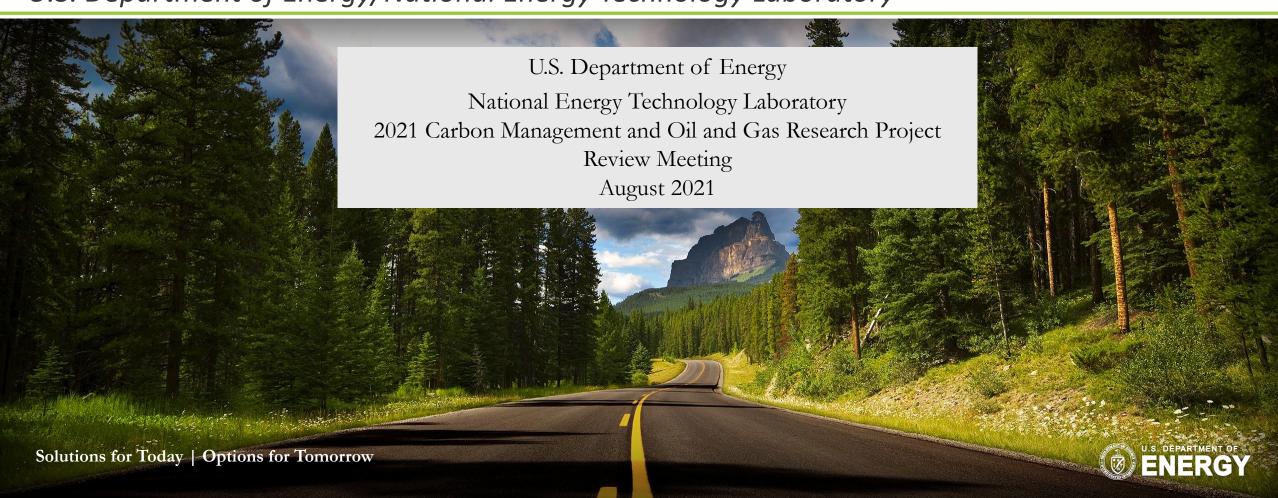
Production of hydrogen and carbon from catalytic flare gas pyrolysis- FWP-1022467

NATIONAL ENERGY TECHNOLOGY LABORATORY

Ranjani Siriwardane

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



Presentation Outline



- Technical approach and status
- Accomplishments
- Lessons learned
- Synergy opportunities
- Project Summary

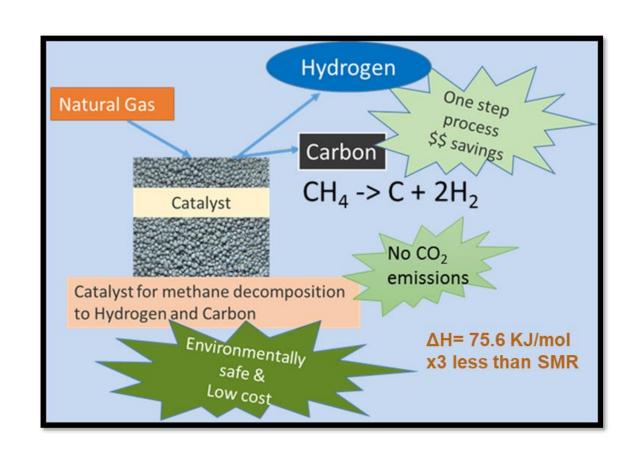


Technical Status

Concept - Catalytic methane pyrolysis (CMP)



- Catalyst decomposes methane to H₂ and carbon
- One step process to produce H₂ and carbon from natural gas
- Two valuable products H₂ and carbon
- Operates at 650-750°C
- Mildly endothermic
- Capable of converting flare gas/natural gas into transportable, value-added products.
- Represent an economical path for decarbonizing flare gas.

