Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

Jerry Y.S. Lin

Arizona State University

DOE Award:

DE-FE0026435

NETL CO_2 Capture Technology Meeting

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Overview

Timeline

- Project start date:
  Oct.1, 2015
- Project end date:
  Dec.31, 2018
- Budget Periods:
  I: 10/1/2015-7/30/2017
  II: 8/1/2017-12/31/2018

Research Area

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

Budget

- Total project funding
  - DOE **$2,471,557**
  - Cost-share: **$620,527**
  - Total**: $ 3,092,084**
- Funding for BP I:
  - DOE **$1,274,869**

Partners

- Arizona State University (ASU)
- University of Cincinnati (UC)
- Media and Process Technology, Inc (MPT)
- Nexant, Inc.

Principal Investigators

Arizona State University
Jerry Y.S. Lin

University of Cincinnati
Junhang Dong

Media Processes and Technologies
Richard Ciora

Nexant, Inc
Gerald Choi

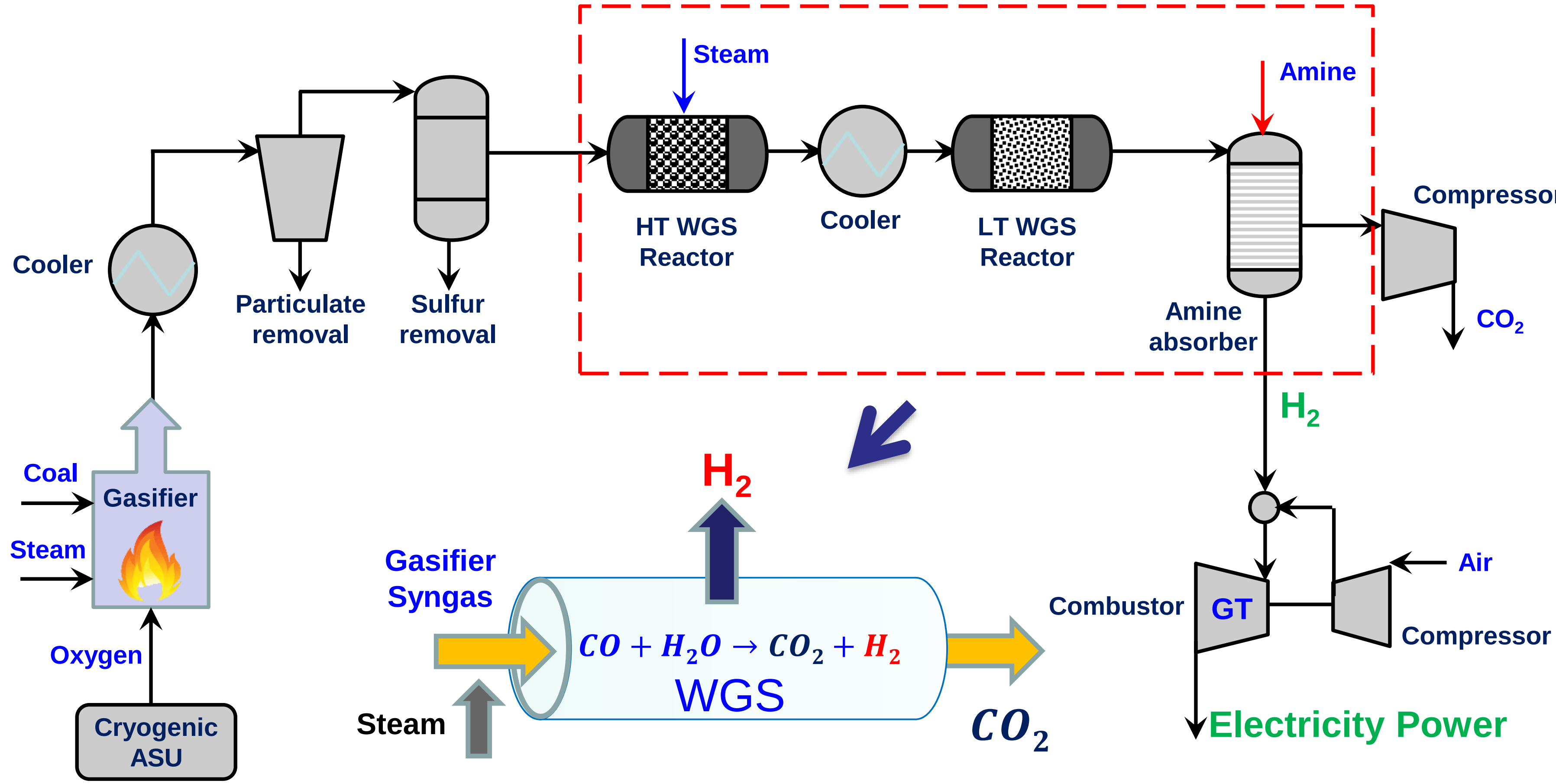
NETL Project Manager
Andrew Jones

Project Objectives

To demonstrate a bench-scale zeolite membrane reactor for WGS reaction of coal gasification gas for hydrogen production for integration with IGCC power plant.

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.

