Arizona State University

Pre-Combustion Carbon Dioxide Capture by a New Dual-Phase Ceramic-Carbonate Membrane Reactor

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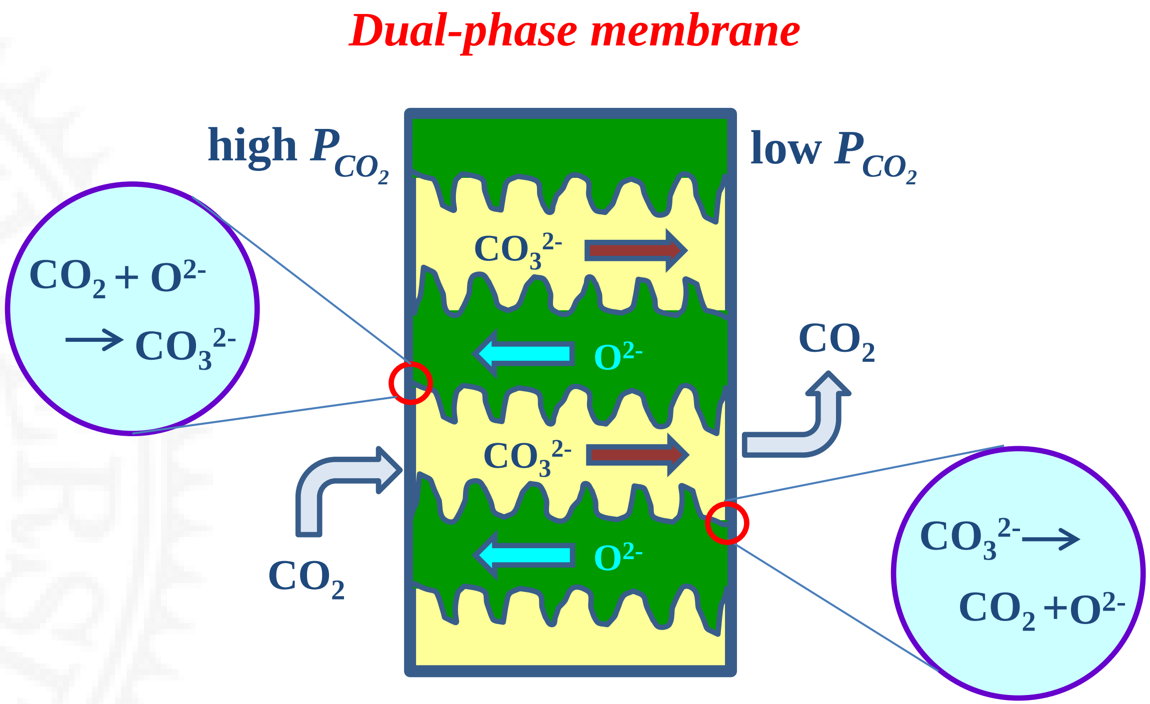
Project Objectives

- Synthesize chemically/thermally stable dual-phase ceramic-carbonate membranes with CO_2 permeance and CO_2 selectivity (with respect to H_2, CO or H_2O) larger than 5×10^{-7} mol/m^2·s·Pa and 500;
- Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications;
- Identify experimental conditions for WGS in the dual-phase membrane reactor that will produce the hydrogen stream with at least 93% purity and CO_2 stream with at least 95% purity.

Technology Background

Ceramic-carbonate dual-phase membrane

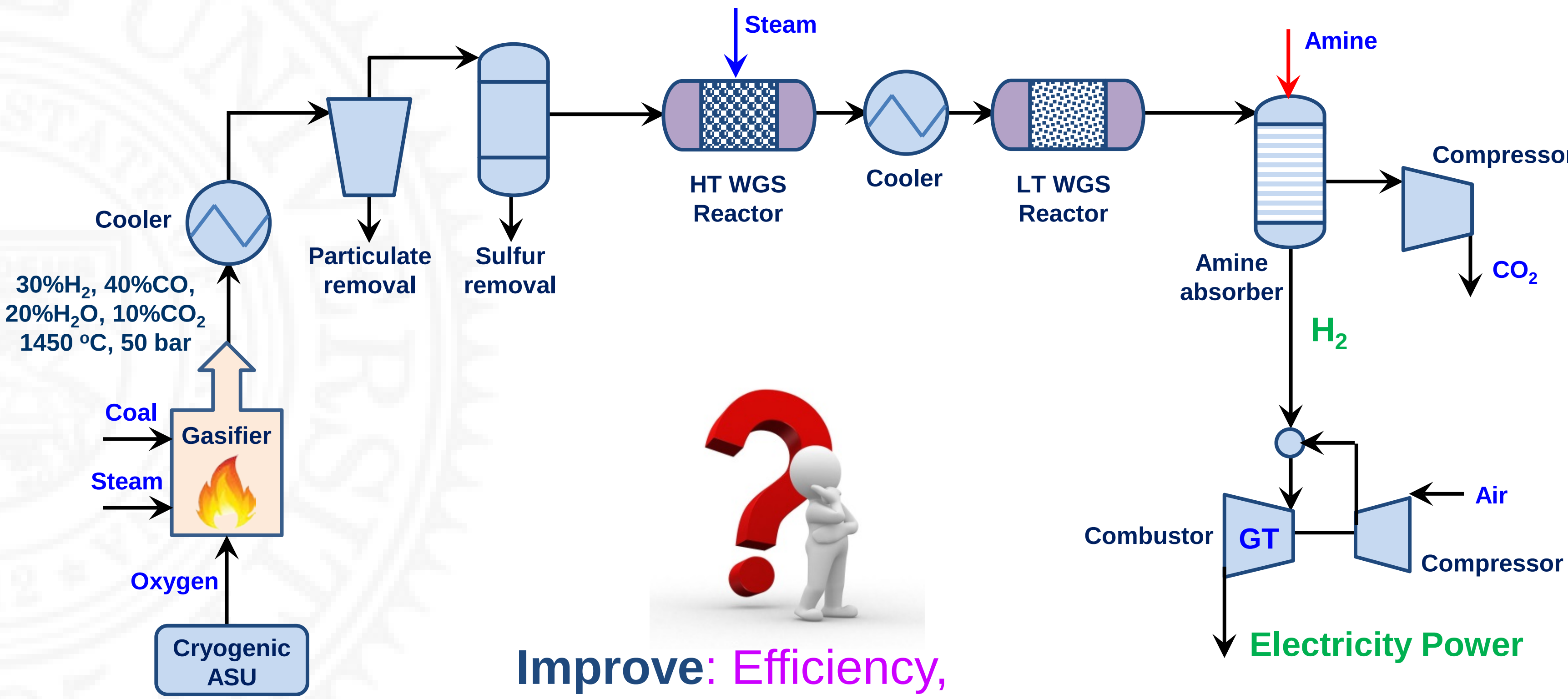


Ceramic phase: oxygen ion conductor, $Sm_{0.2}Ce_{0.8}O_{1.9-\delta}$ (SDC)

