Advanced Reaction Systems

Task 3 – Reaction Intensification: Testing Systems and Enabling Materials

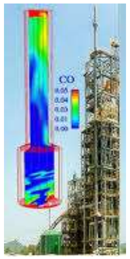
NATIONAL ENERGY TECHNOLOGY LABORATORY

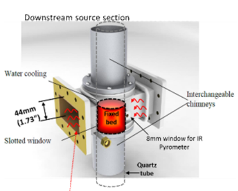
Jonathan W. Lekse

Gasification Annual Meeting, March 20, 2017

Advanced Reaction Systems

Project Overview





Task 1: Project Management

Task 2: Microbial Enhanced Coalbed Systems (MECS)

Task 3: Process and Reaction Intensification

- Microwave enhanced reaction systems
- Non-traditional thermal systems
- Enabling materials and manufacturing technologies
- Oxygen carrier development for chemical looping gasification
- Fischer-Tropsch catalyst synthesis

Task 4: Virtual Reactor Design, Validation, and Optimization

- Basic MFiX code development
- Test system validation with physical experiments
- Optimization toolsets

Task 5: Systems Engineering and Analysis

- Feasibility and baseline study
- Metric development
- Pathway studies

Microwave Reactions for Gasification

Dushyant Shekhawat

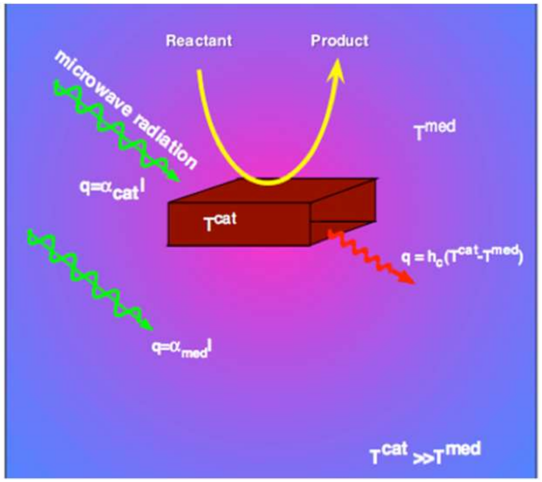
NATIONAL ENERGY TECHNOLOGY LABORATORY

Microwave Reactions for Gasification

Indirect vs. Direct Heating

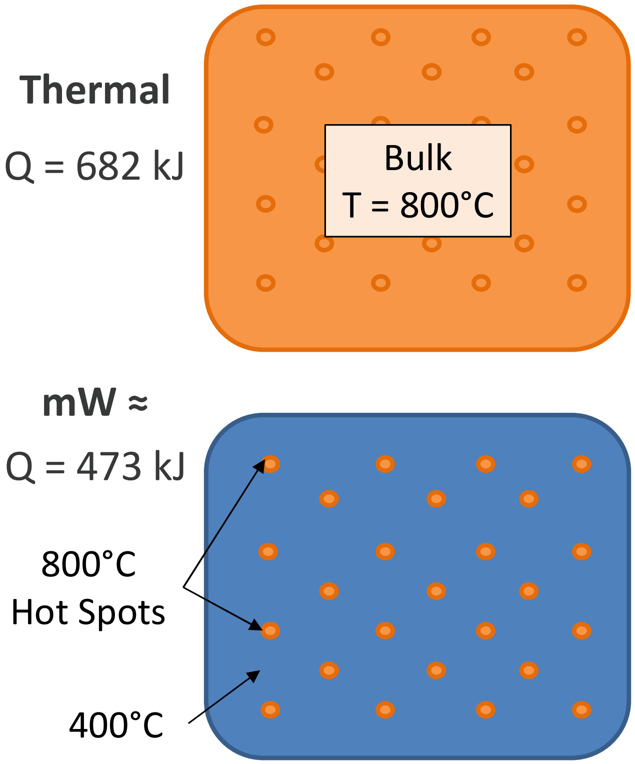
Entire bulk system must be heated, not just reacting species and surface; requires significant heat-up & cool-down times due to indirect heat transfer (lag time); produces lower selectivity

Direct input of energy in non-thermal manner to selectively activate surface sites and reactants shift to more favorable equilibrium conditions and better product selectivity



Microwave Reactions for Gasification

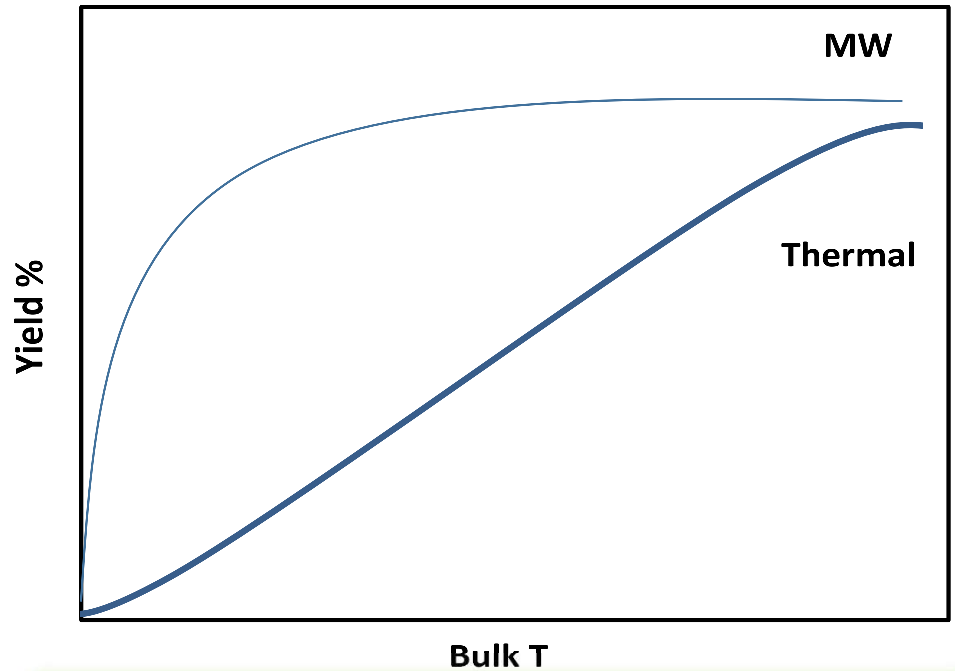
Thermal vs. Microwave Conversion



Assumptions:

C_p = 880 J/kg-K (alumina)
Fluid phase & rxn negligible
Heat losses negligible
Heater Eff ≈ 100%

