Electromagnetic Energy-Assisted Approaches to Convert Fossil Fuels to Low Cost Hydrogen

NETL DE-FOA-0002398

Grant Number: DE-FE-0032061

2023 FECM / NETL Spring R&D Project Review Meeting

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Program Overview

Opportunity: Produce H_2 from fossil fuels without in-situ CO_2 formation

Problem: Thermocatalytic decomposition of CH_4 into H_2 limited by solid carbon formation

- $CH_4(g) \xrightarrow{catalyst} C(s) + 2H_2\ (g)$
- Catalyst deactivation results from excessive carbon deposition

Goal: Prolong the continuous thermocatalytic hydrocarbon conversion process

Solution approach: Use an in-situ electromagnetic (EM) energy-assisted mechanism to regenerate catalysts

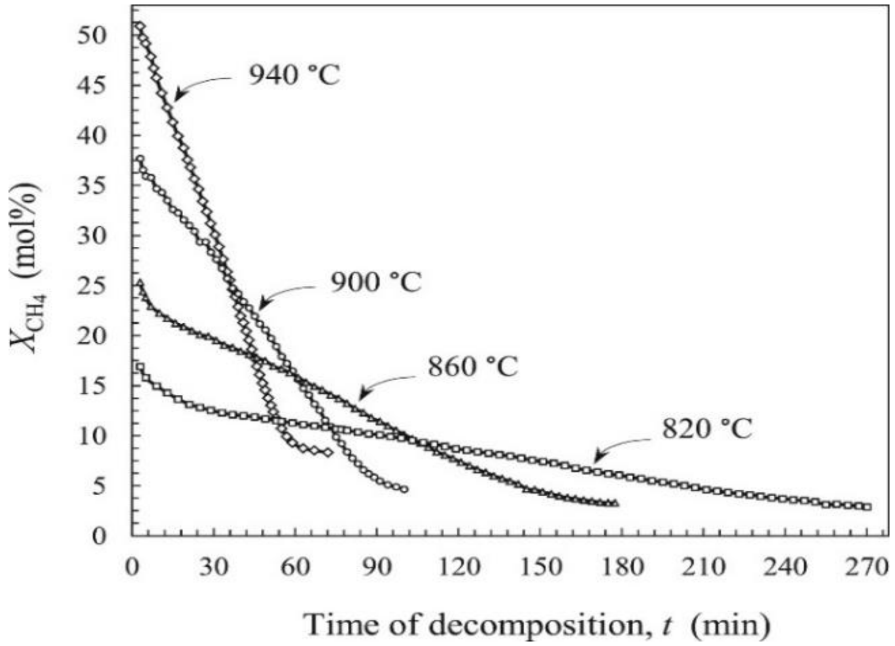
Potential Significance

- Demonstrating use of "alternative energy" in production of H_2 using fossil fuels
- Extend catalyst longevity
- Reduce overall catalyst replenishment cost
- Low-cost, CO_2-free process for H_2 production
- Enable wider adoption of H_2-related technologies from fossil resources
- Applicable to other catalyst-based processes

Background

Thermo-catalytic decomposition of CH_4

- $CH_4(g) \rightarrow C(s) + 2H_2\ (g)$ ΔH_{rxn} = 37 kJ/mol-H_2
  - Electrolysis 285 kJ/mol-H_2
  - Steam methane reforming (SMR) 41 kJ/mol-H_2
- Typically conducted at 500 – 800˚C
  - Typical catalysts include: Transition metals, even C
  - Without catalyst: 1200˚C requirement
- High CH_4 conversion, high C-deposition



Methane decomposition as a function of time (from Al-Hassani *et al.*, 2014)