Zeolite Membrane Reactor for Water-Gas Shift Reaction for CO_2 Capture



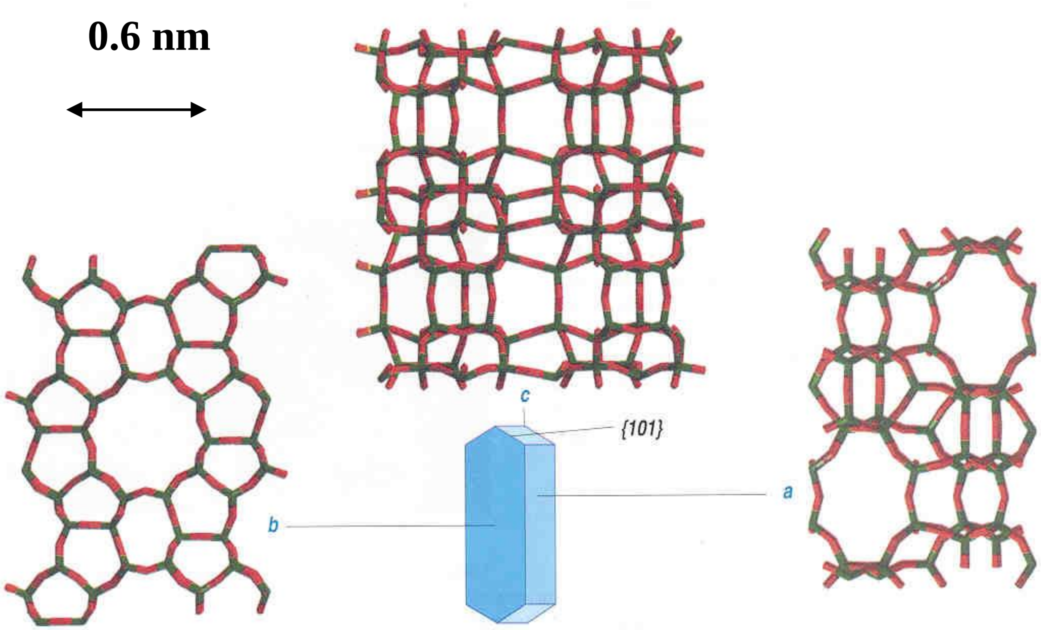
Zeolite membrane for CO_2 capture

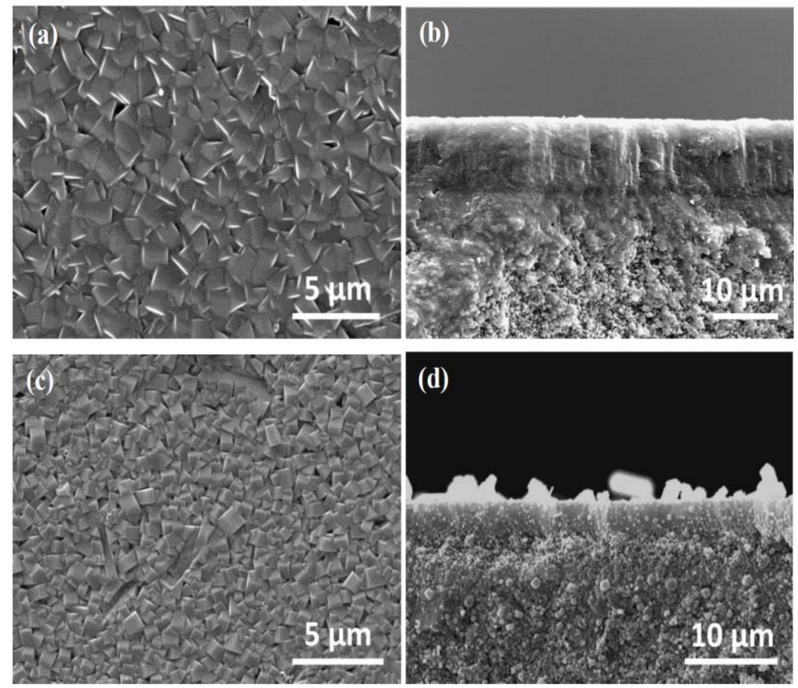
Zeolite Membrane Requirements:

- Operate at 350-550ºC
- Chemically stable in H_2S, thermally stable at ~400ºC
- Hydrogen permeance > 1×10^{-7} mol/m^2.s.Pa (>300 GPU)
- Hydrogen selectivity >25

MFI Type Zeolite

Structure of MFI type Zeolite (ZSM-5 or Silicalite)





Highly chemically and thermally stable (up to 700^{o}C)

Surface and cross-section SEM images of (a, b) templated synthesized random oriented MFI membrane, (c, d) template-free synthesized random oriented MFI membranes (from Lin lab)

Properties of Lab-Scale CVD Modified MFI Zeolite Membranes (Disk Subtrates)

Parameter	Value
H_2 Permeance in ($mol/m^2.s.Pa$)	$1\text{-}4 \times 10^{-7}$
H_2 Permeance in GPU	300-1200
H_2/CO_2 selectivity	20-140
H_2/CO selectivity	50-200
H_2/H_2O selectivity	120-180
H_2/H_2S selectivity	100-180
Tested stability hours in syngas stream at 400 ppm H_2S at 500^oC	600

With equal-molar feed of H_2, CO_2, CO and H_2O at 500^oC and 2 bar feed (Lin and Dong Labs)

Scope of work

1) **Scaling up a zeolite membrane reactor from lab-scale to bench-scale for combined WGS reaction and H_2 separation**
2) **Conducting a bench-scale study using this zeolite membrane reactor 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 L(active)
- A system producing H_2 at rate of about 1-10 kg/day, equivalent to a 1-10 kW_{th} IGCC power plant

General Approach to Scaling up WGS Zeolite Membrane Reactor

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

↓

Intermediate-scale membrane reactor: 3-7 tube membrane module, and WGS reaction in the intermediate-scale reactor

↓

Bench-scale membrane reactor: 21 tube membrane module, and WGS reaction in the bench-scale membrane reactor at NCCC

→ Membrane reactor in IGCC with CO_2 capture - process design and techno-economic analysis