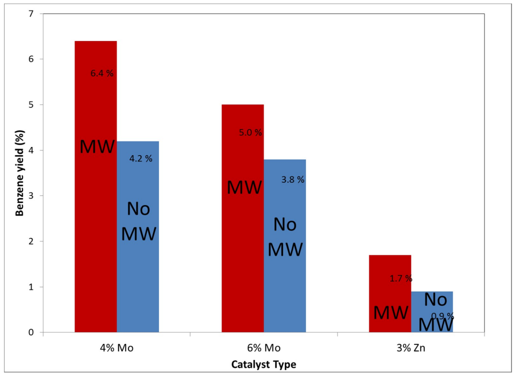
1 wt% Active Phase
Frequency = 2.45 GHz
Reflected power negligible
Magnetron Eff = 70%



MWs allows for *selective heating* of reacting species/sites, which can lower bulk T…can result in higher product yields for rxns that favor lower equilibrium temperatures

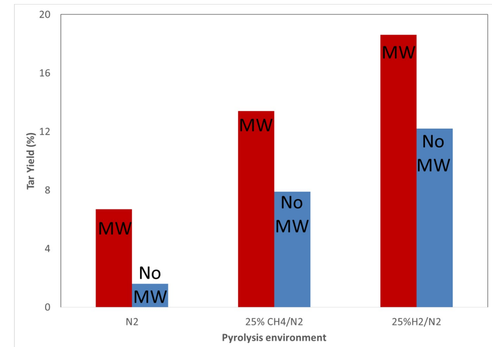
Microwave Reactions for Gasification

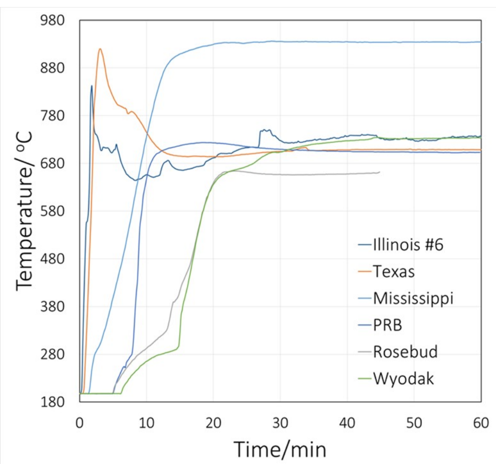
Upgrading in the Presence of Microwaves



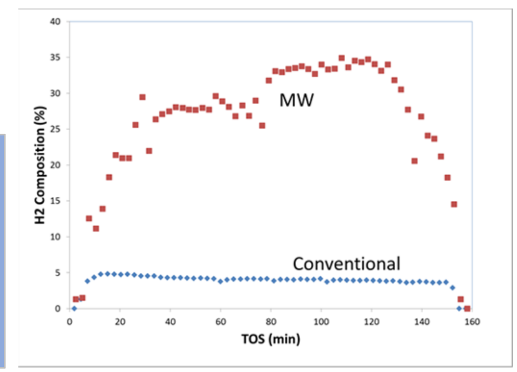
Methane to benzene reaction (700 C): Benzene yield increased significantly in the presence of microwave; Catalyst: 4% Mo, 6% Mo, and 3% Zn supported on HZSM5

Coal pyrolysis in the presence of H2 and CH4 (500C): The product distribution tends to shift to lower molecular weight tars under MW heating





Microwave provides faster fuel conversion rates and different product distribution

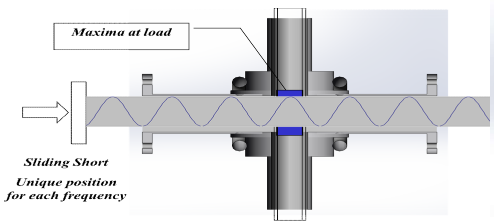


Coal pyrolysis: Low rank coals have relatively faster response in MW; achieved steady state temperatures within seconds.

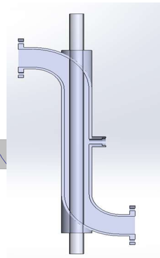
Coal Gasification: MW enhanced the formation of H_2 significantly at low gasification temperature (600 C) and ambient pressure compared to conventional operation

Microwave Reactions for Gasification

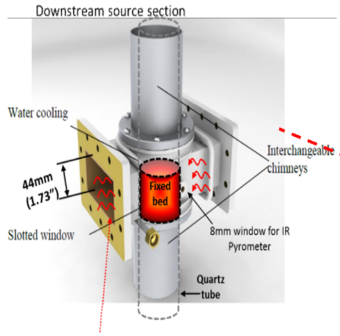
NETL Microwave Capabilities

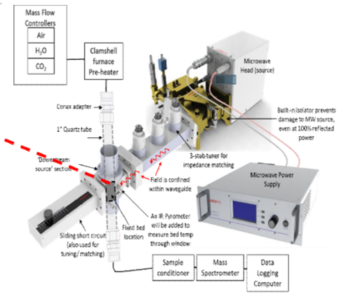


Standing Wave Applicator



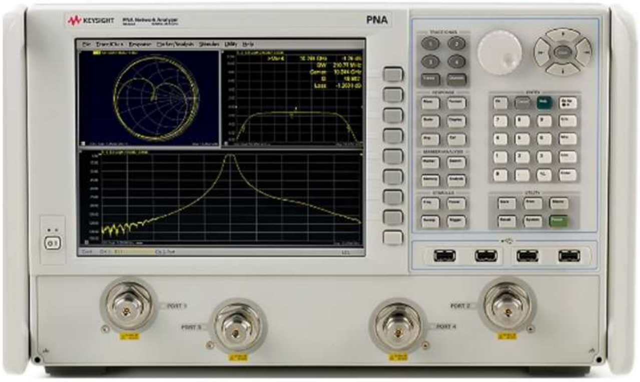
Dual E-Band Applicator





- **Variable frequency MW system**
  - Frequency: 2 to 8 GHz
  - Power: 0 – 0.5 kW
  - Two different applicator configurations: Horizontal and vertical
- **Fixed frequency MW system**
  - Power: 0 - 2kW
  - Frequency: 2.45 GHz

- **Microwave characterization tools**
  - Vector Network Analyzers (Keysight N5231A PNA-L & N5222A PNA)
    - Maximum Frequency: 43.5 GHz
    - Insitu EM response of sample across power and frequency
    - MW sensor hardware verification and tuning
    - To measure electromagnetic (EM) properties of materials
  - Developing a cell to measure the electromagnetic properties up to 1200 C
  - Magnetometry and field dependent electrical transport properties