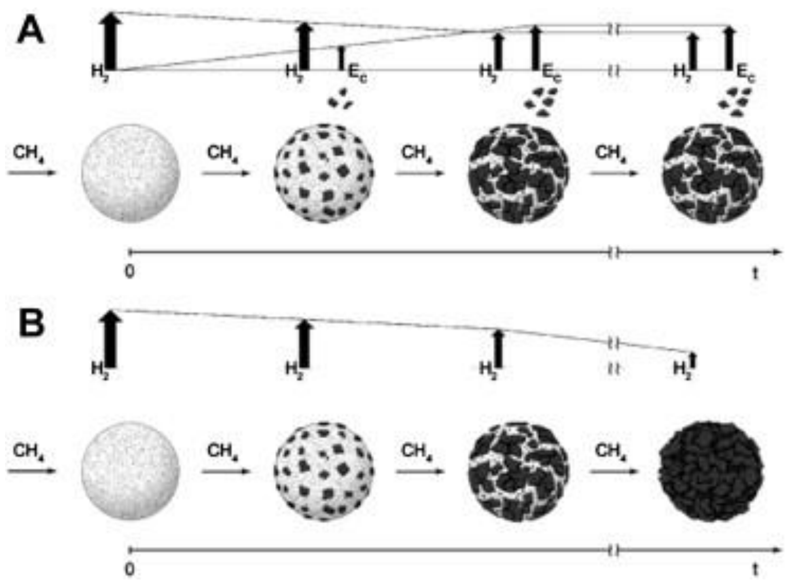
A. A. Al-Hassani, H. F. Abbas, and W. M. A. W. Daud, *Int. J. of Hydrogen Energy* vol. 39, no. 27, pp. 14783-14791, 2014.

Background

Gasification: $C(s) + 2H_2\,(g) \rightarrow$ "$CH_4\,(g)$"

Current "Cleaning" Approaches

- Combust/Gasify carbonaceous deposits or attrit carbon
- Expose metal interface
- *Combustion – CO_2*
- *Gasification – need to decrease H_2 use* (product not reagent)
- Catalyst loss due to attrition
- *Localized & CO_2 free regeneration process essential*



Attrition approach (from Ammendola *et al.*, 2008)

Ammendola, P., Chirone, R., Ruoppolo, G., Russo, G. and Solimene, R., 2008. Some issues in modelling methane catalytic decomposition in fluidized bed reactors. *International journal of hydrogen energy*, *33*(11), pp.2679-2694.

Technical Summary

Task 1: Project Management and Planning

- Subtask 1.1 – Project Management Plan
- Subtask 1.2 – Technology Maturation Plan

Task 2: Catalyst Preparation and Performance Testing

- Subtask 2.1 – Catalyst Preparation
- Subtask 2.2 – Initial High Temperature Catalyst Performance Testing

Task 3: Task 3 – Computational Fluid Dynamics (CFD) Modeling of Conversion System

- Subtask 3.1 – Establish Baseline CFD and Kinetic Model
- Subtask 3.2 – Update CFD and Kinetic Model to Include Effects of the Electromagnetic Energy-Assisted Mechanism

Task 4: Hydrocarbon Conversion Testing using EM Energy-Assisted Thermocatalytic Process

Task 5: Component Identification for Future Work

Task 2: Catalyst Preparation and Performance Testing

Goal

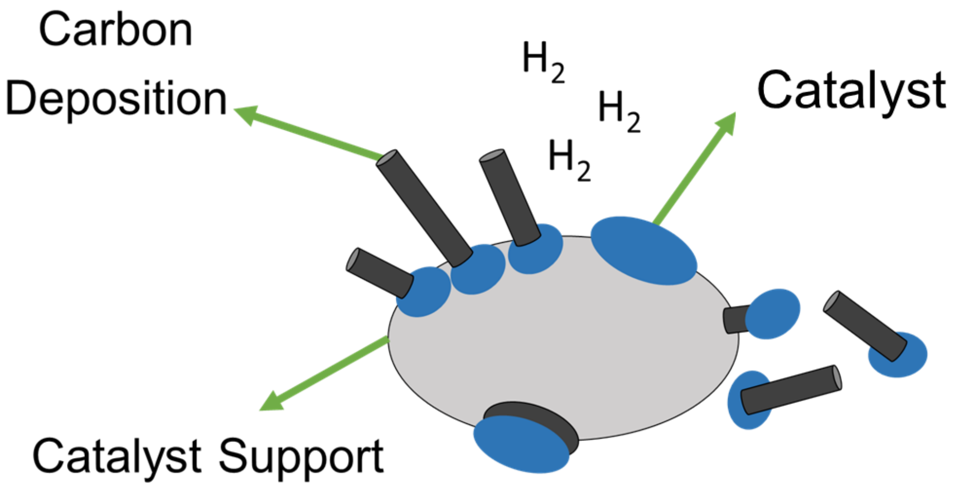
- Identify catalyst/support combinations favoring H_2 production & aligns with EM-Assisted process