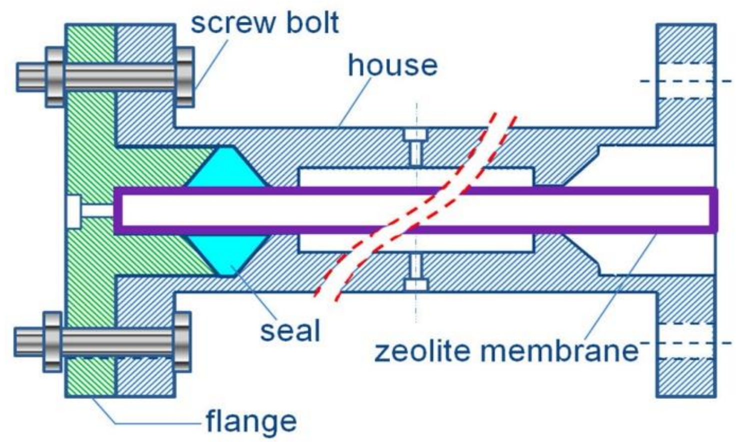
Progress and Accomplishments

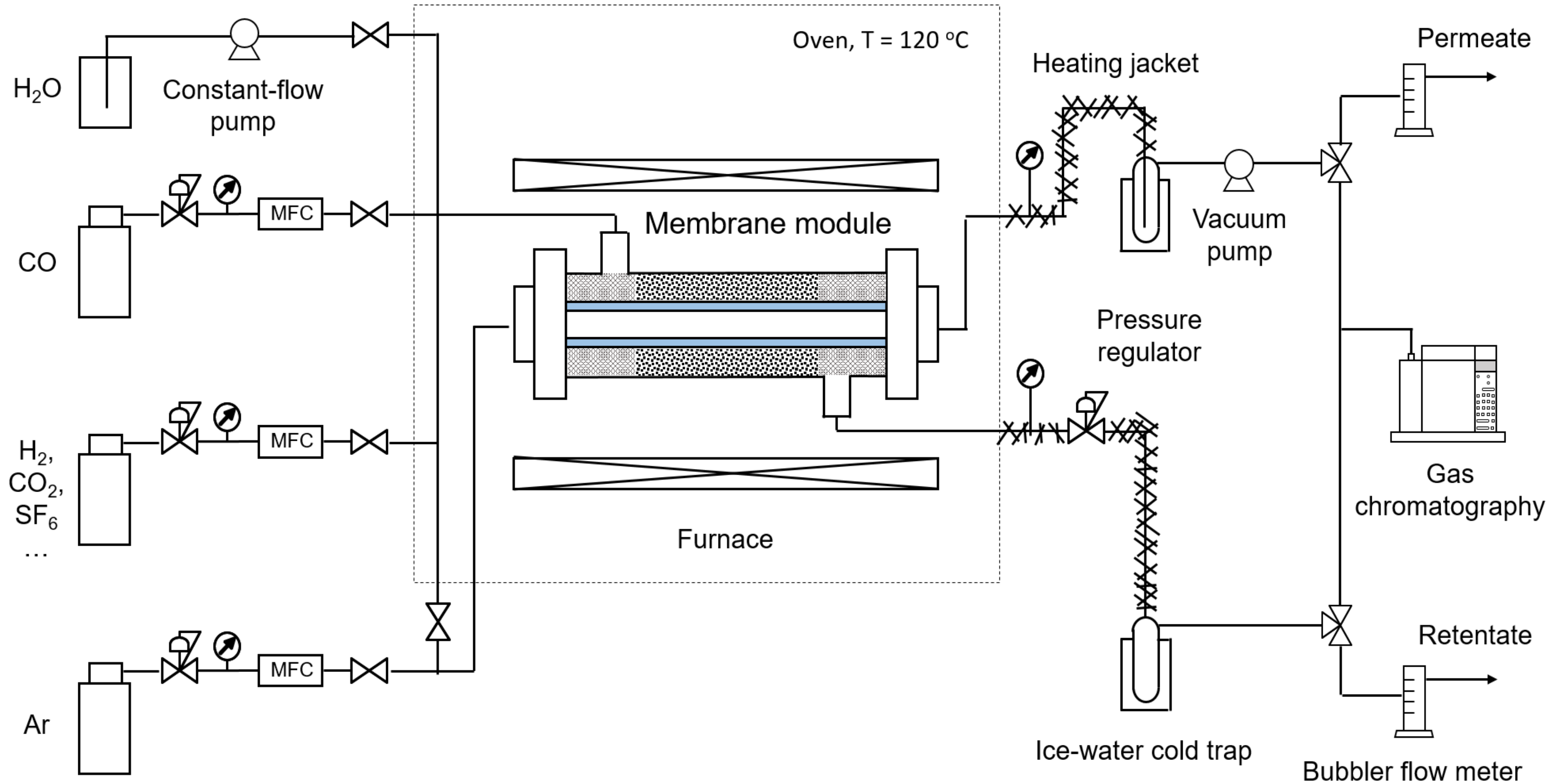
- Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0)
- Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0)
- Optimizing Tubule Support Fabrication (Task 4.0)
- Optimizing Zeolite Membrane Synthesis Methods (Task 5.0)
- Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0)
- Design and Fabrication of Zeolite Membrane Bundles and Modules (Task 7.0)
- Testing Zeolite Tube Bundles under Gasifier Conditions Including Membrane Reactor Configuration (Task 8.0)
- Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0)

Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0)

Subtask 2.1 Setting up high pressure WGS membrane reactor:

Two single-tube zeolite membrane reactor systems were built (400-550ºC, 30 bar), and used to study WGS reaction.

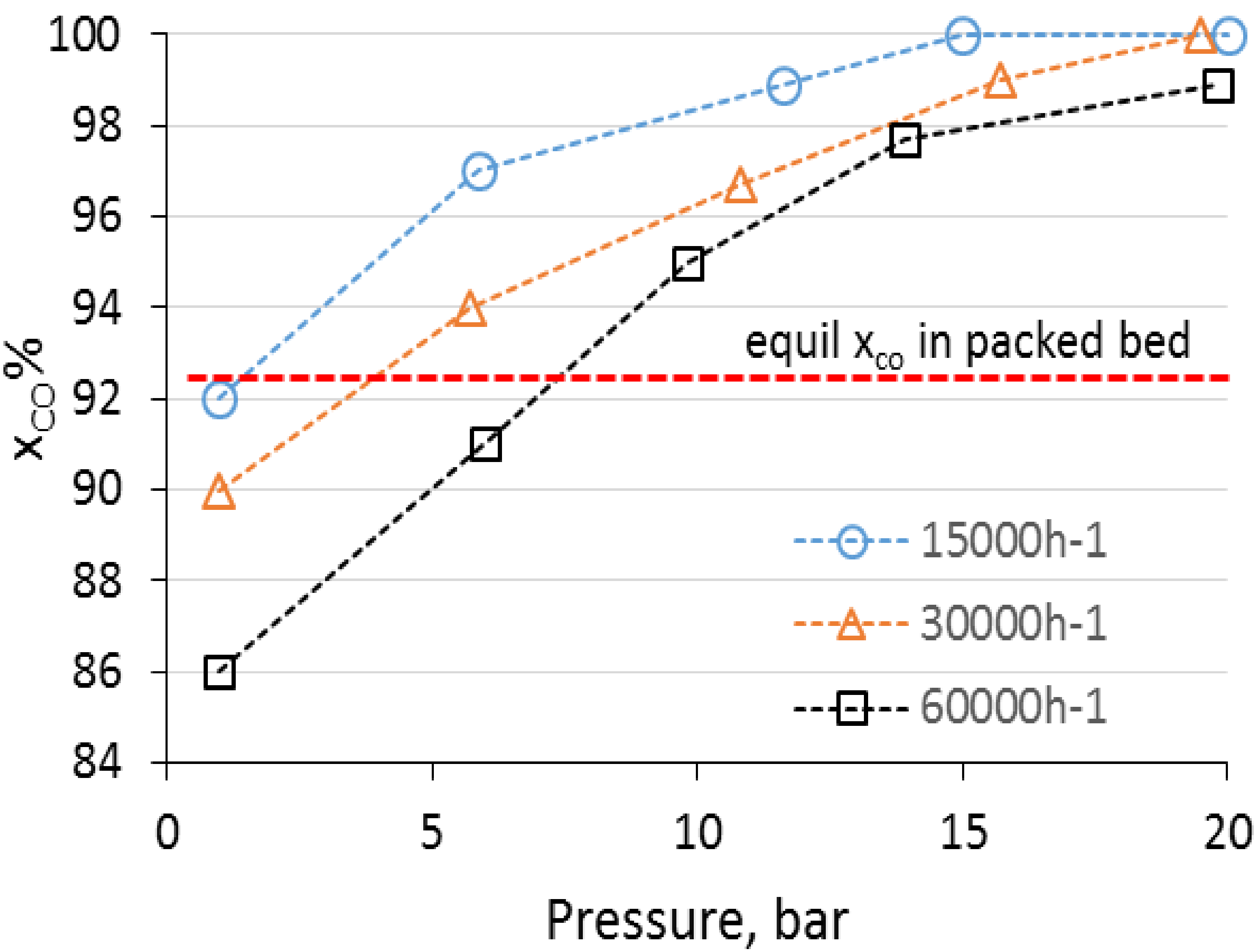




Setup at ASU

Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0) (Cont'd)

Subtask 2.3 Experiments on WGS in lab-scale zeolite membrane reactor



Zeolite membrane:

- $(\alpha_{H_2/CO_2}) = 38$,
- F_{H2} =300 GPU
- Length=8cm

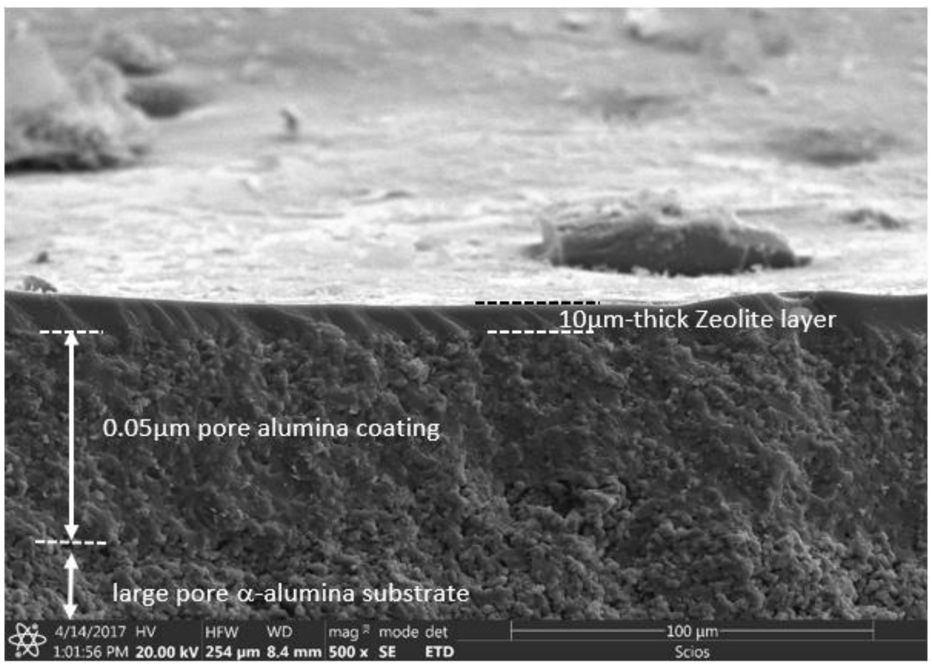
Conditions:

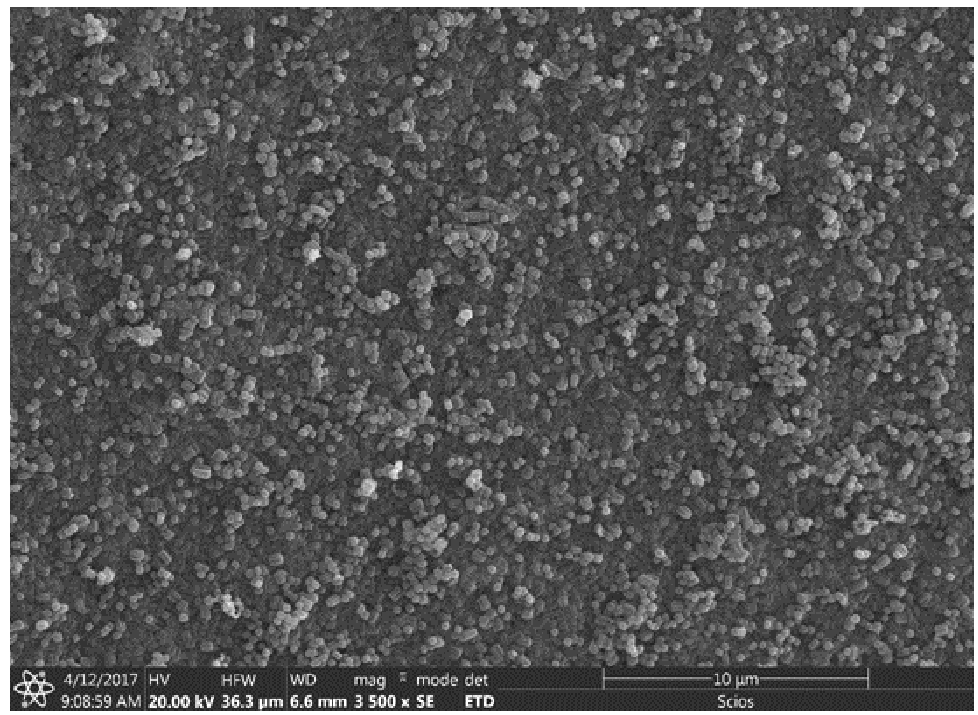
- T=500^{o}C,
- H_2O/CO=3-3.5

Experimental Study on WGS in Lab-Scale Tubule Zeolite Membrane Reactor (Task 2.0) (Cont'd)

Morphology of Zeolite Membranes

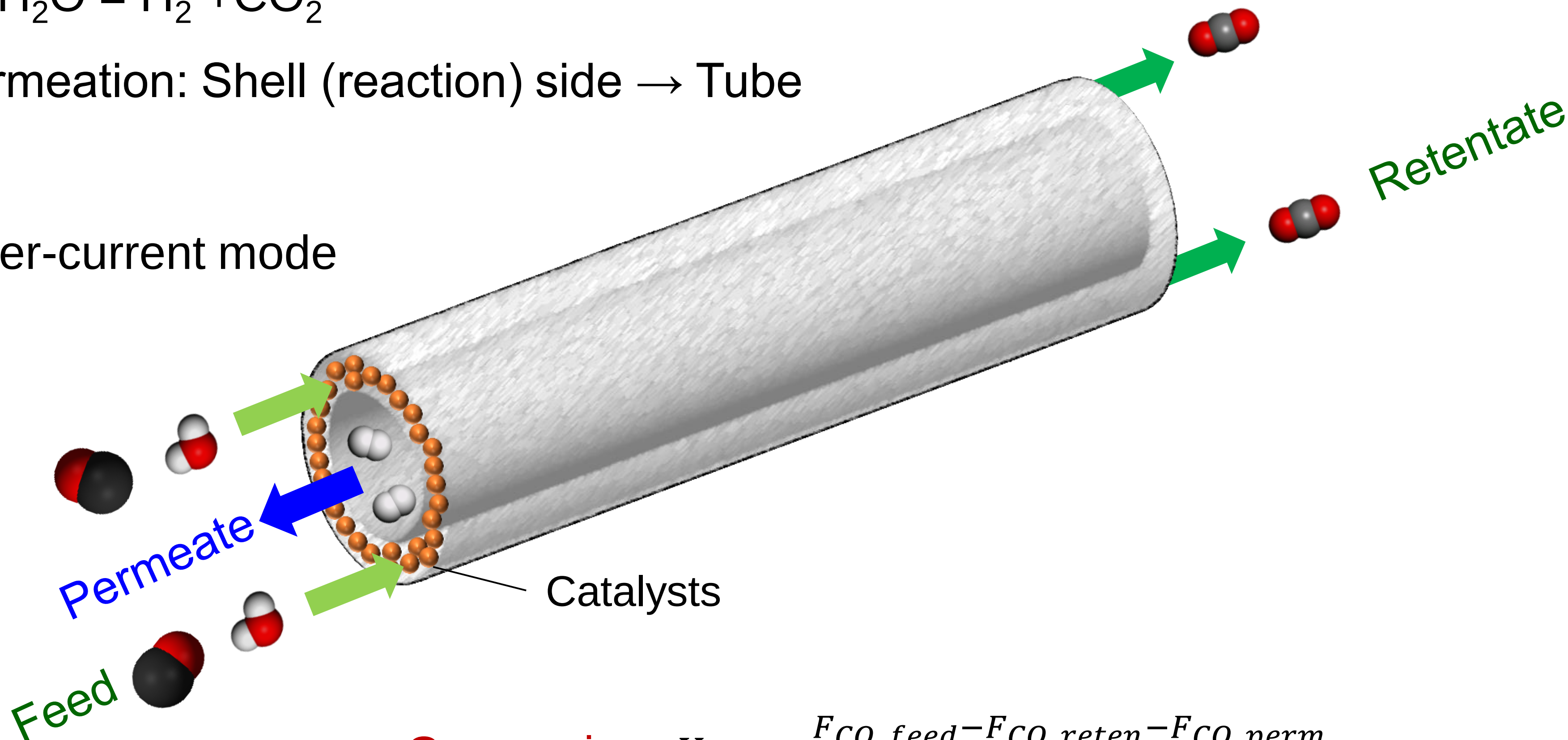
A 10-cm long tubular MFI zeolite membrane was tested for more than six months under WGS reaction conditions at 500^{o}C and reaction side pressure up to 26.5 bar. It was tested for over one week of WGS operation with feed CO containing 1,000 ppm of H_2S.





Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0)

- $CO + H_2O = H_2 + CO_2$
- H_2 permeation: Shell (reaction) side → Tube side
- Counter-current mode



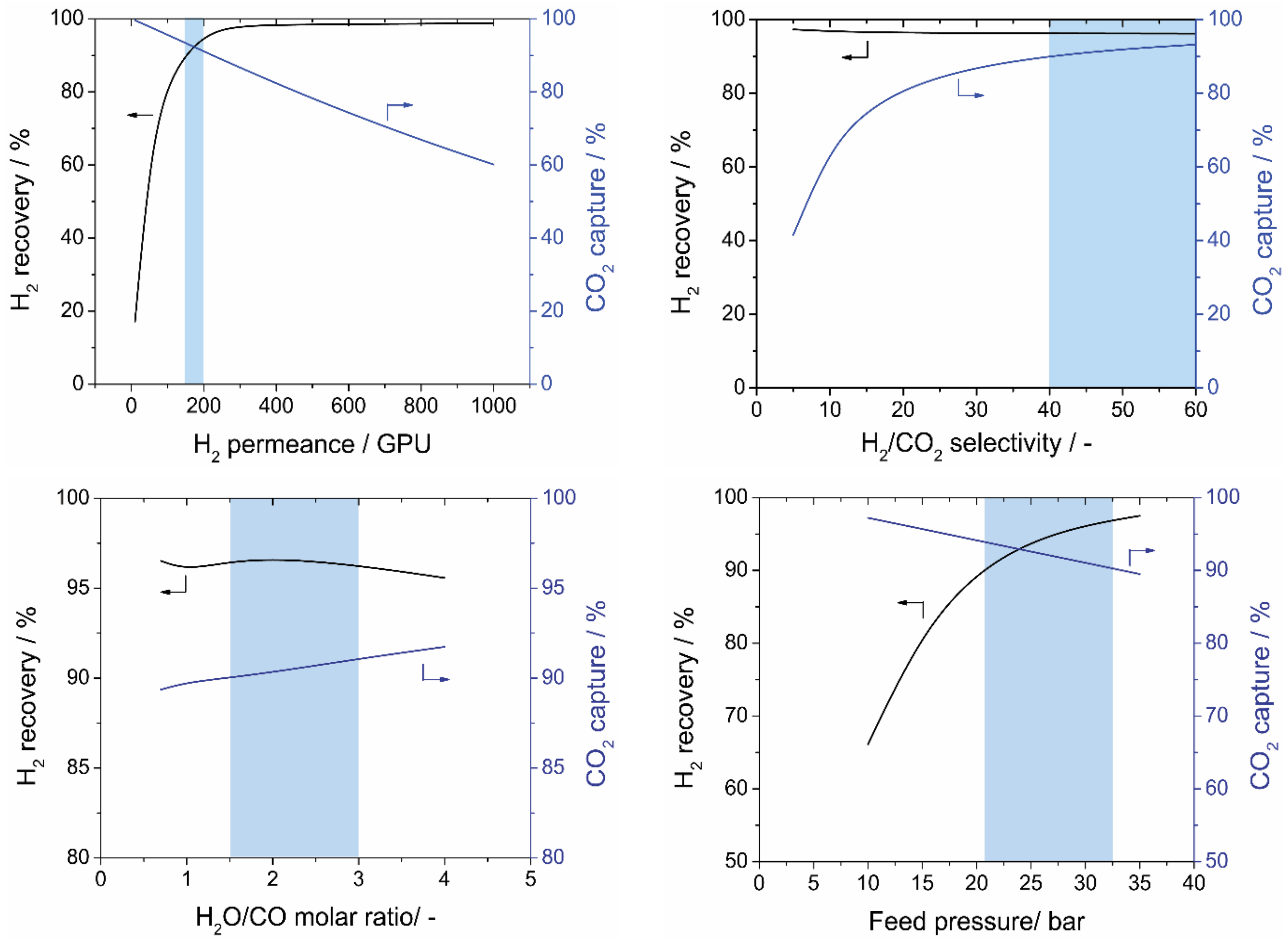
Conversion: $X_{CO} = \frac{F_{CO,feed} - F_{CO,reten} - F_{CO,perm}}{F_{CO,feed}}$

Purity: $G_{H_2} = \frac{F_{H_2,perm}}{F_{total,perm}}$, $G_{CO_2} = \frac{F_{CO_2,reten}}{F_{total,reten}}$

Recovery: $R_{H_2} = \frac{F_{H_2,perm}}{F_{H_2,reten} + F_{H_2,perm}}$ Capture: $R_{CO_2} = \frac{F_{CO_2,reten}}{F_{CO_2,reten} + F_{CO_2,perm}}$

Modeling and Analysis for WGS in Zeolite Tubule Membrane Reactor (Task 3.0) (Cont'd)

H_2 recovery > 92% & CO_2 capture > 90%



Optimizing Tubule Support Fabrication (Task 4.0)

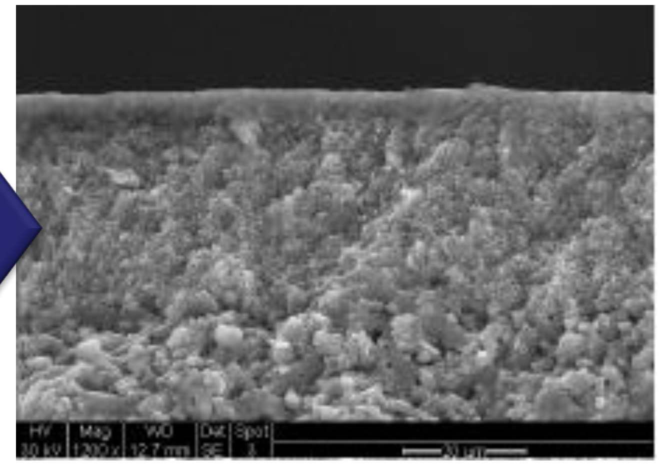
Ceramic Tube Extrusion

Intermediate Layer Deposition
+
Non-porous Tip and End Seals

End Seal (Open end)

Tip Seal (Closed end)

Zeolite Layer Deposition
+
(Silica CCD Modification)