Non-Traditional Thermal Reactors

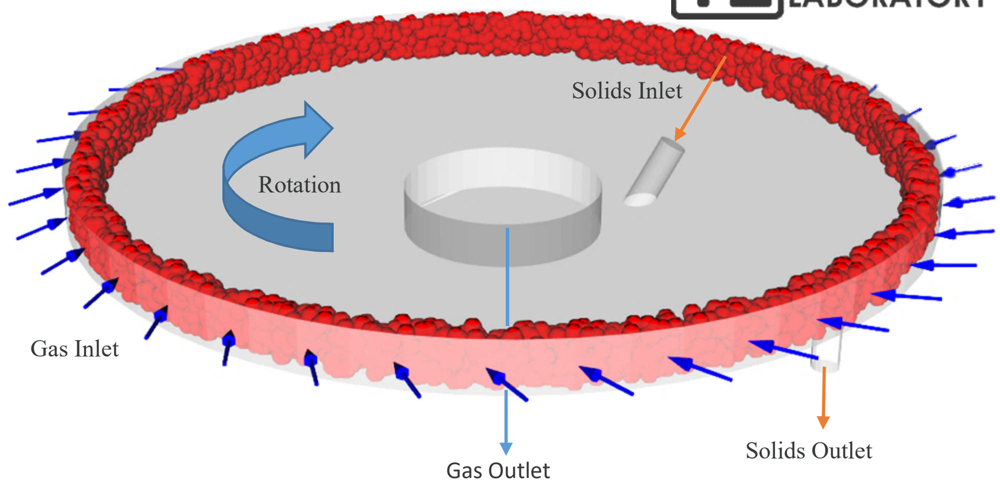
Ronald Breault

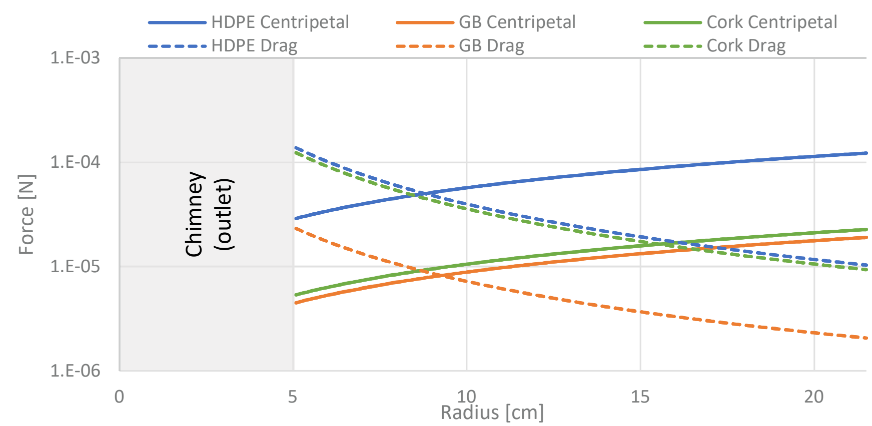
NATIONAL ENERGY TECHNOLOGY LABORATORY

Non-Traditional Thermal Reactors

Rotating Fluid Bed

- **Extremely high gas throughput**
  - Gas-Phase polymerization
  - Drying
  - Catalyst manufacturing
- **Particles experience high Gs (45)**
  - No Bubbles
- **Particle-Particle Separation? Yes!**

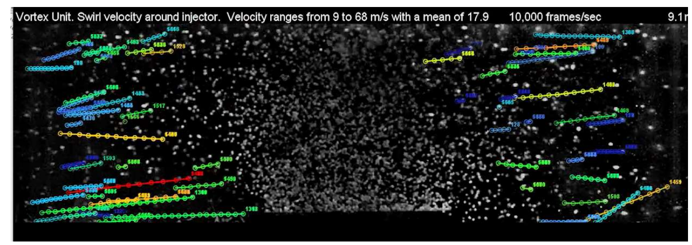


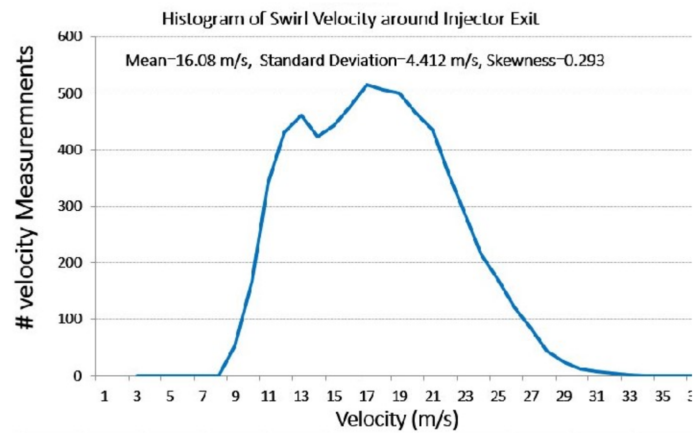


Non-Traditional Thermal Reactors

Vortexing Fluid Bed

- **High gas throughput**
- **Solid Re-Circulation**
- **Huge particle/gas slip ratios**
  - Faster reactions?
- **Currently investigating Hydrodynamics**
  - Particle velocities
  - Pressure distribution



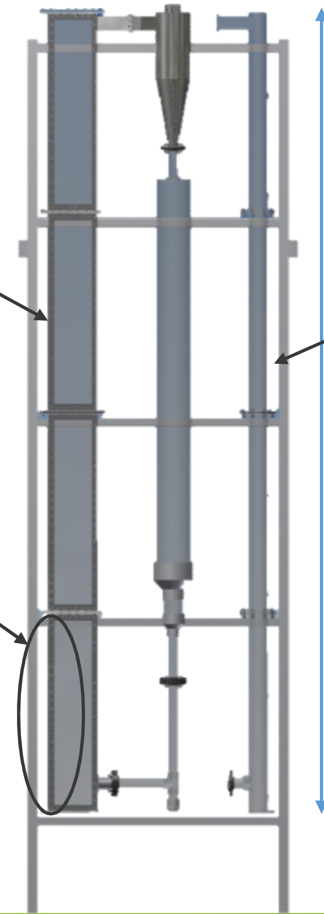


Non-Traditional Thermal Reactors

Riser Cross Section Comparison

4in Round vs. 3in x 12in Rectangular

- **Scale effects**
  - Cluster size/formation
  - L-Valve performance
- **Injector Studies**
- **Starting Shakedown activities**



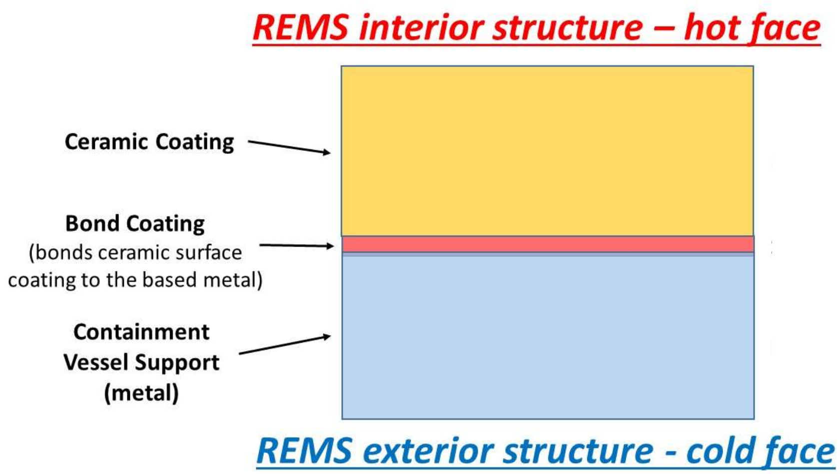
Enabling Materials and Manufacturing Technologies