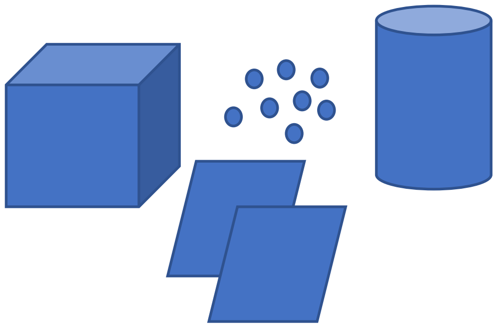
Objective

- Conduct laboratory tests TGA and scaled up systems
- Determine behavior of materials (temperature, gas flow rate, gas composition, structure)

Approach

- Subtask 2.1 – Catalyst Preparation
- Subtask 2.2 – Initial High Temperature Catalyst Performance Testing

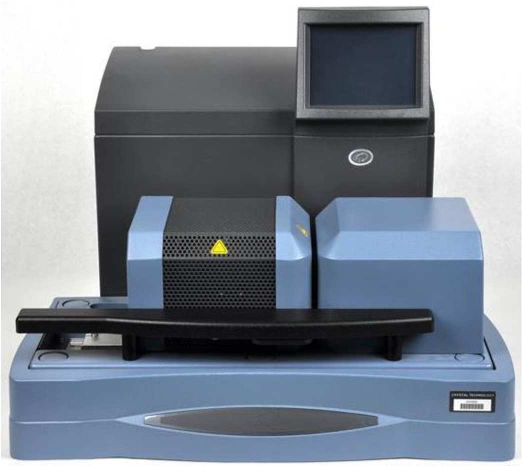




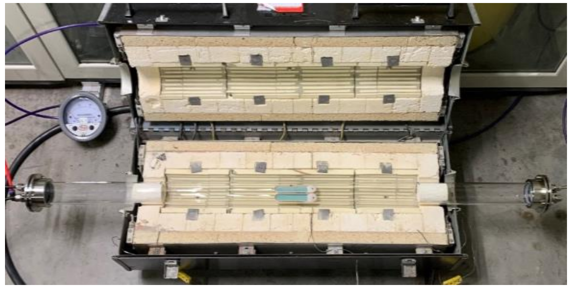
Investigate Catalyst/Support Structures

Task 2: Catalyst Preparation and Performance Testing

- Catalyst/Support structures identified
- Combinations of different supports tested
  - SiO_2, C, Al_2O_3, and Aerogel Supports
- Catalysts
  - Ni, C and Fe
- Identified promising Ni-SiO_2 catalyst
  - Material moldable with binders
  - Binders no effect on catalyst performance
  - Added Cu-promotor – disperses Ni more evenly
- Test conducted using
  - TGA, fixed bed testing and fluidized bed



TGA Tests (TA SDT Q600)



2-inch
tube furnace

Fluidized/Fixed bed testing in 3/8-inch tube reactor

Task 2: Catalyst Preparation and Performance Testing

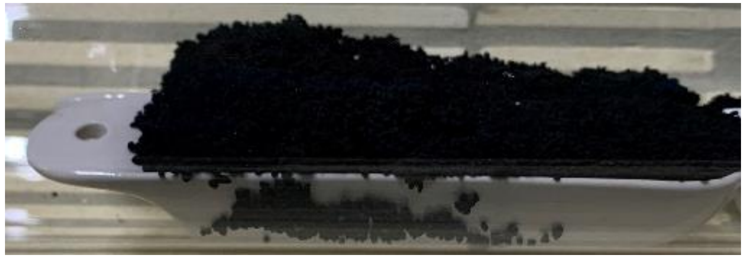
- Kinetics for CFD
- Conduct kinetic study using TGA
  - Eliminate external/bulk diffusion
  - Conduct initial tests – determine optimum flow rate & sample mass
  - 500-650˚C & 30%-50% CH_4 (N_2 balance)
  - Use CFD to develop geometries complementing EM-assisted process
- Result
  - Simple first order rate equation ($r = kP_{CH4}$) suitable for initial decomposition step
  - Pre-exponential factor = 22 mol C/g_{nickel}.min
  - Activation energy = 20 kJ/mol