Package into Multiple Tube Bundle
+
(Silica CCD Modification)

MPT 57-tube Bundle (Carbon Molecular Sieve Membrane)

Optimizing Tubule Support Fabrication (Task4.0) (Cont'd)

Mechanical Strength after Immersion in Zeolite Synthesis Solution

Challenge Conditions: ***T = 180°C; up to 48 hours; various NaOH and Zeolite Synthesis solution***

- *Approach #1: Nominal tube wall thicknesses of 1.1, 1.45, and 1.75mm tested*
- *Approach #2: Higher alumina content in tube (99%)*

Conclusion ***Thicker wall tube may be appropriate but not required.***

Intermediate Layer Integrity/ Material Stability in Zeolite Synthesis Solution

Challenge Conditions: ***T = 180°C; 48 hours; 2.7% NaOH***

Conclusion ***No impact on intermediate layer quality***

Ceramic/Glass Sealant Material Stability in Zeolite Synthesis Solution

Challenge Conditions: ***T = 180°C; 48 hours; 2.7% NaOH***

Conclusion

Glass/Ceramic End Seal

Post Zeolite Solution Challenge

Haze and surface roughness development

Gas tight seal remains.

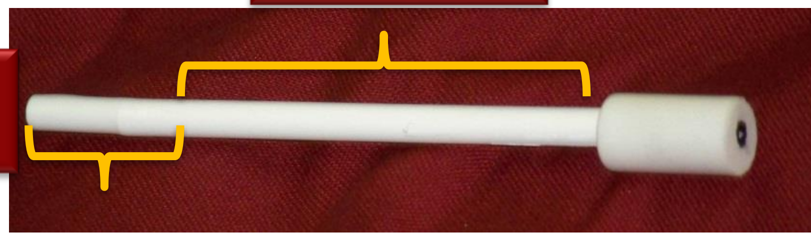
Optimizing Tubule Support Fabrication (Task 4.0) (Cont'd)

Demonstrate High Temperature Hydrothermal Stability of Membrane Bundle Components and Seals