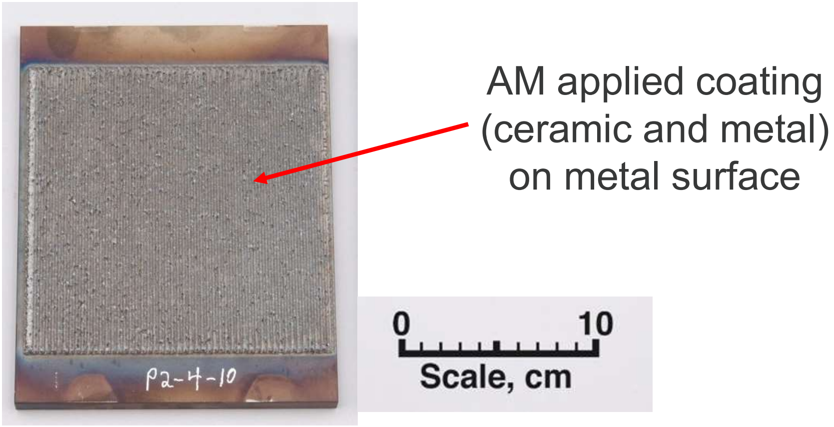
James Bennett

Enabling Materials and Manufacturing

Advanced Material Development

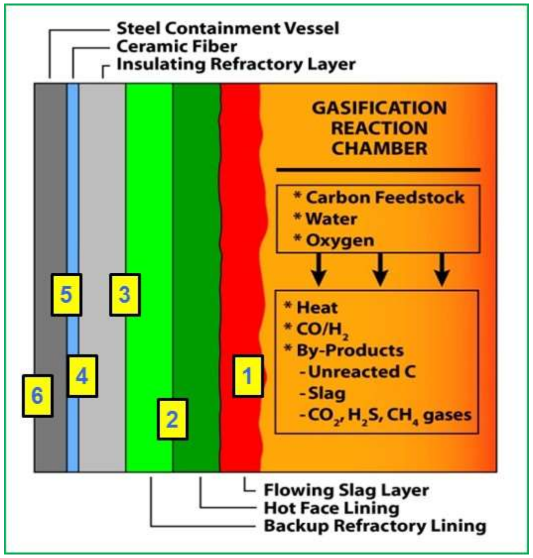
- Identify appropriate materials structure for system evaluation and candidate materials
- Evaluate powder feed Additive Manufacturing as primary manufacturing means; consider conventional and hybrid fabrication technologies
- Evaluating ceramic/metal adherence – *Materials dictate temperature of application, can be a metal/ceramic mismatch of thermal expansion*





Enabling Materials and Manufacturing

Advanced Manufacturing Integration into Modular Processes



Process temperature and system cooling needs will impacts system size

Air cooled slagging gasifier = Refractory temperatures for a given carbon feedstock flow rate and HF brick thickness (9 or 0 in).

In of HF Brick	Temperature (°C) at Location In Gasifier					
	1	2	3	4	5	6
9	1450	929	671	429	257	90
0		1000	718	450	269	90

Key System Variables for Designing a REMS Gasifier

Maximum sizes that can be made by AM, internal gasifier temperature, carbon feedstock flow rates.

- **Factors deciding vessel size are how to cool a structure (air vs water [water needs more infrastructure]), material thicknesses/thermal conductivity, and surface shell temperature.**
- **FHA weight limits for trucks on highways = non permit, 36 tons.**

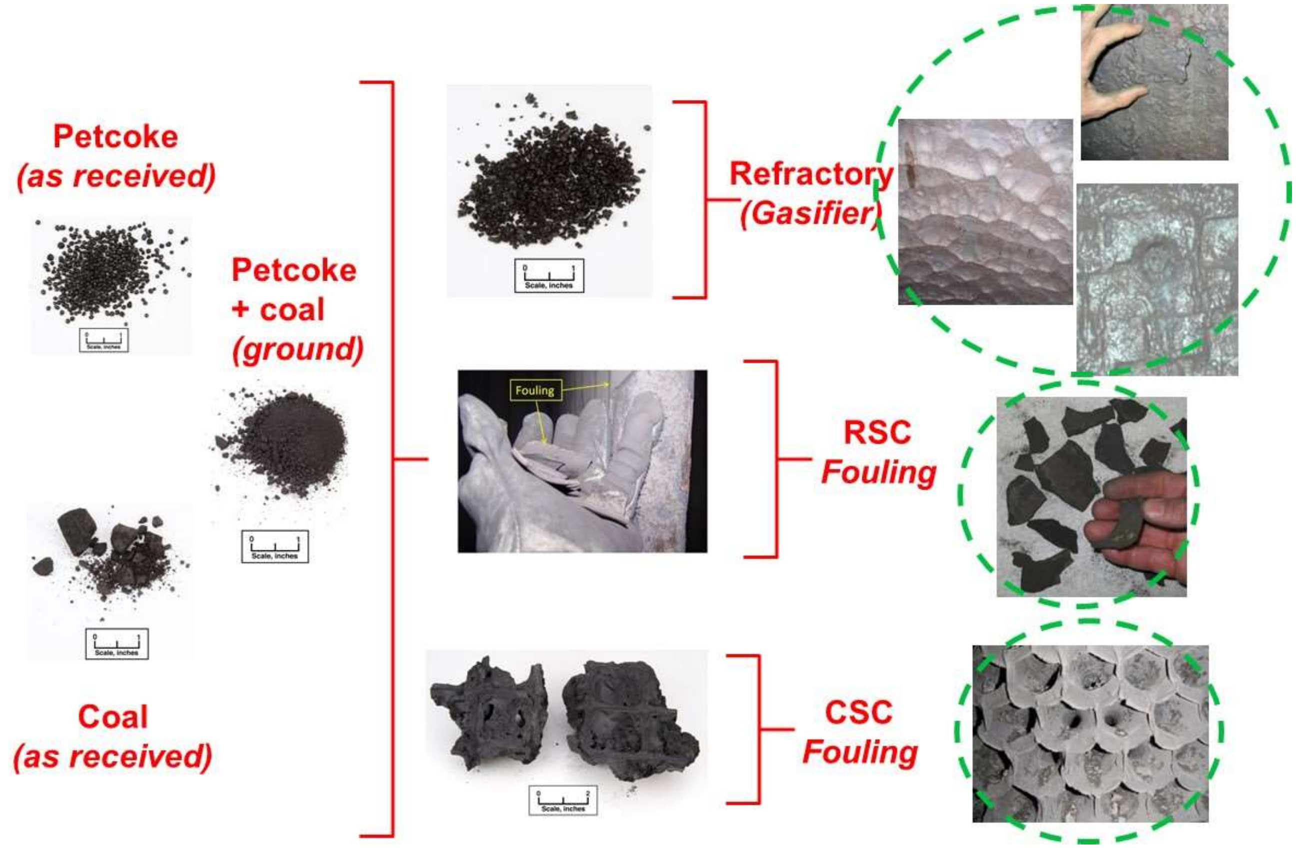
  Air cooled 1450°C slagging gasifier 6 ft dia., outer shell temp. 90°C , 2.5 in steel shell - 1000 psi, 20 ft long, wt is 61.0 tons

  Air cooled 1000°C non-slagging gasifier 6 ft dia., shell temp. 90°C, 0.75 in steel shell - 1 atm, 20 ft long,, wt is 39.1 tons.

