High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

Award No: DE-FE0031634

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Overview

Timeline

- ✓ Project start date:
  Oct. 1, 2018
- ✓ Project end date:
  August. 30, 2022
- ✓ Budget Periods:
  I: 10/1/2018-3/31/2020
  II: 4/1/2020-9/30/2021

Research Area 1

- ✓ Lab-Scale CO_2 Capture Development and Testing on Simulated Syngas

Budget

- ✓ Total project funding
  - ❑ DOE **$800,000**
  - ❑ Cost-share: **$200,007**
  - ❑ Total**: $1,000,007**

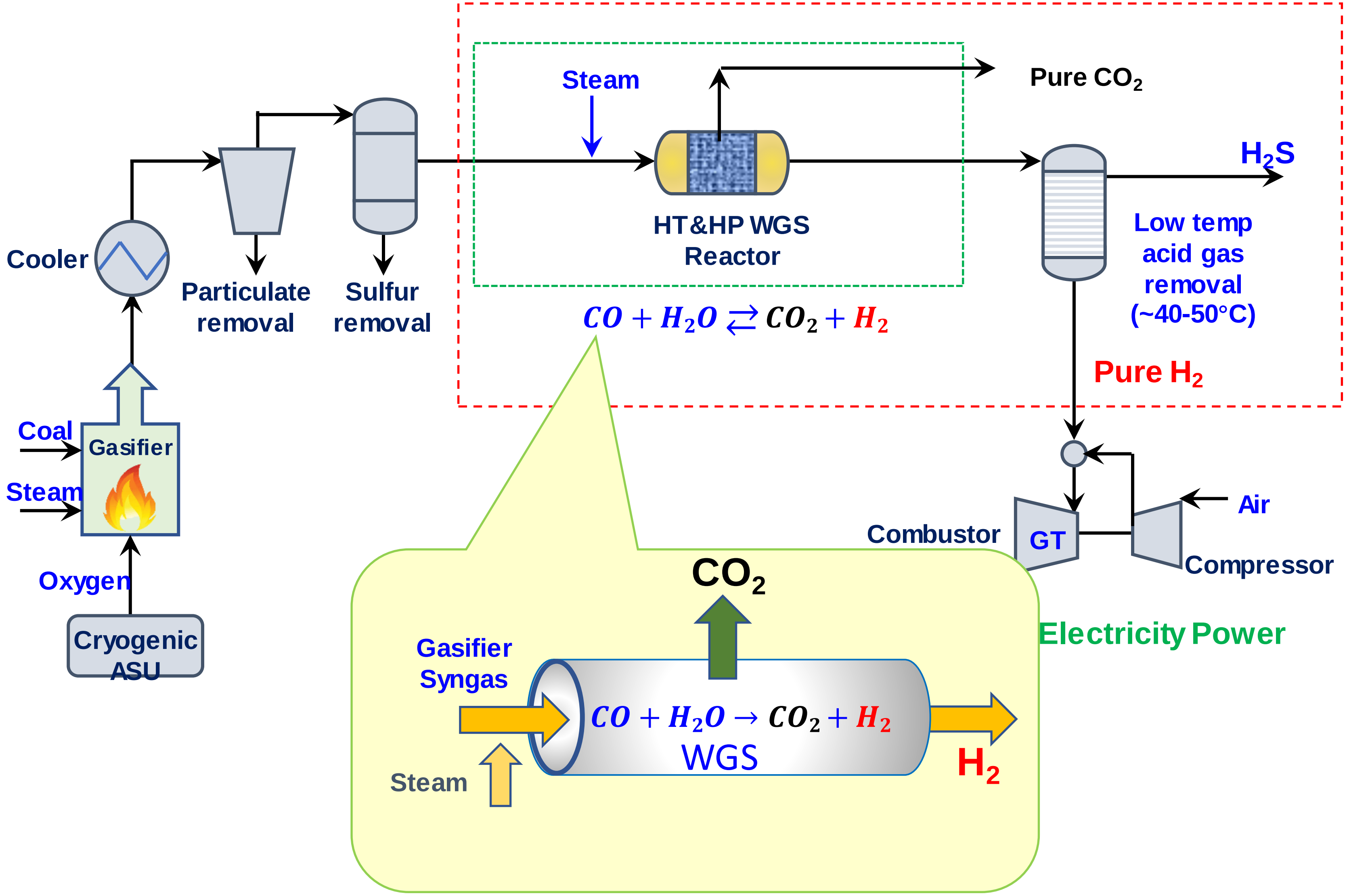
Partners

- ✓ Arizona State University (ASU)
- ✓ University of South Carolina (USC)

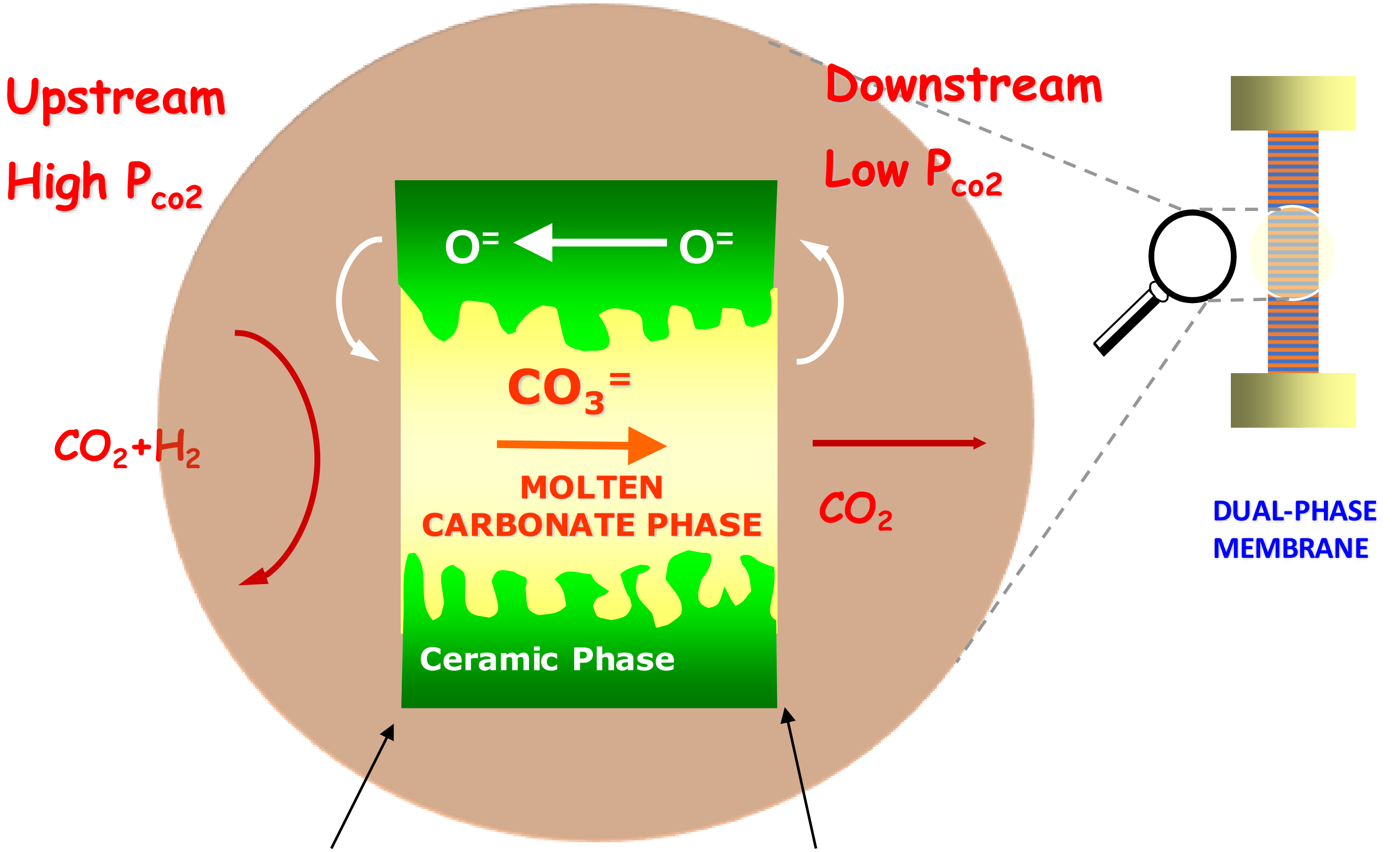
Technology Background
Technical Approach
and
Project Scope