Pre- and post-test with $Ni\text{-}SiO_2$ catalyst

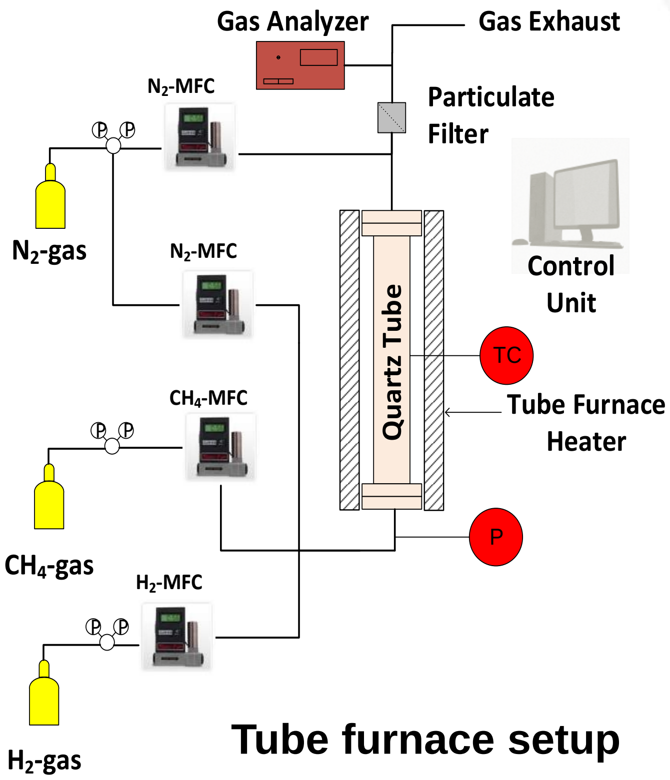
Task 2: Catalyst Preparation and Performance Testing

- TGA testing scaled up to tube furnace
- Tube furnace – easy integration EM Energy-assisted thermocatalytic process
- Just under 70% CH_4 conversion at 650˚C
- Key result - moldable catalyst with suitable performance

Pre-test material



Post-test material with carbon buildup



Tube furnace setup

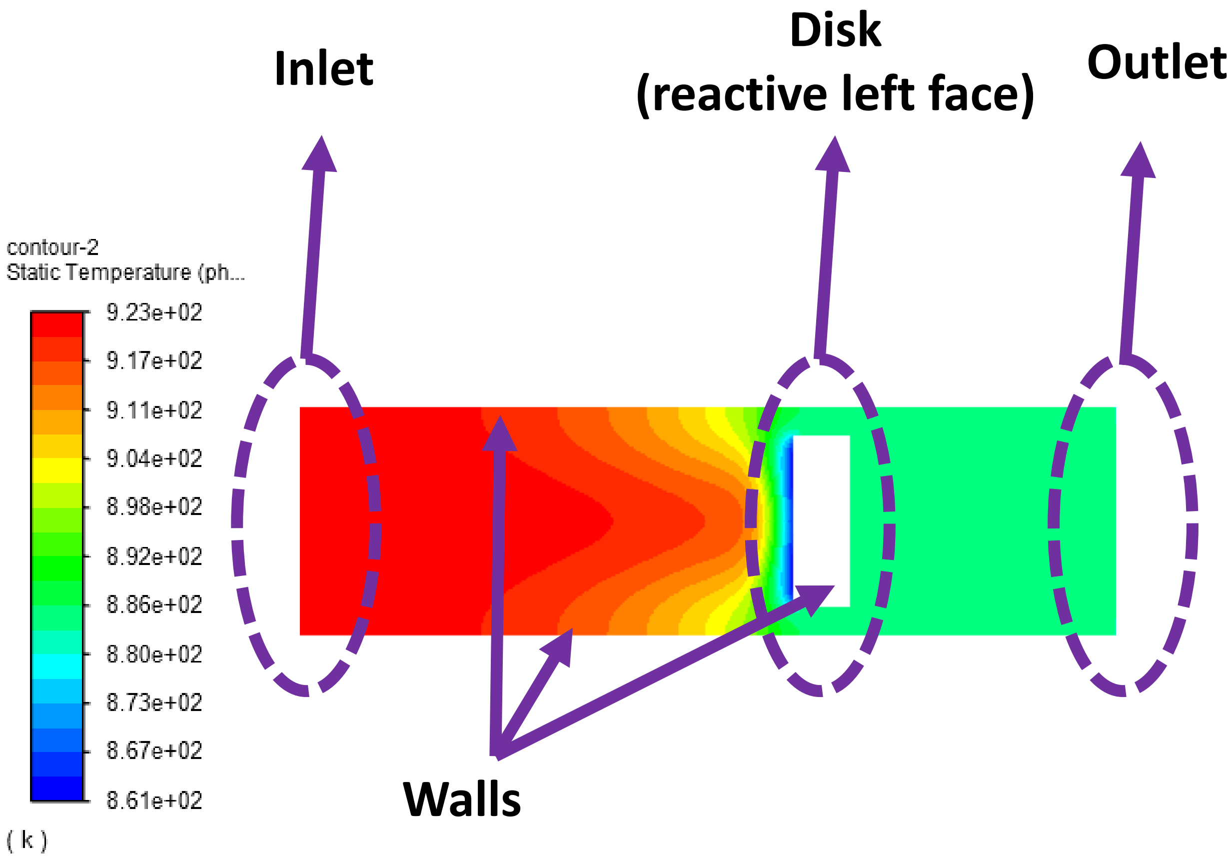
Task 3: Computational Fluid Dynamics (CFD) Modelling of Conversion System