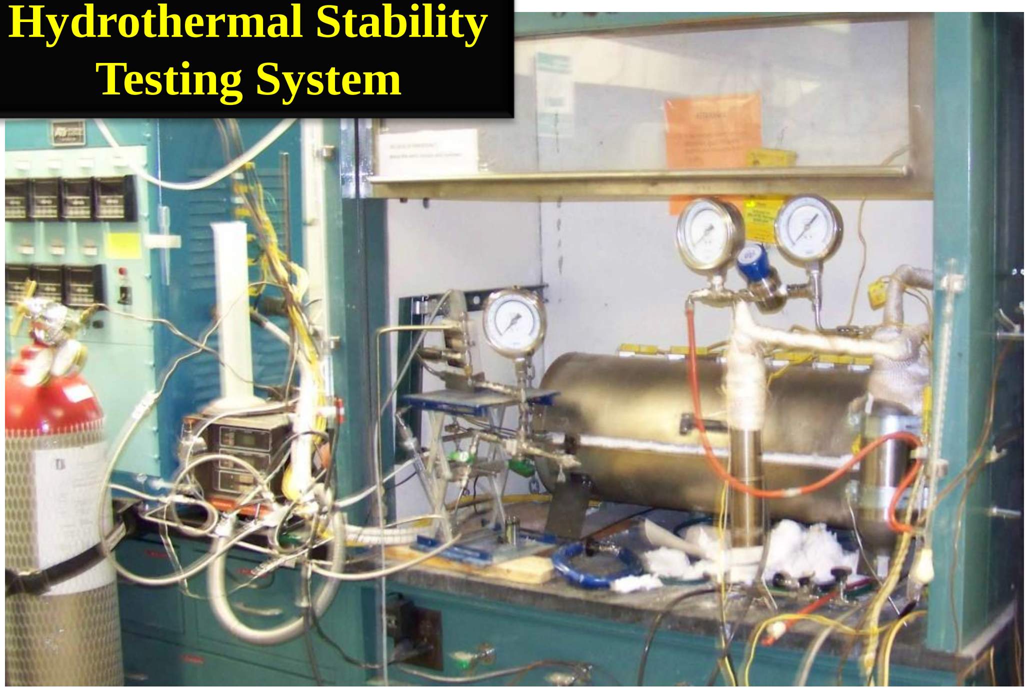
Single Tube Bundle

***Operating Conditions:** T = 450ºC; P = 300 psig; Steam = 80% (in N_2)*

Three Primary Scale-up Seal Components



Hydrothermal Stability Testing System



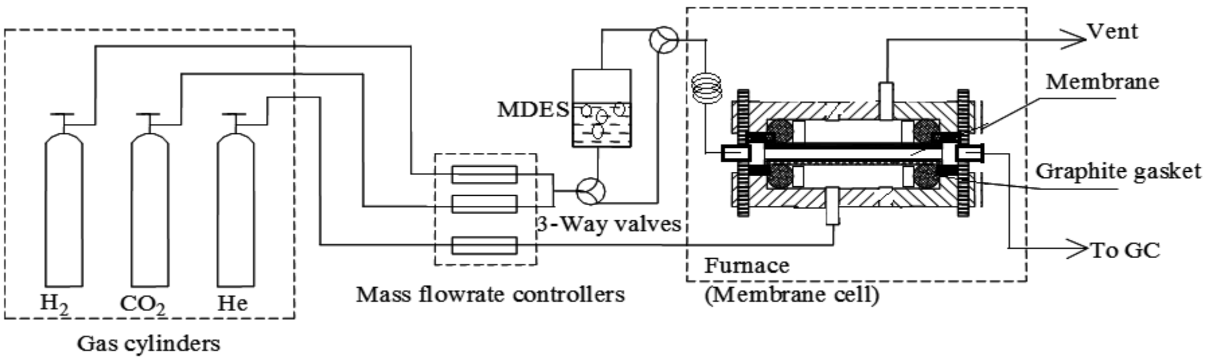
Results/Conclusions

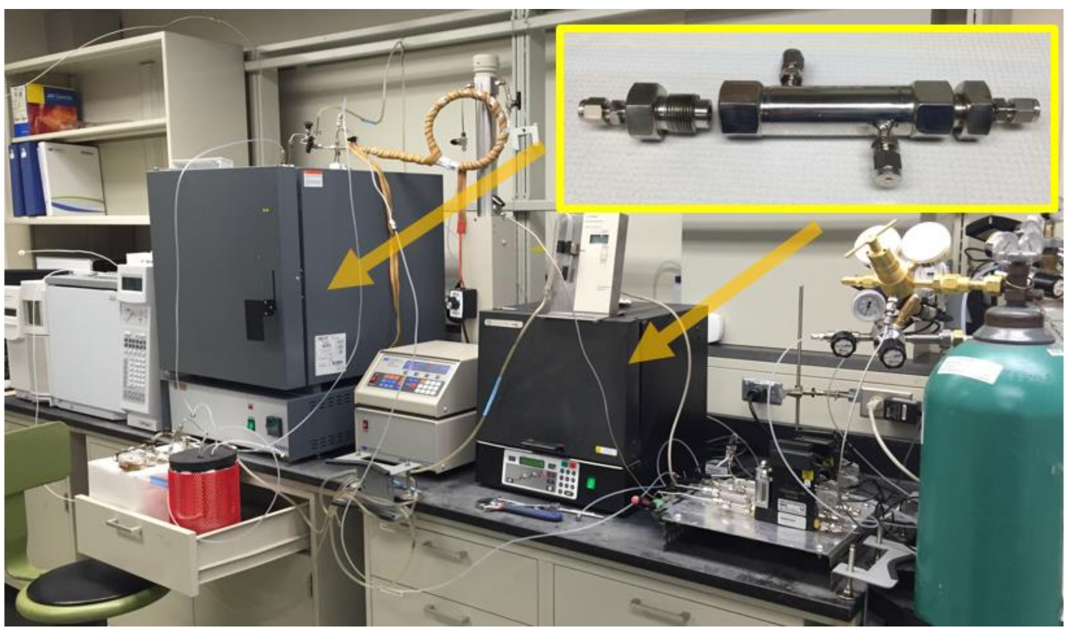
1. *No leak development over 185 days of hydrothermal stability challenge testing.*
2. *All seal component appear to be stable in the testing conditions.*

Optimizing Tubular Zeolite Membrane Synthesis Methods (Task 5.0)

<u>Facility Establishment (design and construction):</u>

- Membrane modification, stability test and WGS reaction system





High temperature high pressure
Membrane modification, test, and WGS reaction

Long term stability
testing system

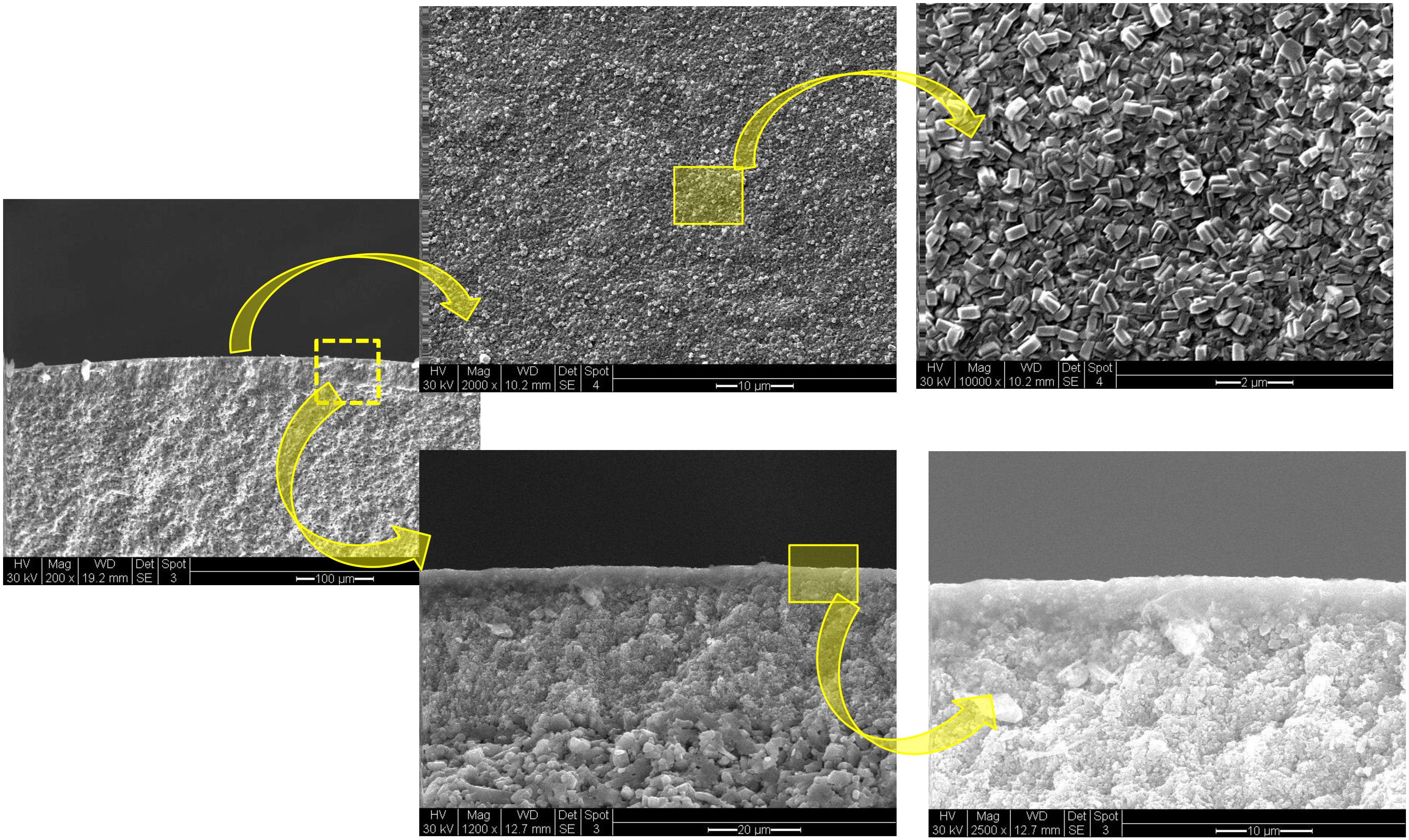
Optimizing Zeolite Membrane Synthesis Methods (Task 5.0) (Cont'd)

— Best results achieved via in-situ synthesis with solutions of high pH (NaOH) and two-step CCD modification at 450 – 500C.

Method	Hydrothermal precursor	Seed layer	Conditions (hydrothermal & CCD modification)	Quality before CCD	Quality post CCD
In situ	**SiO_2+H_2O+ NaOH+TPAOH**	**No**	**Hydrothermal: 180C/8h/rotation CCD: 450 – 500C; two-step**	**Excellent**	**Excellent $\alpha_{H2/CO2}$ ~ 20 - 50**
In situ	SiO_2+H_2O+ $AlCl_3$+NaOH +TPAOH	No	Hydrothermal: 180C/6h/rotation CCD: 450; two-step	Good	Good $\alpha_{H2/CO2}$ ~ 10 - 20
Secondary growth	TEOS+H_2O+ $AlCl_3$+NaOH +TPAOH	Yes; Silica -lite	Hydrothermal: 165C/6h/rotation CCD: 450C; two-step	Excellent	Good $\alpha_{H2/CO2}$ ~ 12
Secondary growth	TEOS+H_2O+ $AlCl_3$+NaOH +TPAOH	Yes; ZSM-5	Hydrothermal: 165C/6h/rotation CCD: 450C; two-step	Average	Poor $\alpha_{H2/CO2}$ < 10

Optimizing Zeolite Membrane Synthesis Methods (Task 5.0) (Cont'd)