Membrane Reactor for IGCC Process with Pre-Combustion CO_2 Capture

- ❑ One single reactor
- ❑ Improvement of kinetic of WGSR at 900°C
- ❑ Improvement of thermodynamics by separating CO_2



Concept of Ceramic-Carbonate Dual-Phase (CCDP) Membrane



$CO_2 + O^= \Rightarrow CO_3^=$

$CO_3^= \Rightarrow CO_2 + O^=$

Typical Composition

Ceramic phase:

$Ce_{0.8}Sm_{0.2}O_{2-\delta}$

Samarium Doped Ceria (SDC)

Carbonate phase:

$(Li/Na/K)_2CO_3$

M Anderson & YS Lin, Proc. *ICIM2006*, pp. 678-681 *(2006); J. Membr. Sci*. 357, 122*(2010)*

Synthesis of Porous Ceramic Supports and CCDP Membrane

Synthesis of ceramic powder by citrate method

↓

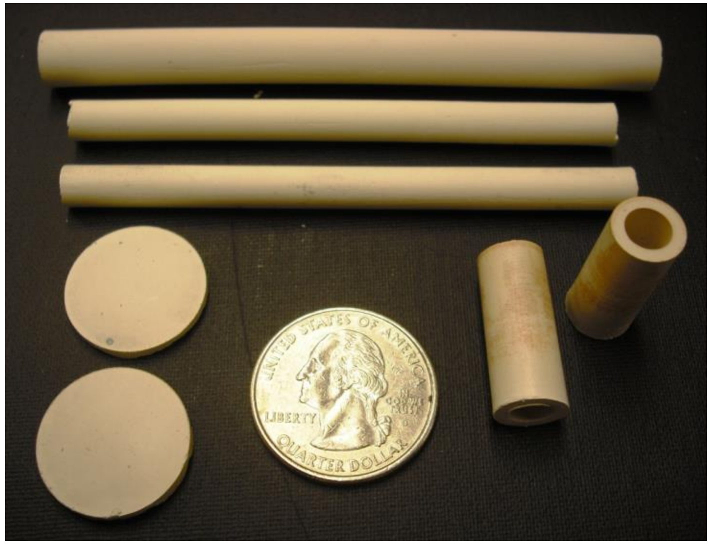
Calcination/heat-treatment to obtain desired phase

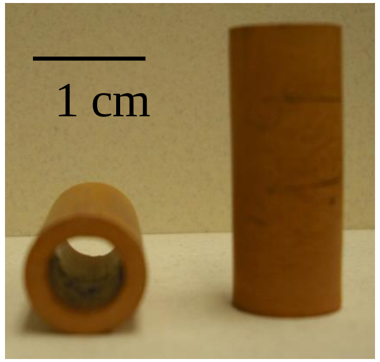
↓

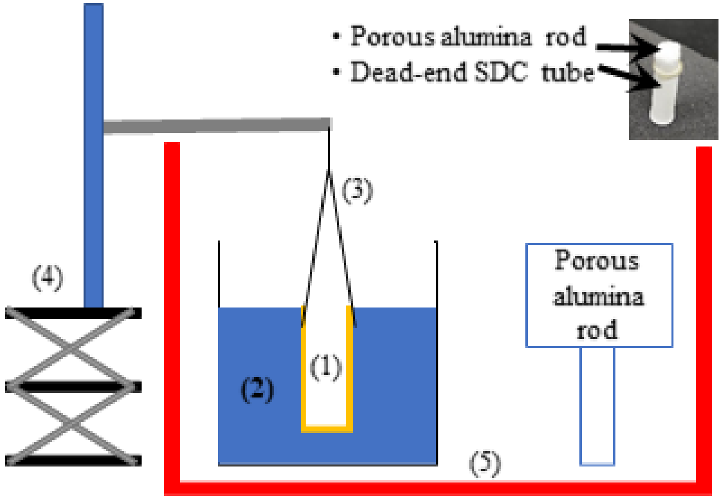
Uniaxial press (disks)	Centrifugal casting (open-end tubes)	Cold-isostatic pressing (dead-end tubes)

↓

Sintering to strengthen the structure and obtain desired porosity







Molten carbonate is infiltrated into porous ceramic supports driven by capillary pressure,

Carbon Dioxide Permeation Flux-Theory

$$J_{CO_2} = \int_{P''_{CO_2}}^{P'_{CO_2}} \frac{\sigma_T RT}{4F^2L} dlnP_{CO2}$$

Total conductance

Experimental conditions

Membrane thickness

Carbonate ion conductivity

oxygen ionic conductivity

$$\sigma_T = \frac{[\gamma_p \sigma_C][\gamma_s \sigma_i]}{[\gamma_p \sigma_C] + [\gamma_s \sigma_i]}$$

Pore or solid volume fraction to tortuosity ratio for solid (ceramic) and pore (molten carbonate) phases

$$\gamma_s = [\frac{\varepsilon}{\tau}]_s$$

$$\gamma_p = [\frac{\varepsilon}{\tau}]_p = [\frac{\varepsilon}{\tau}]_{MC}$$

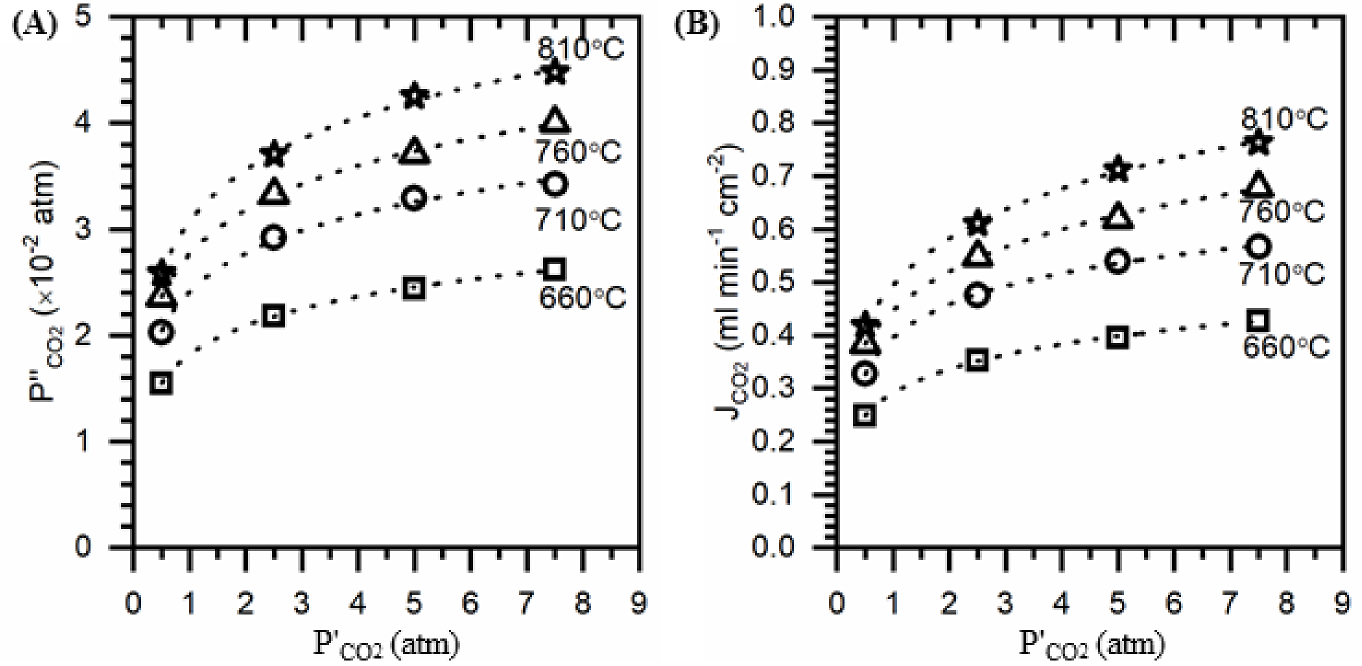
TT Norton, B Lu & YS Lin, , *J. Membr. Sci. 467*, 244 (2014)