Molten carbonate phase: Li, Na, K carbonates

High temperature (>500 ºC) ; Theoretical CO_2 selectivity 100%

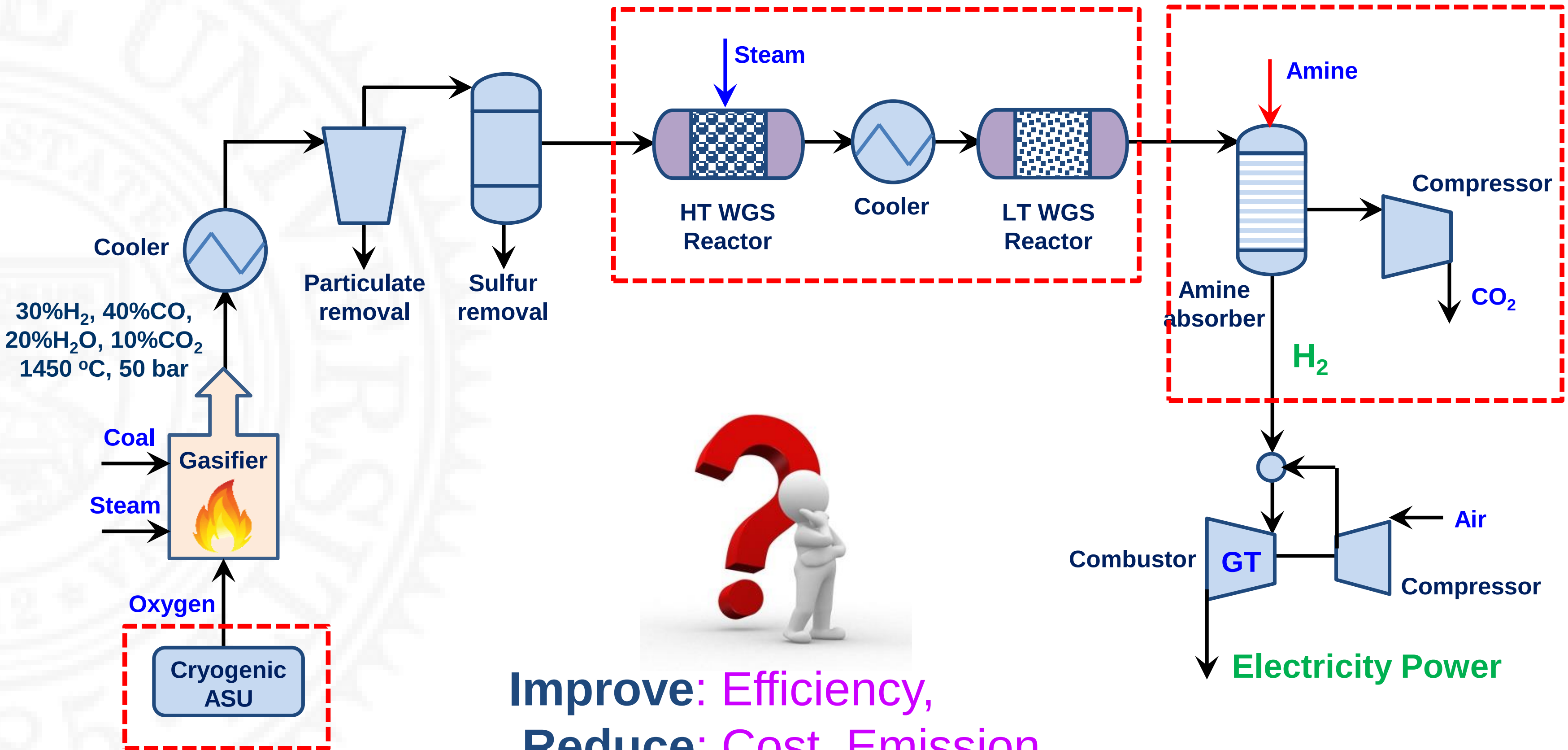
IGCC power plant with CO_2 capture



Improve: Efficiency,

Reduce: Cost, Emission

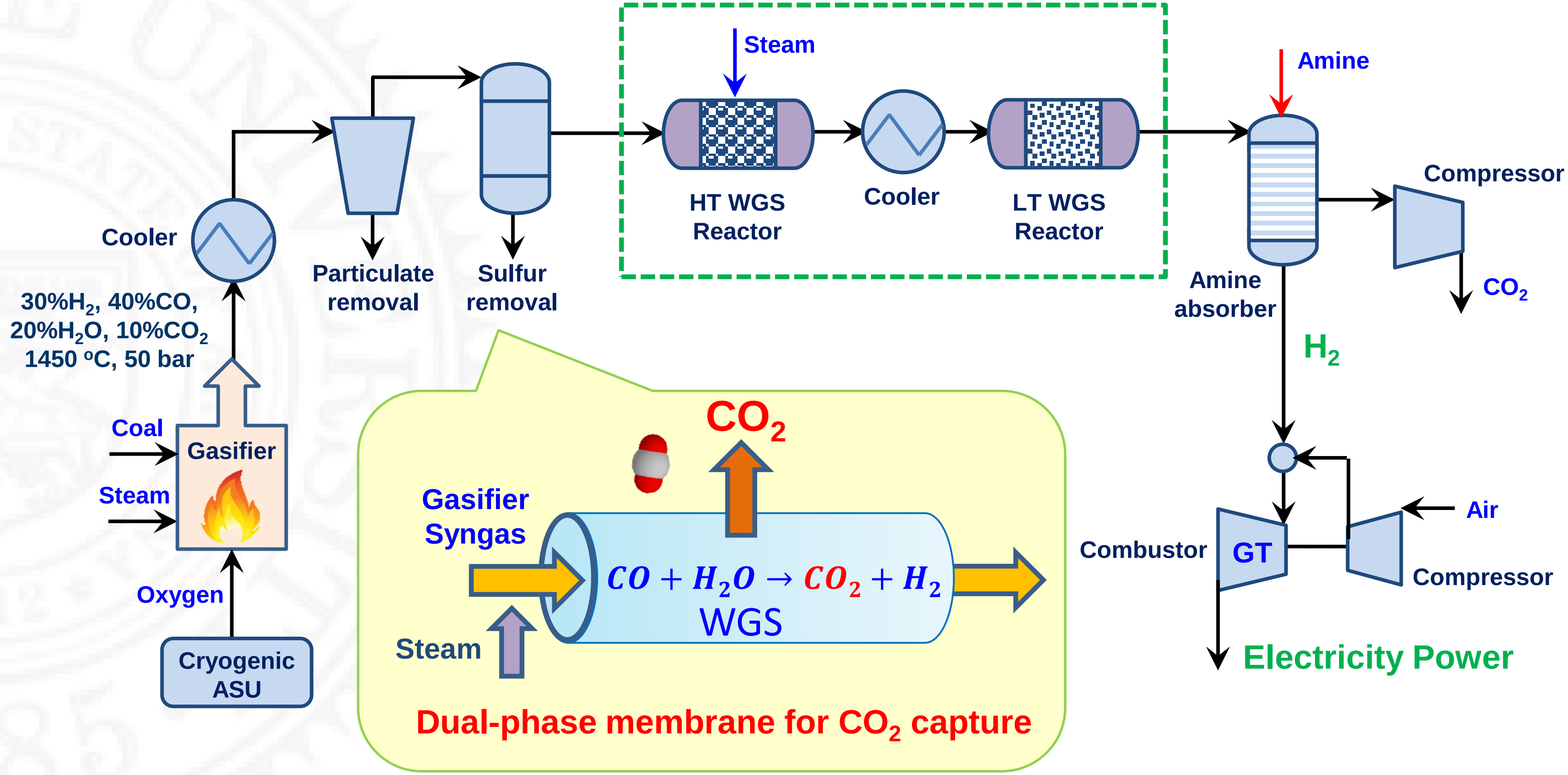
IGCC power plant with CO_2 capture



Improve: Efficiency,
Reduce: Cost, Emission

Advanced membrane technology

Dual-phase membrane reactor for high temperature WGS



900 °C, no catalyst is required

Advantages of dual-phase WGS membrane reactor

- Advantages
  - High thermal and chemical stability
  - High CO_2 permeability (especially under high feed pressure)
  - Removal of pure CO_2
  - Keep H_2 rich stream at high pressure

- Potential impacts
  - **CO conversion** → Reduce the cost of subsequent WGS reaction
  - **CO_2 removal** → Reduce the cost of subsequent CO_2 capture

Progress and Current Status of Project

Tasks

- Task A Synthesis of Dual-Phase Membrane Disks
- Task B Studying Permeation and Separation Properties of Disk Membranes
- Task C Synthesis of Tubular Dual-Phase Membranes
- Task D Gas Separation and Stability Study on Tubular Membranes
- Task E Synthesis and WGS Reaction Kinetic Study of High Temperature Catalyst
- Task F Modeling and Analysis of Dual-Phase Membrane Reactor for WGS
- Task G Experimental Studies on WGS in Dual-Phase Membrane Reactors
- Task H Economic Analysis

Tasks A-D

❖ **Work accomplished**

➢ **Membrane materials**

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)

$Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ (BYS)

Yttria-stabilized zirconia (YSZ)

$La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)

$Sm_{0.2}Ce_{0.8}O_{1.9-\delta}$ (SDC)

➢ **Membrane geometry**

Disk membrane

Tubular membrane

Symmetric thick membrane

Asymmetric thin membrane

➢ **Membrane property**

CO_2 transport property

Long-term stability

CO_2 permeation model

Tasks

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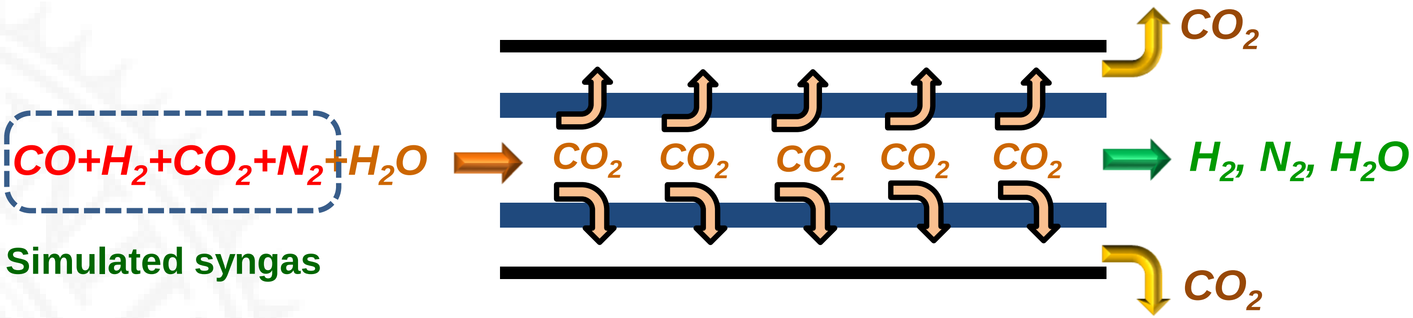
High temperature water gas shift (WGS) reaction