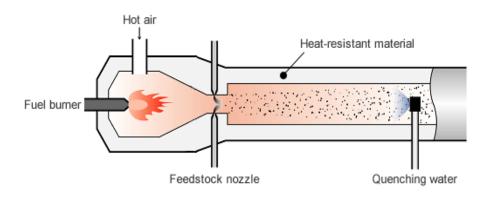


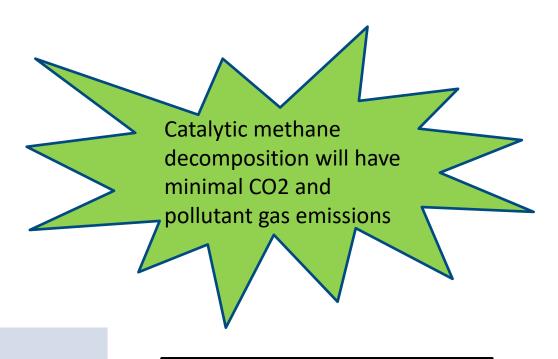


Pros cons & costs associated with conventional approaches for carbon production



Current commercial carbon productionfurnace black method 1300 ^oC (ASAHI Carbon co. ltd.)





- 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.

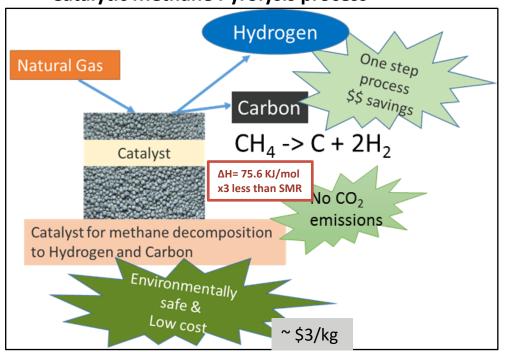
 Current carbon nano fibers and nano tube production methods are expensive, energy intensive and contribute to CO2 emissions



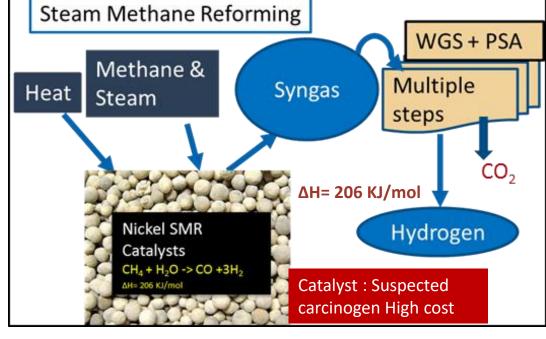
Technical Approach & Status

Advantages of H₂ production from catalytic methane pyrolysis (CMP) vs. steam methane reforming (SMR)

Catalytic Methane Pyrolysis process













Major challenge for CMP is the catalyst development!



Technical Approach & Status

R & D Approach

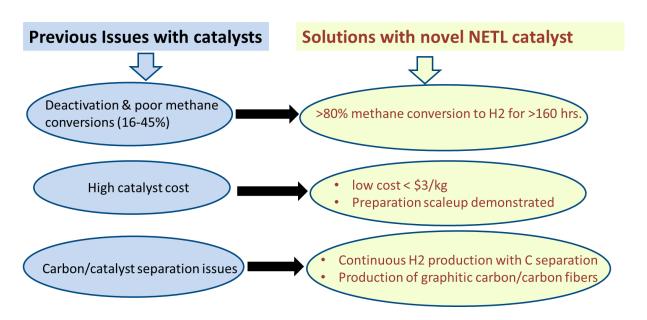


- NETL has developed a very promising novel catalyst (patent pending) for methane pyrolysis
- We have been working under a CRADA with an industrial partner (Birla carbon) who is interested in carbon. CRADA work is continuing.
- Apply the catalytic pyrolysis process for flare gas upgrading
 - Preliminary systems analysis
 - Long term performance with continuous carbon collection
 - Understand the effects of flare gas components on the performance and define strategies to address them
 - Parametric studies to optimize the performance
 - Conduct an in-depth large-scale cost evaluation of the process for operation in a remote site
 - Reactor scaleup using CFD models and pilot scale operation with an industrial partner for commercialization



Research Highlights-Solutions with NETL developed novel patent pending catalyst to major issues with prior catalysts





Recent Research Highlights

- Preliminary systems assessments suggest significant advantages over SMR for H2 production
- Catalyst optimization completed with respect to 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
- Fluid bed test with 75-180 μ catalyst
 - Showed >80% methane conversion to H2 and carbon at 700 °C for 160 hrs. – still continuing
 - Significant accomplishment not reported before
 - Carbon containing fines were continuously collected in the filters
- Evaluated effect of ethane on methane pyrolysis
 - TGA data showed higher ethane decomposition rates
 - Fluid bed data showed positive effect with 100% ethane conversion



Accomplishments - Technical Approach & Status Benefits based on preliminary systems analysis with natural gas

NATIONAL ENERGY TECHNOLOGY TORY

- 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

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.