CO_2 Pressure Dependency of Permeation Flux

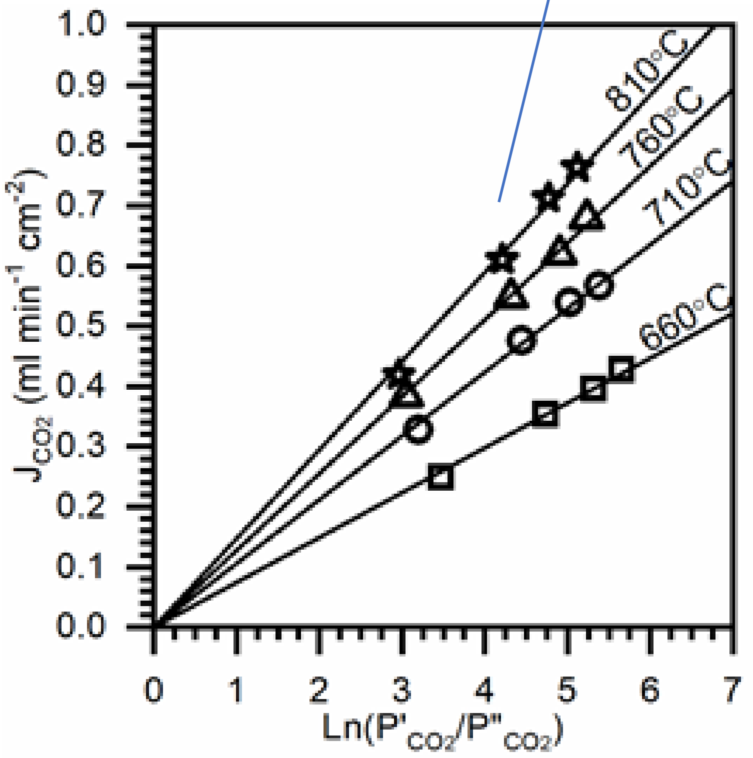
Carbonate phase rate-controlling: $[\gamma_p \sigma_C] \ll [\gamma_s \sigma_i]$

$$J_{CO_2} = \frac{k\ RT}{4F^2L} ln\left(\frac{P'_{CO_2}}{P''_{CO_2}}\right)$$

Feed gas: CO2/N2 (50/50 v%)
Sweep gas: Helium (1 atm)

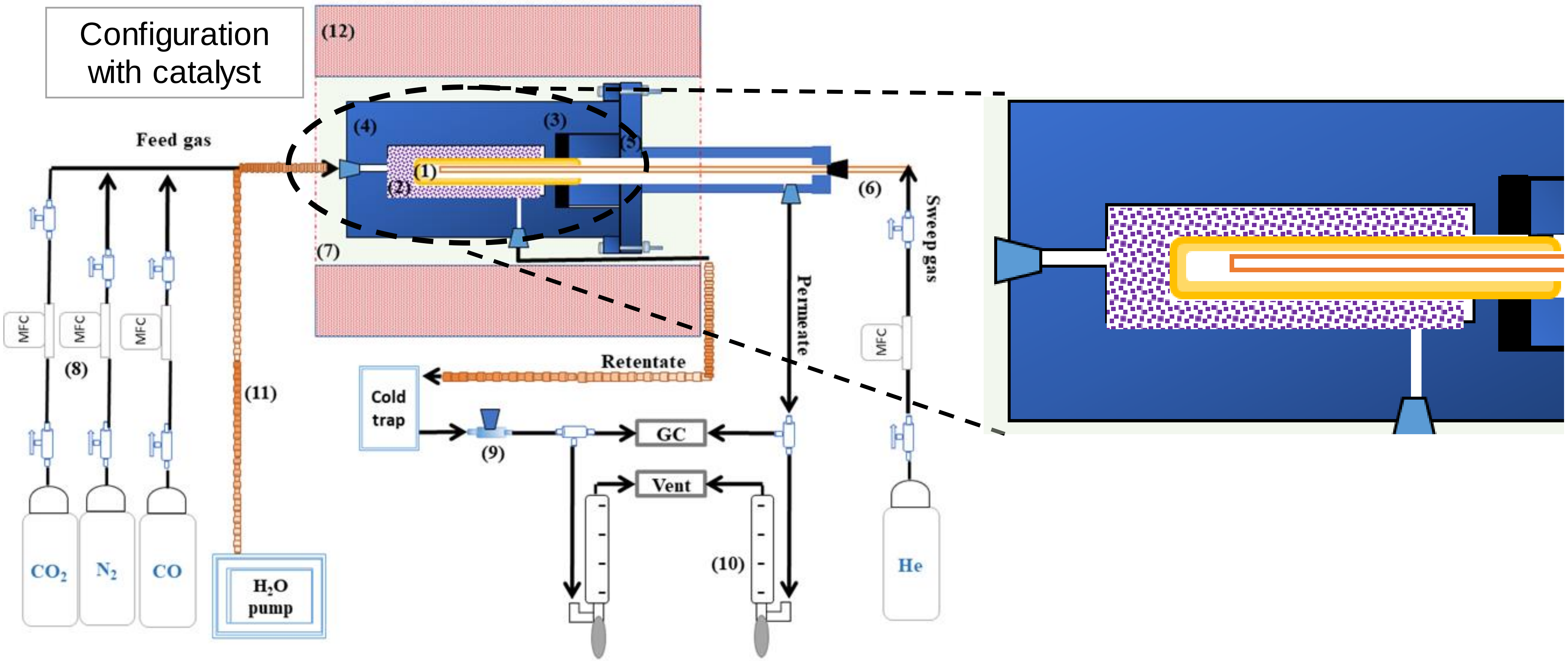


$$k = \frac{4F^2L}{RT}(slope)$$



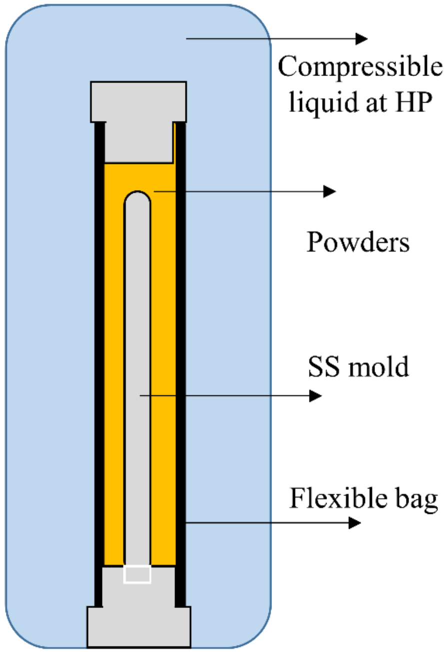
Progress
Accomplishments
and
Current Status

Set-up and Module for High Temperature/High Pressure Membrane Reactor for WGS Reaction Tests



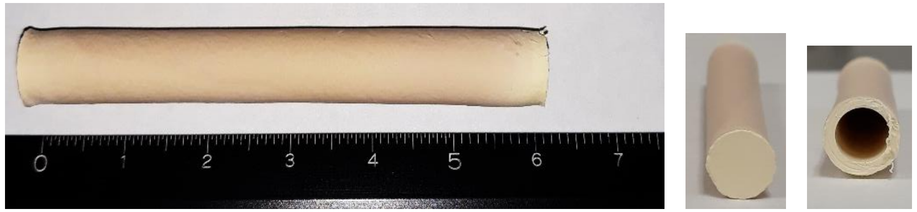
Fabrication of Dead-End Tubular $Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC) Supports

- **Cold Isostatic Press (CIP) method** (dead-end tubes)