Enabling Materials and Manufacturing

Ash Agglomeration

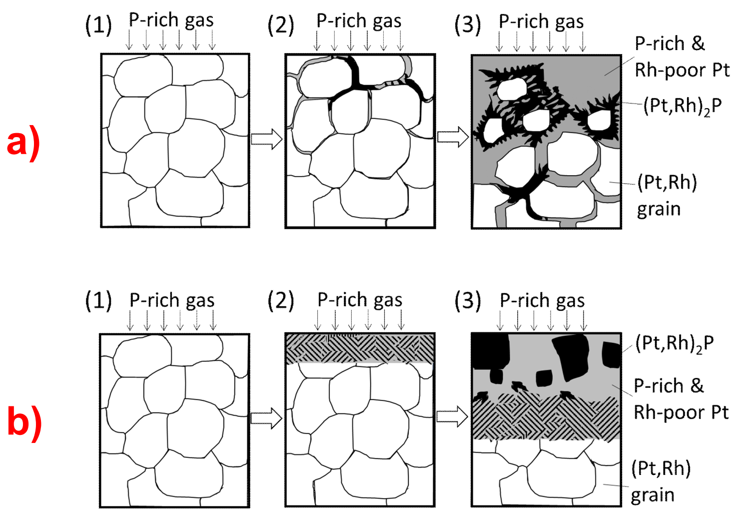
Ash agglomeration/fouling has impacted every gasification process. It is influenced by: 1) the gasification process, 2) the carbon feedstock, 3) process temperature, and 4) process flow rates.



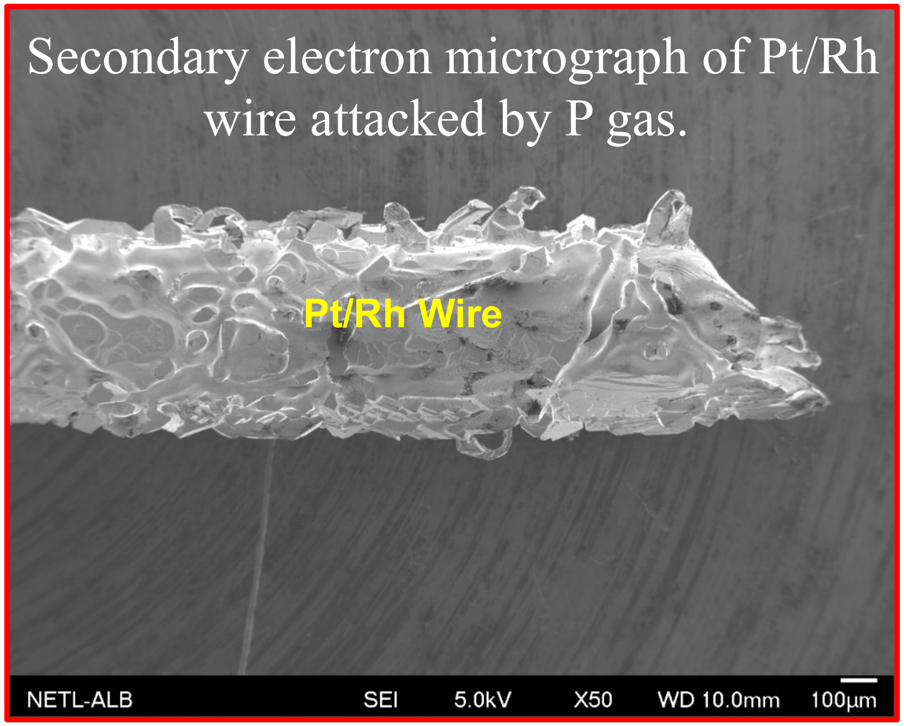
Enabling Materials and Manufacturing

Sensor Evaluation

Efforts to understand and prevent thermocouple sensor attack by the gasification process environment.



Surface attack of Pt/Rh thermocouple wire caused by phosphorus. Two types of diffusion occur, a) P and Rh through grain boundaries, and b) P and Rh through grain lattice, depending on the wire composition. Efforts are directed at preventing attack such as this.



Oxygen Carrier Studies

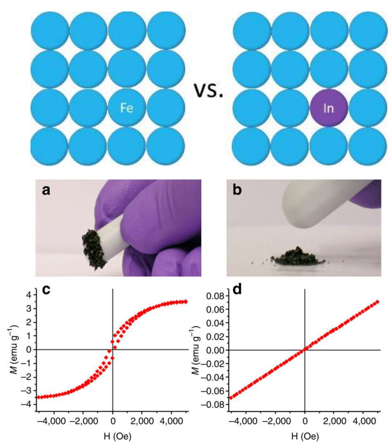
Jonathan W. Lekse and Ranjani Siriwardane

NATIONAL ENERGY TECHNOLOGY LABORATORY

Oxygen Carrier Studies

Project Goals

- We want to understand how changes at an atomic level affect process performance and economics
- We want to use this understanding in order to produce oxygen carriers that are tailored to specific processes
- We are going to use our knowledge to reduce cost and improve efficiency



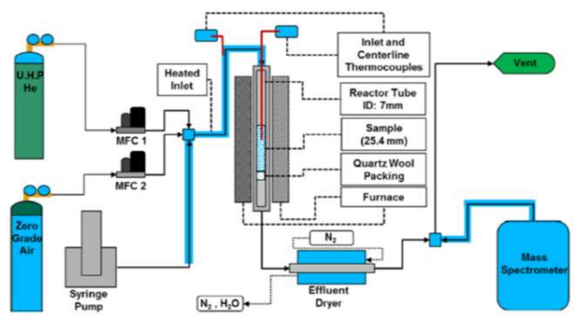


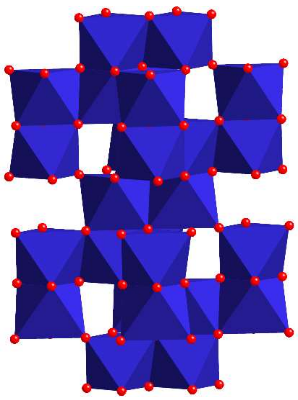
Fig. 4. Schematic of fixed bed reactor system.

