Plasmonic Photocatalysis

N. J. Halas

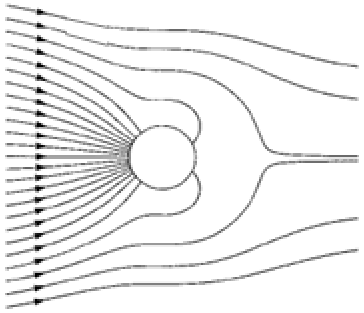
Rice University

Plasmons, not Plasma!

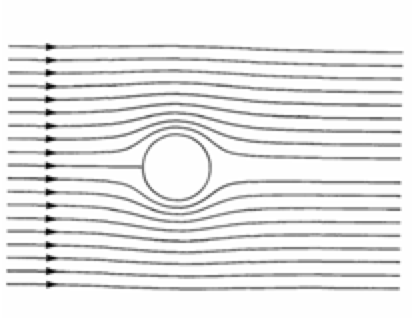
- **Expert in the design and fabrication of nanoparticles that interact with light in specific ways**
- **Professor at Rice since 1990, postdoc at AT&T Bell Labs, graduate fellow at IBM Research**
- **Member of both NAS and NAE (H=157 Google Scholar)**
- **Co-founder of two companies: Nanospectra Biosciences (ultralocalized prostate cancer therapy) and Syzygy Plasmonics (plasmonic photocatalysis for Hydrogen and alternative fuel production)**

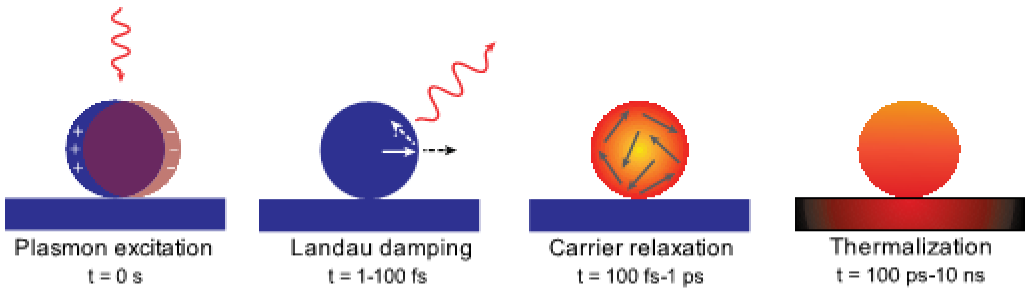
Plasmonic Nanoparticles (Au, Ag, Cu, Al): Optical Frequency Antennas

On Resonance

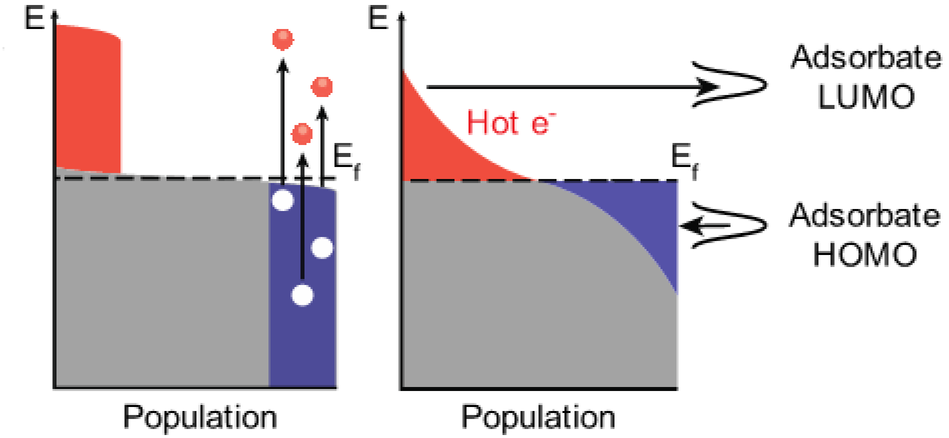


Off Resonance





Photothermal Heating



Hot Carriers

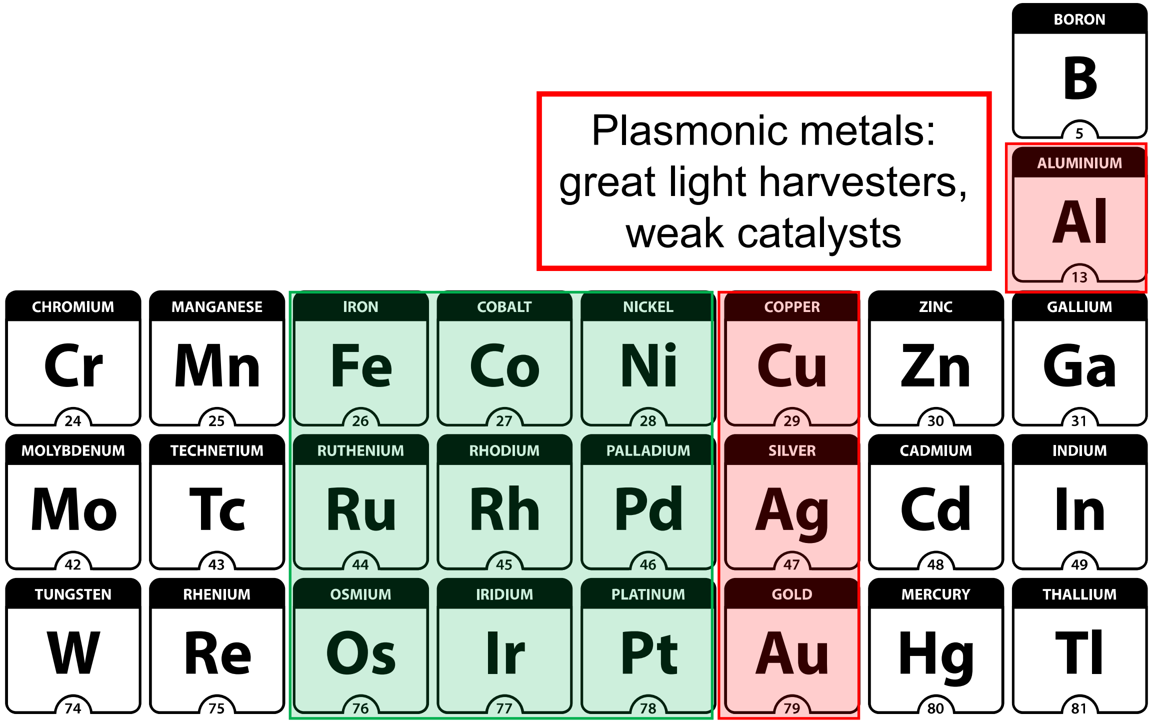
Ideal for photocatalysis!

Bohren and Huffman, *Absorption and Scattering of Light by Small Particles.* Wiley, New York, 1998

M. Brongersma, N. Halas, P. Nordlander, *Nature Nanotech.*, 2015, *10* , 25.

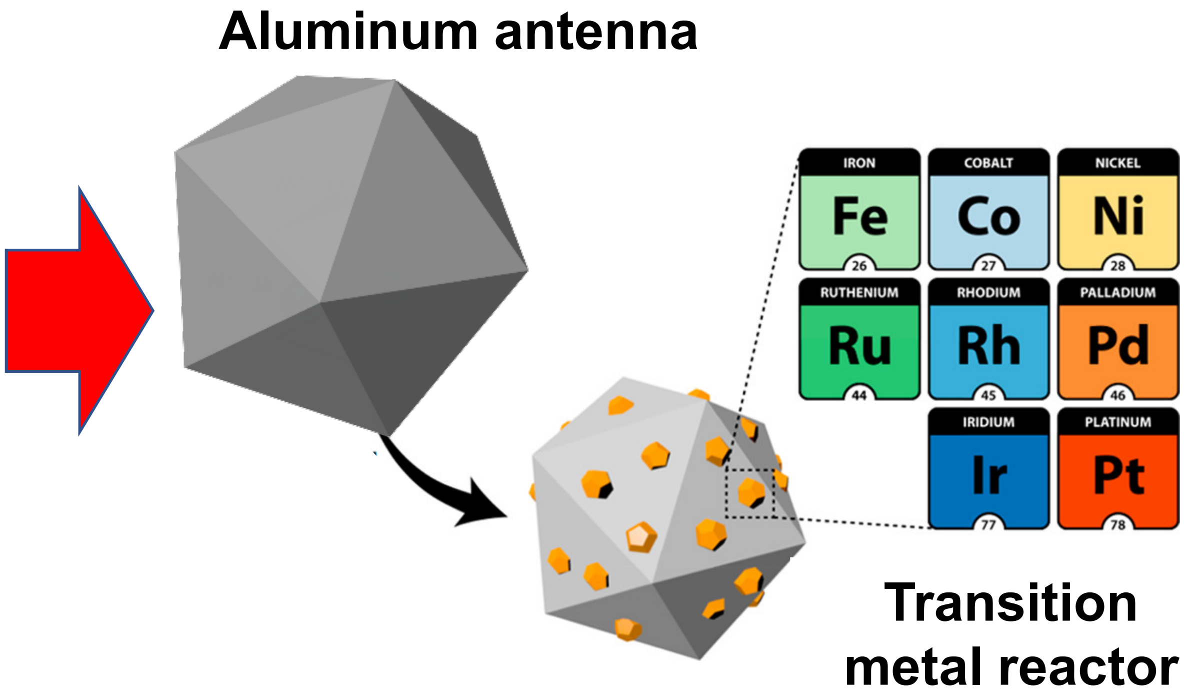
Antenna-reactor for photocatalyst design

Swearer, D.F. *et al.*, Proc. Natl. Acad. Sci. U.S.A. 2016, *113*, 8916–8920



Plasmonic metals:
great light harvesters,
weak catalysts

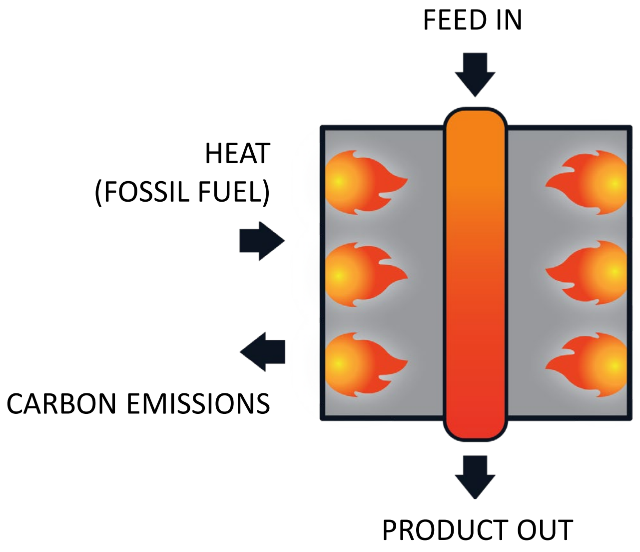
Transition metals:
excellent catalysts, poor
plasmonic materials



Aluminum antenna

Transition metal reactor

Technology based on plasmonic photocatalysis

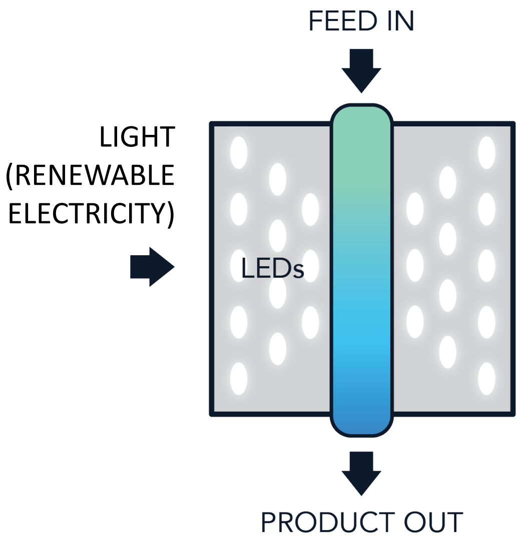


High Pressure / High Temp
(temp at reactor wall ~800°C)

Built from high alloy steel
($42,000 per ton)

Fossil fuel costs vs
long-term carbon pricing

Modest catalyst activity
(Typical TOF of ~1-2)



Low Pressure / Low Temp
(temp at reactor wall ~40°C)

Built from Aluminum
($2,000 per ton)

Renewable costs are
trending down

High catalyst activity
(Demonstrated TOF[1] >30)

Approaching Commercial Scale:

Steam methane reforming
$CH_4 + H_2O \rightarrow CO + 3H_2$

Dry methane reforming
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$
L. Zhou *et al.*, Nature Energy 5, 61-70 (2020).[1]

Ammonia Splitting
$2NH_3 \rightarrow 3H_2 + 2N_2$
L. Zhou *et al.*, Science, 362, 69-72 (2018).