- Goal
  - Model CH_4 decomposition and catalyst regeneration processes
- Objective
  - Use kinetic data from Task 2 and develop CH_4 decomposition model
  - Use catalyst regeneration data from Task 4 and model regeneration process
- Approach
  - Subtask 3.1 – Establish Baseline CFD and Kinetic Model
  - Subtask 3.2 – Update CFD and Kinetic Model to Include Effects of the EM Energy-Assisted Mechanism

Task 3: Computational Fluid Dynamics (CFD) Modelling of Conversion System

Setup (Fluent)

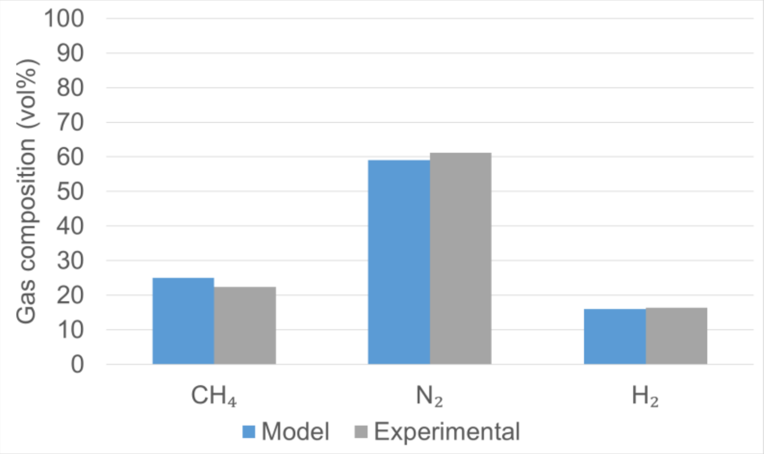
- Model catalyst/support disk perpendicular to gas flow in tube furnace (2-D axisymmetric)
- Operating temperature 650˚C
- Gas composition 33% CH_4 & 67% N_2
- Use kinetics from Task 3
- Temperature decrease on disk's surface – endothermic decomposition



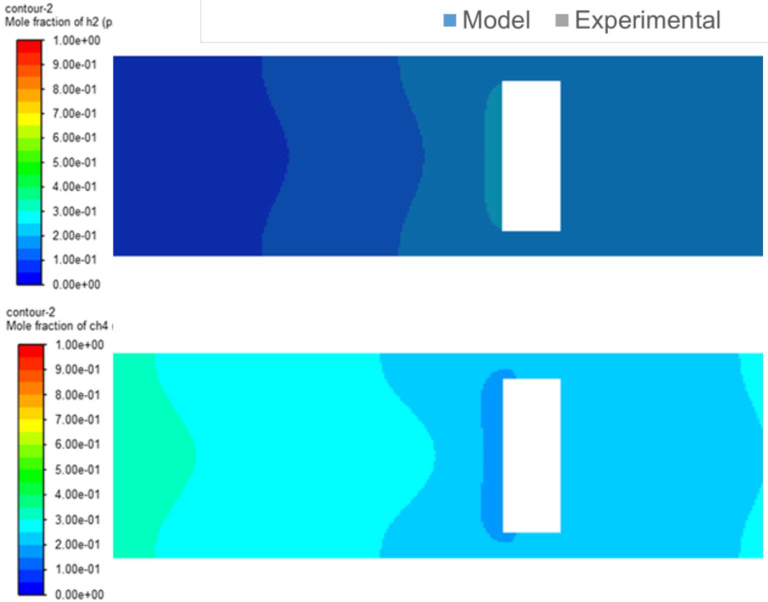
Task 3: Computational Fluid Dynamics (CFD) Modelling of Conversion System