◆ Membrane

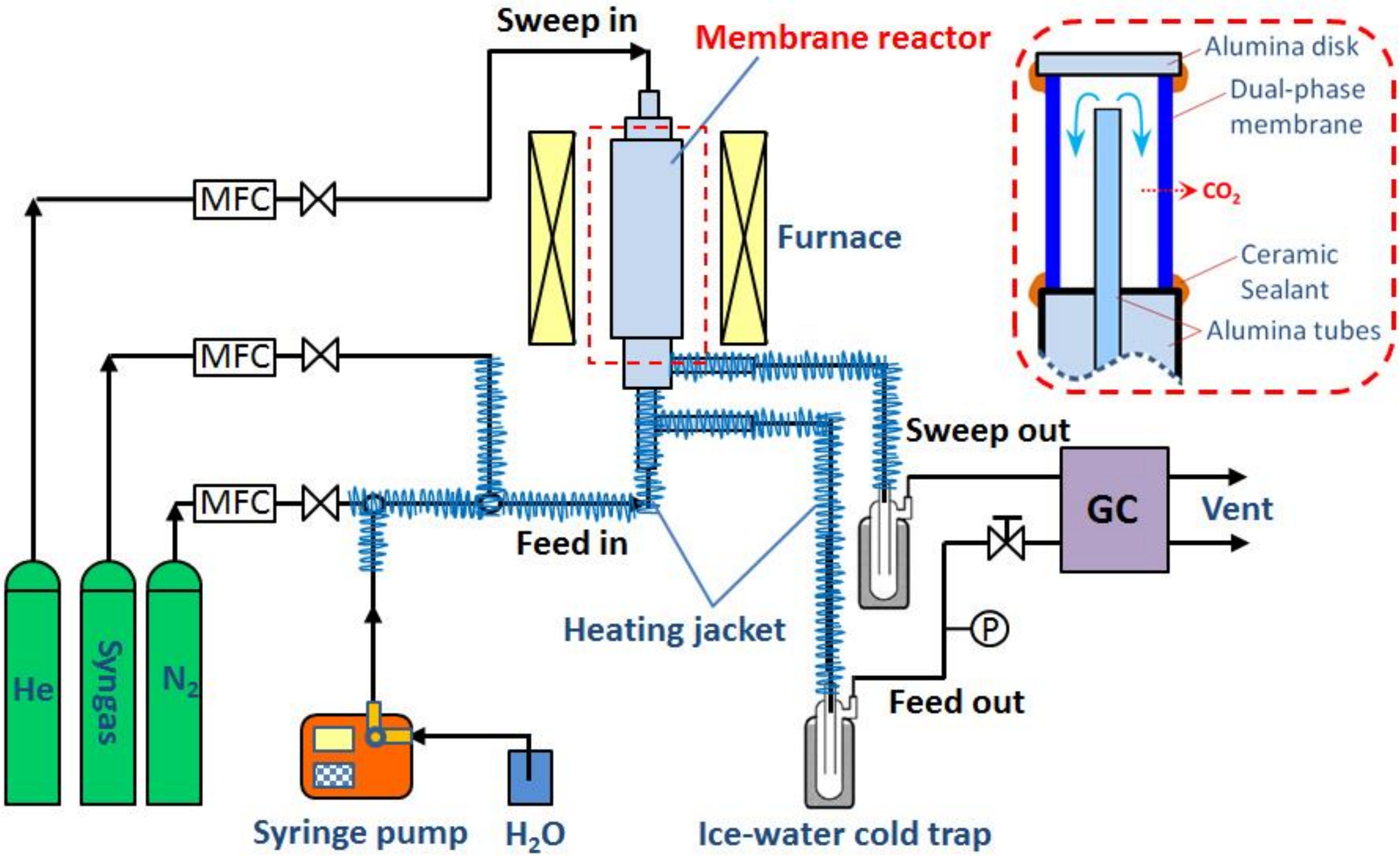
Ceramic: SDC; Carbonate: $Li_2CO_3/Na_2CO_3/K_2CO_3$
OD: 1.1cm; ID: 0.8cm; Thickness: 1.5 mm; Effective length: 2.5cm.

◆ Reaction conditions

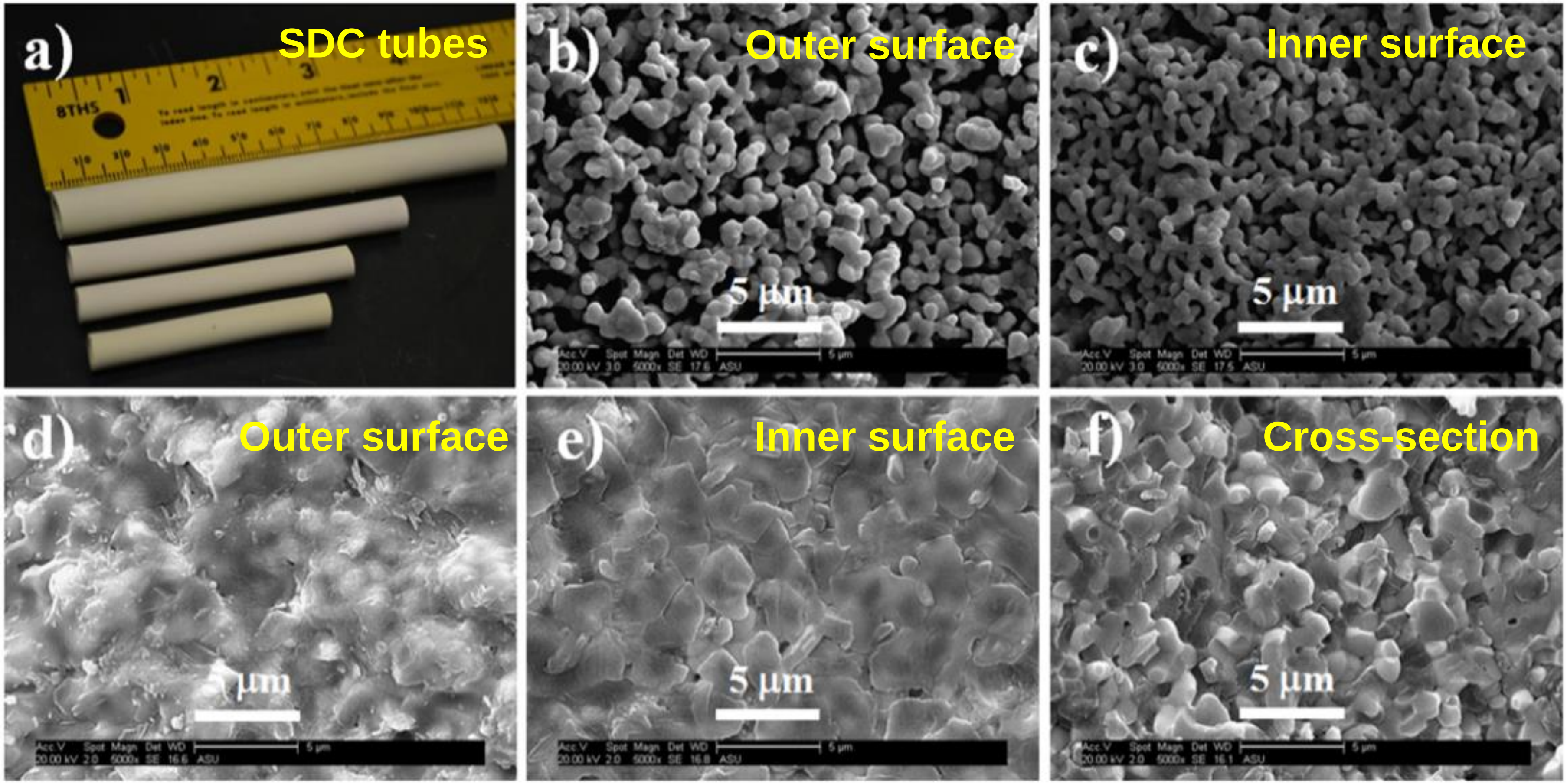
Temperature: 800-900 ^{o}C;
Feed, Sweep side pressure: 1 atm;
Catalyst: No;
Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2 and 4.5% N_2;
Feed side: Syngas flow rate 10-30 mL·min^{-1}, N_2 flow rate 10 mL·min^{-1}, steam to CO molar ratio 1.0-3.0;
Sweep side: He flow rate 60 mL·min^{-1}.