Two Critical Breakthroughs:

1. **Specially designed Plasmonic Photocatalysts (Rice)**
2. **Solid-state Lighting-based Chemical Reactors (Syzygy)**

RICE

What is the current state of development for the technology?

- Technology is licensed and scale up being performed by Syzygy Plasmonics
- Pre-commercial. Only one more scale-up (5 kg to 200 kg) to commercial level.

PHOTOREACTOR DEVELOPMENT PROGRESS

	2018	2019	2020	2021
Productivity per day	milligrams	grams	1 kg	5 kg
Energy Efficiency LHV product / (LHV Feedstock + Electricity)	<1%	~30%	~50%	>55%
Development Level	Micro Reactor	Lab Scale Reactor	Pilot Reactor	Pilot Reactor

Is there an industry sector that your technology would be most applicable to?

- Both small distributed hydrogen production and large centralized production.

What are comparative the advantages of your technology category?

- Can build reactors with low-cost materials like aluminum, glass, and plastic
- Fast start-stop cycles allow for intermittent power -wind, solar- & fast maintenance
- Blue H_2 production: fuel stream eliminated, replaced with renewable electricity
- Green H_2 production: less energy, simpler than current ammonia splitting systems

What specific aspects of your process have the potential to reduce cost of H_2 production?

- Eliminates combustion – Low temperature operation & reduced emissions
- Fast start-stop cycles
- Protection against carbon taxes, regulation

Where are the specific areas where government funding could most accelerate progress?

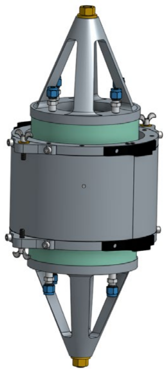
- Market entry – support market entry to demonstrate technology
- New Catalyst Development – fund new catalyst research to new markets

RICE

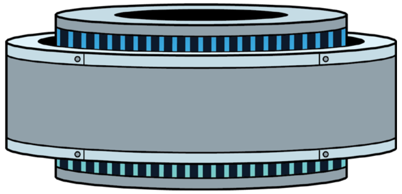
What R&D elements would be required for technology scale-up or scale-down?

- Primary task: scale reactor from 5 kg per day to 200 kg per day
- Only minimal R&D needed to achieve a low-volume, modular reactor
- Significant R&D needed for integration with existing large chemical plants

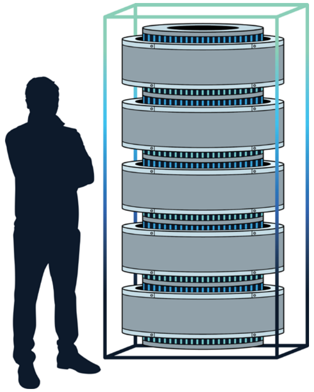
Small Reactor
(Today)



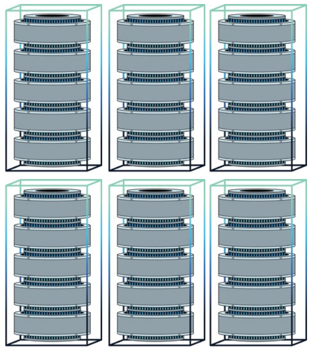
Large Reactor



Reactor Bank



Mass Production



2021	2022	2023	2024
5 kg H_2 / day	~200 kg H_2 / day	>1,000 kg H_2 / day	

What are the biggest barriers, challenges, or risks to your approach?

- Need desulfurization, catalyst is sensitive to sulfur exposure
- Engineering reactors to operate at largest (plant) scale

What are the biggest barriers/challenges/risks aside from the chemical process?

- Achieving costs at economies of scale. Manufacturing costs of first prototype not yet disruptive, economies of scale must be achieved to reach DOE earthshot goals.

What technology development elements would need to start NOW for your approach to reach **$1 for 1 kg of clean Hydrogen within 1 decade?**

- DoE could provide grants for commercial deployment and capital to help scale-up

RICE

What actions external to your process are required to satisfy the net-zero CO_2 emission requirement and other environmental impacts?

- Requires external clean electricity source
- For ‘green’ H_2 – needs ‘green’ ammonia
- For blue H_2 – needs CO_2 utilization or storage
  - This platform technology also has catalysts (NSF SBIR Phase II) for reforming CO_2 into methanol for ‘Double Reforming’: reform methane to get H_2, then reform CO_2 to get methanol.

What are the most important, unrecognized barriers to the other proposed technologies within your technology sector?

- Photocatalysis
  - Other technologies not able to build 3D catalyst beds
  - Semiconductor photocatalysts must overcome bandgap which limits efficiency
  - Catalyst stability of other photocatalysts generally very low
  - Feedstock conversion of other photocatalysts generally very low
- There are only two barriers to success in the greater hydrogen sector
  - Economics – Entire clean hydrogen economy needs ultra-cheap electricity
  - Carbon Intensity – complete lifecycle assessment across H_2 value chain

Microwave Catalysis for Process Intensified Modular Production of Carbon Nanomaterials from Natural Gas

John Hu
West Virginia University

Hydrogen Energy Earthshot Summit

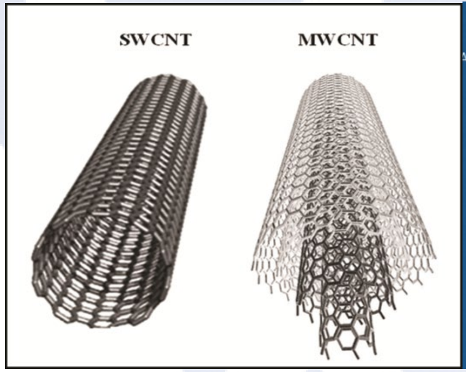
August 31, 2021

The Issue and Need

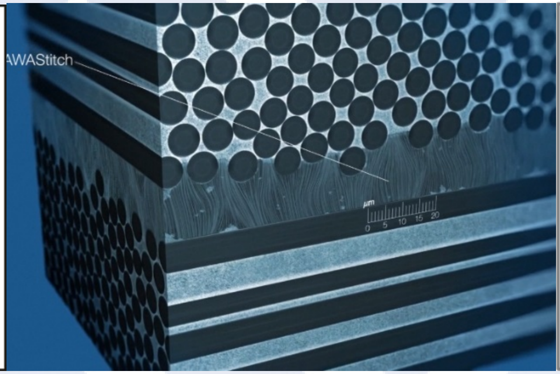
$$CH_4 \rightarrow C_s(Crystalline\ Carbon) + 2H_2$$

Shale Gas Exploration

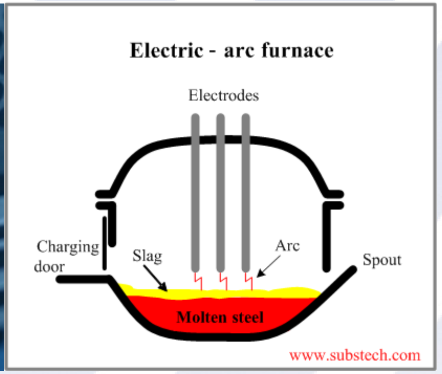
(Bakken, ND)



CNTs



Carbon Composite



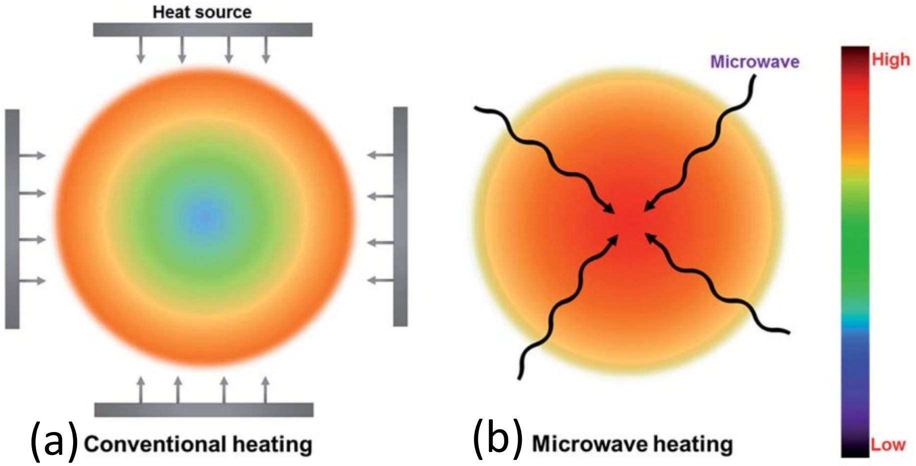
Electrode

- Process intensification at modular scales with the objective of deployment at flare gas location.
- Demonstrate the modular unit operation having a ***large turndown ratio*** which can operate under varying feed rate and composition.