CH_4 decomposition

- CFD model established
- Flow behavior will help assess how to orient EM energy-assisted mechanism
- Future work – use magnetohydrodynamics (MHD) module in Fluent to model EM energy-assisted operation



Post decomposition compositions: Experimental vs. Simulation



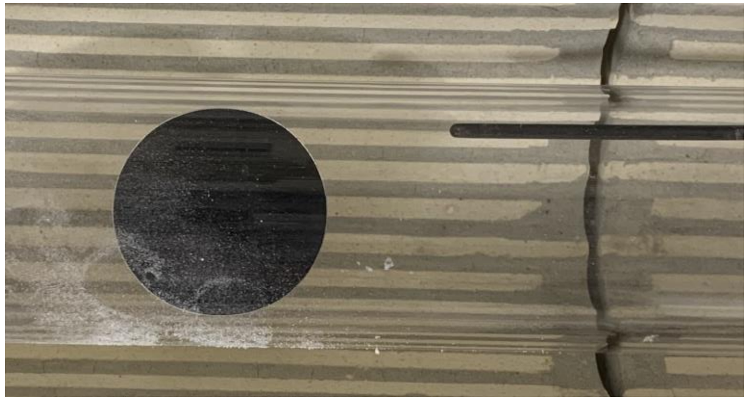
Gas composition in Reactor

Task 4: Hydrocarbon Conversion Testing using EM Energy-Assisted Thermocatalytic Process

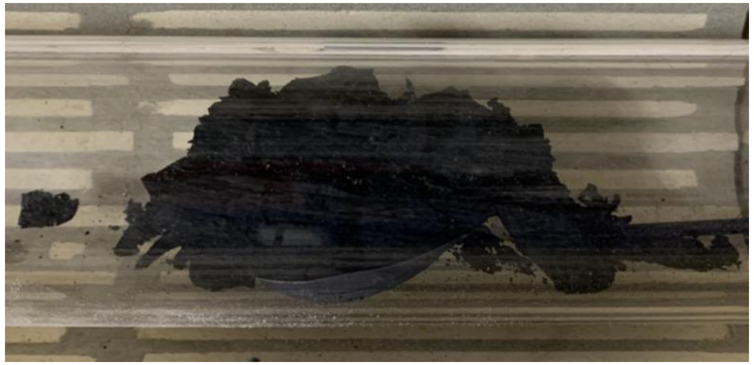
- Goal
  - Evaluate performance of down selected catalyst for EM-assisted testing
- Objectives
  - Conduct **(i)** thermo-catalytic conversion only, **(ii)** conversion at ambient conditions using only EM energy mechanism, and **(iii)** a combination of the two
  - Characterize catalyst test sample before and after tests
- Approach
  - Construct test system using tube furnace as main component – added EM-assisted part
  - Monitor outlet gas composition, analyze catalyst integrity, morphological and chemical changes

Task 4: Hydrocarbon Conversion Testing using EM Energy-Assisted Thermocatalytic Process

- Structured catalyst/support testing
- Initial tests failed (inset images)
  - Aggressive CH_4 decomposition (too long)
  - Refined binding technique
  - Heating protocol in place for slower heating up to set point temperature
- Process refined and latest tests subjected to ~10 minutes of CH_4 decomposition
- Thin layer approach – lines up with CFD and viable C-removal technique