Atomistic Studies Property Testing ⟷ Lab-Scale Process Testing → Large-Scale Performance and Economics

Oxygen Carrier Studies

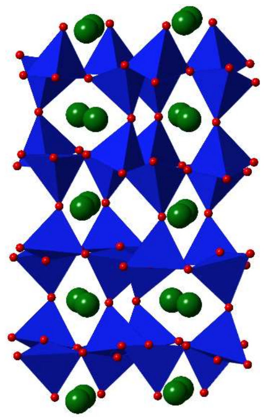
Potential Oxygen Carrier Materials

Binary Oxides



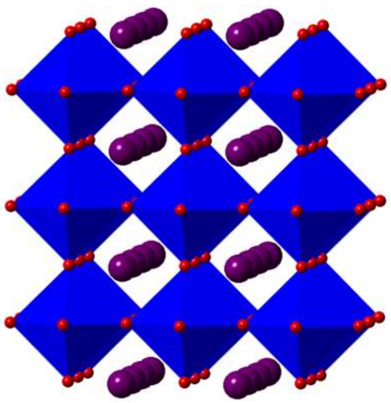
- Inexpensive
- Can have good reactivity
- Limited operating temperature range
- Potential agglomeration

Ferrites



- Can be used for partial oxidation
- Ideal for gasification
- Compositional flexibility
- Stable

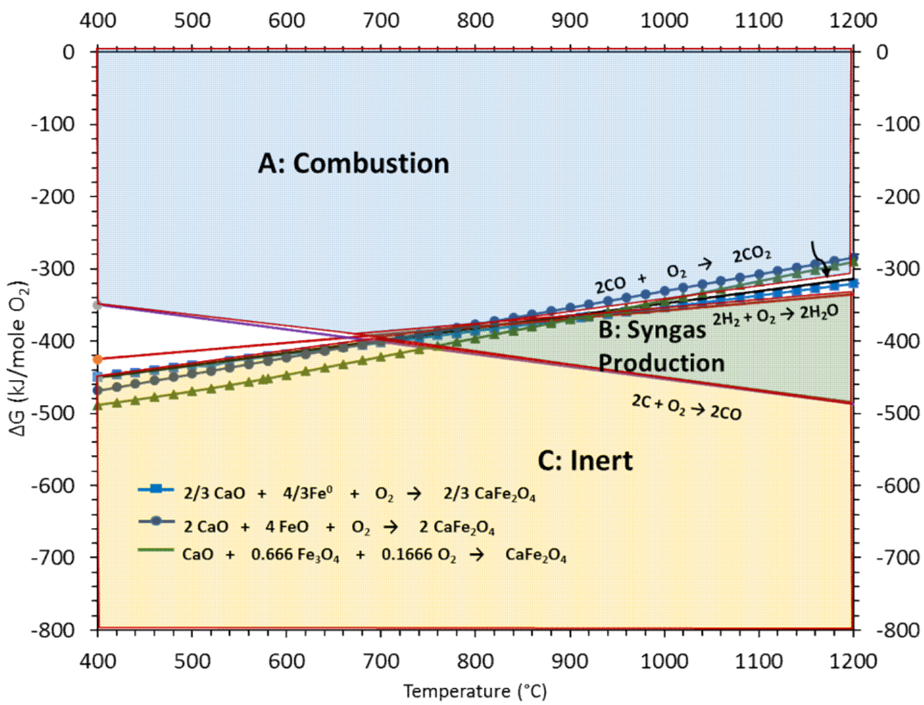
Perovskites



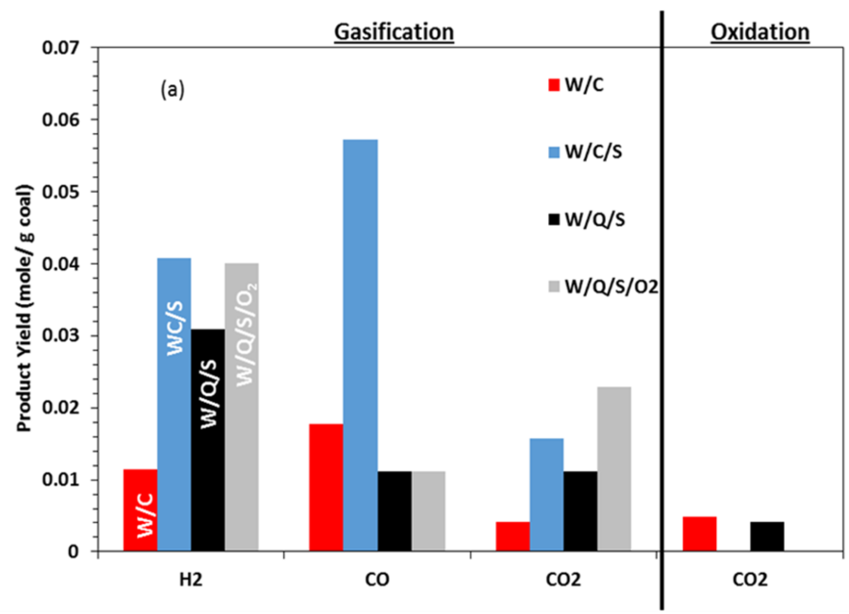
- Easily reduced/oxidized
- Compositional flexibility
- Tuneable oxygen capacity and temperature range
- Stable

Oxygen Carrier Studies

Ferrite Materials for Gasification



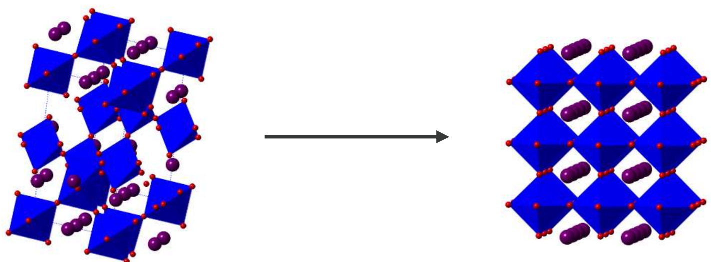
Modified Ellingham diagram for $CaFe_2O_4$ at 700-850 ^0C[1]

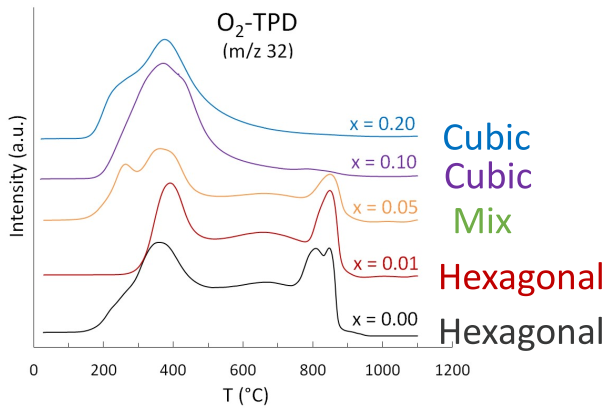


Wyodak coal(W) gasification with calcium ferrite (C) and steam (S) and comparative gasification data with quartz (Q) and 0.75 vol.% gaseous oxygen (O_2)