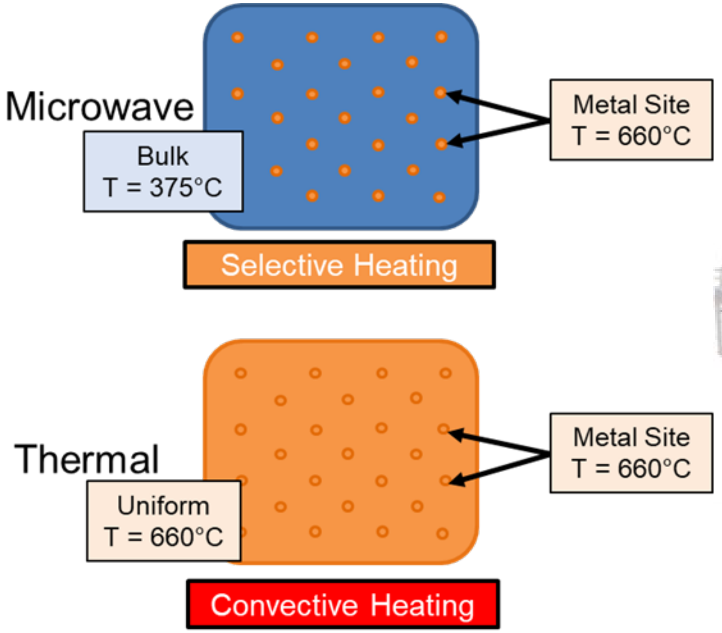
Approach-Microwave Catalytic Process

Advantages of using MW heating

- Volumetric heating
- Rapid, selective heating
- Quick start-up and shut-down-dealing with intermittent feedstock



(a) Conventional heating (b) Microwave heating



Microwave

Bulk
T = 375°C

Metal Site
T = 660°C

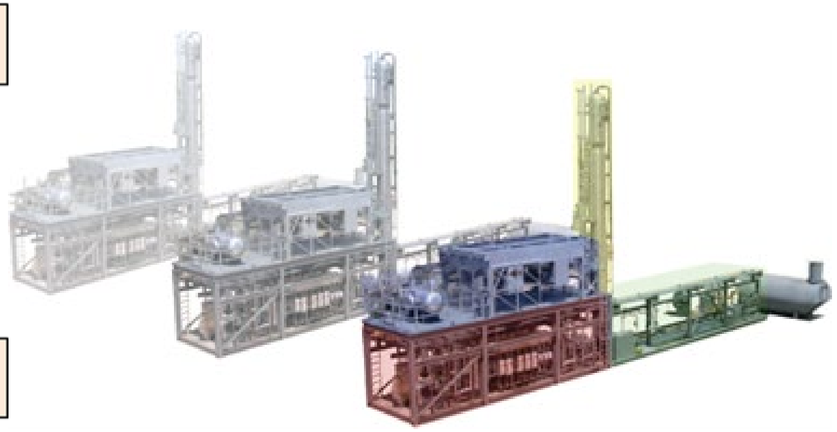
Selective Heating

Thermal

Uniform
T = 660°C

Metal Site
T = 660°C

Convective Heating

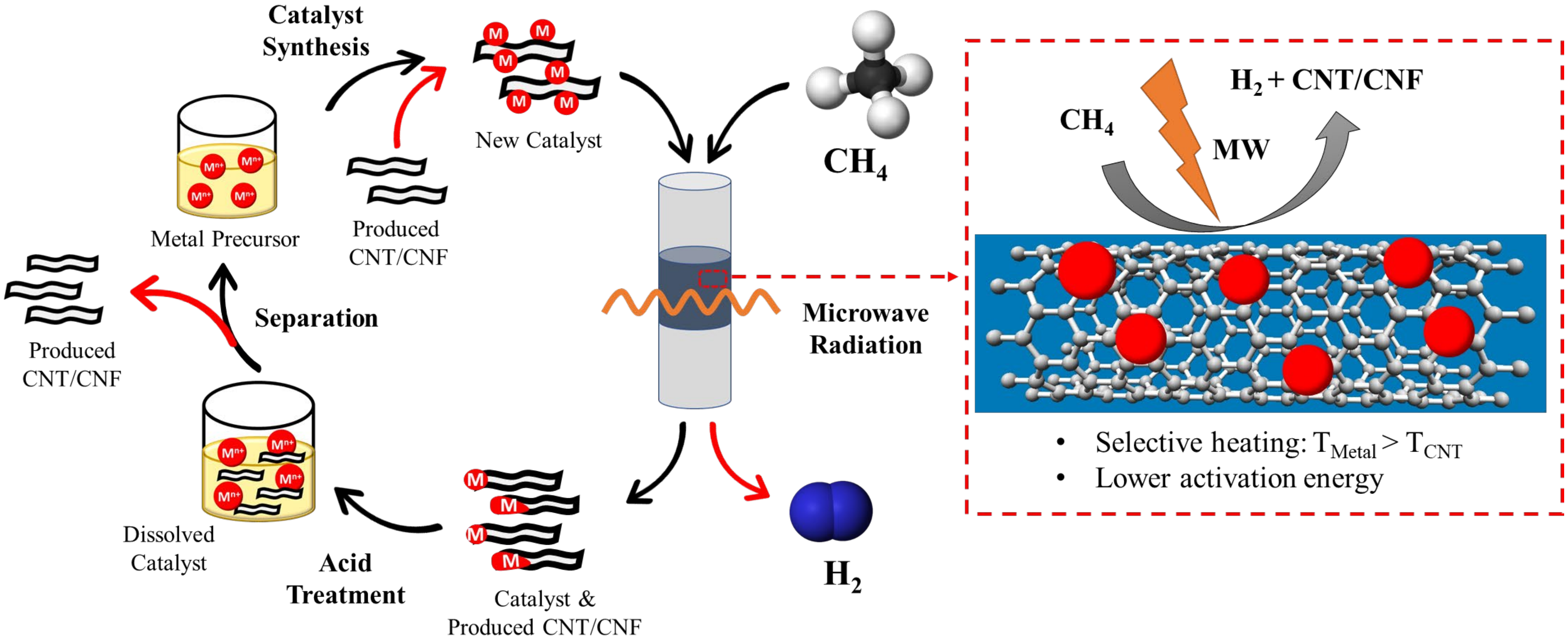


Modular Unit

- Process intensified modular systems provides a route for direct conversion of stranded gas to transportable chemicals. Modular systems are easily deployed and transported to remote locations.

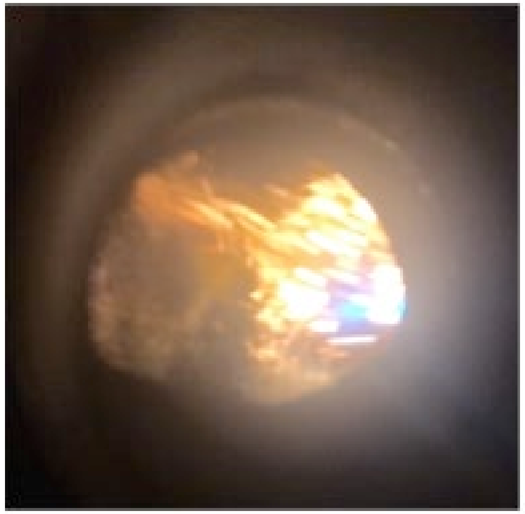
Overcome the Challenges

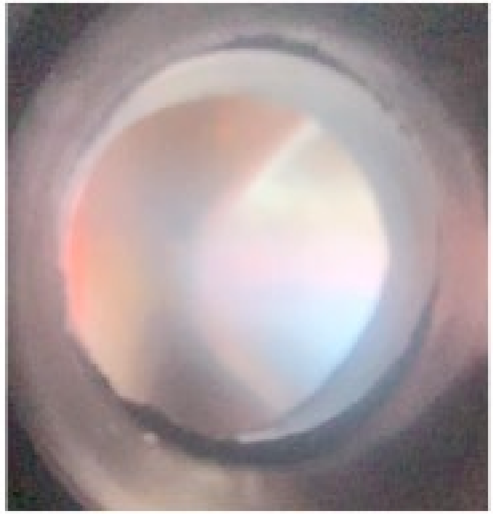
The proposed technology is based on microwave-enhanced, multifunctional catalytic system to ***directly*** convert the light components of stranded natural gas.

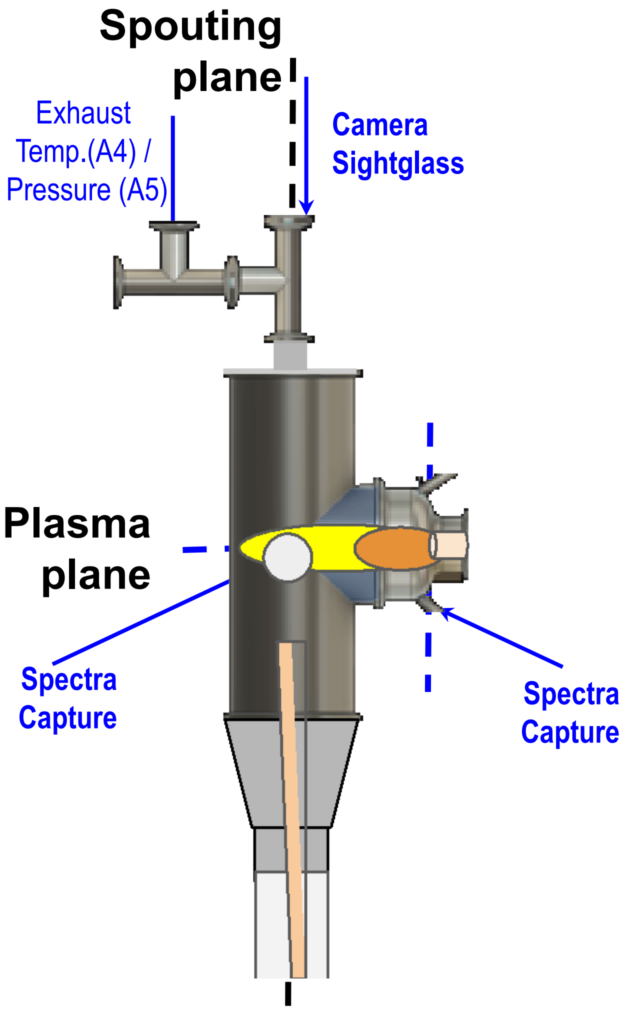


- Selective heating: $T_{Metal} > T_{CNT}$
- Lower activation energy

Microwave Plasma Pilot Demonstration







Spouting plane

Exhaust Temp.(A4) / Pressure (A5)