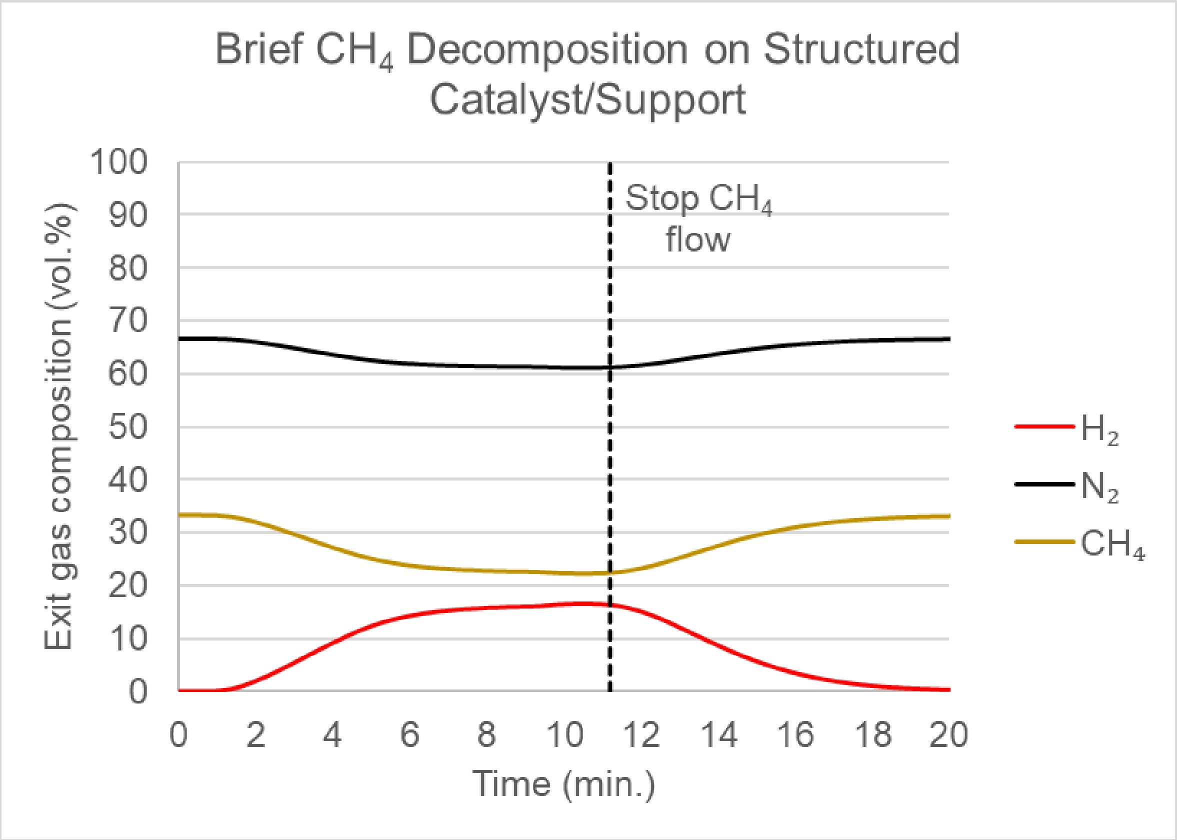
Pre-decomposition structured catalyst/support disk