High temperature syngas WGS reaction

❖ **Schematic diagram**

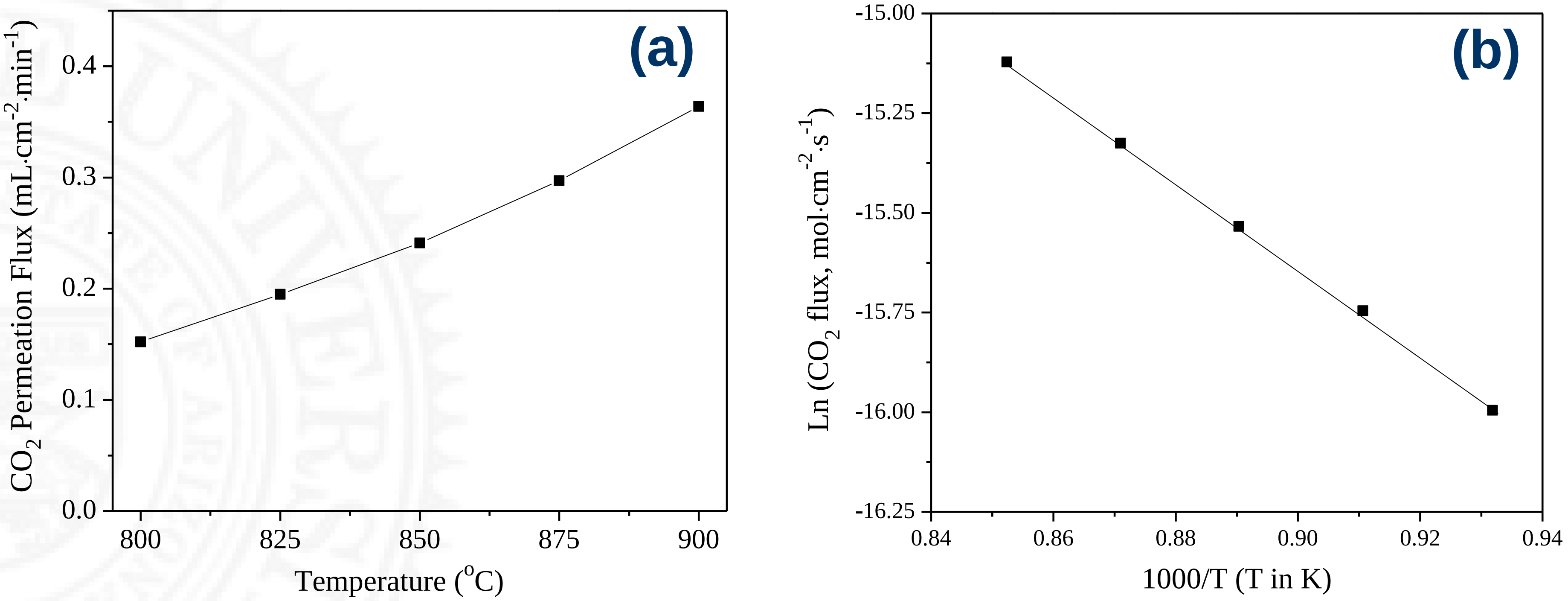


Morphology of tubular dual-phase membrane



a-c: porous supports; d-f: dual phase membrane

CO_2 flux during syngas WGS reaction

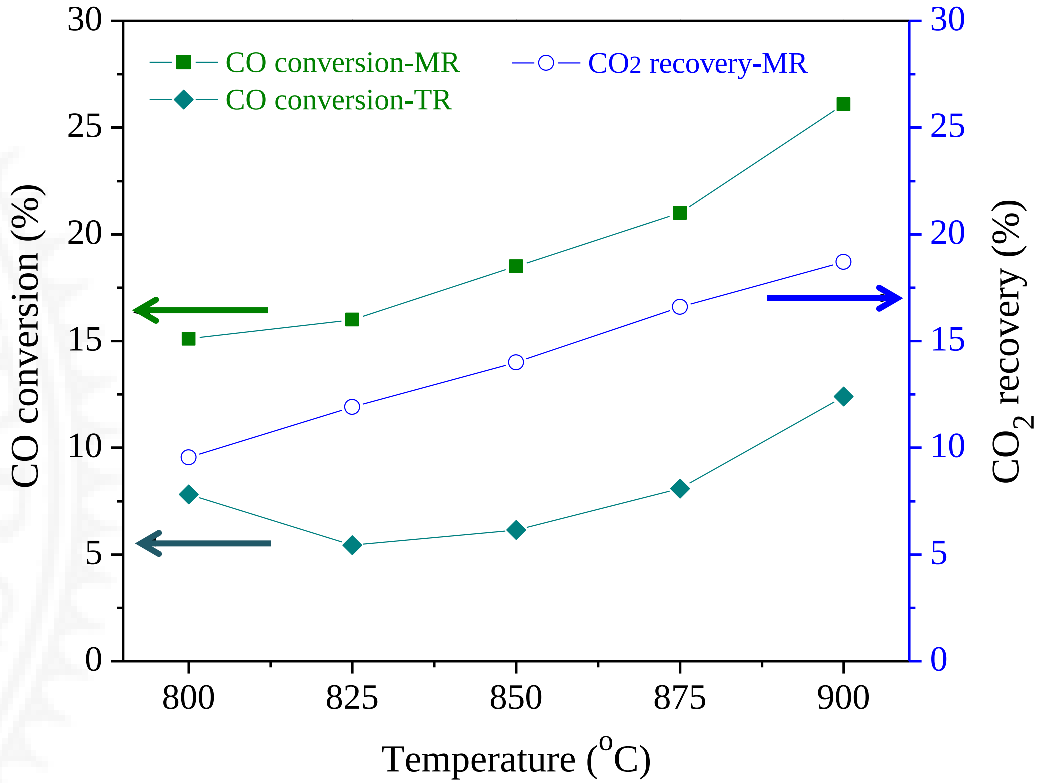


CO_2 flux as a function of temperature during the WGS reaction (a) and the Arrhenius plot (b). Syngas flow rate 20 ml/min, $H_2O/CO=3.0$.

- **900 ^oC, CO_2 flux is about 0.36 $ml \cdot cm^{-2} \cdot min^{-1}$;**
- **CO_2 permeation activation energy is 91 $kJ \cdot mol^{-1}$.**

High temperature syngas WGS performance

❖ **Effect of temperature**

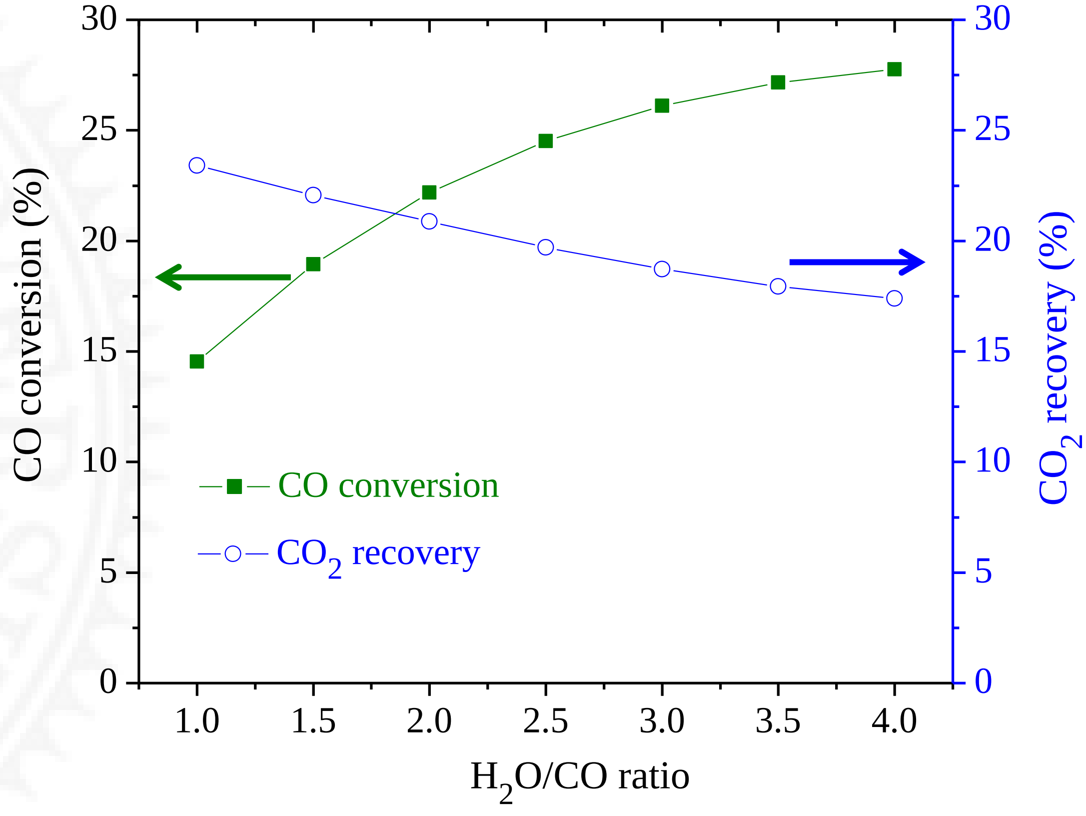


Syngas WGS performance as a function of temperature. Syngas flow rate 20 ml/min; Residence time 1.26 s; H_2O/CO=3.0.

- **900 °C, CO conversion and CO_2 recovery are 26.1% and 18.7%, respectively, in membrane reactor (MR); CO conversion of traditional reactor (TR) is much lower.**

High temperature syngas WGS performance

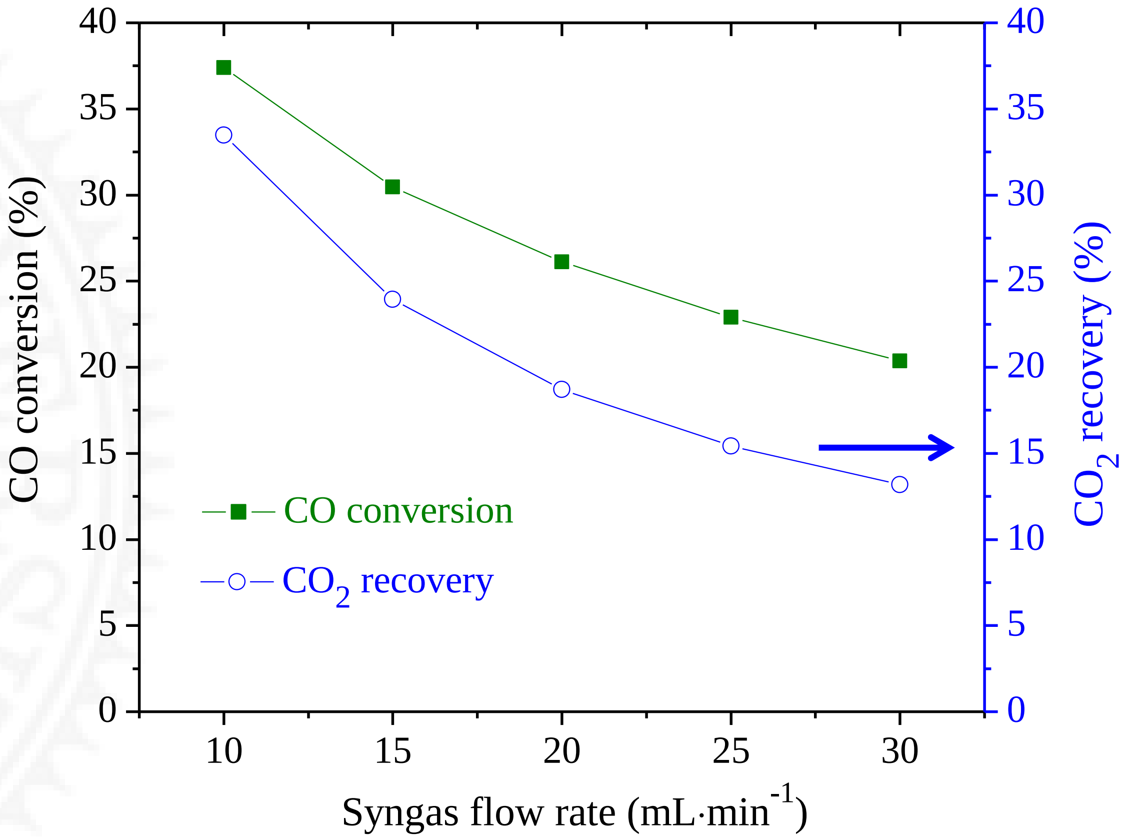
❖ **Effect of H_2O (steam)/CO ratio**



Syngas WGS performance as a function of steam to CO ratio at 900 ^oC. Syngas flow rate 20 ml/min.

