# Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

***Lie Meng*** ***and Jerry Y.S. Lin****

**Arizona State University**

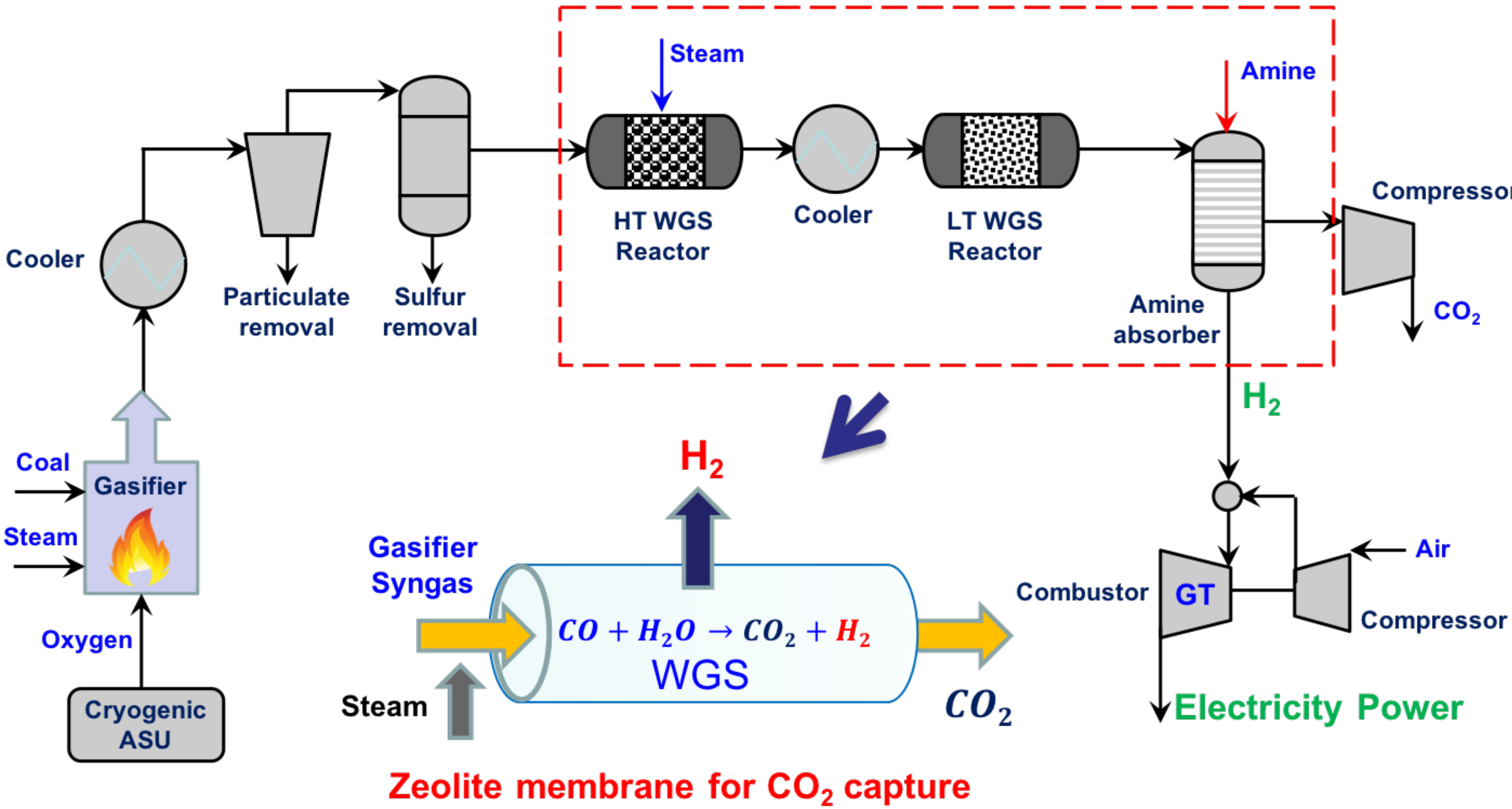
**DOE Award:**

**DE-FE0026435**

**2019 NETL $CO_2$ Capture Technology Project Review Meeting**

**August 27, 2019, Pittsburgh, Pennsylvania**

# Single-stage Zeolite Membrane Reactor for Water-Gas Shift Reaction




Hydrogen-permeable Membrane Requirements:

- Thermally stable at 350-550°C
- Chemically stable in $H_2S$ (>1,000 ppm)
- High hydrogen permeance and selectivity.

# Project Objectives

To demonstrate bench-scale zeolite membrane reactor (ZMR) process for WGS reaction of coal gasification gas for hydrogen production.

To evaluate the performance and cost-effectiveness of this new membrane reactor process for use in 550 MW coal-burning IGCC plant with $CO_2$ capture.

# Overview

## *Timeline*

- Project start date:
  **Oct. 1, 2015**
- Project end date:
  **Dec. 31, 2019**
- Budget Periods:
  **I: 10/1/2015-7/30/2017**
  **II: 8/1/2017-12/31/2019**

## *Budget*

- Total project funding
  - DOE **$2,760,797**
  - Cost-share: **$689,963**
  - Total**: $3,450,760**

## Research Area

2B2: Bench-Scale Pre-Combustion $CO_2$ Capture Development and Testing

## *Partners*

- Arizona State University (ASU)
- University of Cincinnati (UC)
- Media and Process Technology, Inc (MPT)
- Nexant, Inc.
- University of Kentucky Applied Energy Research Center

# DOE Project: Zeolite Membrane Reactor for Pre-Combustion $CO_2$ Capture

Task description

U.S. Department of Energy | NETL

*Project Manager*

***Andrew Jones***

Ceramic Support

Arizona State University

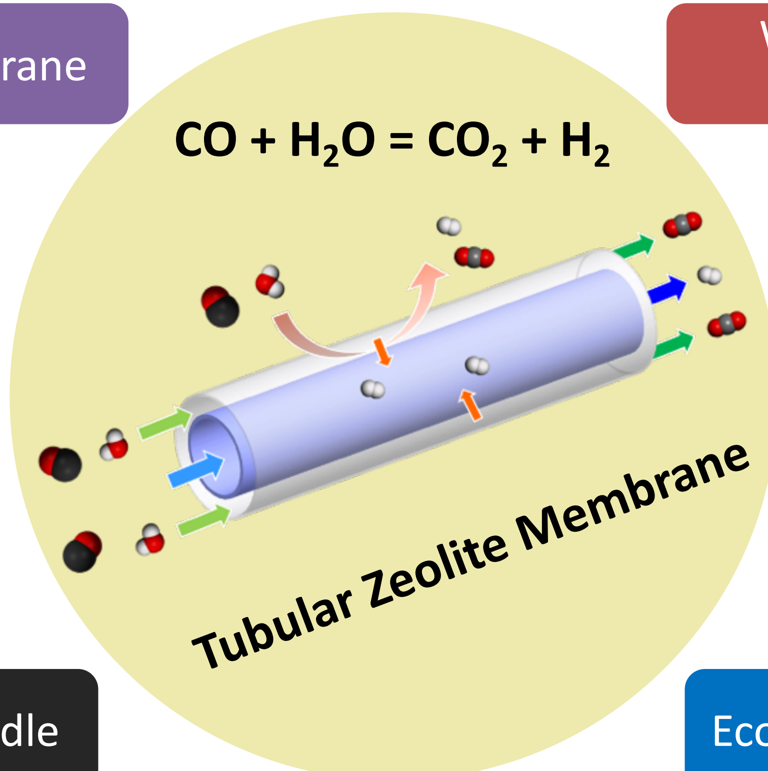
***PI: Jerry Y.S. Lin***

Zeolite Membrane

WGS Kinetics and Catalyst

University of Cincinnati

***PI: Junhang Dong***




Lab-scale ZMR

ZMR Design and Modeling

Nexant

***PI: Gerald Choi***

Membrane Bundle

Economical Analysis

***PI: Richard Ciora***

Media and Process Technology Inc.