Camera Sightglass

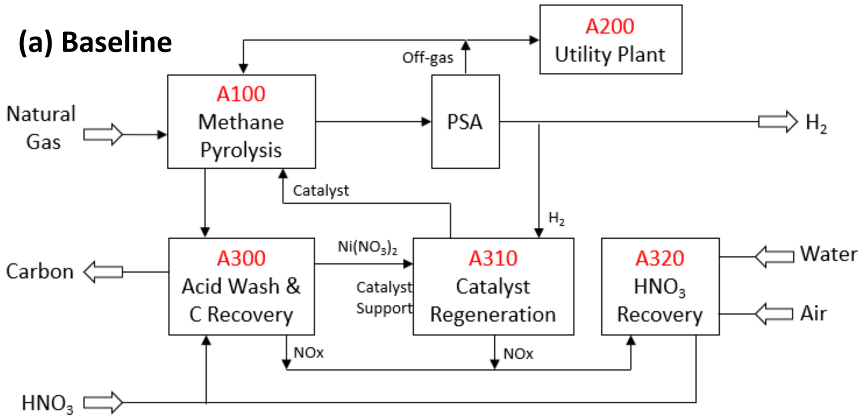
Plasma plane

Spectra Capture

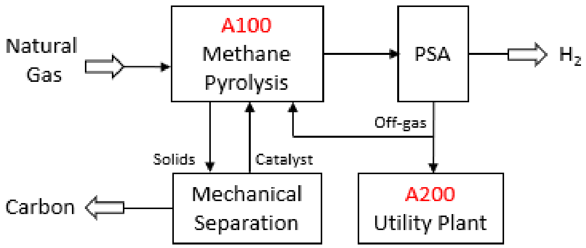
Spectra Capture

TEA-Minimum Carbon Selling Price

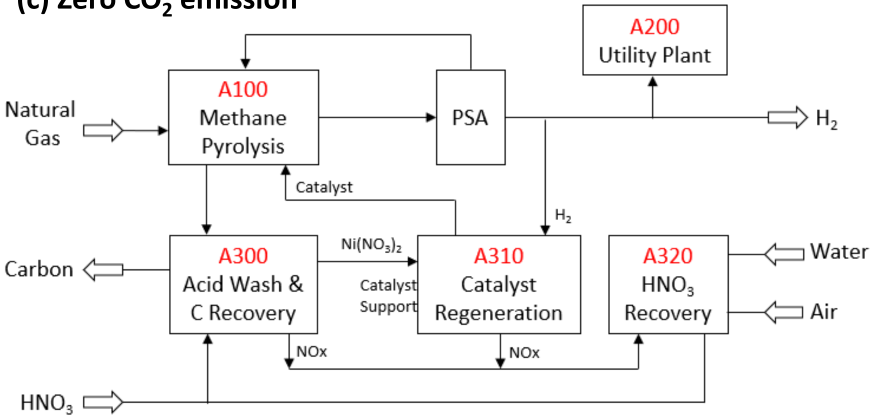
(a) Baseline

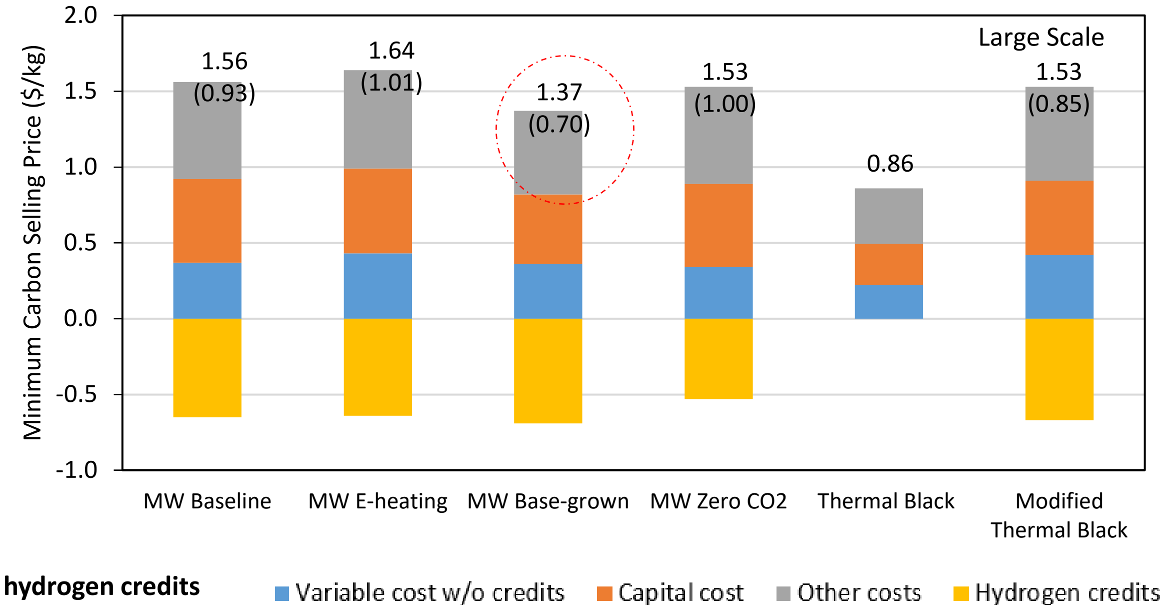


(b) Base-grown



(c) Zero CO_2 emission



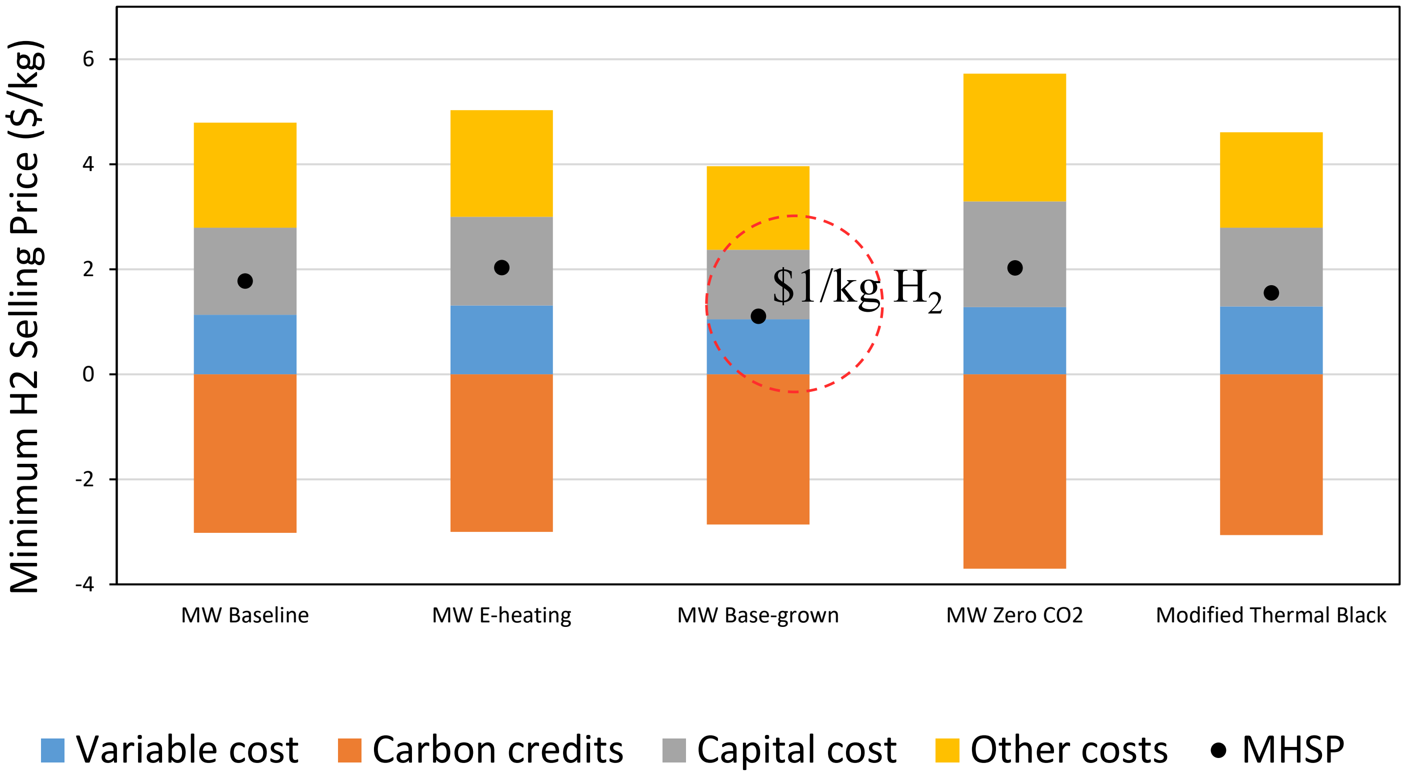


***() MCSP w/ hydrogen credits**

- **The crystalline carbons from our technology will need to be sold at price similar or even lower than carbon black $0.7-1.0/kg**
- **We know these carbon can be sold at price much higher than carbon black.**
- **If benefit from CO_2 tax is considered, economic benefit will be even better.**

Minimum selling price has 15% return built in already

TEA-Minimum H_2 Selling Price



Conclusion:
Hydrogen price can be lower than $1/kg H_2

- Minimum selling price has 15% return built in already
- Carbon credit is set at low grade carbon black price
- Carbon tax is not included in TEA

Minimum selling price has 15% return built in already

Can Hydrogen be Generated *In Situ* from Oil Reservoirs?

Ian Duncan

Bureau of Economic Geology

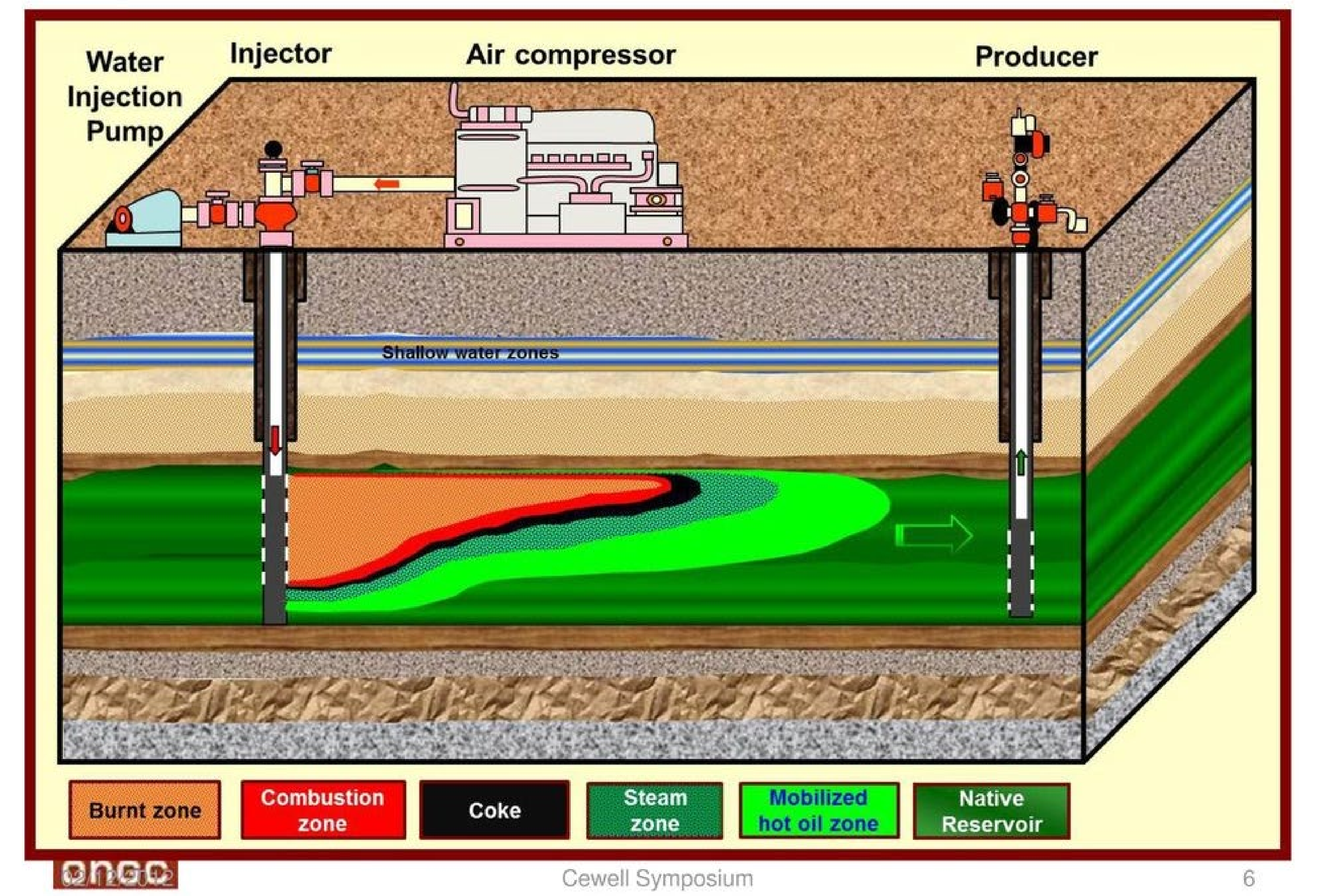
University of Texas

GeoH$_2$

The University of Texas at Austin
Center for Subsurface Energy and the Environment
Cockrell School of Engineering

Bureau of Economic Geology

Cartoon Cross Section of ISC Zone



Can we generate commercially-viable H_2 volumes from ISC using industrial H_2 production as a model?

Industrial Gasification: Reactions

C + ½ O2 → CO (-111 MJ/kmol) exothermic

$C + 2H_2 = CH_4$ (-75 MJ/kmol) exothermic

Industrial Steam Methane Reforming (SMR) Reactions

- $CH_4 + H_2O = CO + 3H_2$, +206 kJ/mol, (SMR)
- $CO + H_2O = CO_2 + H_2$, + 41 kJ/mol, (WGS)

Water Gas Shift

Both use Pt or Ni catalysts, temperatures ~ 1,000 °C

Generating about 95% H_2 in U.S.