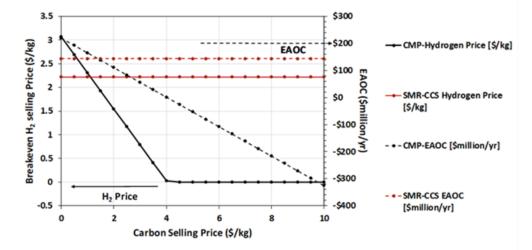
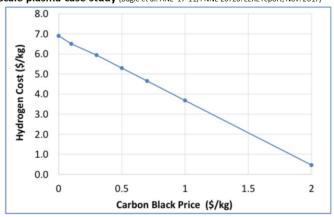


Table ES.1. Market Analysis for Potential Carbon Products (K = thousand, M = million, MT = metric ton) (Dagle et al. ANL-17-11/PNNL-26726. EERE report, Nov. 2017)

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 • ~ 2M MT (2017)	U.S. market • 0.67M MT
			Global market • 12M MT (2014) • 16.4M MT (2022)	Global market • 4M MT (2014) • 5.4M MT (2022)
Graphite [4]	Lithium-ion batteries	\$10+/kg	Global market • 80K MT (2015) • 250K MT (2020)	Global market • 27K MT (2015) • 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 • 70K MT (2016) • 100K MT (2020)	Global market • 23.3K MT (2016) • 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 • 5K MT (2014) • 20K MT (2022)	Global market • 1.7K MT (2014) • 6.7K MT (2022)
Needle coke [10]	Graphite electrodes for electric arc steel furnaces	~\$1.5/kg	Global market • ~1.5M MT (2014)	Global market • ~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 net hydrogen cost for the small-scale plasma case study (Dagle et al. ANL-17-11/PNNL-26726. EERE report, Nov. 2017)



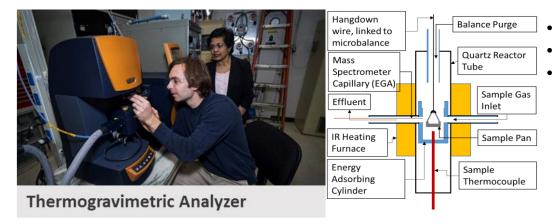


Facilities



Catalyst preparation facility
- Prepares Kg quantities





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

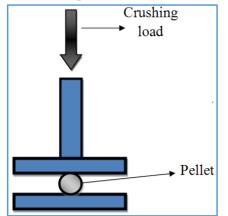
In-Situ XRD-Identification of graphitic carbon

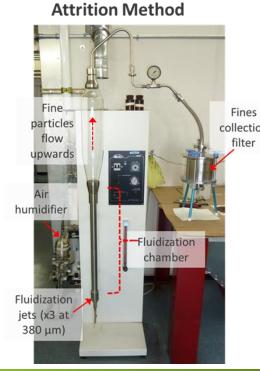


NETL Raman Spectrometer

Identify nano carbon structures

Crush strength measurements





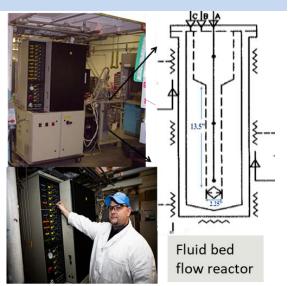
ASTM 5757-11

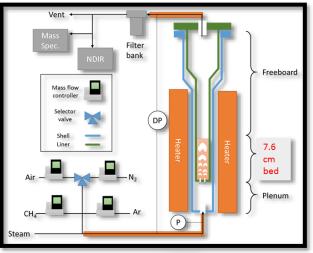


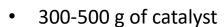
Facilities



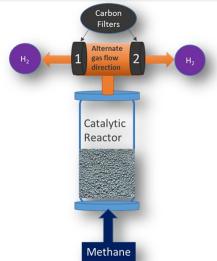
Fluidized Bed Flow Reactor







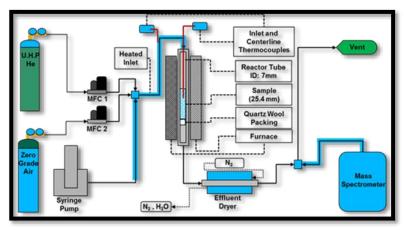
- Operate at 1.5-3x Umf
- Continuous operation with collecting carbon in dual filters switching effluent gas flow direction