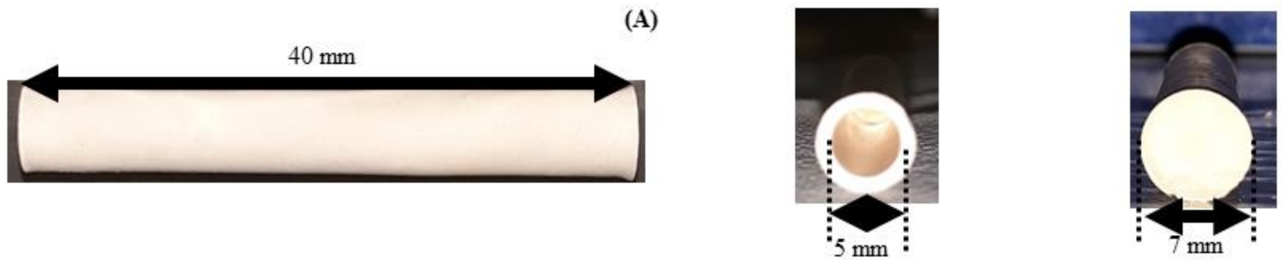


- ✓ Press: 20kpsi (~1500bar)
- ✓ Long tubes
- ✓ High mechanical strength
- ✓ Dead-end tubes
- ✓ One compressing seal

Green dead-end tube



Sintered dead-end tube (1200 °C)



Water Gas Shifting (WGS)

$$CO + H_2O \rightarrow CO_2 + H_2$$

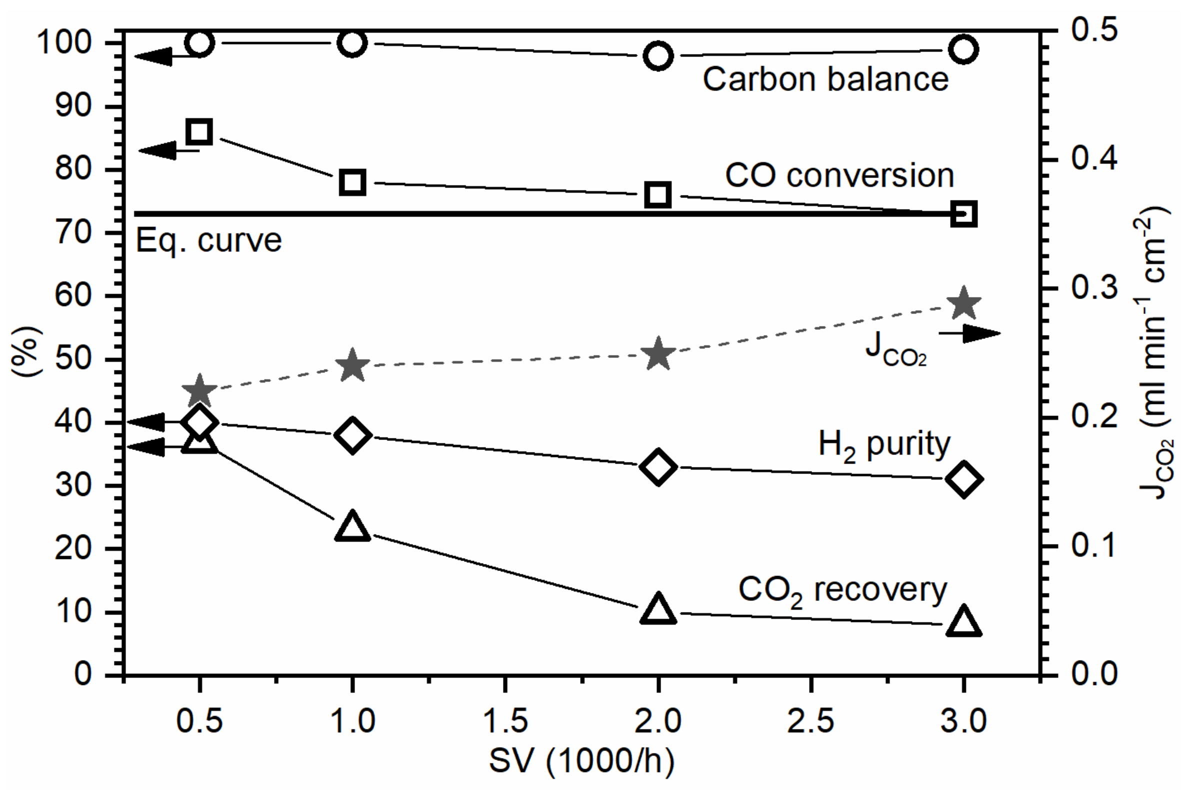
- **Tubular Membrane**

  Ceramic: $Sm_{0.2}Ce_{0.8}O_{1.9-\delta}$ (SDC) (Low Porosity)
  Carbonate: $Li_2CO_3/Na_2CO_3/K_2CO_3$
  OD: 0.7 cm, ID: 0.5 cm, Length: 4.0 cm
  Wall thickness: 1 mm;

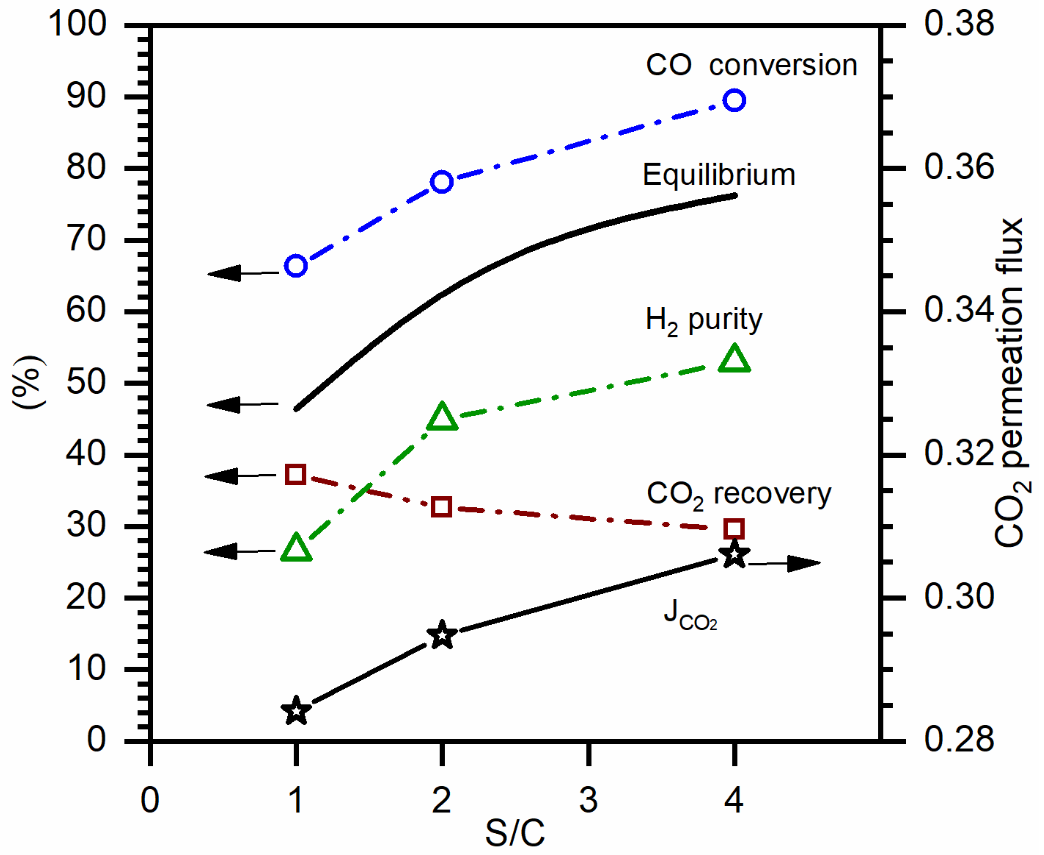
- **Reaction conditions**

  Temperature: 700-950 ^{o}C;
  Feed pressure: 1-15 atm;
  Sweep pressure: 1 atm
  Catalyst: Co-Mo-Mg(AlO2)$_2$ (SSK-10) (Haldor Topsoe)
  Feed side Space Velocity: 150-2100 h^{-1}
  Sweep side: He: 50-200 mL·min^{-1}.