BP's 1985 ISC Pilots

- **1980's BP, Cold Lake, heavy-oil reservoir**
  - In-situ combustion pilots
  - Wet-oxygen and wet air
  - "most wells", intermittent, high-level H_2, up to 20 mole% (alternating with methane)

- **Main findings:**
  - Thermal cracking … not a significant producer H_2
  - H_2 likely produced by methane shift reaction

Interpretation BP Results

- When H_2 + CO_2 levels are high, the CH_4 levels are low, and vice versa.
- Consistent with the SMR reaction
- Factors controlling hydrogen versus methane?
- Temperatures generated by in situ oxidation unknown

Duplicating Industrial Hydrogen Production in Oil Reservoirs

Need:

- Heat source… in-situ combustion (ISC)
- Recent research shows temperatures of 400 to 500 °C needed
- Gas phase generated by ISC needs to have CO and/or CH_4
- Ability to control oxygen and water fugacity
- Strategy for production wells to entrain H_2 rich gas

Strategies to Manipulate Oxygen Fugacity, Temperatures, and Reaction Rates

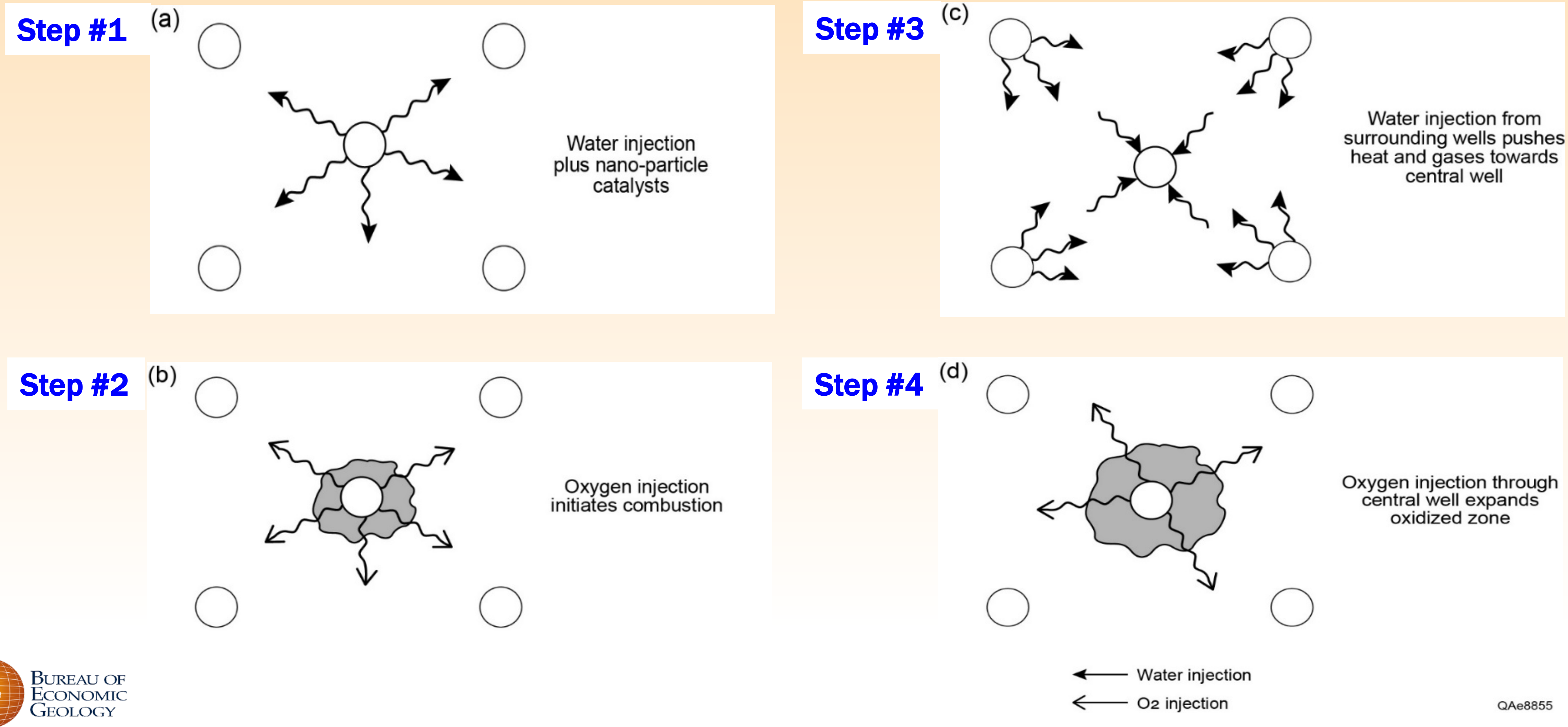
1) Ratio of injected pure O_2 to compressed air… controls Oxygen fugacity and influences temperature

2) Use of Nano-catalysts to lower effective temperature of reactions

3) Water injection can move heat and gases to reaction zones

Innovation: Reverse Injection of Water Versus Oxygen

Sequence of Injection of Oxygen and Water



Step #1

Step #2

Step #3

Step #4

Bureau of
Economic
Geology

Two other important technologies to be investigated by our collaborators:

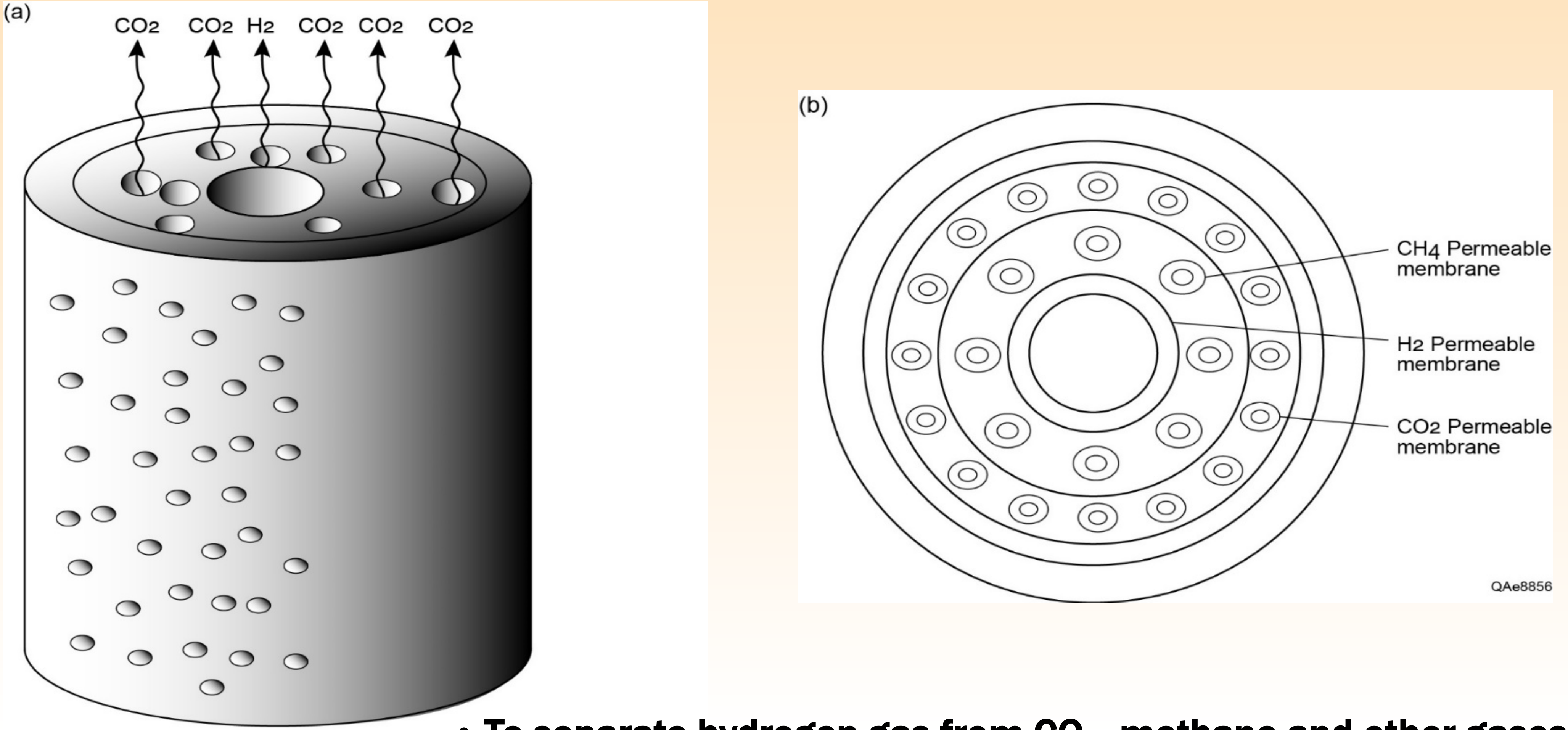
(1)High temperature H_2 selection ceramic membranes

(2)Nano-particle catalysts

Injected Nano Catalysts

Process Catalyzed	Catalyst	Additional Catalysts
Oxidation	Calcite	Copper
Gasification	Nickel, Copper (and/or Cu-K/Al_2O_3 based catalysts	Calcite
Methane Shift Reactions	Nickel (and/or $NiAl_2O_4$ based nanoparticles)	Z_n

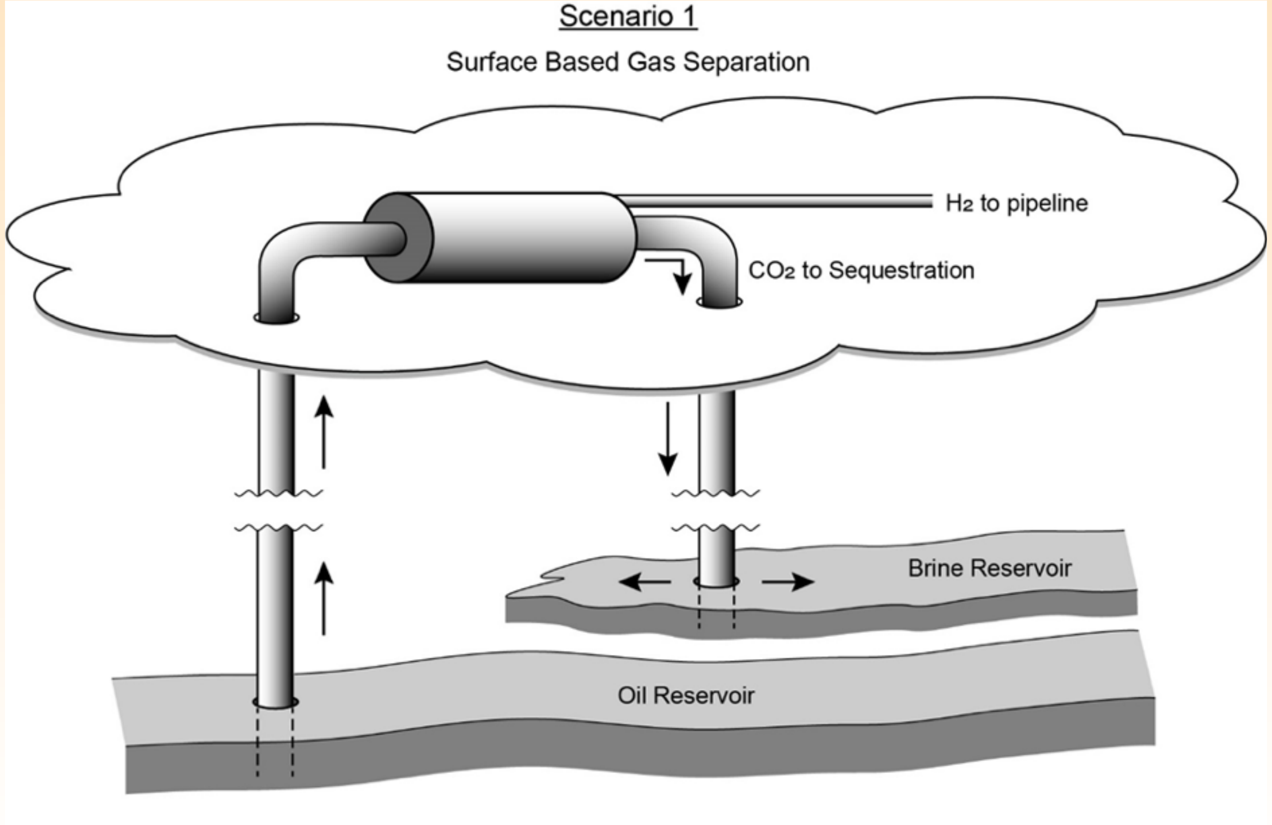
Ceramic Membranes



- To separate hydrogen gas from CO_2, methane and other gases
- Possible geometries of selected permeable ceramic membranes