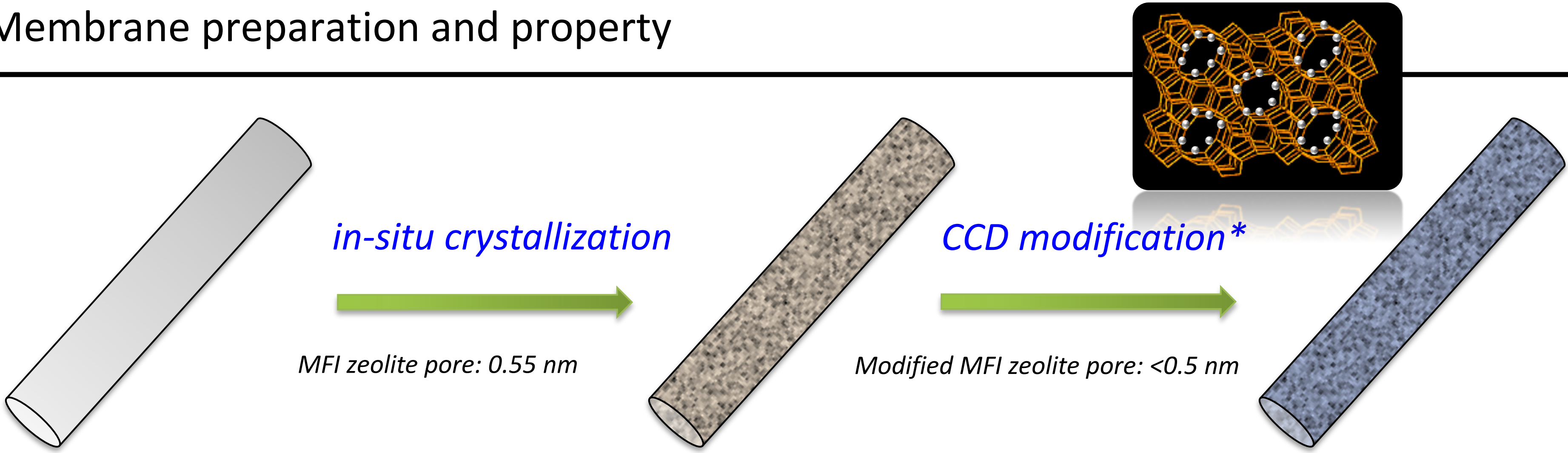
***PI: Kunlei Liu***

University of Kentucky

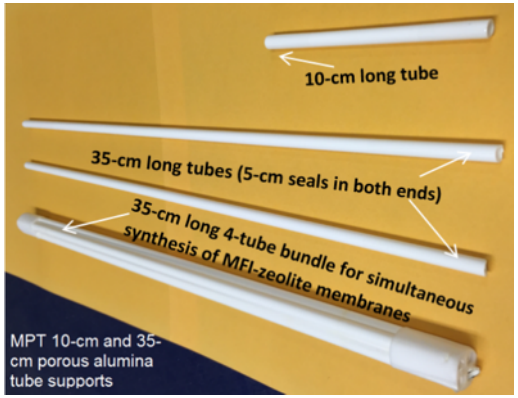
Bench-scale ZMR

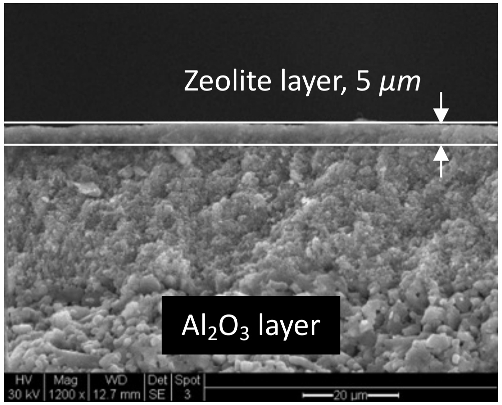
# Tubular MFI-type Zeolite Membranes

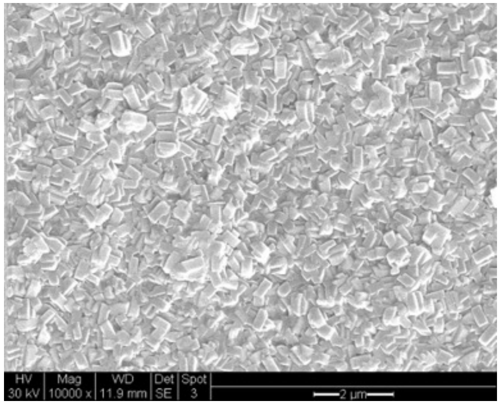
## Membrane preparation and property




| $Al_2O_3$ tubular support | MFI zeolite membrane | Modified zeolite membrane |
|---|---|---|



| $Al_2O_3$ tubular support | MFI zeolite membrane | Modified zeolite membrane |
|---|---|---|
| OD =5.7 mm; ID =4.7 mm | 25°C: $H_2/CO_2$ < 1.0 | 25°C: $H_2/CO_2$ = 1.5-3.0 |
| Pore size < 100 nm | 450°C: $H_2/CO_2$ = 3.0-4.7 | 450°C: $H_2/CO_2$ = 4.7-200 |

*Catalytic Cracking Decomposition of Methyldiethoxysilane (MDES)

# Scope of work

1) **Scaling up zeolite membranes from lab-scale to bench-scale for combined WGS reaction and $H_2$ separation**

2) **Conducting a bench-scale study using ZMRs for hydrogen production for IGCC with $CO_2$ capture.**

Goal is to demonstrate effective production of $H_2$ and $CO_2$ capture by the bench-scale zeolite membrane reactor from a coal gasification syngas at temperatures of 400-550°C and pressures of 20-30 atm:

- Bench-scale zeolite membrane reactor: 21 zeolite membrane tubes of 3.5 ID, 5.7 OD and 25-cm long (active)

- A system producing $H_2$ at rate of about 2 kg/day, equivalent to a 2 $kW_{th}$ IGCC power plant

# General Approach to Scaling up WGS-ZMR

Single-tube zeolite membrane reactor: study WGS up to 30 atm by experiments and modeling

↓

Intermediate-scale zeolite membrane reactor:  3 and 7 tubular membrane modules for WGS reaction

↓

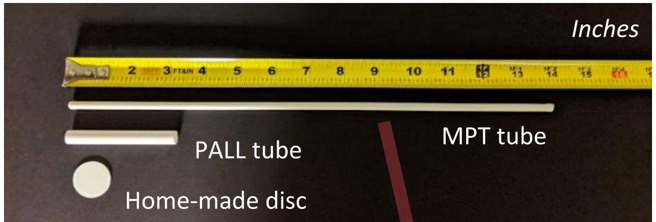
Bench-scale zeolite membrane reactor:  21 tube membrane module for WGS reaction at UK-CBTL

→ Zeolite membrane reactor in IGCC with $CO_2$ capture - process design and techno-economic analysis

# Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

## Scaling-up strategy: batch synthesis of multiple tubular MFI zeolite membranes

Different membrane supports



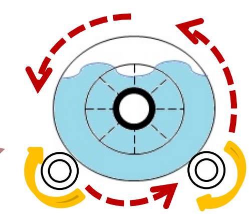

3-tube assembly

Teflon-lined SS autoclaves

**Dimensions and active areas of porous α-alumina supports**

**(L0: total tube length; Lm: active membrane section length; OD and ID: outer and inner diameter, respectively; Am: active membrane area)**

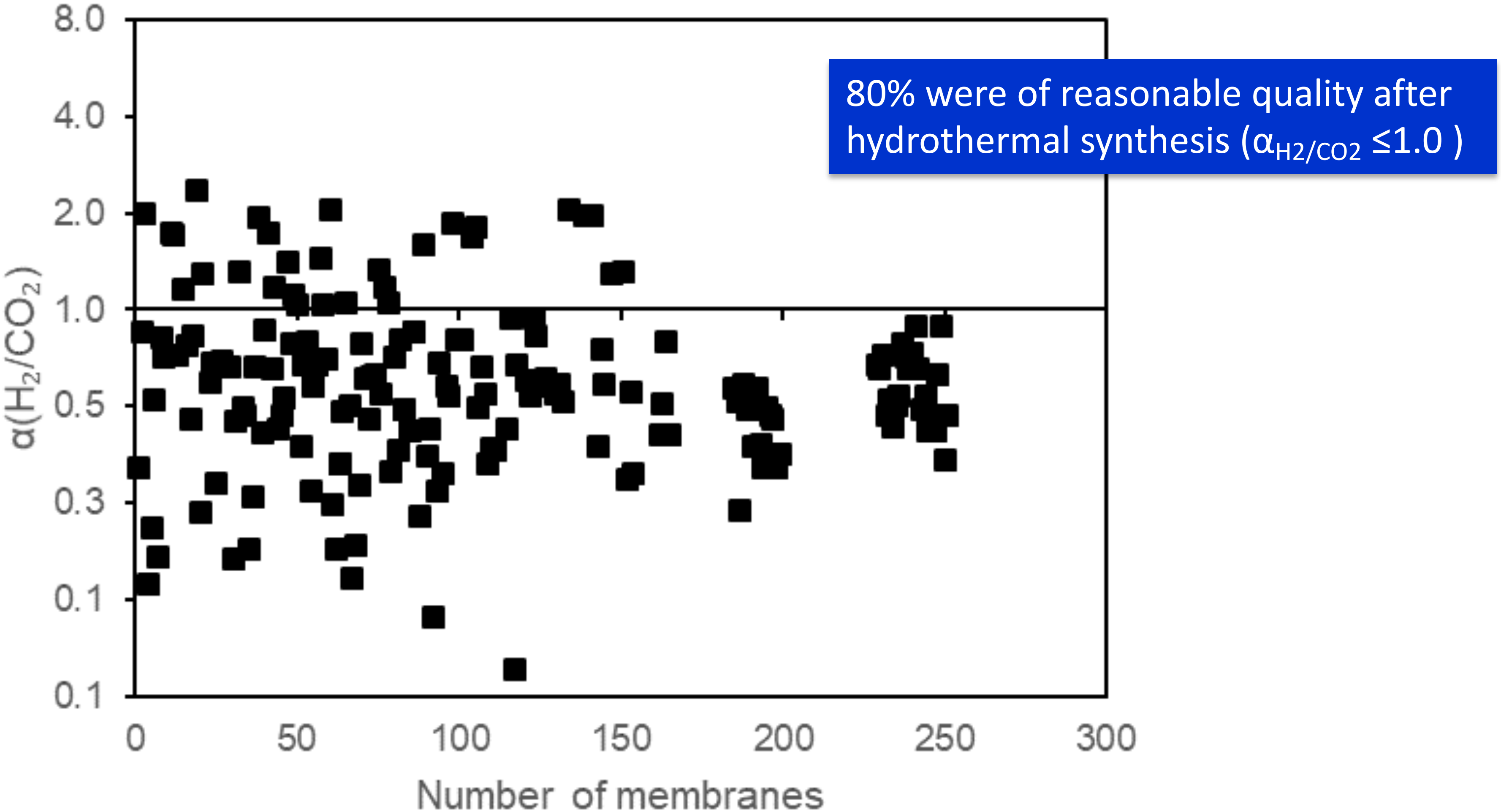
| Support | $L_0$ (cm) | $L_m$ (cm) | OD(mm) | ID(mm) | $A_m$(cm$^2$) |
|---|---|---|---|---|---|
| Disc (UC) | - | -- | --- | - | 2.5 |
| PALL tube | 10 | 2.0 | 10 | 7 | 4.4 |
| MPT tube | 10 | 5.0 | 5.7 | 3.7 | 8.9 |
| MPT tube | 35 | 25 | 5.7 | 3.7 | 44.4 |