Results of WGS in Membrane Reactor – Effect of SV and S/C

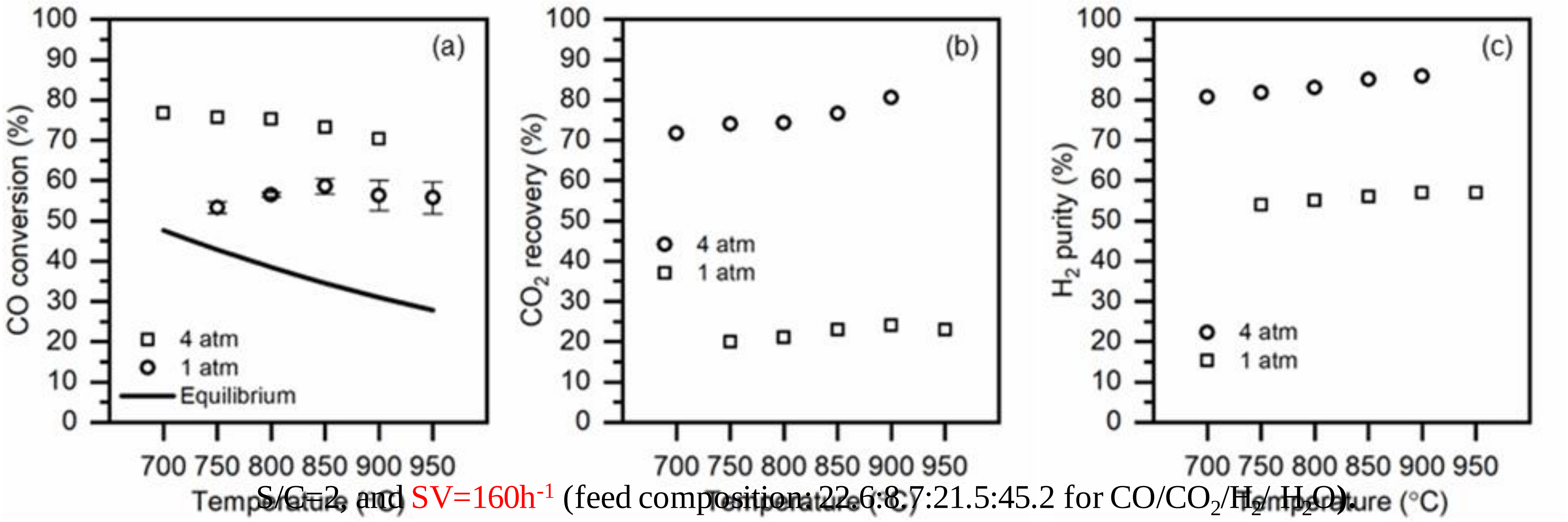


with a catalyst at 850 °C, 7 atm, and S/C=4 at different space velocities (feed composition: 45.7:13.1:41.3:182.8 for $CO/CO_2/N_2$/steam).



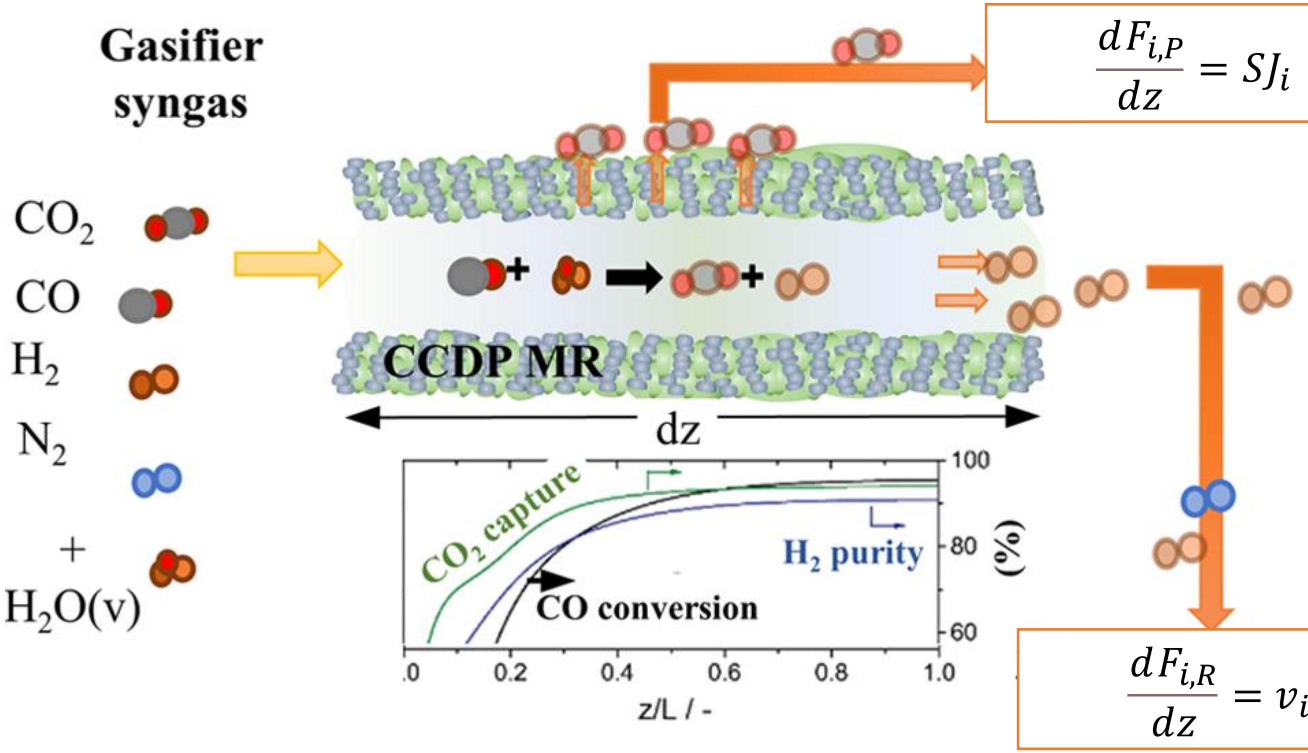
with the catalyst at 900°C and 5 atm as a function of steam to carbon ratio (S/C). The permeate side was vacuumed at 85 mTorr, SV=500 1/h

Results of WGS in Membrane Reactors – Effect of Temperature and Pressure



S/C=2, and SV=160h^{-1} (feed composition: 22.6:8.7:21.5:45.2 for $CO/CO_2/H_2/H_2O$).

Predicting Performance at High Pressure by Modeling from Low Pressure Experimental Data



$$\frac{dF_{i,P}}{dz} = SJ_i$$

$$\frac{dF_{i,R}}{dz} = v_i A r_{CO} - SJ_i$$

WGS Reaction Kinetics

$$r_{CO} = k_0 exp\left(\frac{-37.99}{RT}\right) P_{CO}^{0.50} P_{H_2O}^{0.32} P_{CO_2}^{-0.12} P_{H_2}^{-0.11} (1-\beta)$$

CO_2 Permeation Flux

$$J_{CO_2} = \frac{\alpha RT}{4F^2 L} Ln\left(\frac{p_{CO_2,R}}{p_{CO_2,P}}\right)$$