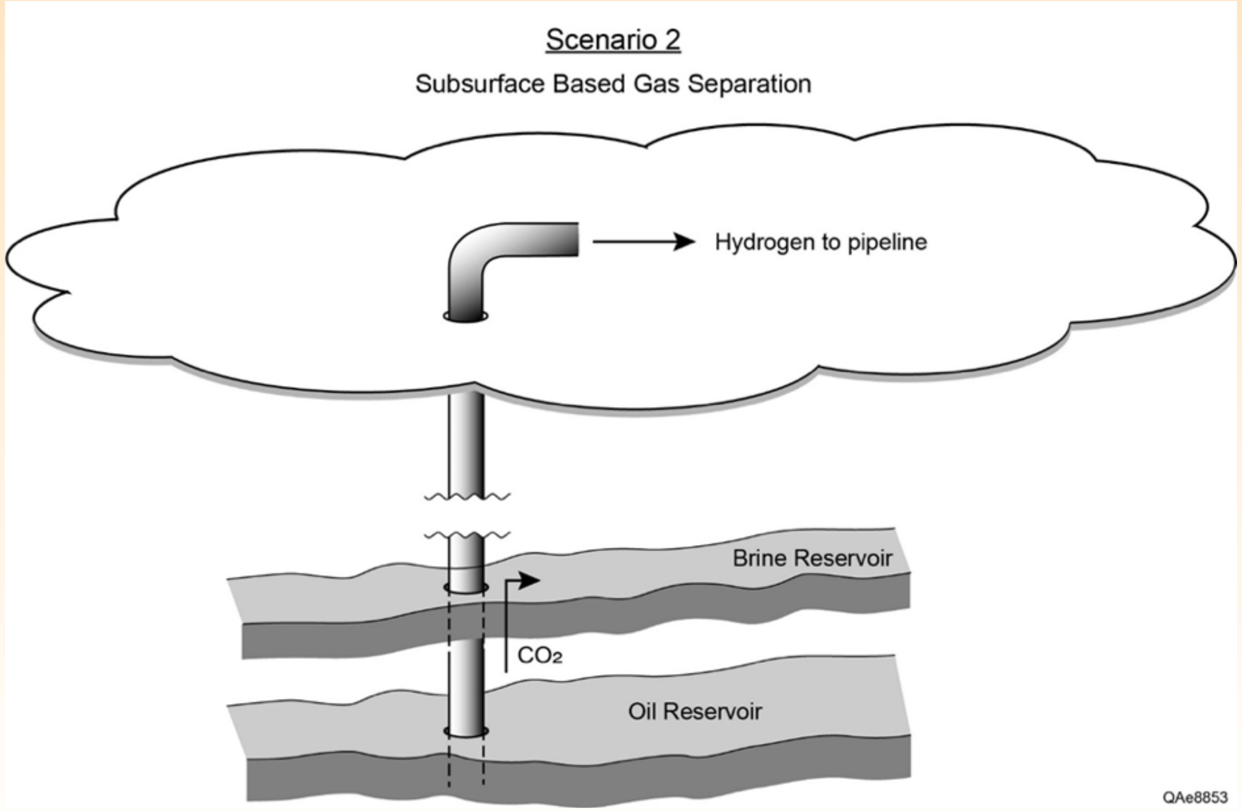
Bureau of Economic Geology

Sequestrating/ Processing Associated CO_2



Scenario 1

Surface Based Gas Separation

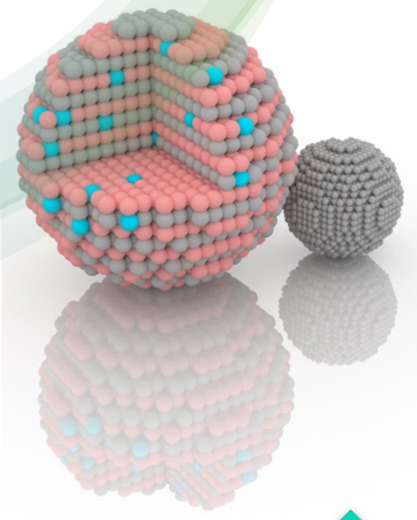


Scenario 2

Subsurface Based Gas Separation

Discussion and Conclusions

- Potential for low-cost hydrogen generation with integrated CO_2 sequestration
- Currently underutilized oil reservoirs (heavy oil, depleted fields) may become valuable sources for hydrogen
- Would build on existing oil field infrastructure and skilled personnel



Chemical Looping Technology for Hydrogen Production

L. S. Fan

Department of Chemical and Biomolecular Engineering

The Ohio State University

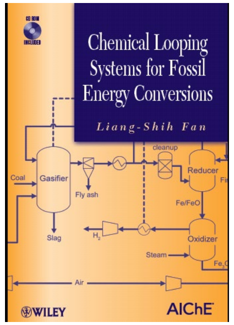
Columbus, Ohio 43210

USA

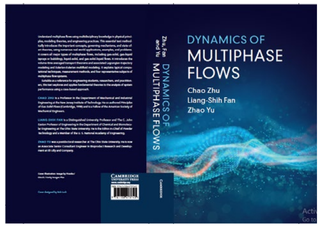
Hydrogen Energy Earthshot Summit Panel

August 31, 2021

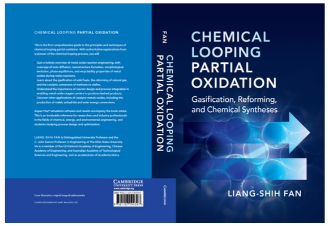
Wiley/AIChE 2010

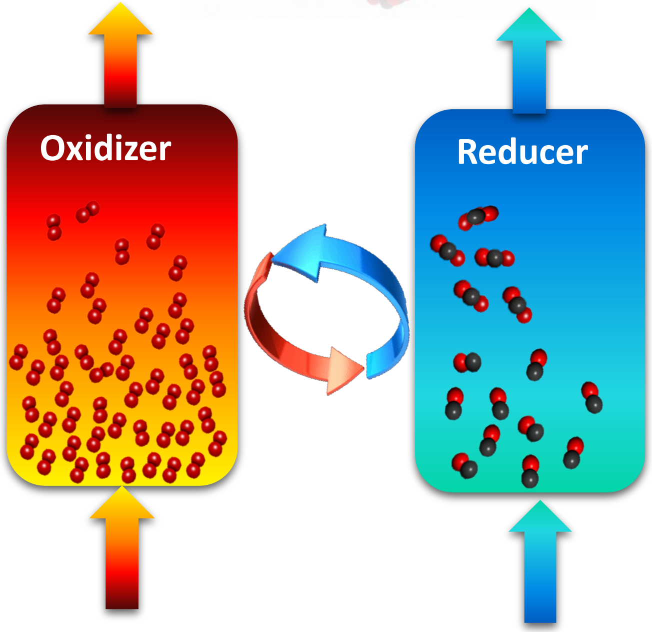


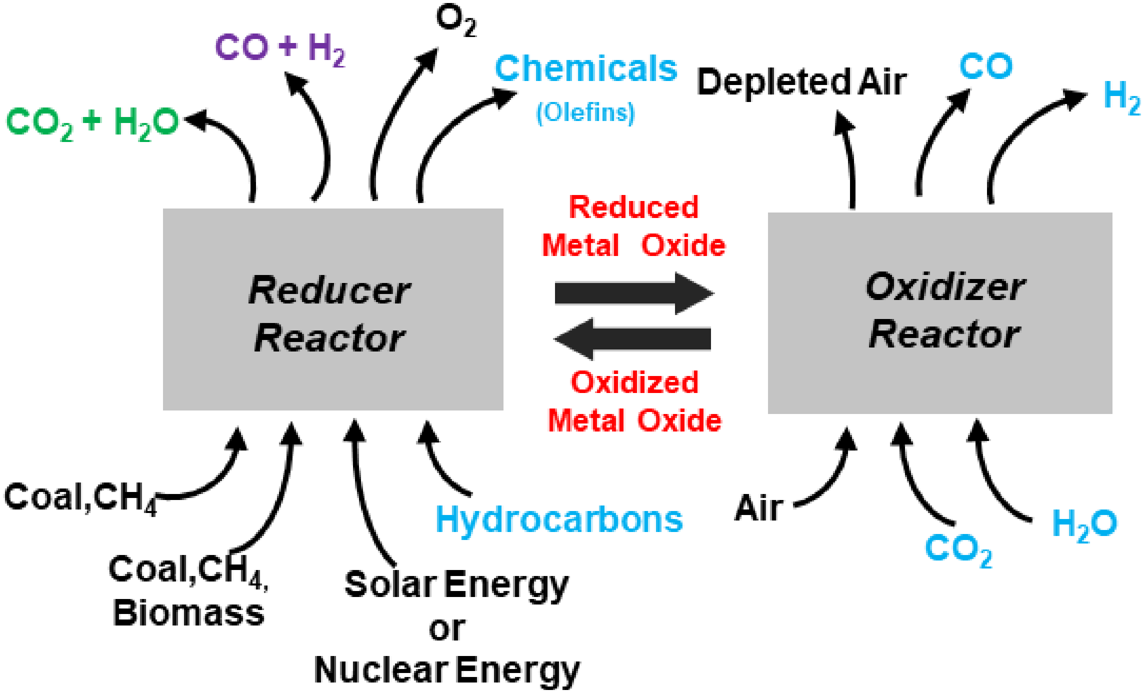
Cambridge University Press 2021



Cambridge University Press 2017







$CO_2 + H_2O$

$CO + H_2$

O_2

Chemicals (Olefins)