Rotated hydrothermal synthesis of long-tube MFI zeolite membranes

**Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module**

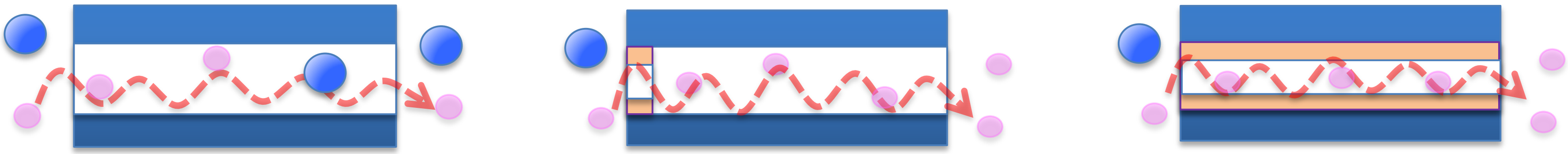
$H_2/CO_2$ selectivity for membranes before CCD modification at 25°C

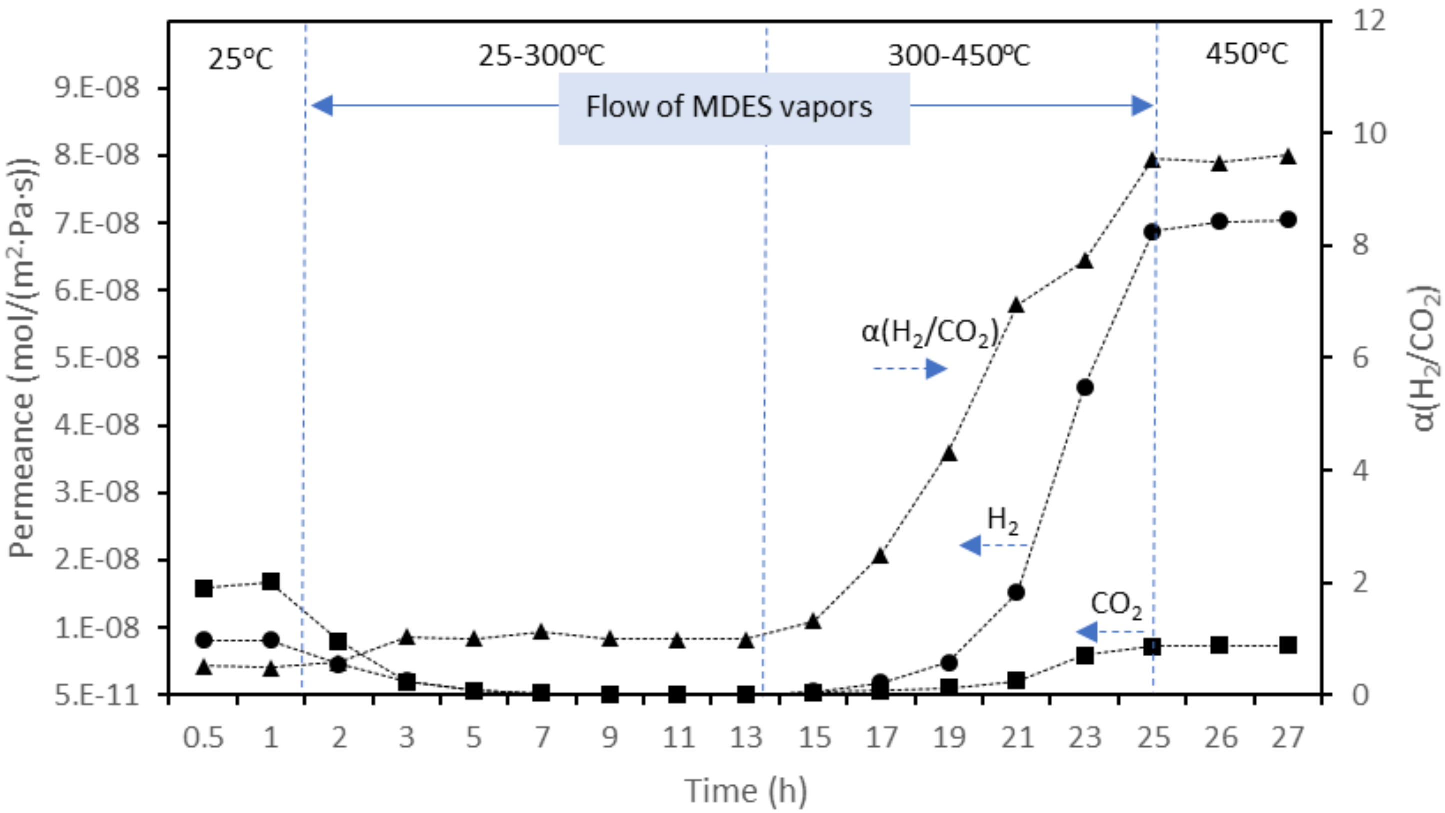



- Selective towards the strongly adsorbing $CO_2$ if nonzeolitic large pores are insignificant.
- Membranes remained free of pinholes and large inter-crystal spaces.

## Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

Quality control: CCD modification procedure for MFI zeolite membranes






- Mono-silica modifier deposition expected deep in the channels and more modifier deposition in microdefects.

# Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

$H_2/CO_2$ selectivity for membranes after CCD modification at 450°C

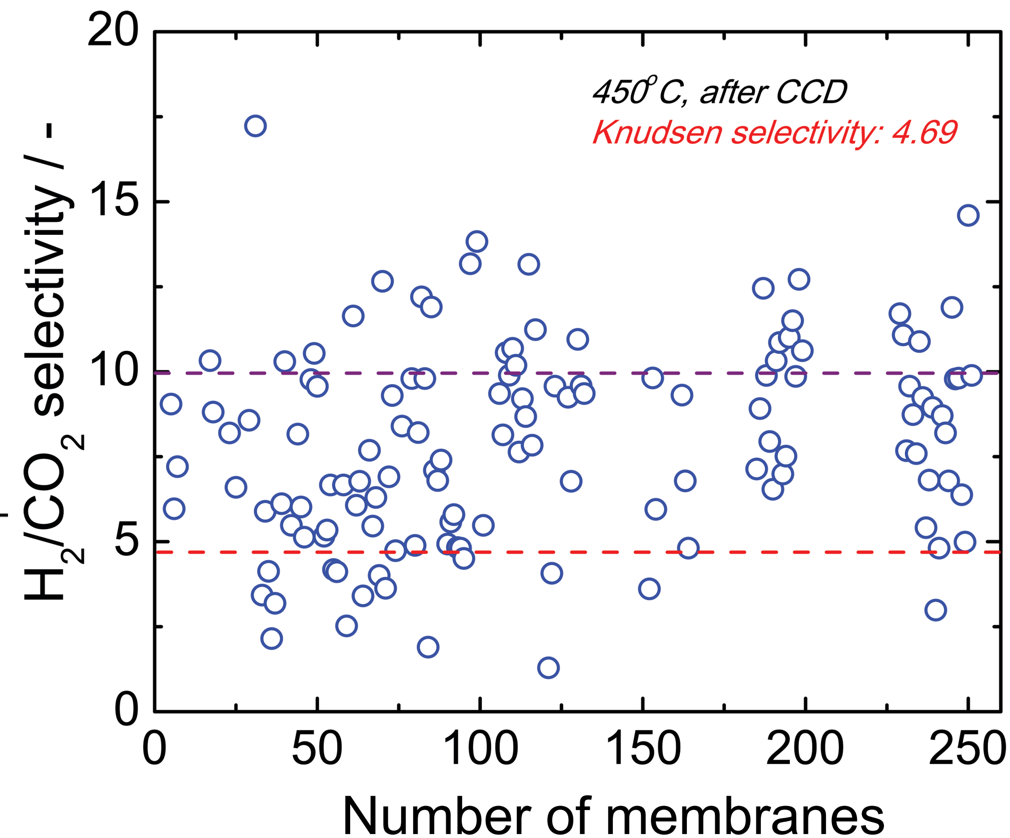
- Most CCD-modified membranes

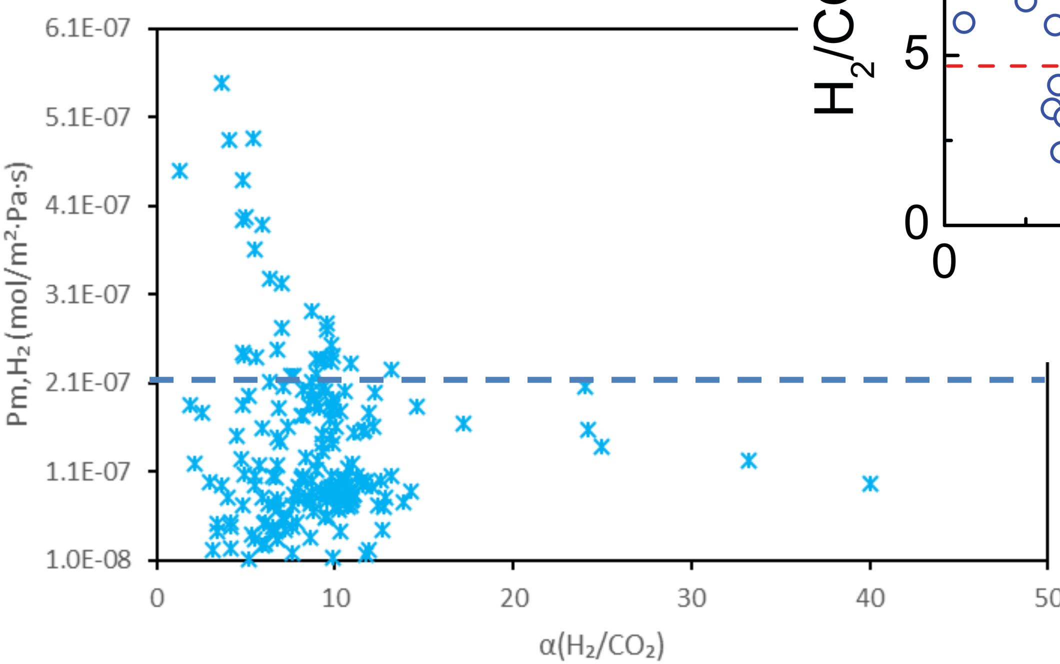
  $H_2$ permeance:

  ~2.0 x $10^{-7}$ mol/(s.m$^2$.Pa)

  (600 GPU)

  $H_2/CO_2$ selectivity: ~10.