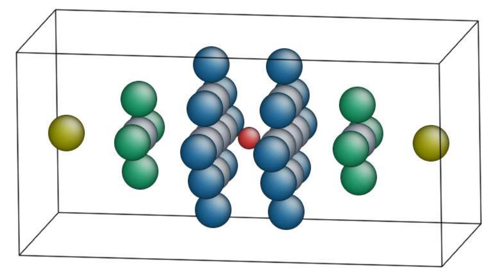
Oxygen Carrier Studies

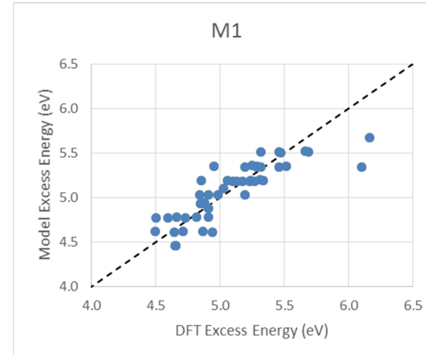
Tuning Oxygen Desorption in Perovskites





Substitution can control structure which can be used to "tune" oxygen desorption properties





- **Collaboration with CMU and IDAES**
  - Dominic Alfonso (NETL)
  - De Nyago Tafen (NETL)
  - David Miller (NETL)
  - Christopher Hanselman (CMU)
  - Chrysanthos Gounaris (CMU)
- **Using computational tools to investigate substitutional motifs in perovskite materials**

IDAES Institute for the Design of Advanced Energy Systems

CARNEGIE MELLON UNIVERSITY PITTSBURGH PENNSYLVANIA 1900

NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

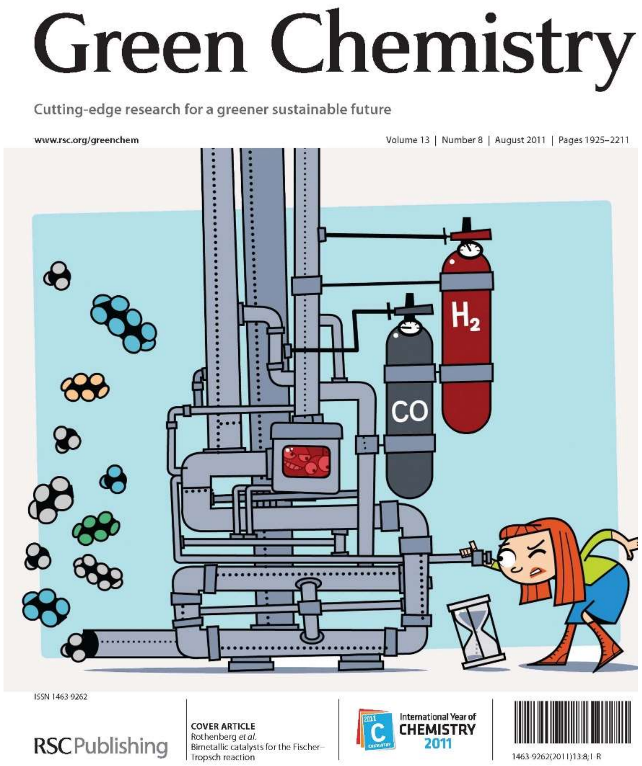
Fischer-Tropsch to Olefins

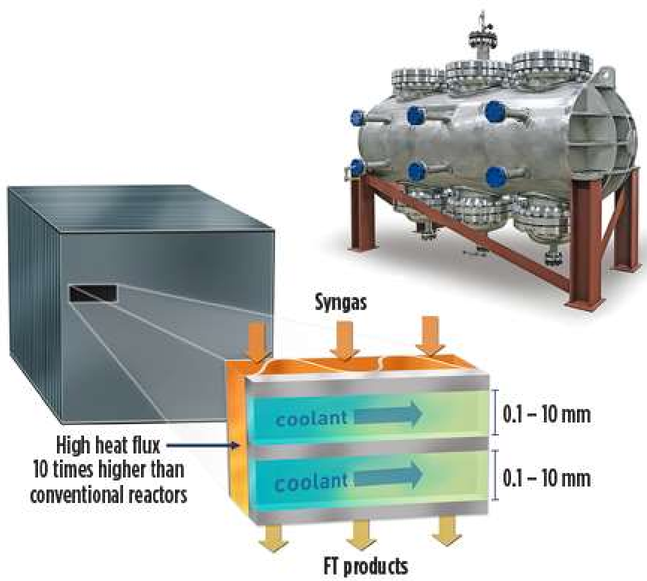
Christopher Matranga and Congjun Wang

NATIONAL ENERGY TECHNOLOGY LABORATORY

Fischer-Tropsch to Olefins

Fischer-Tropsch Synthesis





Sustainable method to produce ultraclean liquid fuels and chemicals from coal, natural gas and biomass with potential for significant CO_2 reduction.

FT to olefin process (FTO) is also the only technologically available method* to synthesize industrially important light olefins ($C_2^= – C_4^=$) directly from syngas, which can reduce the cost of production as well as the dependence on petroleum for these chemicals.

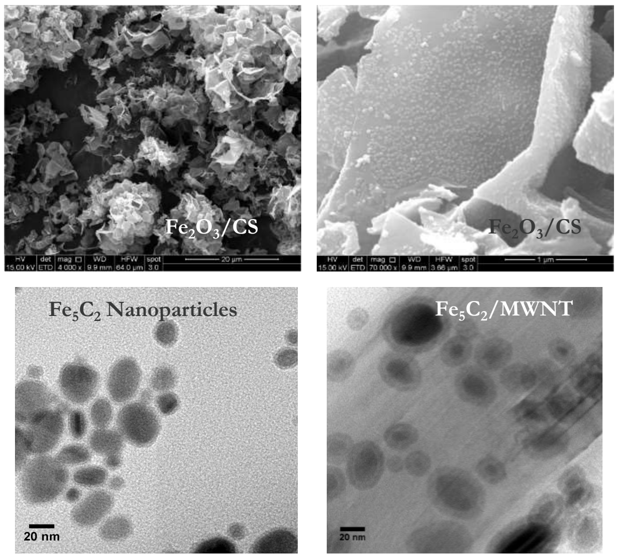
*There are hybrid processes using composite catalysts, e.g., the OX-ZEO process reported in *Science* 351, 1065 (2016).

The FT and FTO processes and catalysts are especially suitable for modular catalysis systems with enhanced mass and heat transfer properties.