High temperature syngas WGS performance

❖ **Effect of syngas flow rate**

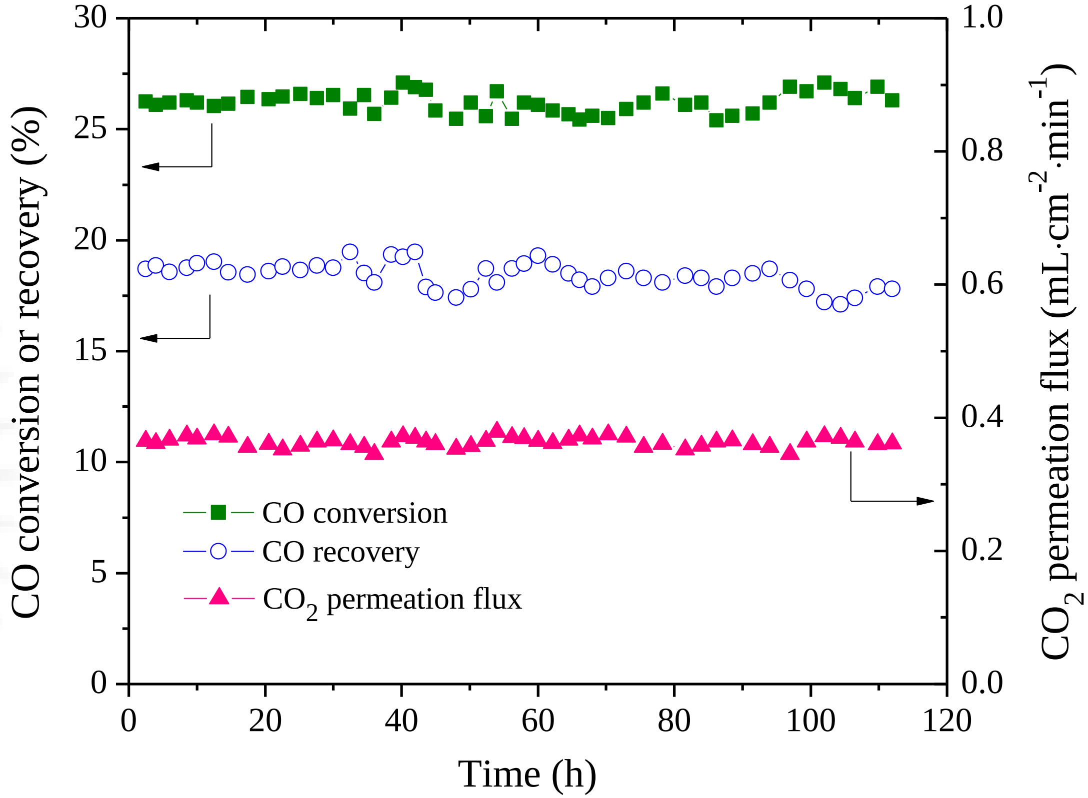


Syngas WGS performance as a function of syngas flow rate at 900 °C. H_2O/CO=3.0. Residence time from 2.16 s to 0.89 s.

High temperature syngas WGS performance

❖ **Long-term stability**

Cycle	Time
1	0-30 h
2	30-58 h
3	58-84 h
4	84-112 h



Long-term stability of the WGS membrane reactor at 900 ^oC. Syngas flow rate 20 ml/min, H_2O/CO=3.0.

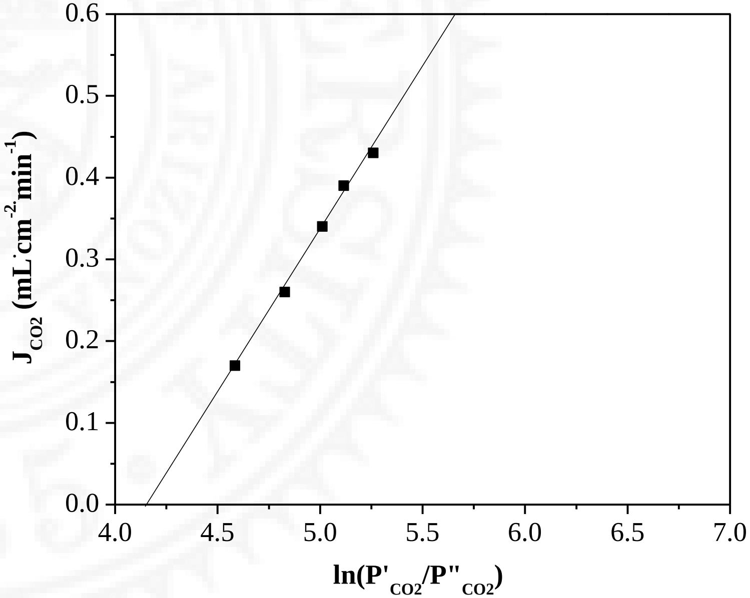
- **900 ^oC, CO conversion and CO_2 recovery and CO_2 flux maintain at around 26.2%, 18.4% and 0.36 mL·cm^{-2}·min^{-1}, respectively, for more than 110h.**

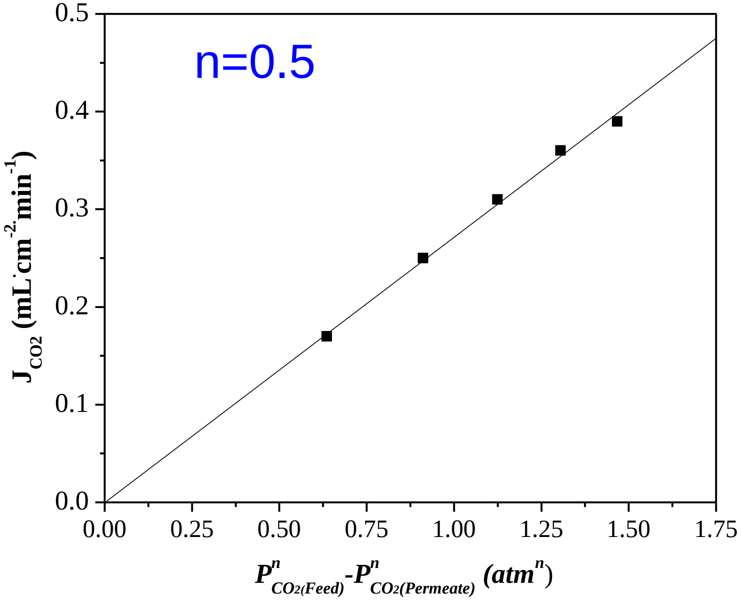
Modeling

❖ **New CO_2 permeation equation**

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

$$J_{CO_2} = k' \cdot \frac{RT}{4F^2L} \cdot ({P'_{CO_2}}^n - {P''_{CO_2}}^n)$$





*Lin and co-workers, J. Membr. Sci. 467(**2014**) 244.*

Modeling

❖ **Kinetic equation for WGS reaction without catalyst**

$$\gamma = F k_f [CO]^{0.5}[H_2O](1 - \frac{[CO_2][H_2]}{K_{eq}[CO][H_2O]})$$

F: a correction factor used to account for the catalytic activity of membrane materials;

k_f: forward reaction rate constant based on the study of Bustamante et al.;