# Task 14: Building Bench-Scale Zeolite Membrane Reactors

## Assembly and Testing of Bench Scale Zeolite Bundles

>300 tubular substrates fabricated
>250 modified zeolite membranes prepared and QC tested
>20 bundles of 3-, 7-, and 21-tube variants prepared

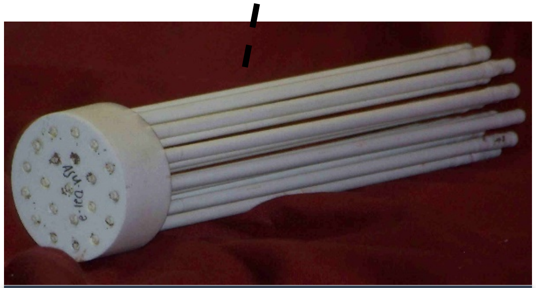
*Summary of Multiple Tube Bundles Prepared in the Project*

| Bundle ID | # of Tubes | Tube Type | Status/Availability |
|---|---|---|---|
| ZM-D21-1 | 21 | Dummy; shorty, Zeyon | Available. Used in preliminary Reactor Module shakedown. |
| ZM-D21-2 | 21 | Dummy; standard, Zeyon | Available. |
| | | | |
| ZM-D21-x | 21 | Dummy; Swagelok (rods) | Available. NOTE…Swagelok module size. |
| ZM-K21-3T | 3 | 3 tubes in 21-tube puck | Available. Used in preliminary Reactor Module shakedown. |
| ZM-K3-3 | 3 | Zeolite | Damaged. |
| ZM-K3-6 | 3 | Zeolite | Available. |
| ZM-K3-7 | 3 | Zeolite | Available. Shakedown testing completed 2Q2019 |
| ZM-K3-8 | 3 | CCI Modified | Available. |
| ZM-C3-9 | 3 | CCI Modified | Available. ZMR testing completed 2Q2019 |
| | | | |
| ZM-K7-1 | 7 | CCI Modified | Available. Long term performance stability completed. |
| ZM-C7-2 | 7 | CCI Modified | Available. ZMR testing completed 2Q2019 |
| | | | |
| ZM-K21-1 | 21 | Zeolite | Available. Shakedown testing completed 2Q2019 |
| ZM-K21-2 | 21 | Zeolite | Available. Shakedown testing completed 3Q2019 |
| ZM-K21-3 | 21 | Zeolite | Available. To shakedown testing. |
| ZM-C21-4 | 21 | CCI Modified | Available. To shakedown testing. |
| ZM-C21-5 | 21 | CCI Modified | Available. To shakedown testing. |

# Task 14: Building Bench-Scale Zeolite Membrane Reactors

## ZMR Housing and Seals: Thermal and Hydrothermal Stability

21-Tube ZMR Housing

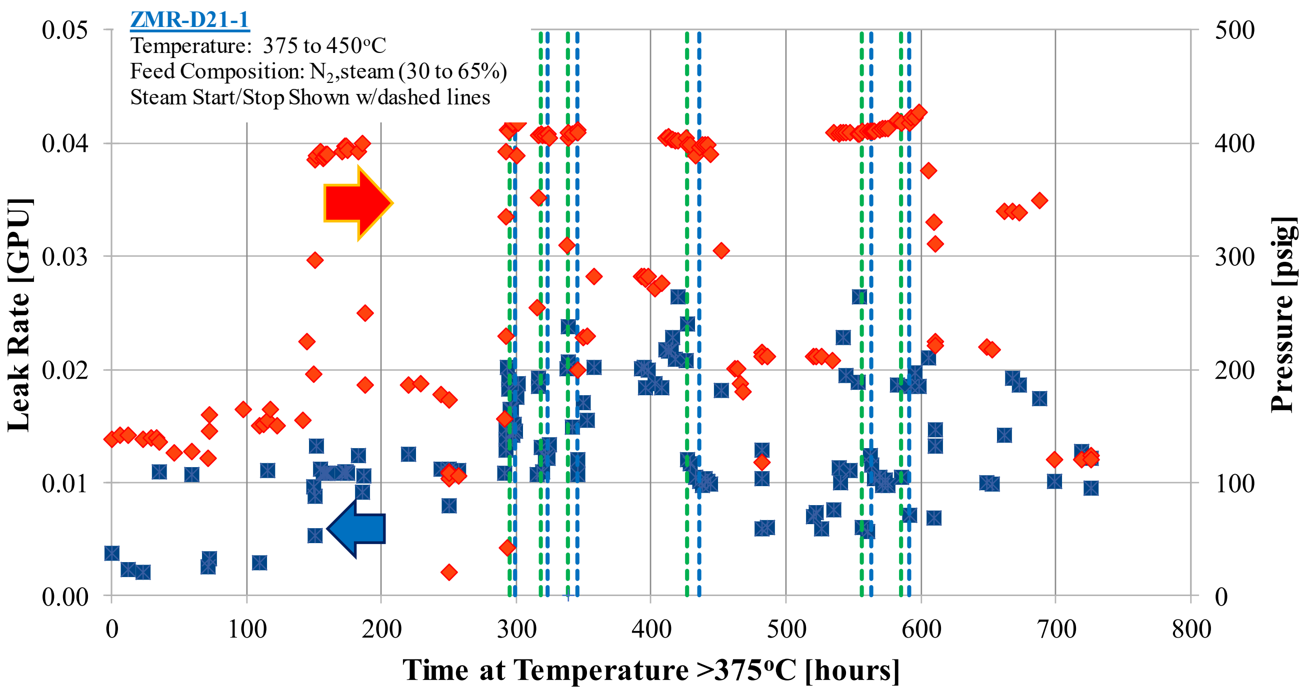


21-Tube Dense Dummy Bundle (Impermeable)

### Housing and Bundle Leak Rate during Challenge Testing

*Testing Conditions:*

*T = 375 to 450°C; P = 150 to 400 psi; Steam content 40 to 65%*




*No leak development in the seal components was observed in nearly 350 hours of challenge testing.*

# Task 14: Building Bench-Scale Zeolite Membrane Reactors

## Fabrication and Performance Testing of Zeolite Membrane Bundle

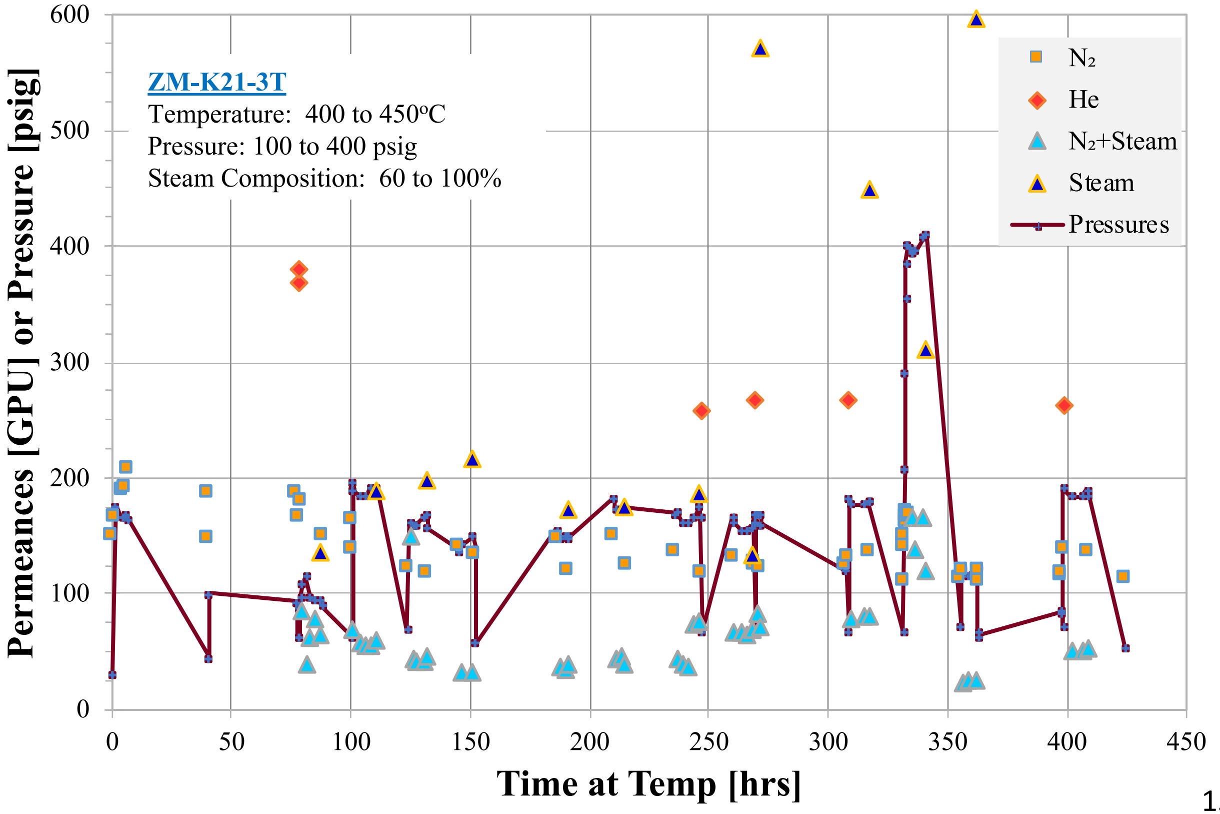
3-tube membrane bundle (ID: ZM-K21-3T)