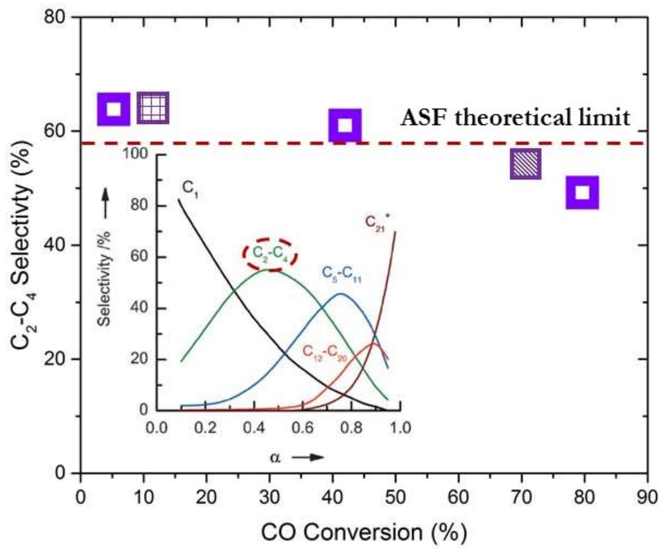
Fischer-Tropsch to Olefins

Selectivity and Activity of Fe-based Nanocatalysts

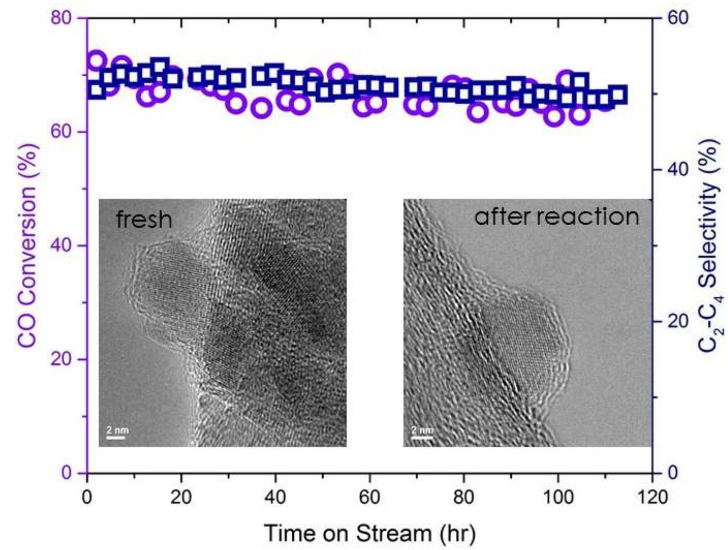
NATIONAL ENERGY TECHNOLOGY LABORATORY



Electron microscope images of catalyst materials.



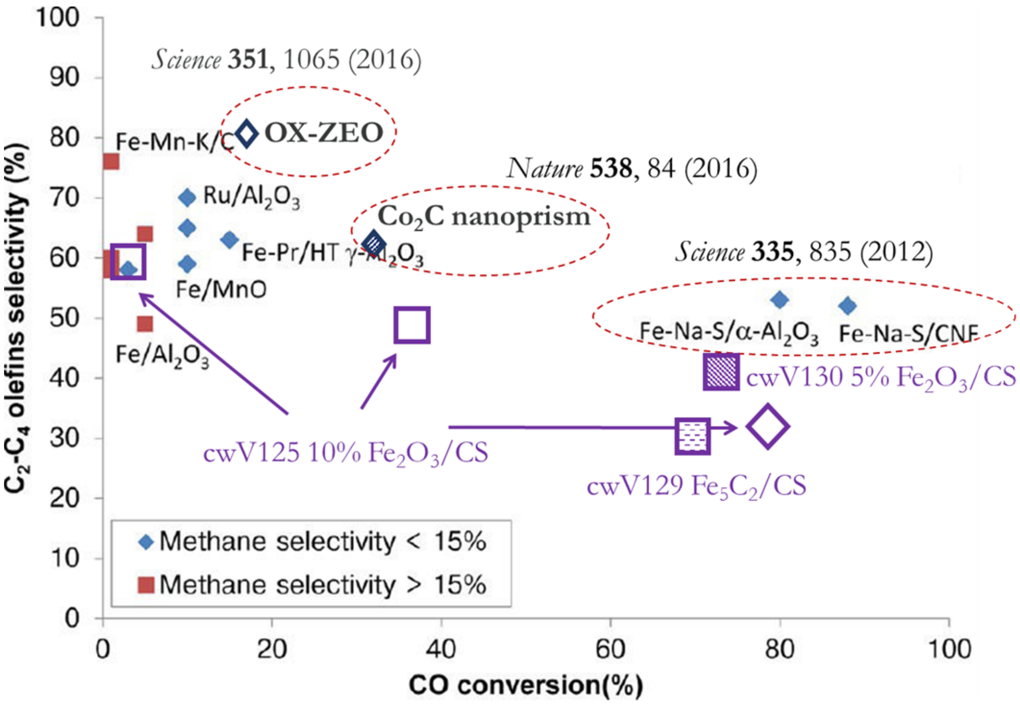
Catalysts meet or exceed the Anderson-Schulz-Flory distribution limit.



Some catalysts remain robust for up to > 400 hrs on stream.

Fischer-Tropsch to Olefins

Comparison with State of the Art



Catalyst	Reaction Condition	CO Conversion	C_2-C_4 Selectivity ($C_2^=$-$C_4^=$)	CH_4 Selectivity (wt. %)	Iron Time Yield ($\mu mol_{CO}/g_{Fe}\cdot s$)*	Stability (hr)
Fe_2O_3/CNT	H_2, 350 °C, 3h RC 1(?)	7	~12	50	NA	~10
10% Fe_2O_3/CS (CWV 125)	H_2, 400 °C, 3h RC1	38.7	55.8 (45.9)	29.7	112	40 (?)
5% Fe_2O_3/CS (CWV 130)	H_2, 400 °C, 3h RC2	72.6	53.5 (41.2)	29.9	1355#	> 200
Fe_5C_2/CNT	10% H_2/N_2, 350 °C, 3h, RC3	46.8	38.4 (18.9)	56.3	150	(?)
Fe_5C_2/CS (CWV 129)	H_2, 400 °C, 3h RC2	70.4	46.0 (28.9)	44.1	1092#	> 400
5% Fe_2O_3/CS (P) (CWV 132)	H_2, 400 °C, 3h RC2	12.4	63.5 (54.9)	9.7	240	~18
Fe_5C_2/CS (P) (CWV 131)	H_2, 400 °C, 3h RC1	10.7	64.9 (50.0)	21.6	103	< 10

Time yields are higher for NETL Catalysts than State of the Art literature materials

Questions?

NATIONAL ENERGY TECHNOLOGY LABORATORY