Post-decomposition structured catalyst/support disk

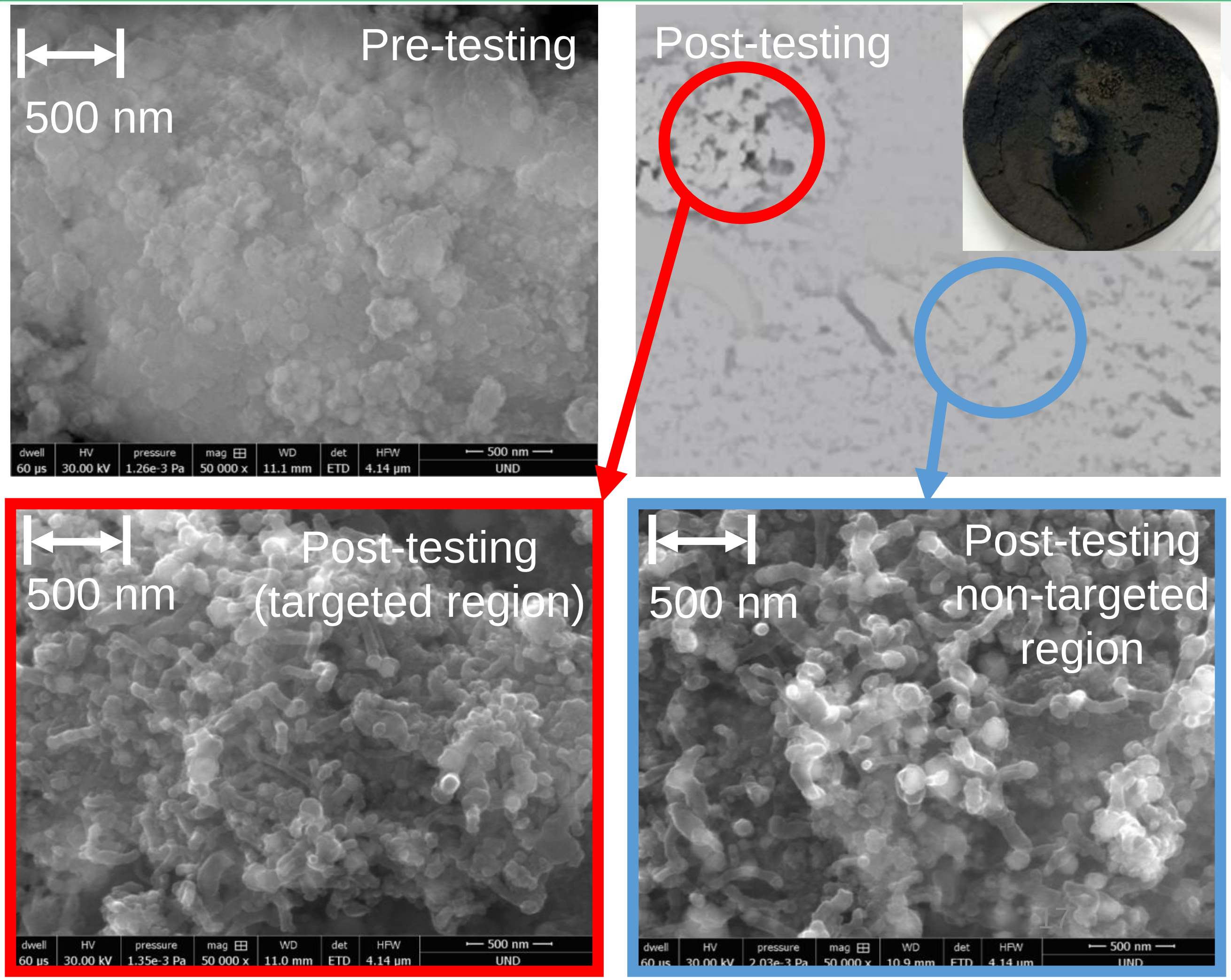
Task 4: Hydrocarbon Conversion Testing using EM Energy-Assisted Thermocatalytic Process

- Structured catalyst/support testing
- CH_4 decomposition at 650˚C
- Tube furnace with 33% CH_4 and 67% N_2
- Short duration test – coat structured surface with thin carbon layer
- Lower CH_4 conversion (~25%) compared to bulk material – this case structured surface
- Follow up with EM energy-assisted mechanism for C-removal



Task 4: Hydrocarbon Conversion Testing using EM Energy-Assisted Thermocatalytic Process

- EM-assisted mechanism tested on structured catalyst
- Ambient testing – no effect
- At 650˚C visible surface changes
- C-based pieces observed in reactor
- SEM-EDX conducted at removal area and non-removal area
- Tubular-shaped C visually detected both cases
- EDX inconclusive (rough surface)
- Follow up: TGA analysis of materials to determine reactivity of targeted/non-targeted regions



Task 5: Component Identification for Future Work

- Goal
  - Assess large-scale thermo-catalytic reactor/ catalyst geometries for prolonged operation
- Objective
  - Identify suitable geometry (using CFD-based kinetics/deposition models)
  - Target regions with greatest deposition probability for the specific geometry
  - Assess impact factors including temperature, entrance/internal geometries
- Approach
  - Use numerical modeling to study the selected geometry in detail.
  - Determine placement/intensity of EM energy-assisted mechanisms to circumvent deposition
  - Study long-term performance of catalysts under varying degrees of blockages

Summary

Task 2

- Identified formable catalyst/support structure for use in CH_4 decomposition
- Material exhibits properties that complement the EM Energy-Assisted Thermocatalytic Process

Task 3

- Developed CFD model for decomposition reaction
- Model can be used to explore different geometries of structured material

Task 4

- EM-assisted effect observed on catalyst/support
- Additional quantification required to assess the outcome of the result

Acknowledgement

- *This material is based upon work supported by The United States Department of Energy, Office of Fossil Energy's University Training and Research for Fossil Energy Applications Program (Project DE-FE000032061)*
  - *Project Manager – Maria Reidpath (DOE/NETL)*
  - *FECM 2023 Organizers*
  - *Kaiser Ahmed Bhuiyan, GRA (UND)*
  - *Dr. Gautham Krishnamoorthy (UND)*
  - *Dr. Srivats Srinivasachar (Envergex LLC)*

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Thank you

Questions?

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