3-Tube Bundle in 21-tube Potting Configuration

*Performance Verification of the 21-Tube ZMR Bundle*

*Three Tube Bundle in 21-tube Potting Configuration*

*<u>Testing Conditions:</u> T = 400 to 450°C; P = 100 to 400 psi; Steam content 40 to 65%*




*No deterioration in performance throughout the 425-hour challenge test.*

# Task 14: Building Bench-Scale Zeolite Membrane Reactors

## Fabrication and Performance Testing of Zeolite Membrane Bundle

7-tube membrane bundle (ID:  ZM-K7-1)


*Pure Gas Performance of the Individual Tubes and Corresponding 7-tube Bundle*

| Tube ID | RT He | RT $N_2$ | 200°C He | 200°C $N_2$ |
|---|---|---|---|---|
| **B11-1** | 2.05 | 1.73 | 1.22 | 0.75 |
| **B11-2** | 1.73 | 1.32 | 1.43 | 0.70 |
| **B11-4** | 1.40 | 1.14 | 1.21 | 0.63 |
| **B11-7** | 1.87 | 1.55 | 1.57 | 0.80 |
| **B11-11** | 2.28 | 1.83 | 1.73 | 0.95 |
| **B11-12** | NA | NA | 1.69 | 0.90 |
| **52B** | 0.51 | 0.22 | 1.31 | 0.68 |

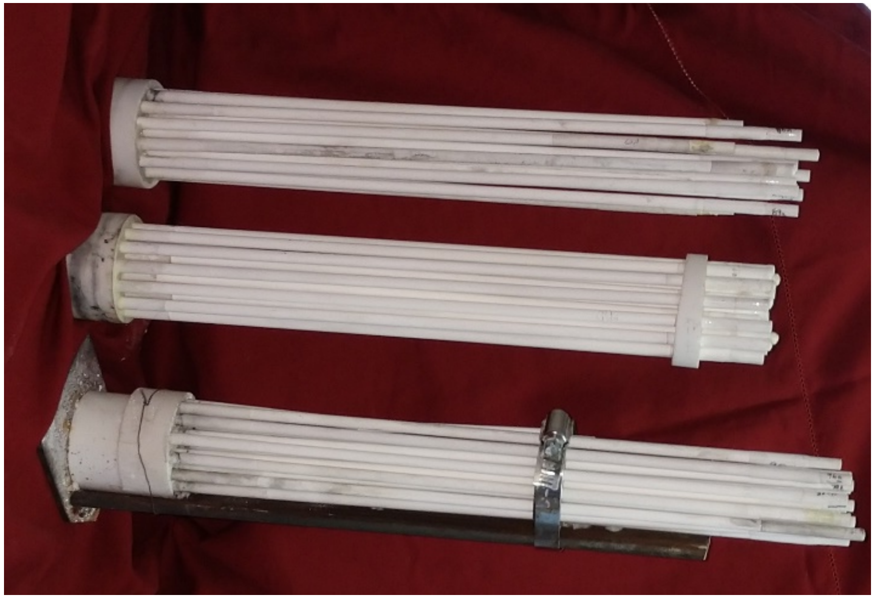
| | | | | |
|---|---|---|---|---|
| *Average* | *1.64* | *1.30* | *1.45* | *0.77* |
| *He/$N_2$* | | *1.26* | | *1.88* |

| Bundle ID | RT He | RT $N_2$ | 200°C He | 200°C $N_2$ | 450°C He | 450°C $N_2$ |
|---|---|---|---|---|---|---|
| ZM-K7-1 | 0.87 | 0.49 | 1.28 | 0.68 | 1.76 | 0.75 |
| | *He/$N_2$* | 1.76 | *He/$N_2$* | 1.90 | *He/$N_2$* | 2.33 |

## Task 14: Building Bench-Scale Zeolite Membrane Reactors
Fabrication and Performance Testing of Zeolite Membrane Bundle

21-tube membrane bundle (ID: ZM-K7-1)

| Performance of the ZMR-K21-1 bundle at 400°C. | | | | | |
|---|---|---|---|---|---|
| **Run Time [hour]** | **He [GPU]** | **$N_2$ [GPU]** | **$CO_2$ [GPU]** | **$He/N_2$ [-]** | **$He/CO_2$ [-]** |
| 8 | 247 | 109 | 122 | 2.3 | 2.02 |
| 30 | 260 | 110 | 122 | 2.4 | 2.13 |
| 74 | 258 | 114 | 123 | 2.2 | 2.10 |



**ZMR-K21-6 (under construction)**

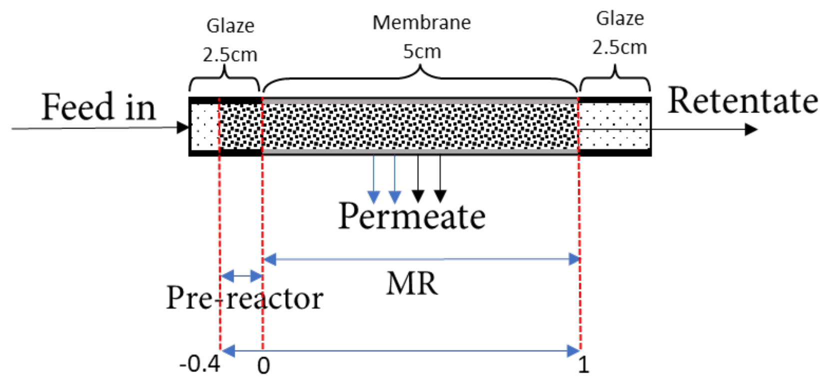
**ZMR-C21-5**

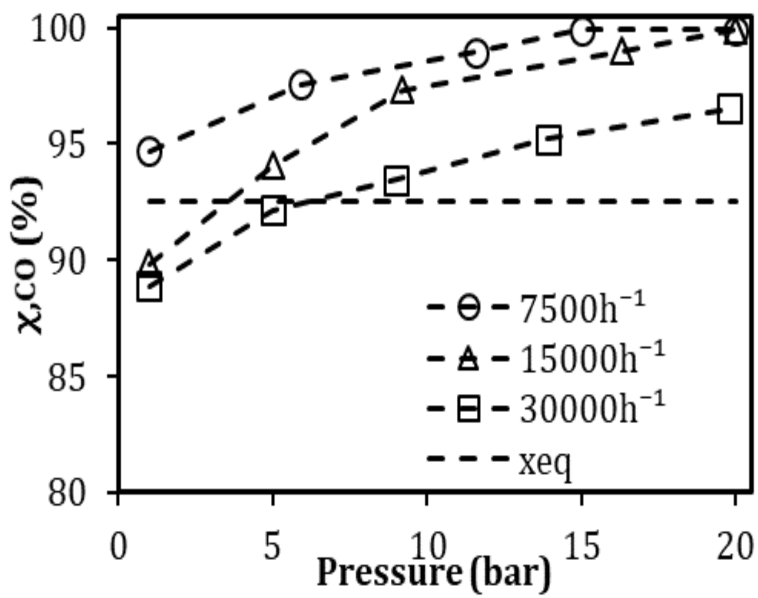
**ZMR-C21-4**

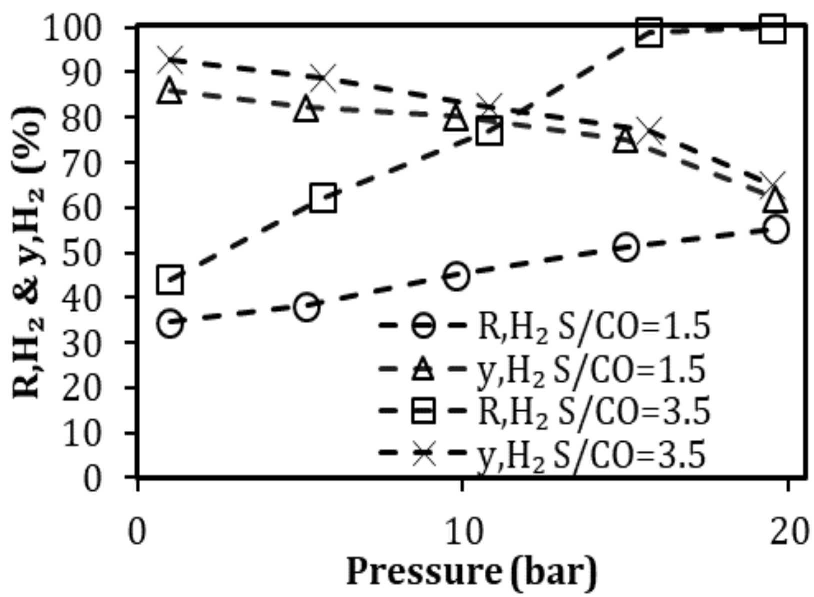
# Task 14.2: Assembling and Testing Bench Scale Zeolite Membrane Reactor

High pressure WGS reaction in zeolite membrane reactor

**Complete CO conversion by high temperature and high pressure WGS reaction in ZMR with $\alpha_{H2/CO2}$ = 20 ~ 45, $P_{m,H2}$ ~ 200 UPU.**




Results of WGS reaction in the tubular MR at 500°C:

$\chi_{CO}$ >99.5% achieved at pressure >15 bar for S/CO = 3.5 and at >20 bar for S/CO = 1.5

# Task 14: Building Bench-Scale Zeolite Membrane Reactors

## Modification and Installation of Bench-Scale Reactor Test Skid

Back View: Major Bench Scale Reactor Test Skid Subsystems

Pressure Control Panel

Mass Flow Meter Enclosure

Reject and Permeate Liquid Knockout Pots

Steam Injection Subsystem

Water Sampling Subsystem

Front View: Oven Chamber with Membrane Test Module and a 3” x 85-tube Membrane Bundle for Perspective