Fixed Bed Flow Reactor



- 8-10 g of catalysts (160-600 μ)
- 100 sccm of 15-17 vol.% methane in Helium at 650-750 C
- Measured effluent gas concentrations with mass spectrometer

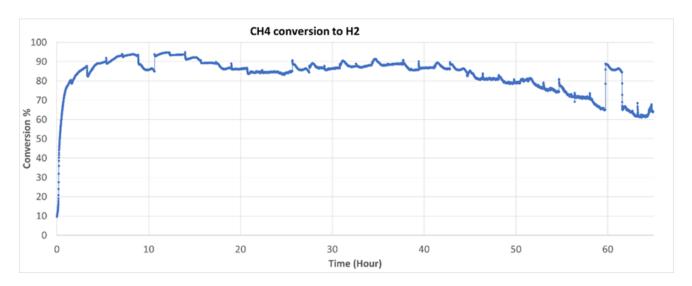




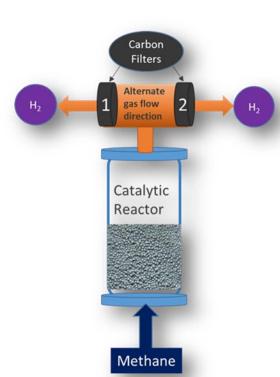
Fluidized bed tests data with NETL catalyst particle size 180-600 μ



Percentage of CH4 conversion to H2 during 65 hr. fluid bed methane pyrolysis test with NETL catalyst (425 g) at 700 °C



- High methane conversion 80-90% to H2 for about 50 hrs. and over 60% for 65 hrs. not reported in literature
- Carbon was collected continuously in the filters during the test
 - Total carbon collected was 600 g

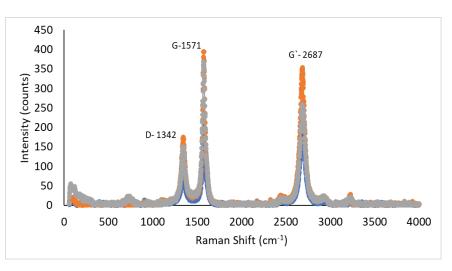




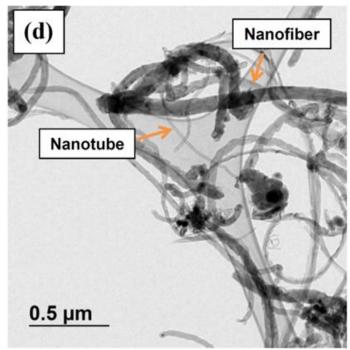
Confirmed Valuable Carbon Formation by various spectroscopic analysis



Raman Spectroscopy



Transmission electron micrographs(TEM)





X-ray diffraction data

Stood

Position[*2theta][Cu]

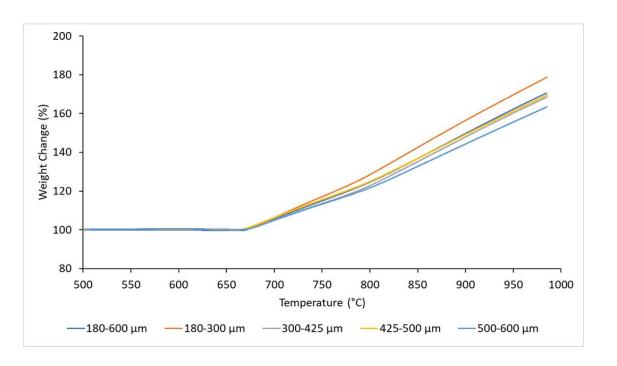
- Carbon containing fines were collected continuously in filters
- XRD identified graphitic carbon
- Raman spectroscopy and TEM identified carbon nano fibers/tubes