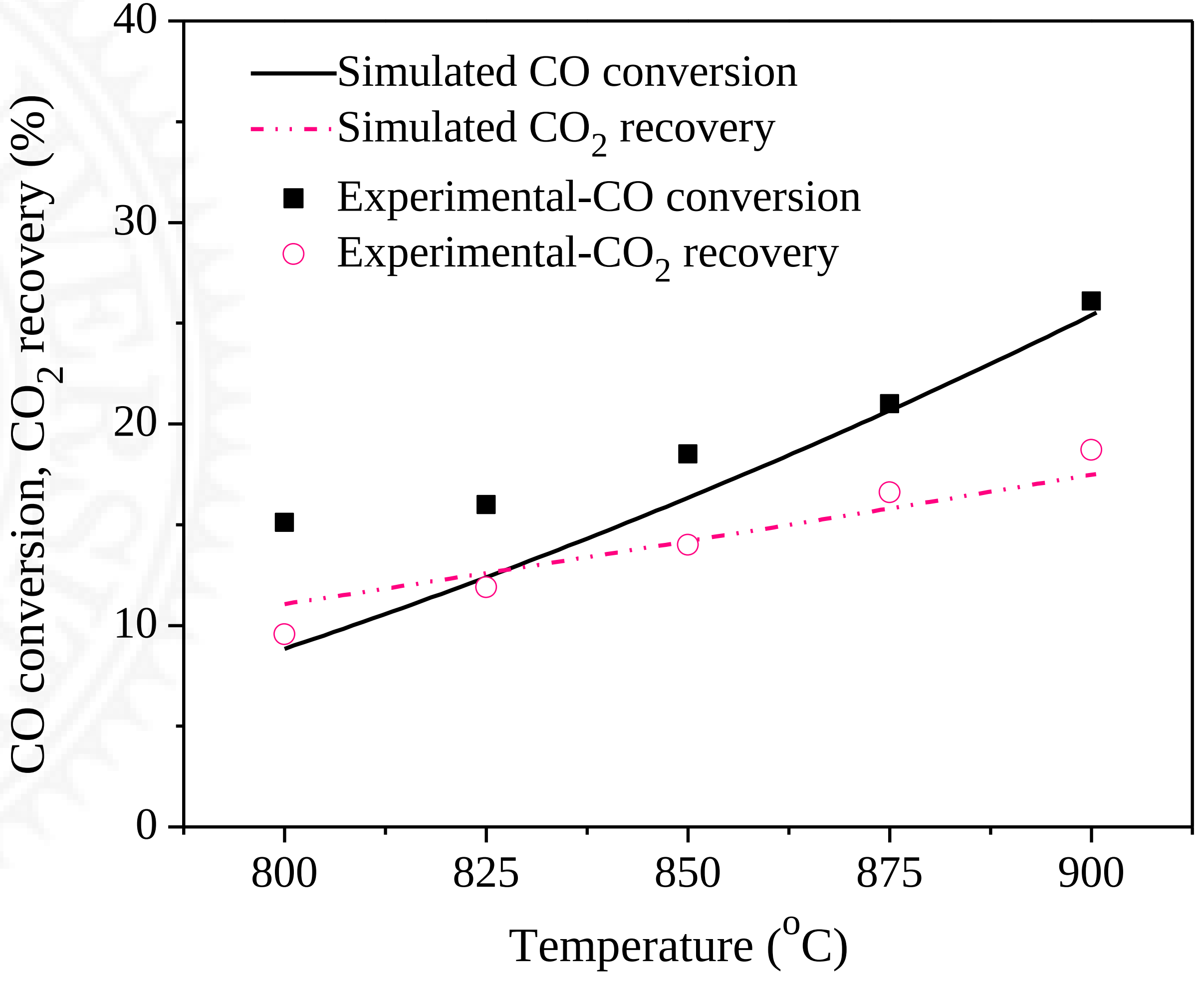
$$k_f = k_o e^{-Ea/RT}$$

K_{eq}: temperature-dependent WGS equilibrium constant.

*Iyoha O., H_2 production in palladium & palladium-copper membrane reactors at 1173K in the presence of H_2S, PhD thesis, University of Pittsburgh, (**2007**); Bustamante et al., AIChE J., 51 (**2005**) 1440.*

Comparison of Experimental and Modeling Results

❖ **Reliability of the modeling**



Simulation Conditions

◆ Membrane

SDC/Carbonate tubular membrane;
OD: 1.1cm; ID: 0.8cm; Thickness: 1.5 mm; Effective length: 2.5cm.

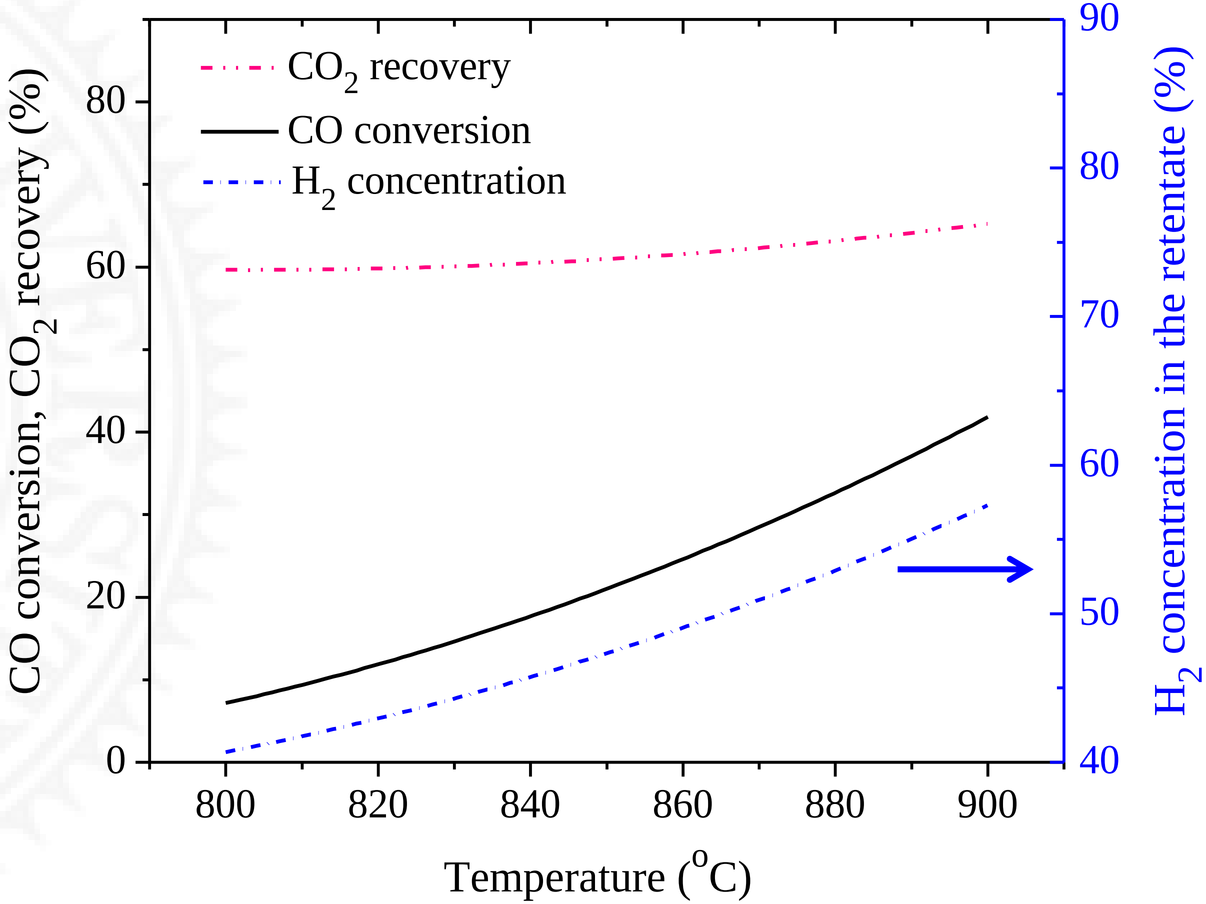
◆ Reaction conditions

Temperature: 900 ºC;
Feed pressure: 1, 10, 20, 30, 40 atm;
Sweep side pressure: 1 atm;
Catalyst: No;
Syngas: 56.5% CO, 8.2% CO_2, 35.3% H_2;
Feed side: Syngas flow rate 10-40 mL·min^{-1}, steam to CO molar ratio 1.0-4.0;
Sweep side: He flow rate 60 mL·min^{-1}.

Siefert and Litster, Applied Energy 107 (2013) 315.

Modeling Results

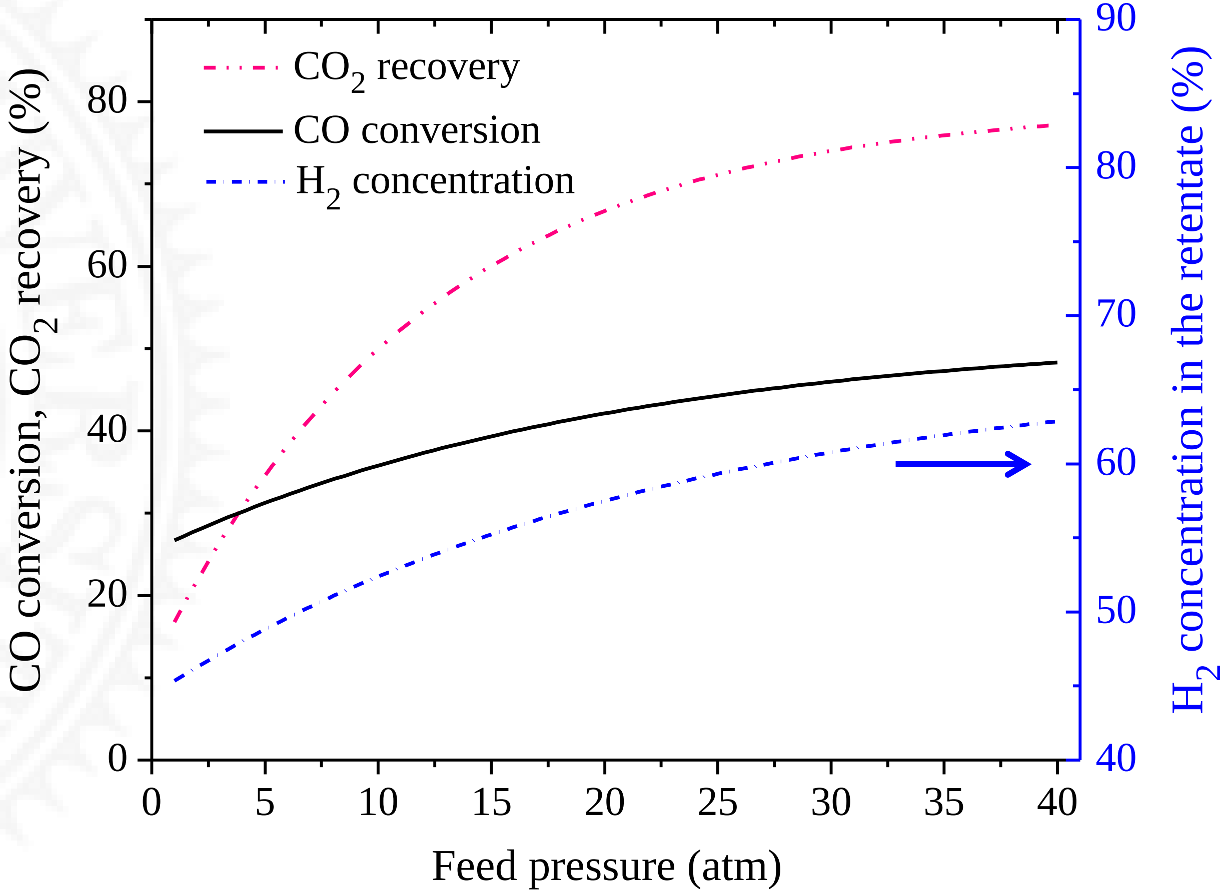
❖ **Effect of reaction temperature**



20 atm; Steam to CO ratio of 3; Syngas flow rate 25 mL/min; Residence time 1.12 s.