Oven Controls

3” x 85-tube Membrane Bundle

Power Distribution Skid

Monitoring and Control Panel

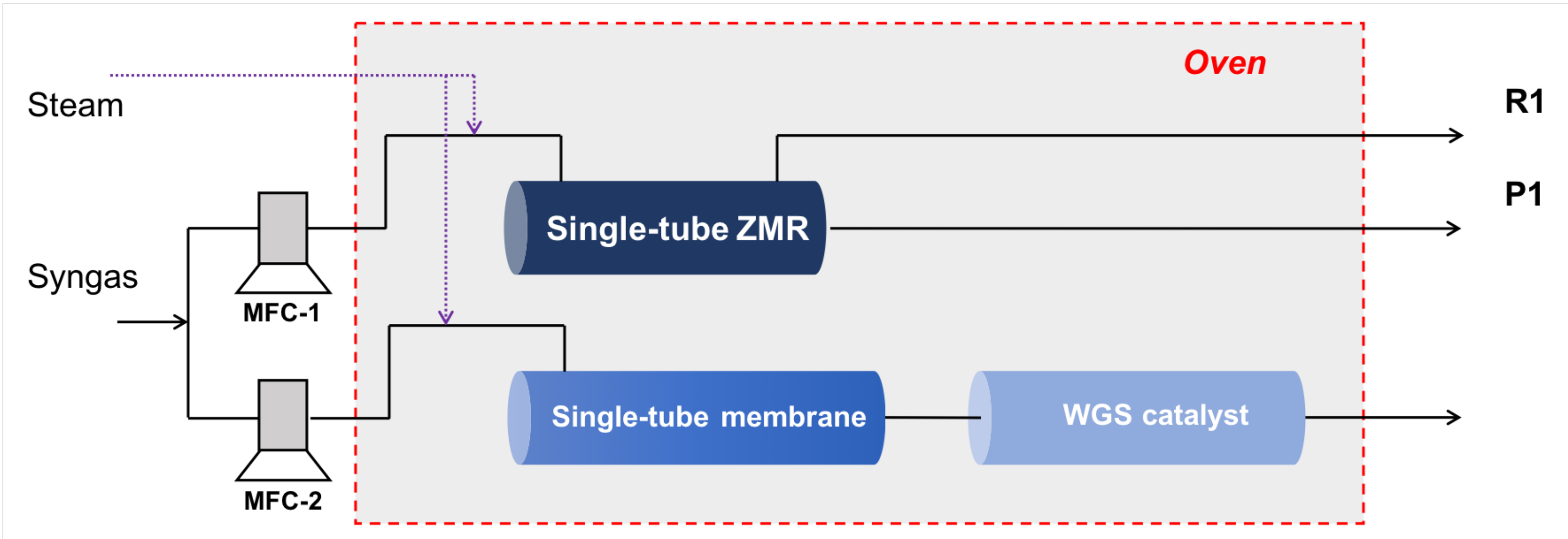
# Task 14: Building Bench-Scale Zeolite Membrane Reactors

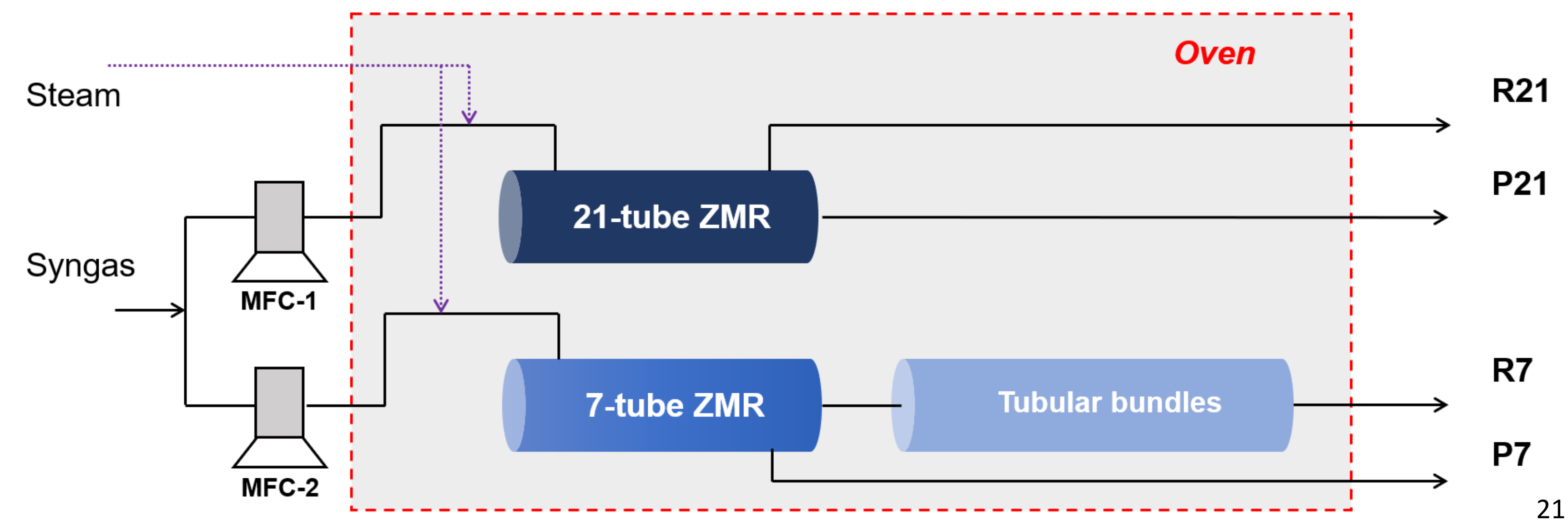
Modification and Installation of Bench-Scale Reactor Test Skid

Bench-scale Unit at the UK-CBTL Facility

# Task 15: Testing WGS Reaction in Bench-Scale Membrane Reactor

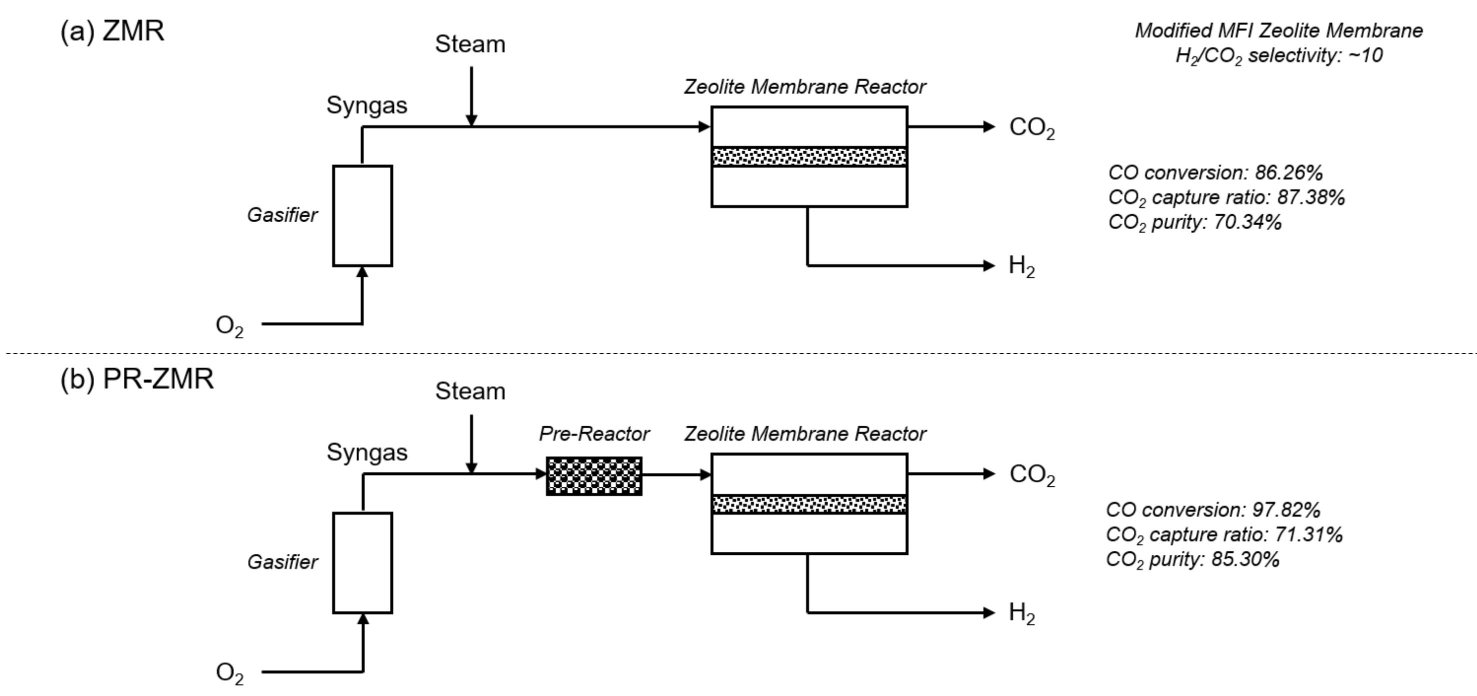
Test plan for WGS-ZMR process at UK-CBTL