Catalyst Particle Size Effect



TGA Data during temperature ramps in methane - catalyst with various particle sizes

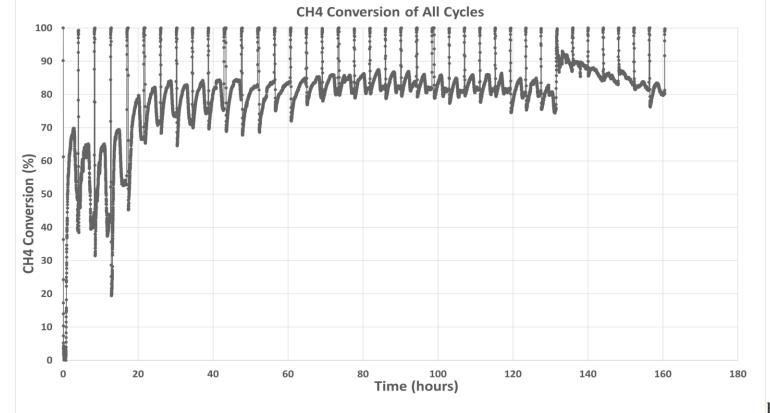


- Rate of methane pyrolysis has some effect on the particle size.
- Particle size <300 μ had better rate
- No change in the 300-500 μ range
- 500-600 μ had a slightly lower rate



Fluidized bed results at 700 $^{\circ}\text{C}$ with NETL catalyst with particle size 75- 180 μ





Major Accomplishment!

- High methane conversion of 80-90% to H2 for about 160 hrs. with 75-180 μ
 - more reaction time than that with 180-600 μ
- Significantly higher than reported in literature.
- Carbon containing fines were collected continuously in the filters during the test

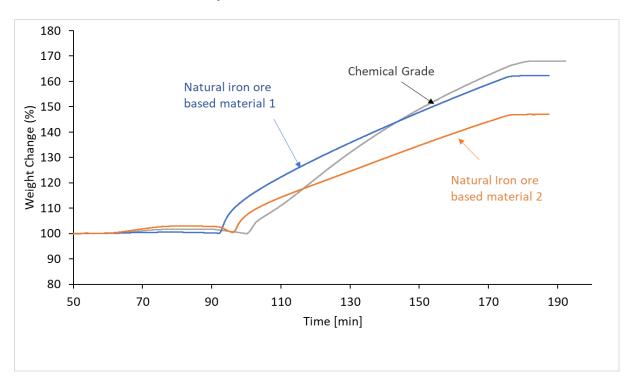
Catalyst	Preparation	Reactor Bed	Catalyst Lifetime	CH ₄ Conversion
Fe/MgO	Impregnation	Fixed	150 minutes	45%
2Ni-1Fe-1Al	Co-precipitation	Fixed	150 hours	40%
Fe/SiO ₂	Impregnation	Fixed	150 minutes	95%
Fe/MgO	Impregnation	Fixed Bed	200 minutes	25%
Fe/Al ₂ O ₃	Fusion Nitrates	Fluidized	6 hours	18%
Ni-Fe-SiO 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%
	0 0			



Effect of raw material purity on reactivity



TGA reactivity data at 700 °C with 10% CH4

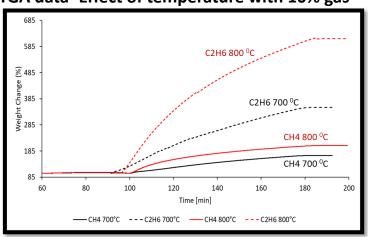


- Chemical grade material has >99% purity
- Mineral grade materials
 - Low purity
 - Low cost ~38 times lower than with chemical grade
- One natural mineral based material had similar performance as chemical grade – Low-cost option
- Some natural grade materials had no activity
- Trace impurities affect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

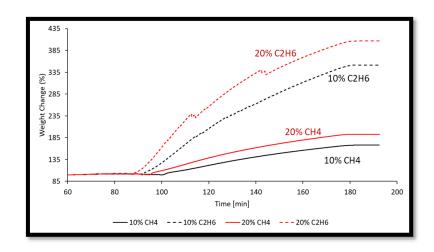


Effect of ethane on methane pyrolysis

TGA data -Effect of temperature with 10% gas



TGA data- Effect of concentration at 700 °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)