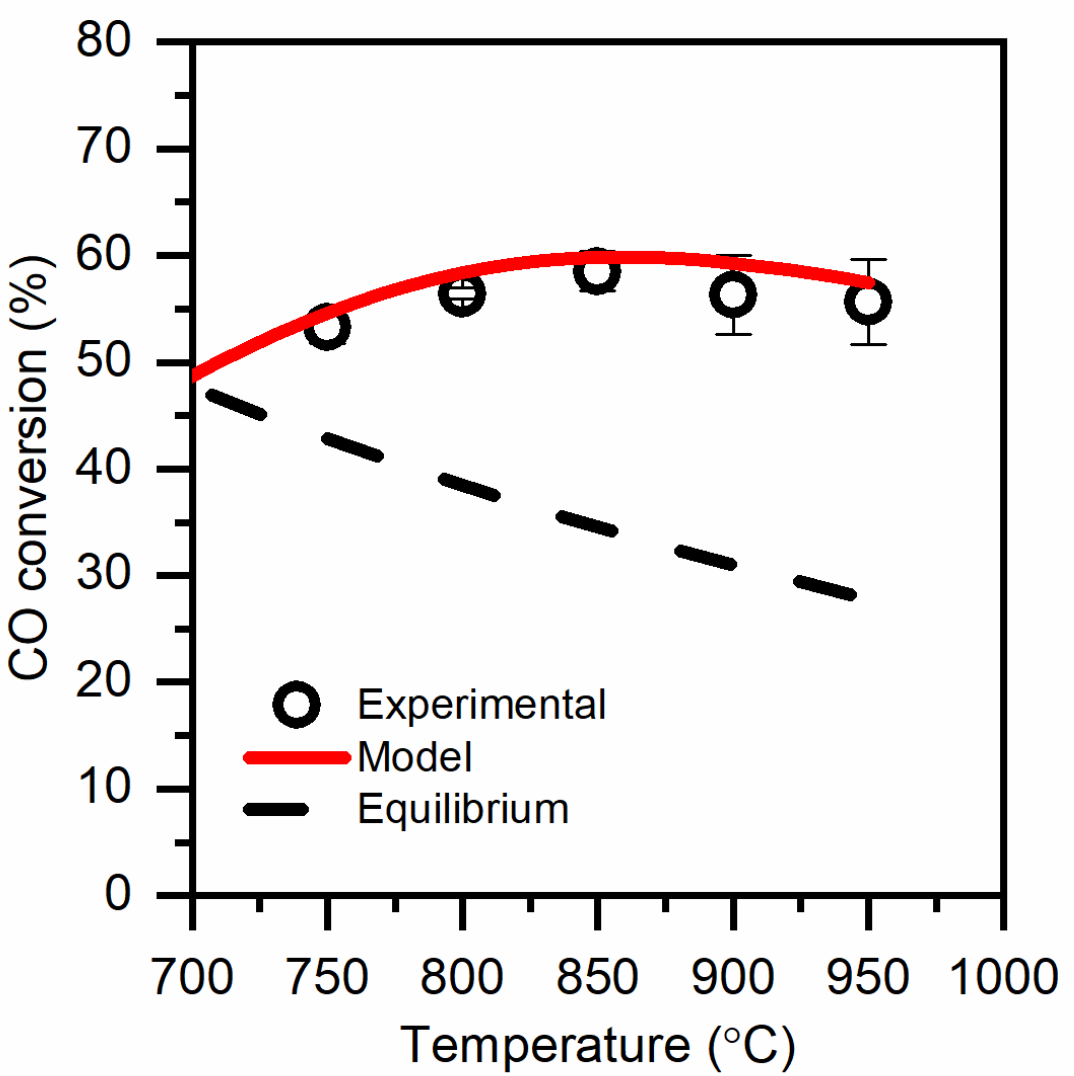
Both measured experimentally in our lab

Predicted Results of WGS Reaction in Membrane Reactor
in Comparison with Experimental Data

Feed gas	Mol %
CO	25.0
CO2	9.7
H2	24.0
N2	0
H2O	38.9

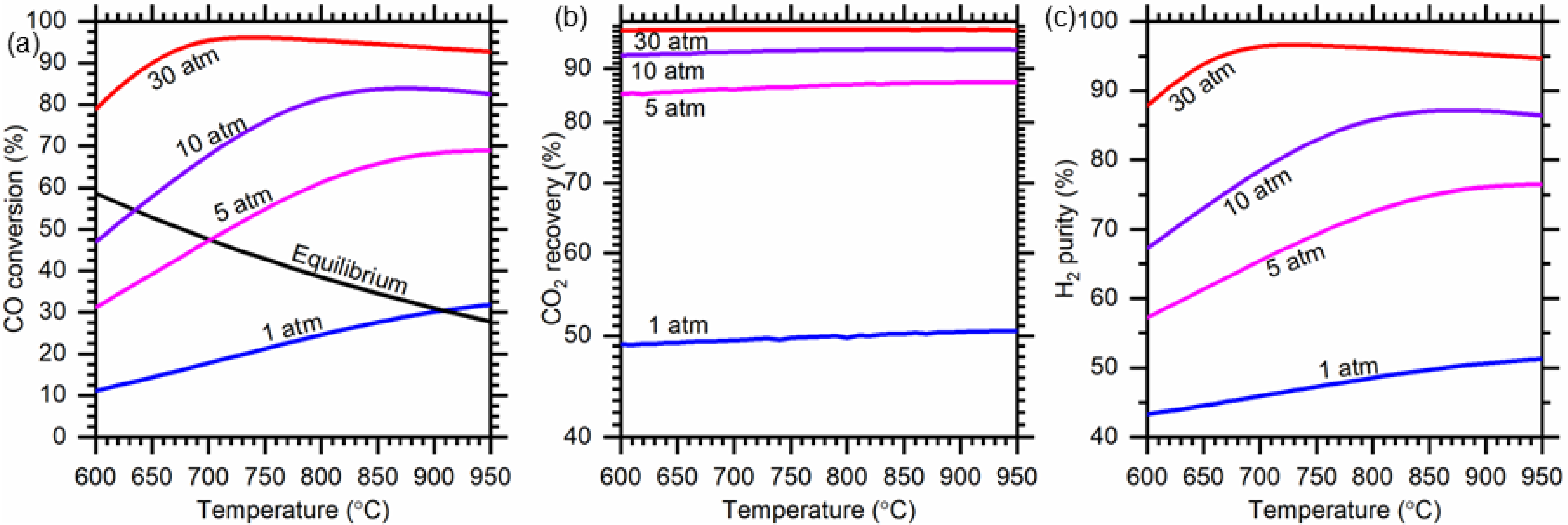
S/CO = 2

Sweep gas: He 50 ml/min
Catalyst: 4gr
SV: 160 h-1
Feed and sweep pressure: 1 atm



Modeling Results at High Pressures

Modeling results for WGS reaction in CCDP MR with catalyst using a feed gas of $CO/CO_2/H_2/H_2O$ (22.6:8.7:21.5:45.2) at $SV=700\ h^{-1}$ as a function of temperature and different total feed pressures.