Modeling Results

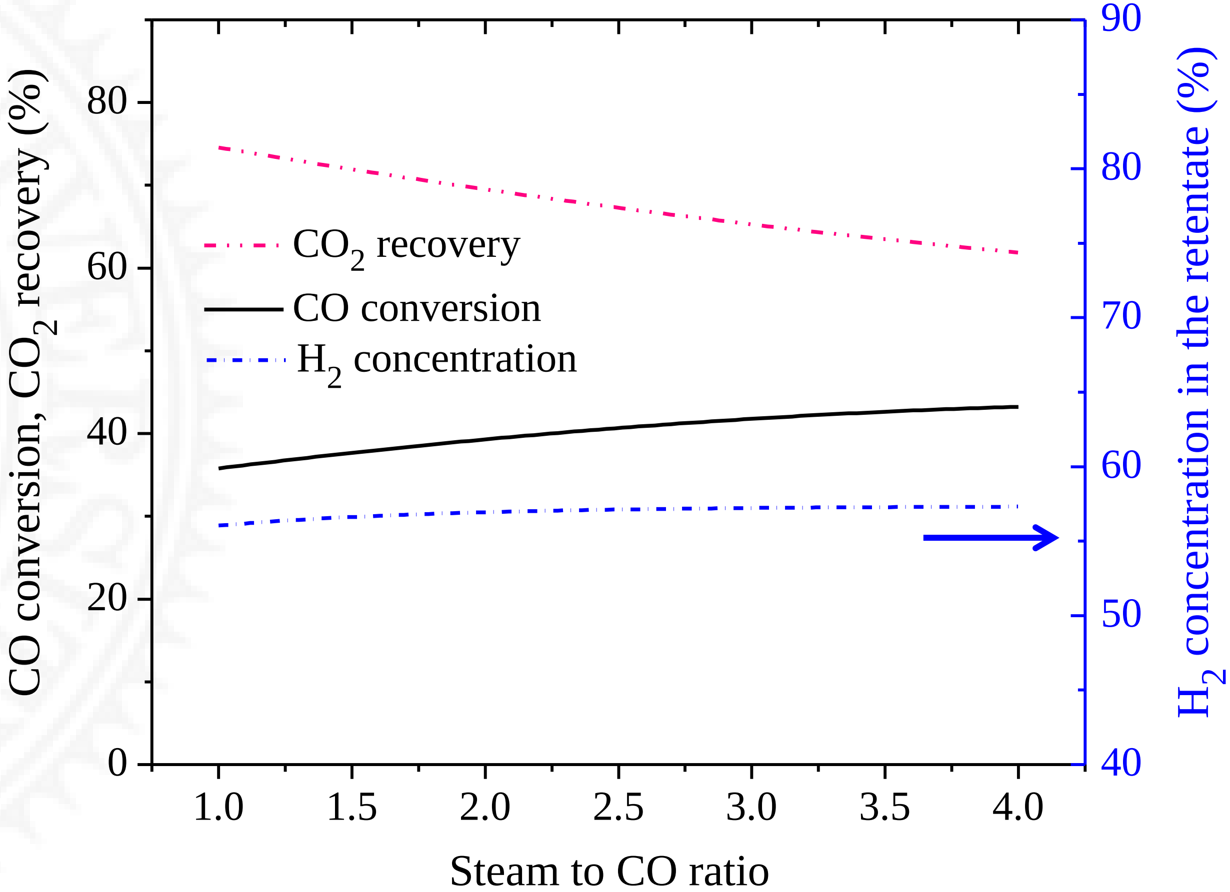
❖ **Effect of feed pressure**



900 °C; Steam to CO ratio of 3; Syngas flow rate 25 mL/min.

Modeling Results

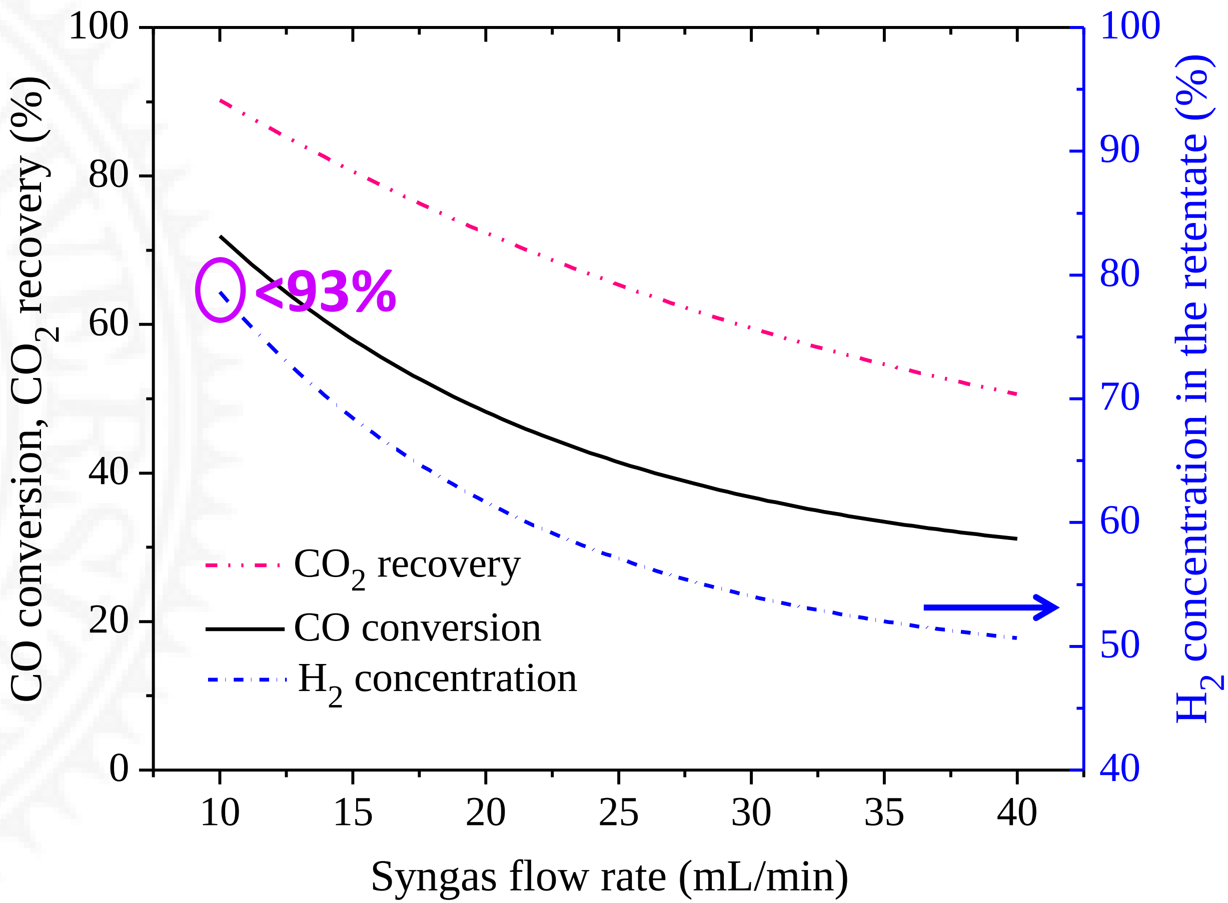
❖ **Effect of Steam to CO ratio**



900 °C; 20 atm; Syngas flow rate 25 mL/min.

Modeling Results

❖ **Effect of syngas flow rate**

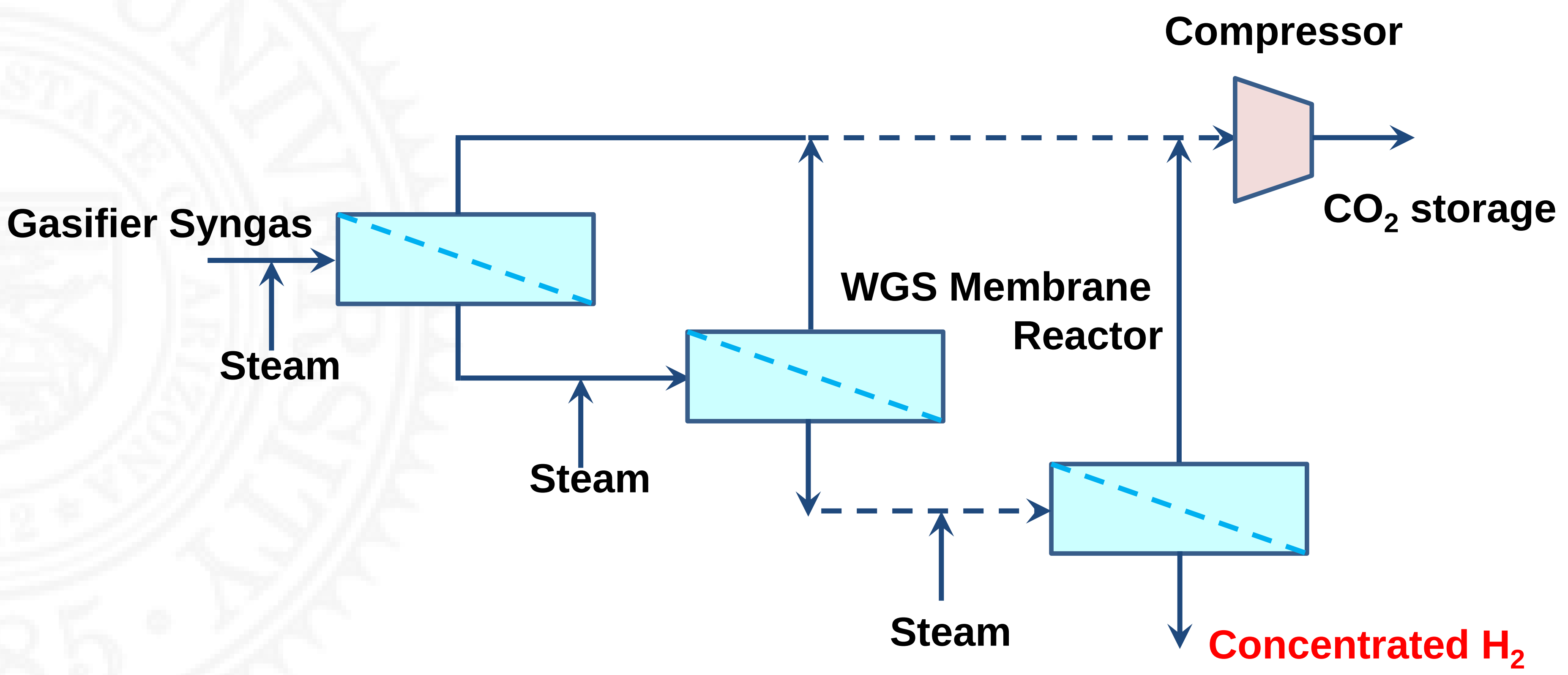


900 °C; 20 atm; Steam to CO ratio of 3; Residence time from 2.8 s to 0.7 s.