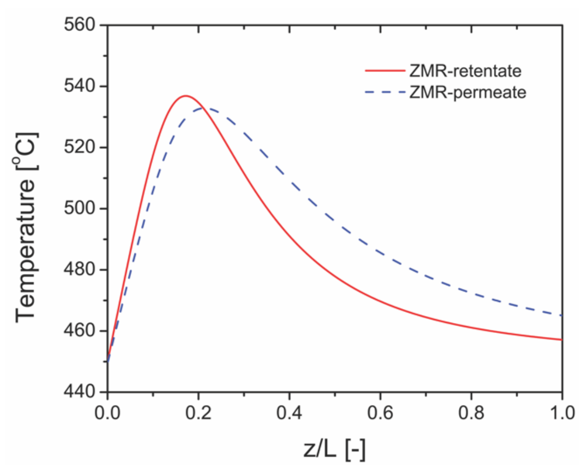


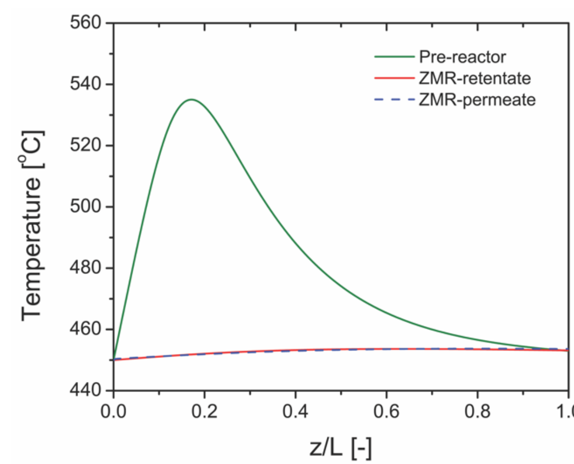



# Task 15: Testing WGS Reaction in Bench-Scale Membrane Reactor

## Modification and Installation of Bench-Scale Reactor Test Skid

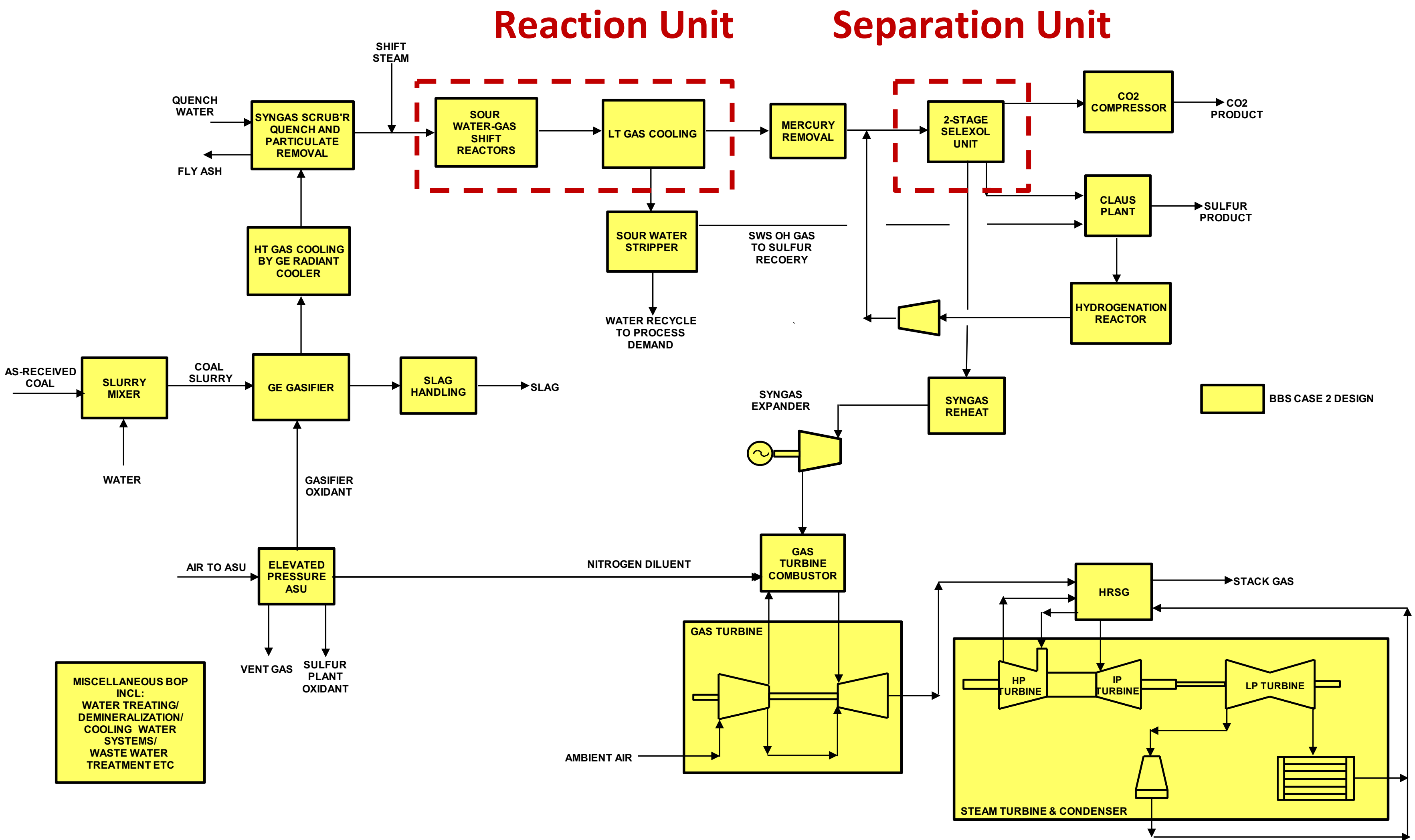


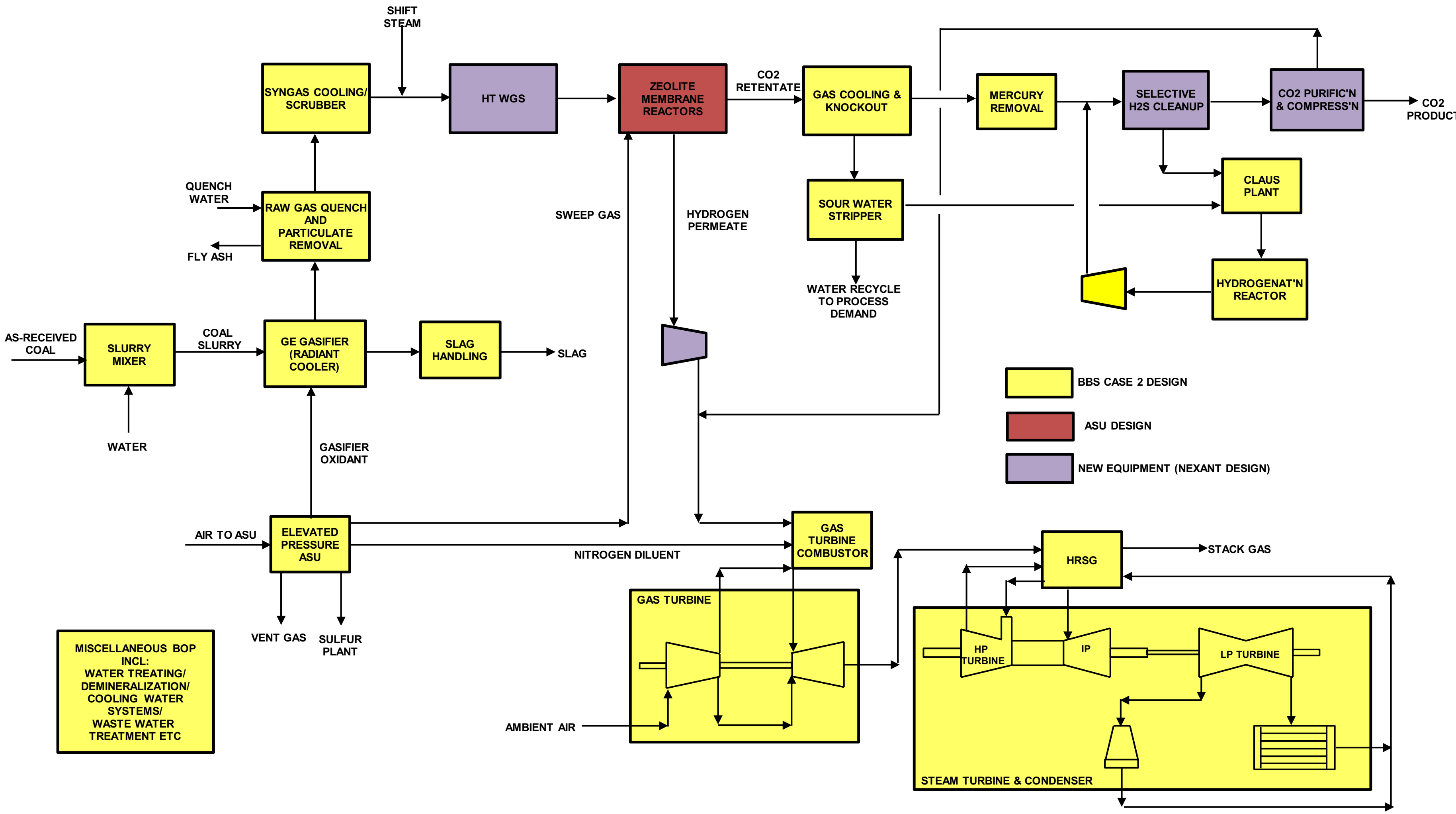
# Task 16: Process Design, Techno-Economic and EH&S Analyses

Block Flow Diagram – Reference DOE Case 2 GE IGCC with $CO_2$ Capture



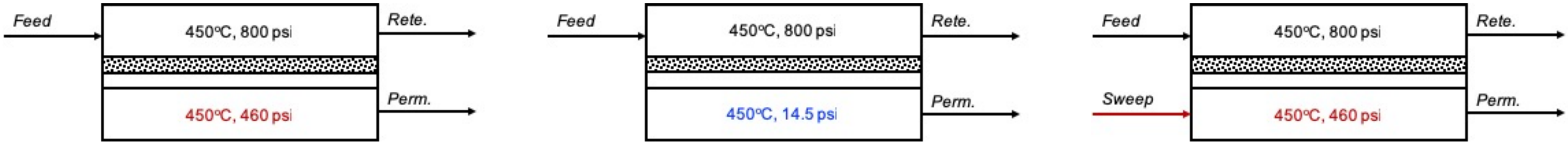
# Task 16: Process Design, Techno-Economic and EH&S Analyses