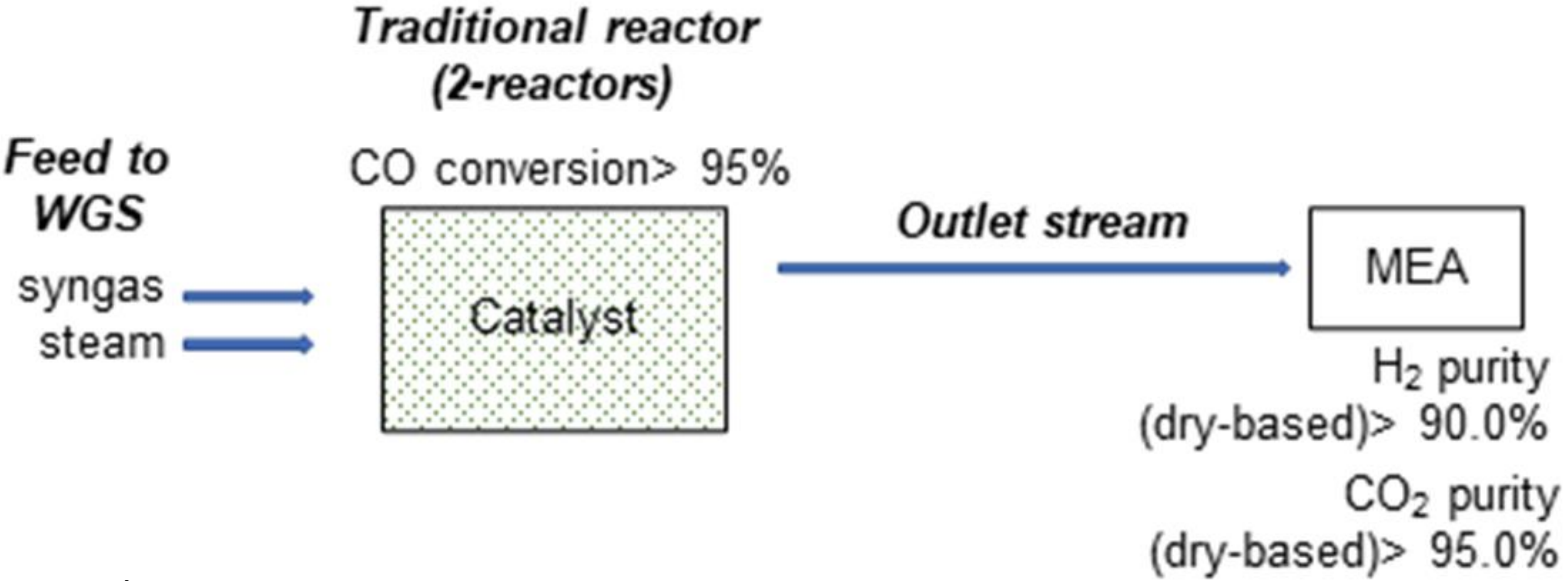


Syngas Feed and Operation Conditions for Membrane Reactor

(for 550 MW Power Plant)

Operating conditions	Feed Gas (Syngas)	Steam Addition
Temperature (°C)	232	288
Pressure (bar)	30	30
Flow rates (mol/s)		
CO_2	884	0
CO	2296	0
H_2	2187	0
H_2O	3545	1047
Inert (including H_2S)	201	0

Target for WGS for H_2 Production with CO_2 Capture



Baseline Case B5B

Ref: Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminouscoal and Natural Gas To Electricity, **Netl-Pub-22638, Sept. 24, 2019**

Performance of CCDP Membrane Reactor for WGS with CO_2 Capture in one Device

Key Parameter: Feed Pressure: 30 atm, Sweep Pressure: 1 atm, Temperature: 650-900°C

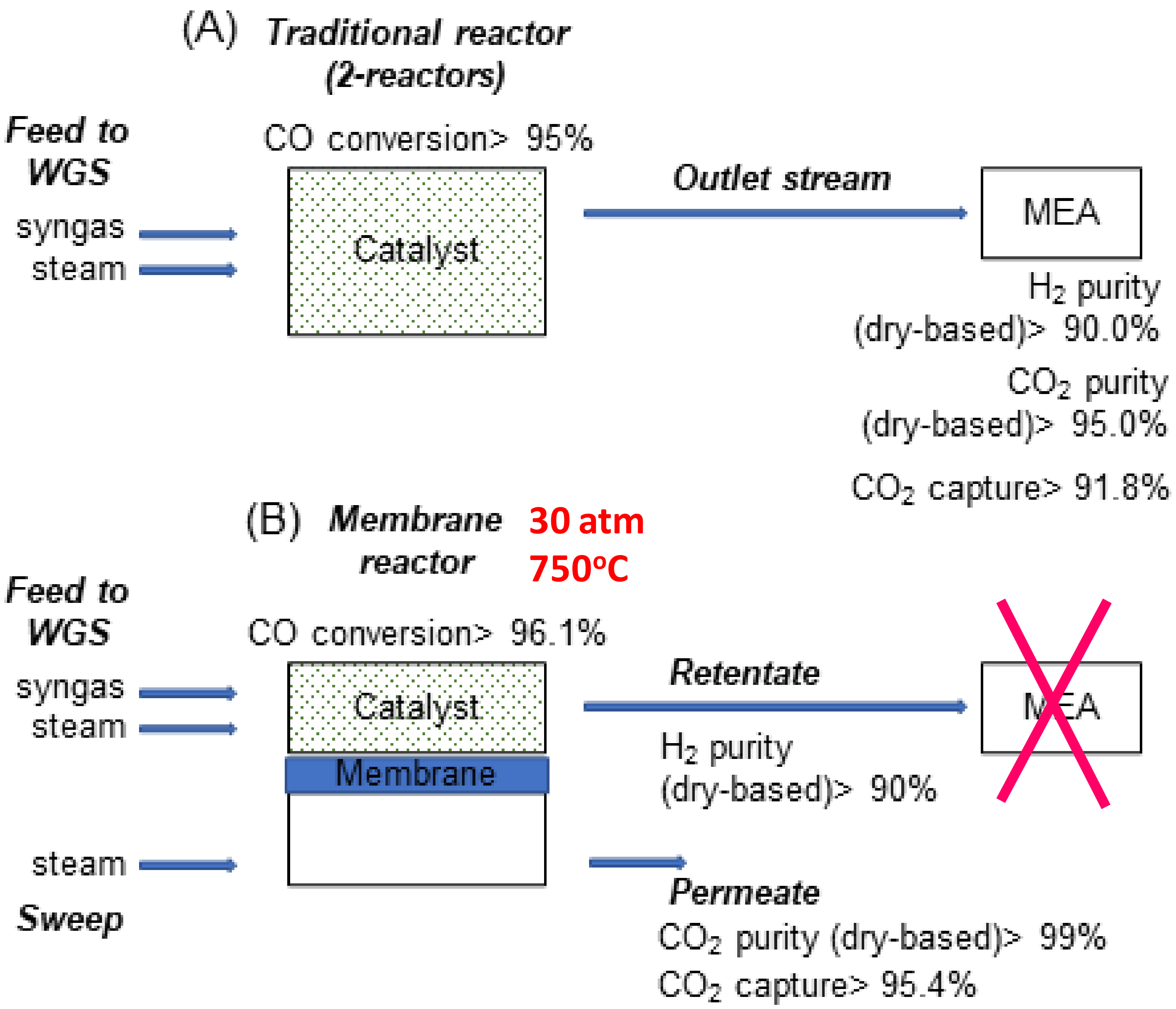
	CCDP Membrane CO_2 permeance coefficient (α_k)(mol/s·m^2·K)	Membrane surface area to catalyst volume ratio (φ)(m^2/m^3)	Space velocity (SV) (h^{-1})	Sweep flow to feed flow rate ratio (R) (mol/mol)
Base Case	0.0052	234	250	0.83
Case 1	0.0125	234	700	1.42

Results of Membrane Reactor Meeting the Performance Criteria

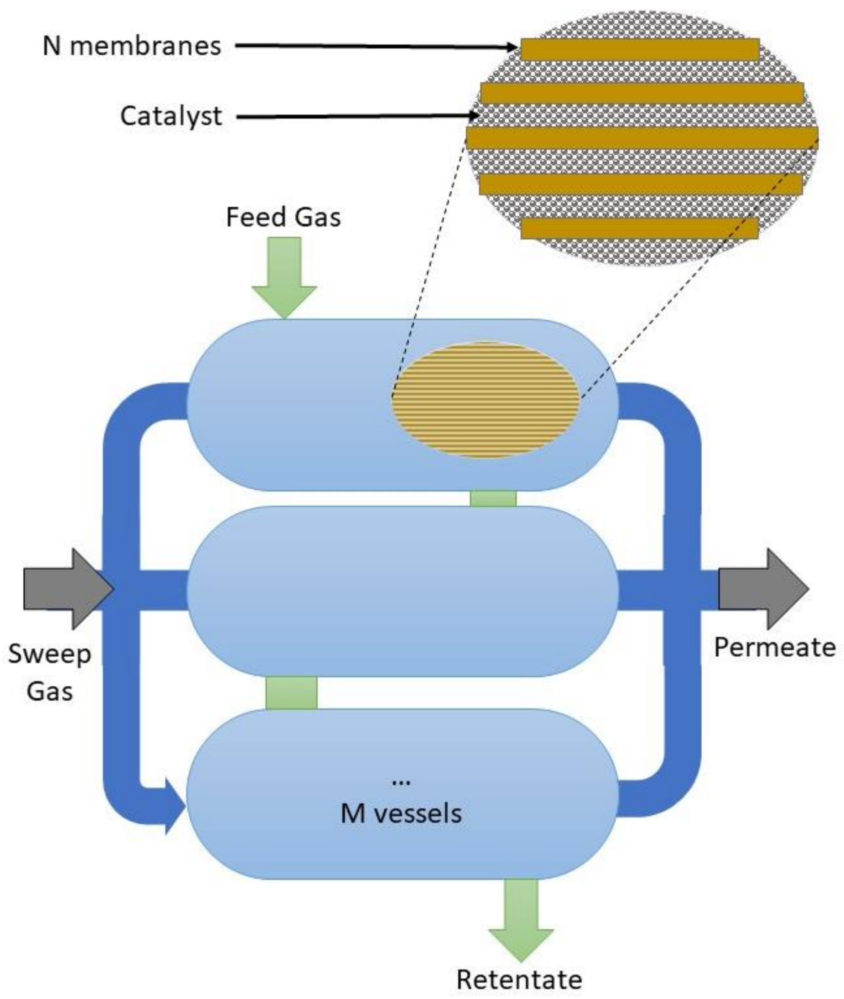
	Average $\bar{J}_{CO_2}$ (cm^3/min.cm^2)	CO conversion (%)	C recovery (capture) (%)	Dry-based H_2 purity# (%)
Base Case	0.5	95.01	94.12	91.86
Case 1	1.5	96.10	95.54	92.76