Depleted Air

CO

H_2

Reducer Reactor

Reduced Metal Oxide

Oxidized Metal Oxide

Oxidizer Reactor

Coal, CH_4

Coal, CH_4, Biomass

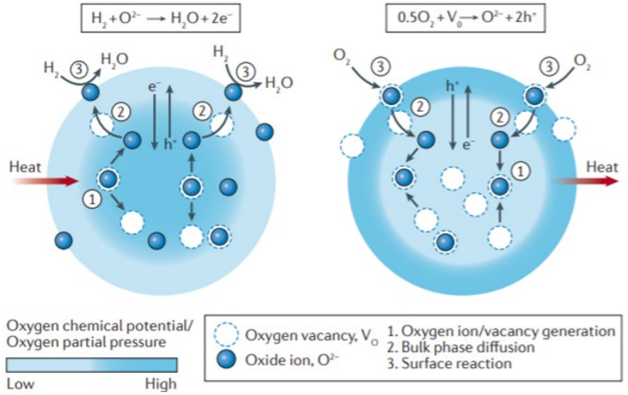
Solar Energy or Nuclear Energy

Hydrocarbons

Air

CO_2

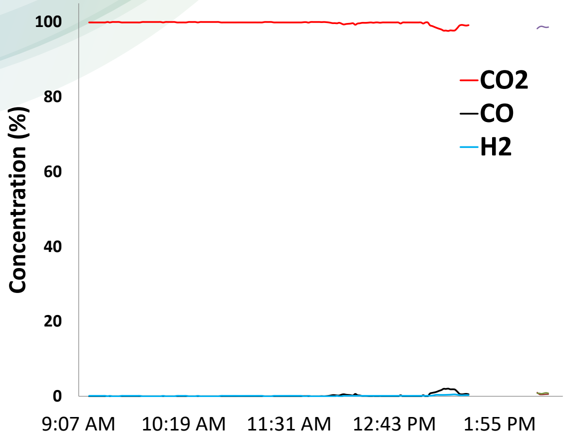
H_2O



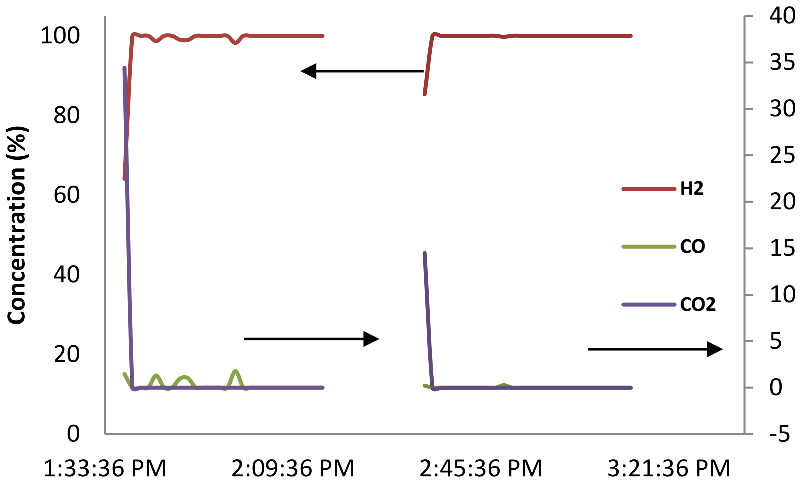
Zeng and Fan et al., Nature Review Chemistry, 2018; Fan, Books, 2010, 2017
Chung and Fan et al. Energy & Environmental Science 10, 2318-2321, 2017
Qin and Fan et. al. J. Mater. Chem. A, 38, 20153–20160, 2017

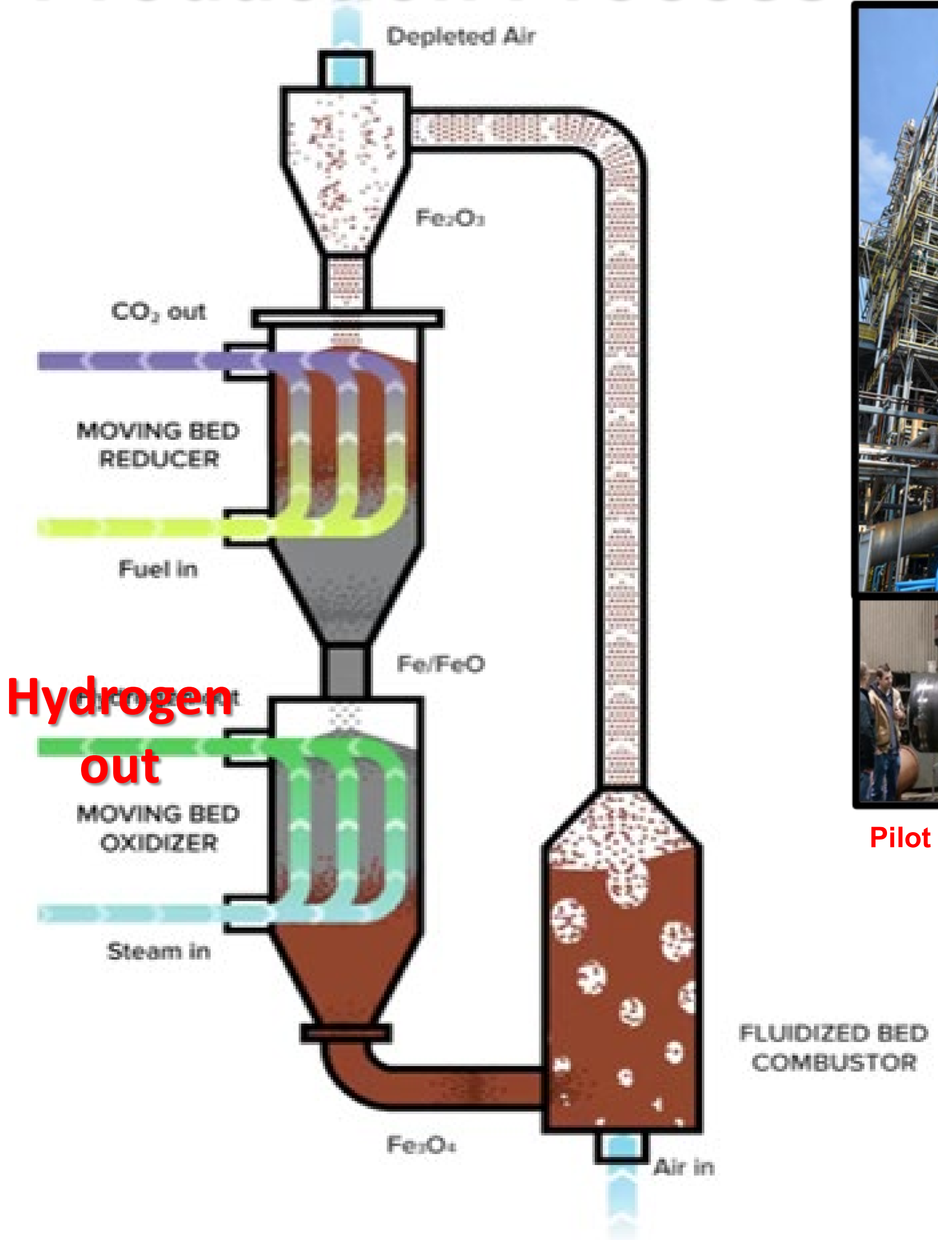
OSU 3-Reactor Chemical Looping Hydrogen Production Process

> 99% CO_2 purity in Reducer



>99.99% H_2 purity in Oxidizer



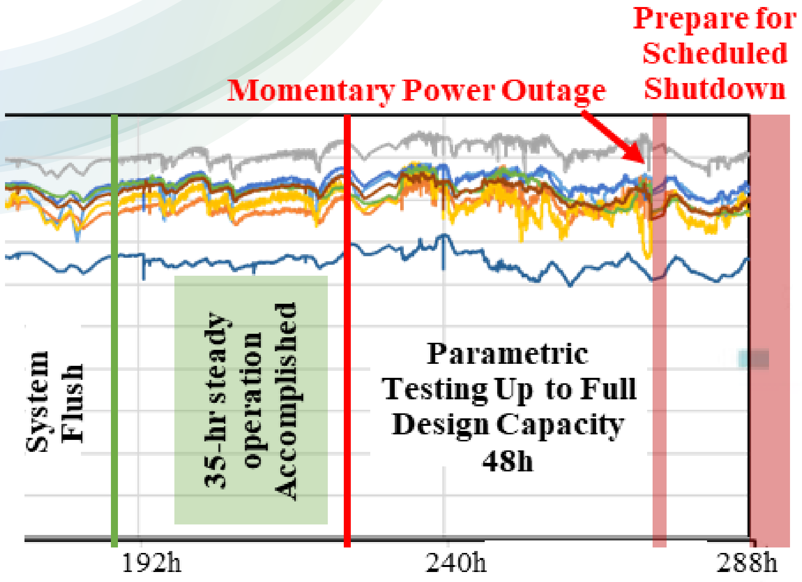


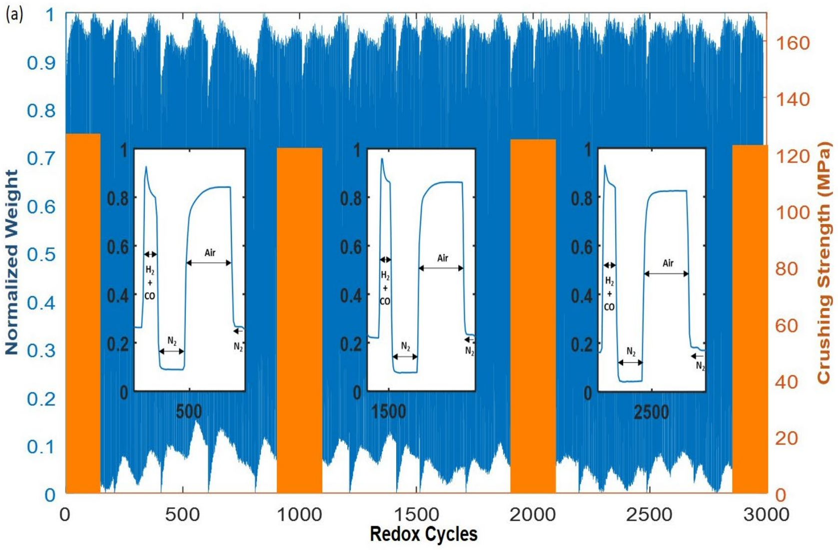
Pilot demonstration at National Carbon Capture Center, AL