## Block Flow Diagram – ZMR Case IGCC with $CO_2$ Capture



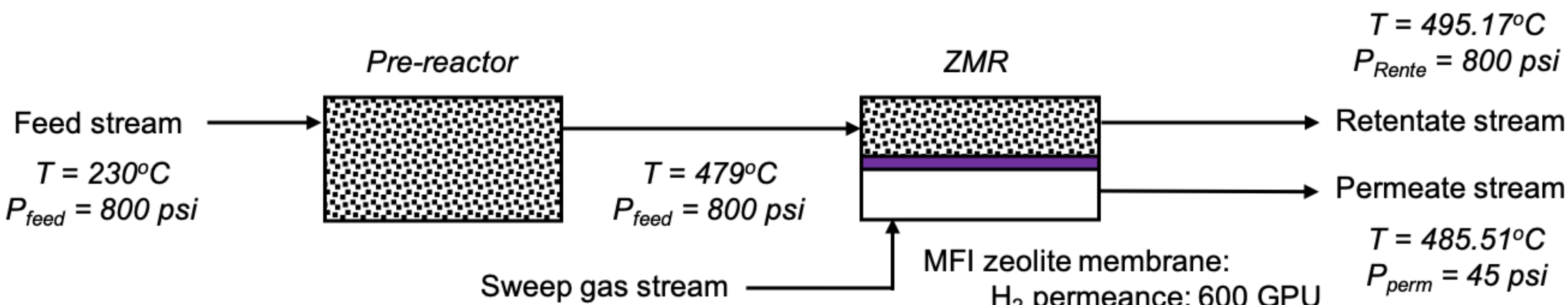
# Task 16: Process Design, Techno-Economic and EH&S Analyses

## WGS-ZMR modeling: Comparation of operation models




| Variable | Value | | |
|---|---|---|---|
| Permeate side pressure / psi | 460 | 14.5 | 460 |
| Sweep/feed gas flow rate ratio | 0 | 0 | 3 |
| CO conversion / % | 78.05 | 97.06 | 95.07 |
| $H_2$ recovery / % | 10.12 | 96.78 | 89.91 |
| $H_2$ purity / % | 69.32 | 91.86 | 90.51 |
| $CO_2$ capture / % | 95.04 | 89.49 | 88.41 |
| $CO_2$ purity / % | 38.03 | 91.14 | 81.59 |

# WGS-ZMR modeling: Base case




| Syngas Feed Gas Composition | |
|---|---|
| $H_2$ mol ratio [%] | 21.56 |
| CO mol ratio [%] | 22.74 |
| $CO_2$ mol ratio [%] | 8.73 |
| $H_2O$ mol ratio [%] | 45.48 |
| $N_2$ mol ratio [%] | 0.48 |
| $CH_4$ mol ratio [%] | 0.07 |
| $H_2S$ [%] | 0.44 |

| Simulation Results | |
|---|---|
| CO conversion [%] | 98.12 |
| $H_2$ recovery [%] | 95.87 |
| $H_2$ purity [%] | 92.25 |
| $CO_2$ capture [%] | 93.06 |
| $CO_2$ purity [%] | 88.39 |

| ZMR Feed Gas Composition | |
|---|---|
| $H_2$ mol ratio [%] | 38.37 |
| CO mol ratio [%] | 6.15 |
| $CO_2$ mol ratio [%] | 25.48 |
| $H_2O$ mol ratio [%] | 29.00 |
| $N_2$ mol ratio [%] | 0.48 |
| $CH_4$ mol ratio [%] | 0.00 |
| $H_2S$ [%] | 1.02 |

| Retentate Gas Composition | |
|---|---|
| $H_2$ mol ratio [%] | 3.27 |
| CO mol ratio [%] | 0.86 |
| $CO_2$ mol ratio [%] | 51.99 |
| $H_2O$ mol ratio [%] | 41.18 |
| $N_2$ mol ratio [%] | 0.87 |
| $CH_4$ mol ratio [%] | 0.00 |
| $H_2S$ [%] | 1.84 |

| Permeate Gas Composition | |
|---|---|
| $H_2$ mol ratio [%] | 90.9 |
| CO mol ratio [%] | 0.36 |
| $CO_2$ mol ratio [%] | 4.65 |
| $H_2O$ mol ratio [%] | 1.43 |
| $N_2$ mol ratio [%] | 2.62 |
| $O_2$ mol ratio [%] | 0.01 |
| Ar mol ratio [%] | 0.00 |

## Task 16: Process Design, Techno-Economic and EH&S Analyses

ZMR-based IGCC – Overall Cost of Electricity

| COE Components | Final TEA ZMR IGCC | Nexant Case 2 IGCC | NETL/DOE Case 2 IGCC |
|---|---|---|---|
| **CAPEX, $MM** | | | |
| Total Installed Cost (TIC) | 1,302 | 1,351 | 1,345 |
| Total Plant Cost (TPC) | 1,716 | 1,800 | 1,792 |
| Total Overnight Cost (TOC) | 2,123 | 2,230 | 2,220 |
| **OPEX, $MM/yr (100% CF BASIS)** | | | |
| Fixed Operating Cost ($OC_{fix}$) | 66 | 69 | 68 |
| Variable Operating Cost Less Fuel ($OC_{var}$) | 62 | 59 | 58 |
| Fuel Cost ($OC_{Fuel}$) | 146 | 146 | 147 |
| **Power Production, MWe** | | | |
| Gas Turbine | 462.5 | 464.2 | 464.0 |
| Expander | 0 | 6.5 | 6.5 |
| Steam Turbine | 257.9 | 245.3 | 263.5 |
| Total Power Output | 720.3 | 715.9 | 734.0 |
| Auxiliary Power Consumption | 208.1 | 191.0 | 190.8 |
| Net Power Output | 512.3 | 524.9 | 543.3 |
| Power Generated, MWh/yr (MWH) | 4,487,683 | 4,598,086 | 4,758,870 |
| Net Plant Efficiency, HHV | 30.8% | 31.5% | 32.6% |
| **COE, excl $CO_2$ TS&M, mills/kWh** | **138.3** | **138.6** | **133.1** |
| **COE, incl $CO_2$ TS&M, mills/kWh** | **147.3** | **147.3** | **141.5** |

*MM: million*

*HHV: Btu/lb*

*1 mill = $0.001*

# Task 16: Process Design, Techno-Economic and EH&S Analyses

## ZMR-based IGCC – Permeate Pressure Dependency

| | 45 psia Permeate Pressure | 100 psia Permeate Pressure | 200 psia Permeate Pressure |
|---|---|---|---|
| **Permeate and Retentate Conditions** | | | |
| $H_2$ Recovered in Permeate, % total | 92% | 86% | 71% |
| $CO_2$ Purity in Retentate, mol% dry | 84% | 78% | 66% |
| $H_2$ % in Retentate, mol% dry | 11% | 17% | 29% |
| **Membrane Area, $m^2$** | **8001** | **8589** | **10461** |
| **Affected Major CAPEX Component TPC, $MM Incremental** | | | |
| ASU/Oxidant and Nitrogen Compression | -- | -2.7 | -2.7 |
| ZMR | -- | +2.8 | +11.5 |
| $CO_2$ Compressor | -- | +6.7 | +14.1 |
| Nitrogen Sweep Gas Compressor | -- | +4.1 | +6.0 |
| Permeate Compressor | -- | -6.5 | -12.5 |
| Selexol Acid Gas Removal | -- | +23.4 | +36.0 |
| **TOTAL INCREMENTAL CAPEX COMPONENT, $MM** | **--** | **+27.8** | **+52.4** |
| **INCREMENTAL POWER PRODUCED, MWe** | **--** | **+4.0** | **+6.8** |
| **INCREMENTAL COE, mills/kWh (% vs 45 psia Case)** | **--** | **+0.4 (+0.3%)** | **+1.3 (+0.9%)** |

# Task 16: Process Design, Techno-Economic and EH&S Analyses

ZMR-based IGCC – Membrane Selectivity Dependency

| Affected Auxiliary Loads at Various ZMR Membrane $H_2/CO_2$ Selectivities, MWe | $H_2/CO_2$ Selectivity = 70 | $H_2/CO_2$ Selectivity = 200 |
|---|---|---|
| **Permeate and Retentate Conditions** | | |
| $H_2$ Recovered in Permeate, % total | 92% | 91% |
| $CO_2$ Purity in Permeate, mol% dry | 4.3% | 1.6% |
| $CO_2$ Purity in Retentate, mol% dry | 84% | 84% |
| $H_2$ % in Retentate, mol% dry | 11% | 11% |
| **Membrane Area, $m^2$** | **8001** | **8038** |
| **Affected Major CAPEX Component TPC, $MM Incremental** | | |
| ZMR | -- | +0.2 |
| Permeate Compressor | -- | -0.9 |
| $CO_2$ Compressor | -- | -1.5 |
| Selexol Acid Gas Removal | -- | -9.7 |
| **TOTAL INCREMENTAL CAPEX COMPONENT, $MM** | **--** | **-11.9** |
| **INCREMENTAL POWER PRODUCED, MWe** | **--** | **+3.6** |
| **INCREMENTAL COE, $/MWh (% vs Base Case)** | **--** | **-1.5 (-1.1%)** |

# Summary

- 25-cm long CCD-modified zeolite membranes scaled up on alumina substrates.
- Multiple-tube ZMRs assembled and evaluated, and test skid for bench-scale test modified.
- Process design and Techno-Economic Analysis of ZMR-based IGCC plant was nearly completed.

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# Thank You!