Temperature 750°C, CO_2 stream purity (dry base) is >99% because CCDP only permeates CO_2

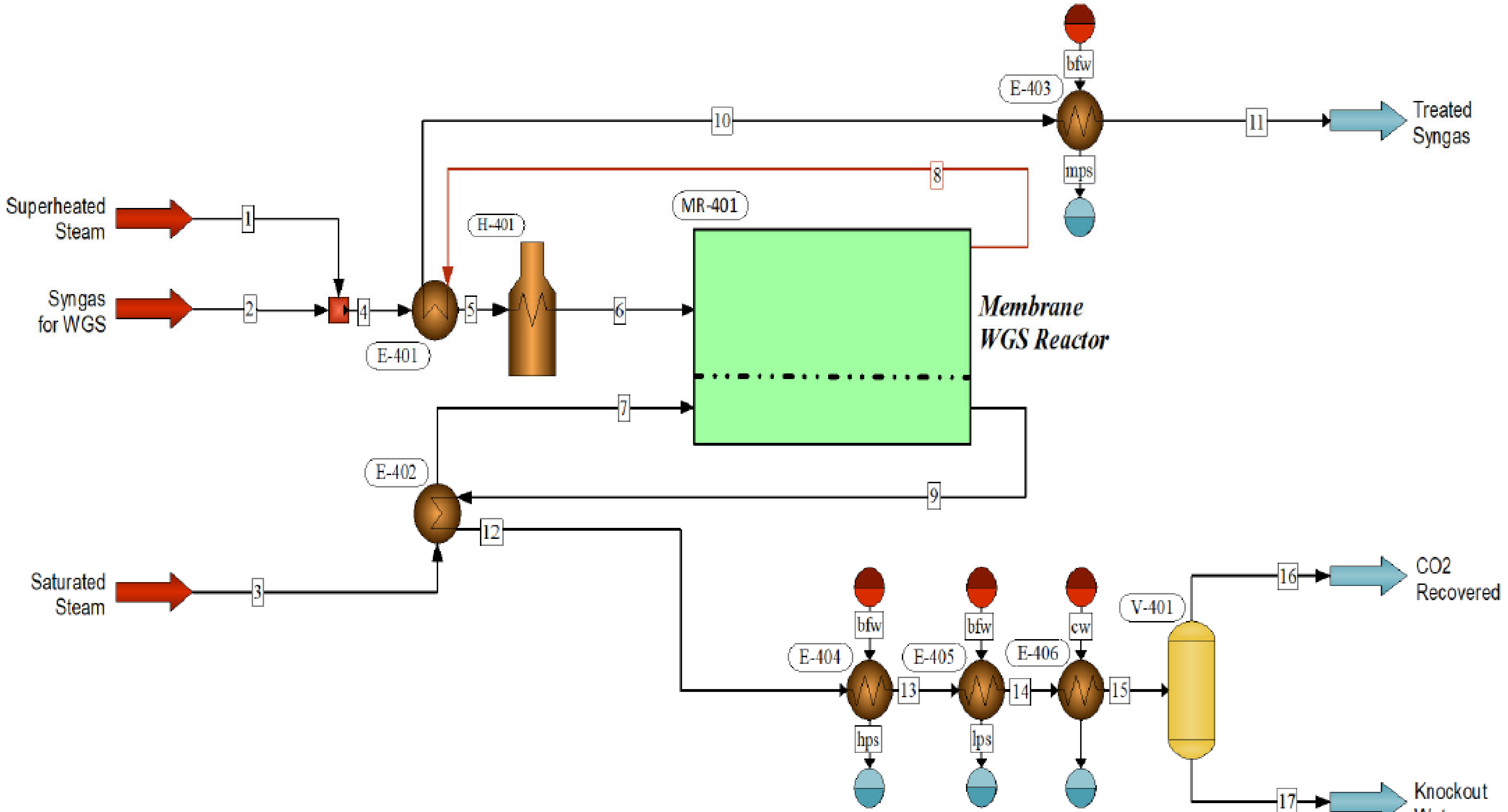
Membrane Reactor for WGS for H_2 Production with CO_2 Capture



Tube-Shell Membrane Reactor



Process Design of Membrane Reactor for WGS



WGS System Design Configuration, Performance and Cost Comparison

550 MW Coal-Fired IGCC Power Plant: Gasified Syngas as Feed for WGS
(819,302 M^3/h)

Membrane fabrication capital cost

	Base Case	Case 1
Membrane Area (Mm^2)	819,302	292,872
Membrane tubes #	4,429,022	1,583,375
Membrane cost (M$)	355	130

Tube dimension: 1 cm x 5 m

	WGS + MEA	MR System
WGS Trains	1	1
WGS Stages	HTS & LTS	HTS
WGS Reactors	9	12
WGS CO Conversion	0.95	0.95
WGS Reactor Pressure	30 bar	30 bar
WGS Catalyst	H-T SSK-10	H-T SSK-10
WGS Catalyst initial charge	3602 m^3	3279 m^3
Membrane area	-	764,425 m^2
CO_2 Recovery Trains / Type	1 MEA	-
Carbon Capture (%)	91.8	94.1
WGS Reactors	240 M$	951 M$
CO_2 Recovery & Energy	287 M$	56 M$
Total Plant	527 M$	1007 M$

Membrane reactor base case

Summary

- CCDP Membrane Reactor can enhance significantly WGS reaction with in-situ CO_2 capture
- Performance of membrane reactor depends on membrane permeance, catalyst activity, and operation conditions (feed pressure, space velocity and membrane surface to catalyst volume ration)
- High pressure favors performance of the membrane reactor.
- At 30 bar and other conditions similar to fixed-bed reactor, the membrane reactor can meet WGS reaction/CO_2 capture target without subsequent CO_2 separation unit
- Membrane reactor process has much lower operation costs but higher capital costs compared to the conventional Process

Acknowledgement

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- Prof. Gregory Raupp
- John Morgen
- Prof. Kevin Huang

Thank You!

Project Objectives

- To synthesize the chemically/thermally stable Ceramic Carbonate Dual-Phase (CCDP) membranes.
  - ✓ CO_2 permeance > 2000 GPU (6.5×10^{-7} $mol/m^2 \cdot s \cdot Pa$)
  - ✓ Selectivity > 500
  - ✓ Resistant to H_2S
- To fabricate tubular CCDP membrane reactor modules.
  - ✓ High-temperature >700 °C
  - ✓ High-pressure > 20 atm
  - ✓ WGS membrane reactor applications.
- To identify conditions for WGS in membrane reactor with
  - ✓ 99% purity of CO_2 stream
  - ✓ 90% purity of H_2 stream