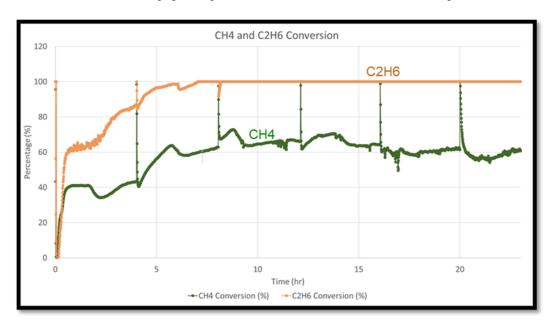
Species	Dissociating Bond ^a	0 K	298.15 K	Uncert.
Methane, CH ₄	H-CH ₃	432.373	438.892	± 0.065
Methyl, CH ₃	H-CH ₂ (to ^{eq} CH ₂)	457.21	463.14	± 0.13
	H-CH ₂ (to ³ CH ₂)	457.21	463.14	± 0.13
	H-CH ₂ (to ¹ CH ₂)	494.87	500.66	± 0.13
Species	Dissociating Bond ^a	0 K	298.15 K	Uncert.
Ethane, CH ₃ CH ₃	H-CH ₂ CH ₃	415.25	421.77	± 0.26
	CH ₃ -CH ₃	367.87	376.66	± 0.19
Ethyl, CH ₃ CH ₂	H-CH ₂ CH ₂	146.08	150.59	± 0.27
	CH ₃ CH-H (to ^{eq} CH ₃ CH)	446.57	452.61	± 0.82
	CH ₃ CH-H (to ³ CH ₃ CH)	446.57	452.59	± 0.82
	CH ₃ CH-H (to ¹ CH ₃ CH)	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



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



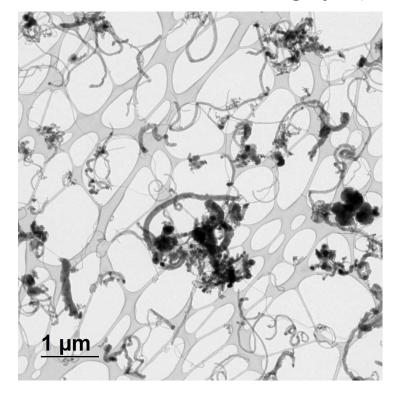
Percentage of CH4 conversion to H2 during fluid bed methane/ethane pyrolysis test with NETL catalyst at 700 °C



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)





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
- Particle size $<300 \mu$ had better performance than that with 300-600 μ
- Fluid bed tests with catalyst 75-180 μ showed >80% methane conversion to H₂ 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 H₂ production in a fluid bed reactor tests
- Ethane (component in flare gas) had a positive effect on the catalytic decomposition performance
 - TGA ethane decomposition rate was faster than that with methane at both 700 °C and 800 °C and the effect was more significant at 800 °C
 - Fluidized bed test conducted with a mixture of methane to ethane (4:1 ratio) showed 100% ethane conversion and 60% methane conversion indicating preference of the catalyst for ethane decomposition.
- Preliminary Systems assessments suggest significant advantages over SMR for H₂ production.



Lessons Learned



Challenges

- Carbon purity
- Catalyst disposal procedures and cost
- Gas separations (e.g., methane and H2) to obtain 100% H2
- Performance evaluation in a prototype reactor with continuous H2 production
- Scale up and commercialization



Synergy Opportunities



- Current industrial partner Birla carbon USA primary interest in carbon products
- Fuel cell company has also expressed interest and NDA in progress for discussions



Next Steps

- Complete evaluation of the process with key flare gas components including propane and trace amounts of CO2
- Optimization of catalyst performance and demonstrate long-term bench scale fluid bed tests with major flare gas components
- Obtain TGA experimental data with flare gas components and complete reaction modeling analysis to determine kinetic rate parameters required for system economic assessment
- Complete system assessment incorporating experimentally verified rate expressions and kinetic parameters. Determine technical/economic feasibility of modular field deployable systems at relevant scale.
- Construct a prototype reactor and demonstrate the technology
- Conduct an in-depth large-scale cost evaluation of the process for operation in a remote site
- Reactor scaleup using CFD models and pilot scale operation with an industrial partner for commercialization