Syngas flow rate 10 $mL \cdot min^{-1}$: CO conversion, CO_2 recovery and H_2 concentration are 72%, 90% and 78%, respectively.

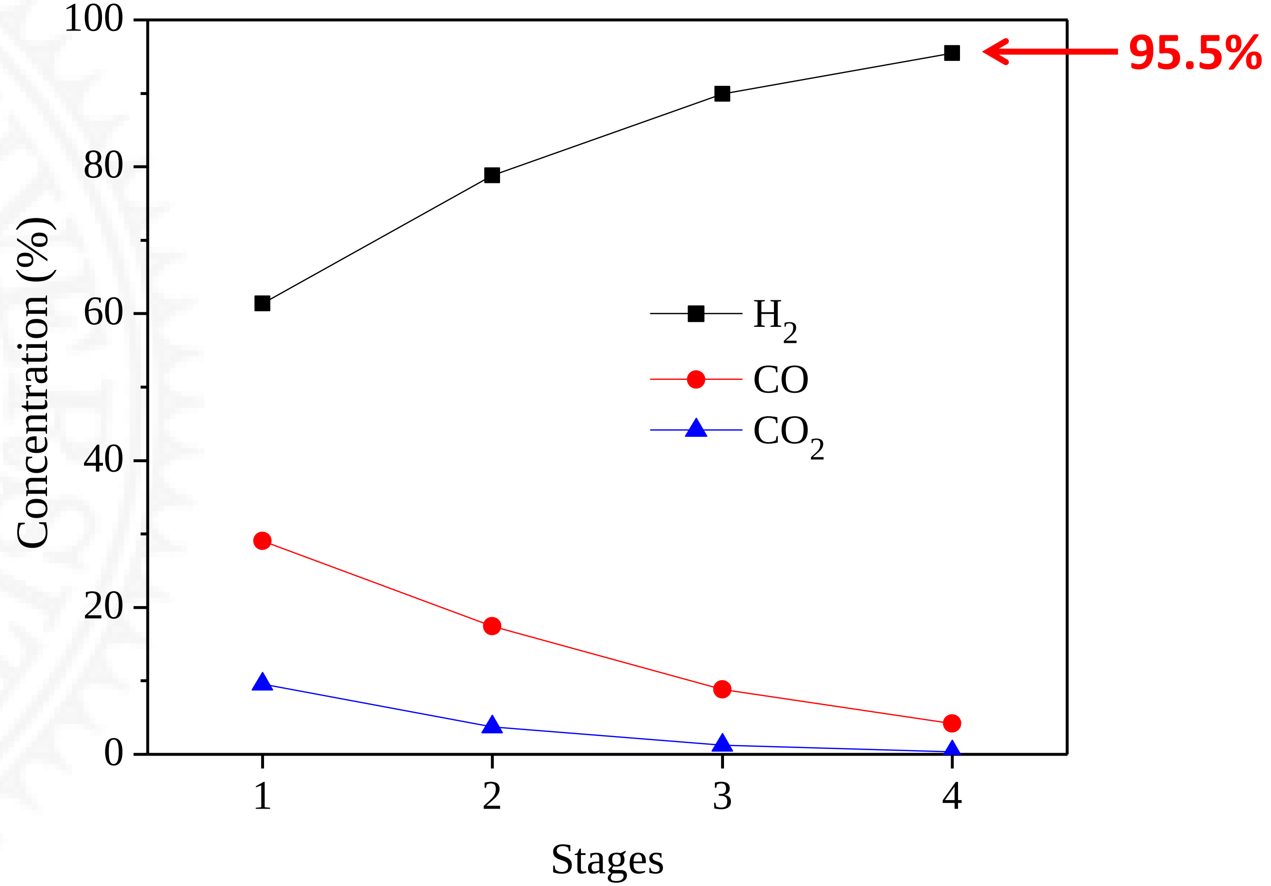
Modeling Results

❖ **Schematic of multi-stage membrane reactor**



Modeling Results

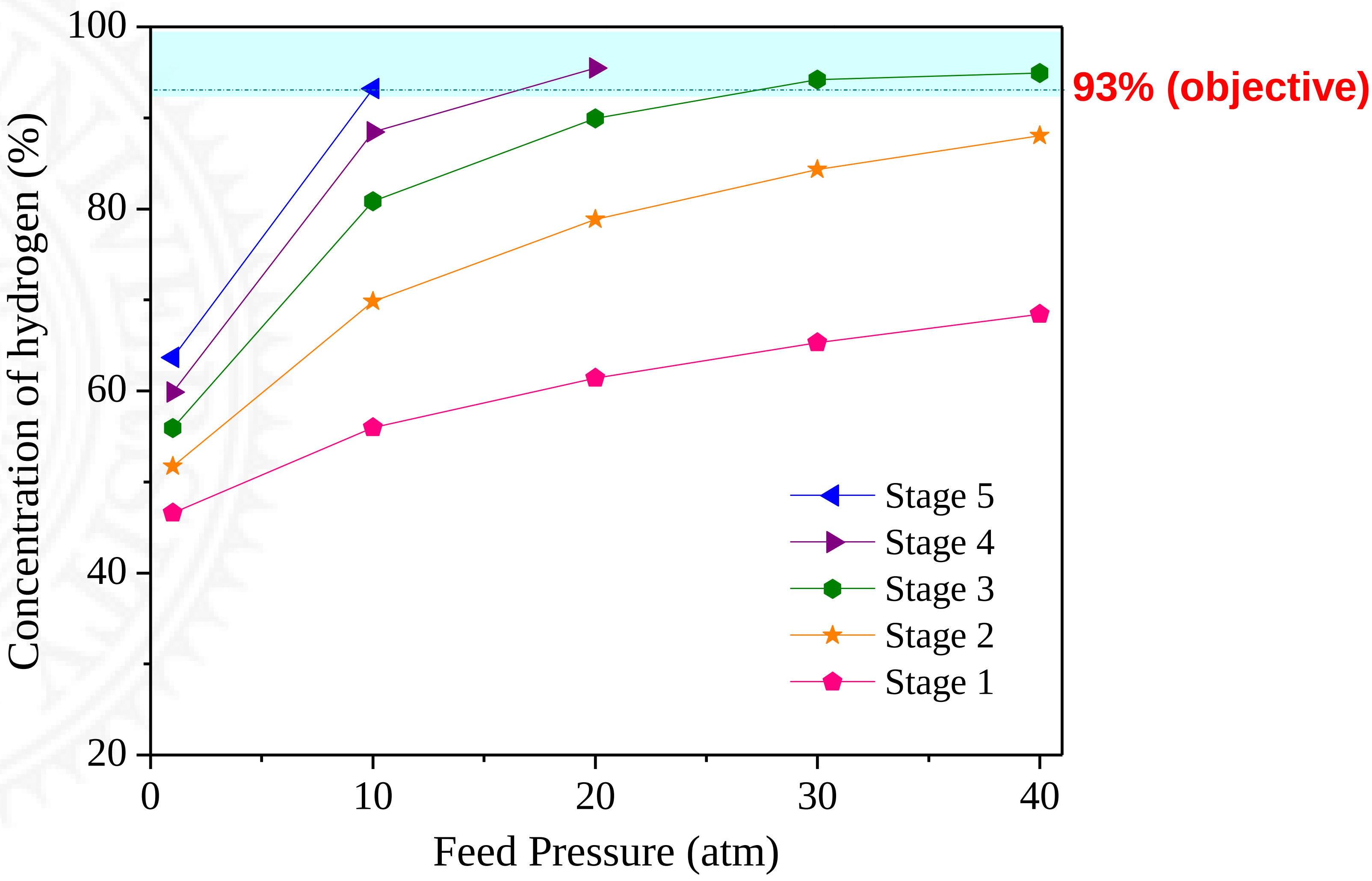
❖ **Multi-stage membrane reactor**



900 ºC; 20 atm；syngas flow rate 20 mL/min; Steam to CO ratio of 3.

Modeling Results

❖ **Multi-stage membrane reactor**



900 ^oC; syngas flow rate 20 mL/min; Steam to CO ratio of 3.

Summary

- In the membrane reactor, the removal of CO_2 by membrane promotes the conversion of CO, facilitating the H_2 production and CO_2 capture.
- Syngas WGS reaction was successfully operated in the tubular membrane reactors. SDC-carbonate membranes showed good CO_2 flux and high thermal and chemical stability.
- Experimental conditions for WGS membrane reactor to produce 93% hydrogen stream were identified by modeling analysis.
- SDC-carbonate dual phase membranes are promising for high temperature CO_2 separation in industrial processes, such as IGCC.