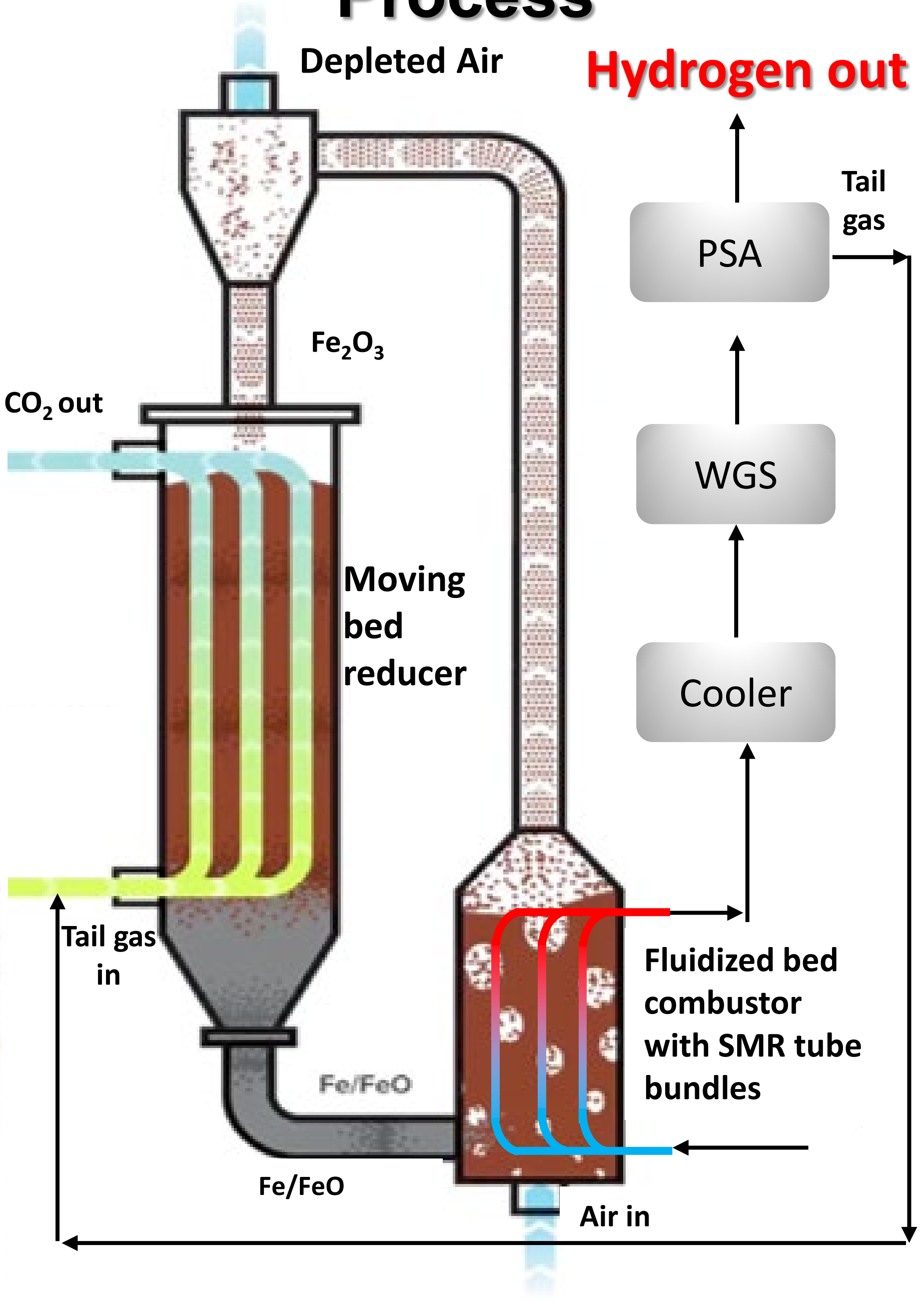
Cost of Low Pressure H2 Production with CO_2 Capture Can be less than \$1.5/Kg H_2

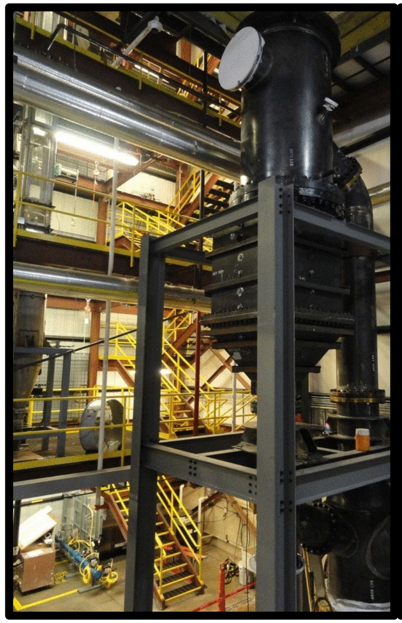
Hsieh and Fan et al., Applied Energy, 2018.
Li and Fan et al., AIChE Journal. 2010
Tong and Fan et al., Fuel. 2013.
Kong and Fan et al., Fuel. 2020

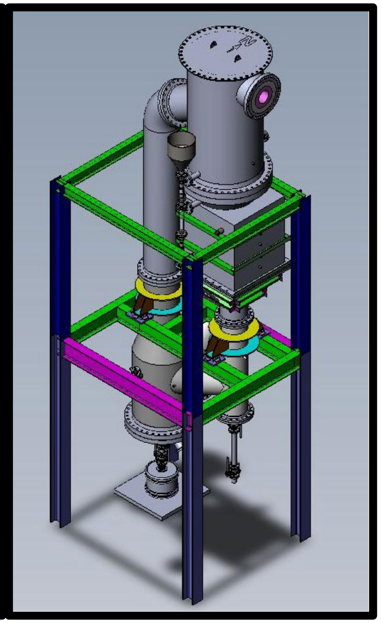
OSU 2-Reactor Chemical Looping coupled SMR Hydrogen Production Process











250 kW_{th} B&W CDCL Pilot Plant Testing

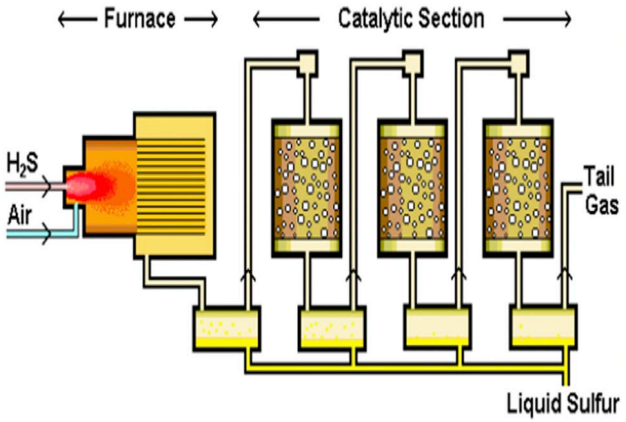
- **Simplicity**
- **Unique Reducer Configuration: Moving Bed**
- **Non-Mechanical L-Valve**

Cost of Hydrogen production with CO_2 capture can be less than \$1.0/kg H_2

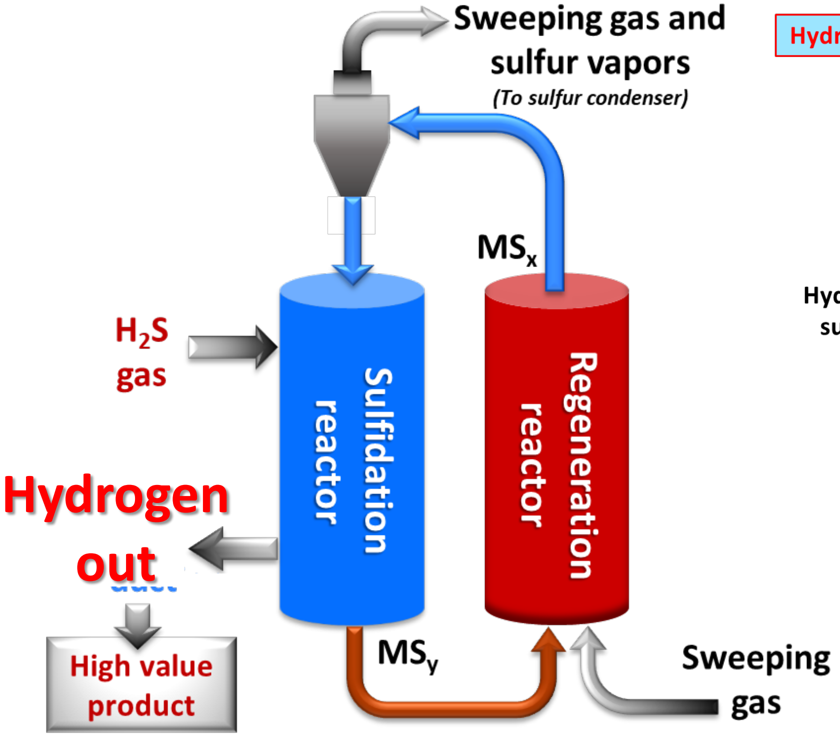
Fan, L.-S., Zeng, L., Luo, S. *AIChE Journal*. 2015.
Zhang and Fan et. Al. Applied Energy, 2021
Kim and Fan et. al. Fuel, 2013
Bayham and Fan et. al. Energy Fuels 2013

THE OHIO STATE UNIVERSITY

OSU Chemical Looping Sulgen Process for Hydrogen Generation from Hydrogen Sulfide

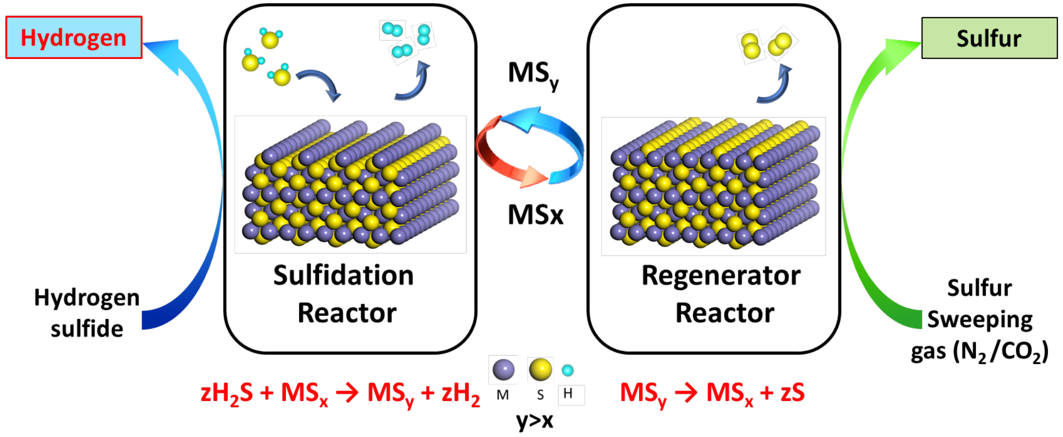


Conventional H_2S treatment using the Claus process

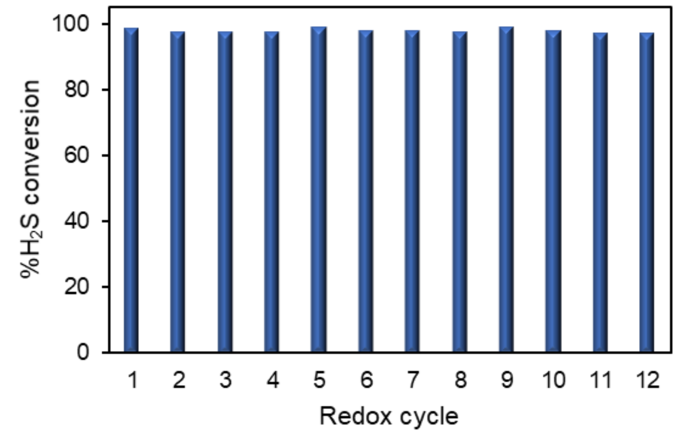

Sweeping gas and sulfur vapors
(To sulfur condenser)
MS_x
H_2S gas
Sulfidation reactor
Regeneration reactor
Hydrogen out
High value product
MS_y
Sweeping gas

Chemical looping Sulgen process for H_2 generation from H_2S

Overall Reaction
$H_2S \rightarrow H_2 + 0.5\ S_2$


Hydrogen
Hydrogen sulfide
Sulfidation Reactor
MS_y
MSx
Regenerator Reactor
Sulfur
Sulfur Sweeping gas (N_2/CO_2)
$zH_2S + MS_x \rightarrow MS_y + zH_2$
M S H
y>x
$MS_y \rightarrow MS_x + zS$

>98% H_2S conversion in Sulfidation step



H_2S conversion into H_2 over 12 sulfidation (T: 400°C) and regeneration (T: 950°C) cycles using iron-based sulfur carrier

Key advantages over the Claus process:

- Production of H_2 instead of steam
- ~99% reactive separation of H_2S into H_2 from syngas, natural gas, acid gas and hydrocarbon (C_2-C_4) stream
- Significant reduction in processing units, cost and energy requirement

Nadgouda SG, Jangam KV, Fan L.-S. Systems, methods and materials for hydrogen sulfide conversion. 2018 (62/716,705 (US), patent pending).
Jangam and Fan et al., ACS Sustainable Chem. Eng. 2021
Jangam and Fan et al., Chem. Eng. J., 2021
Sassi and Gupta, Am. J. Environ. Sci.,2008