Appendix



Benefits to Program



Program Goal	Potential solutions with the NETL catalytic methane decomposition process
Compactness	High reaction rates (Figure 2-3B), simple one reactor system, and operation with continuous product removal will contribute to a compact design. Proven existing technologies used to create module. Low risk in terms of R&D efforts on reactor design and integration.
Integration	All process steps are integrated to a single process, enabling modularity.
Modularity	Process operation with one reactor system with inlet and outlet gas steams that do not require additional processing should make the components easy to assemble, disable, and transport to multiple locations. Potential for entire integrated process to fit onto field deployable trailer
Operability	Process does not require an external heat source or external power supply for operation. Simplicity of the operation should contribute to minimal operational oversite and minimal intervention at site.
Low Cost	Production of two valuable products, carbon and hydrogen would contribute to significantly lower costs with high profitability better than current commercial processes, as indicated by preliminary systems analysis). Product commodities production cost is estimated to be below market value, enabling high profit margins.



Project Overview Goals and Objectives



- Major objective: Conduct field tests of a fully integrated pilot scale unit to demonstrate NETL patent pending catalytic pyrolysis process for generating H2 and carbon from flare gas
- Specific project goals
 - Evaluate effect of all the components in flare gas including propane and trace amounts of CO2 on the performance
 - Work on effect of ethane on methane pyrolysis has been completed
 - Work on effect of propane and CO2 on methane pyrolysis is in progress
 - Catalyst optimization completed with respect to particle size and low cost raw materials
 - Demonstrate long-term cycle (30 hours) stability on bench scale tests with flare gas to meet the net hydrogen yield target of > 25% defined by EERE as (mol H2 produced-mol H2 used in process)/(2 mol CH4).
 - Obtain TGA kinetic rate parameters of all flare gas components required for TEA
 - Complete system assessment incorporating kinetic data





Organizational Chart

- Key staff at NETL Ranjani Siriwardane (PI), Jarret Riley (Che. Eng.), Chris Atallah (Chem. Eng.), Nicole Kirby (Chem.), Engineering technicians
- Industrial partner: Birla carbon USA
 - CRADA
 - Expertise in carbon analysis, application tests and techno economic analysis
- New industrial partner in fuel cell development work
- NETL systems analysis group- future support in technoeconomic analysis
- NETL CFD team for reactor design and scaleup





Gantt Chart

UNAG Task 2 Production of Hydrogen and Carbon from Catalytic Flare Gas Pyrolysis ★ Go/No Go Milestone Actual (Flexibility) Select a period to highlight at right. A legend describing the charting follows. Period Highlight: Plan Duration Actual Start % Complete EY20 EY21 EY22 EY24 EY23 Q4 Q3 Q3 PERCENT Task **ACTIVITY** PS PD AS AD **PERIODS** COMPLETE 8 10 11 12 13 14 15 16 17 **Baseline System Study** 100% 1 1 1 1 Effect of Flare gas components on CMP Performance 1 6 1 6 50% Reactor Performance Evaluations 1 6 1 6 50% 2.2.1m Milestone (EY21.2.A) 6 1 6 1 50% 2.2.2 TGA Kinetic Studies 1 7 1 7 50% 2.2.2m Rate Parameters of all flare gas compoents 7 1 7 1 30% **Catalyst Optimization** 10% 1 4 1 4 System Assessment 2 8 2 8 0% Go/No Go (EY22.2.B) 0% 9 1 9 1 **Reactor Prototyping** 0% 7 5 7 5 2.5m Shakedown and batch operation (EY23.2.C) 0% 11 1 11 1 **Protoype Continuos Operation** 0% 10 6 10 6 2.6m Go/No Go (EY24.2.D) 15 2 15 2







- R.V. Siriwardane, W. Benincosa, J. Riley, "Novel iron based catalysts for production of carbon and hydrogen from decomposition of methane, Submitted to U.S. patent office, April 2019
- 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
- Publications are restricted due to the corporative research & development agreement (CRADA) with the industrial partner Birla carbon