ZSM-5 Membranes on MPT Tubes



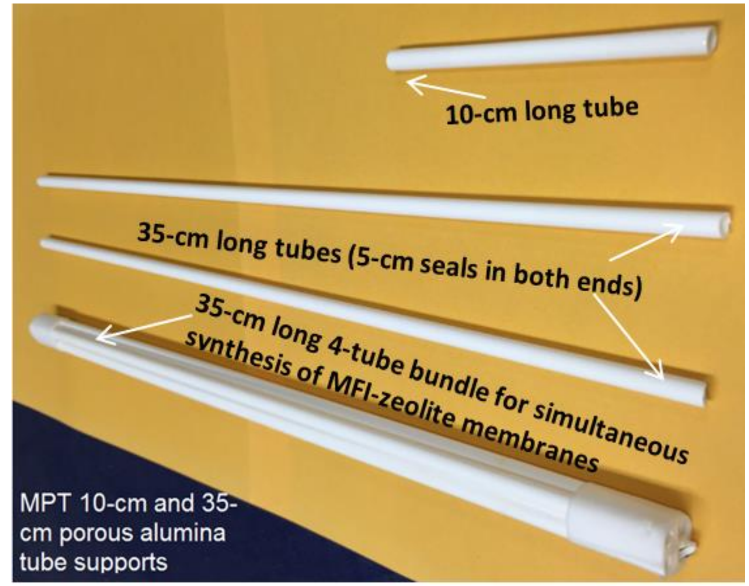
Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0)

Previous synthesis of 2.5-cm-diameter disc and 2-cm long ϕ1.0-cm tube (Pall Corp) membranes

Different size and geometry and surface chemistry of MPT tubes needs changes in: (1) zeolite precursor chemistry, (2) hydrothermal synthesis conditions, (3) calcination conditions, and (4) CCD modification conditions

Synthesis of 10-cm long ϕ1.0-cm tube (Pall Corp) membranes

Long tube and multi-tube synthesis (dead-ended and open-ended): (1) zeolite precursor chemistry, (2) hydrothermal synthesis conditions, (3) calcination conditions, and (4) CCD modification conditions



Preparation of 35-cm long tube membranes on MPT ϕ=0.57-cm tubes and scale-up to making multi-tubes in single batch

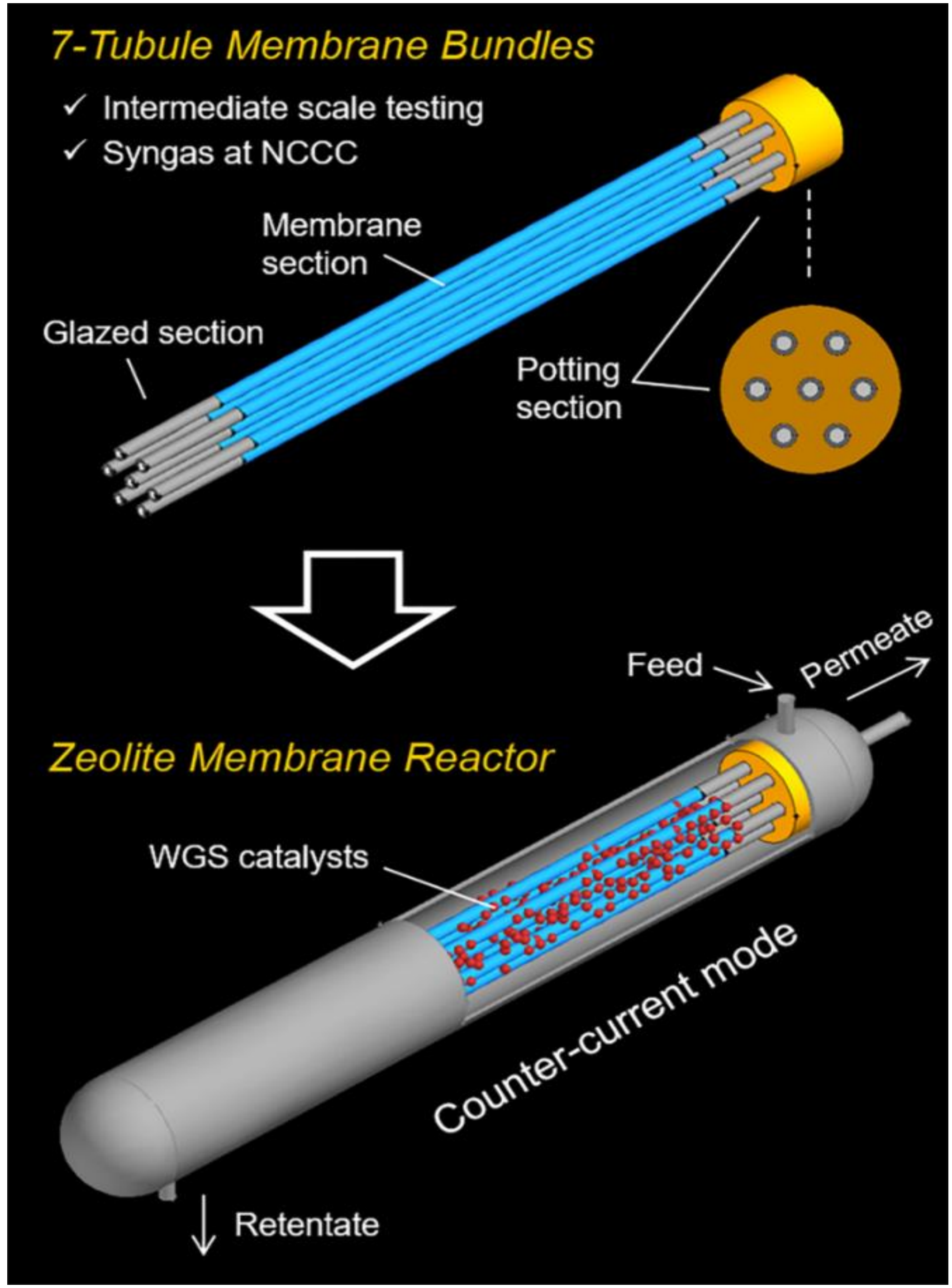
Scaling up Synthesis of High Quality Zeolite Membranes (Task 6.0) (Cont'd)

Performances demonstrated on the modified MFI zeolite membranes of different scale up stages – for separating 50v/50v H_2/CO_2 mixture at 450°C and 1 atm (1GPU=3.35×10^{-10} mol/m$^2\cdot$s$\cdot$Pa)

Support	**Dimensions**	**Support Maker**	**A_m (cm^2)**	**$\alpha_{H2/CO2}$**	**$P_{m,H2}$ (GPU)**	Target	
						$\alpha_{H2/CO2}$	$P_{m,H2}$ (GPU)
Disc	D = 2.5-cm	UC lab	2.5	62	~390	--	--
Tube	L=8cm; L_m =1.5 cm; OD=1cm; ID=0.7 cm	Pall Co.	4.7	>100	~806	--	--
Tube	L=8cm; L_m =6 cm; OD=1cm; ID=0.7 cm	MPT	11.0	45±5	360±50	45	600
Tube	L=35cm; L_m =25 cm; OD=1cm; ID=0.7 cm	MPT	44.8	41±5	725±50	45	600

Design and Fabrication of Zeolite Membrane Bundles and Modules (Task 7.0)

Single, 3- and 7-tube alumina membrane “bundles” for use in the high temperature hydrothermal pressure testing.

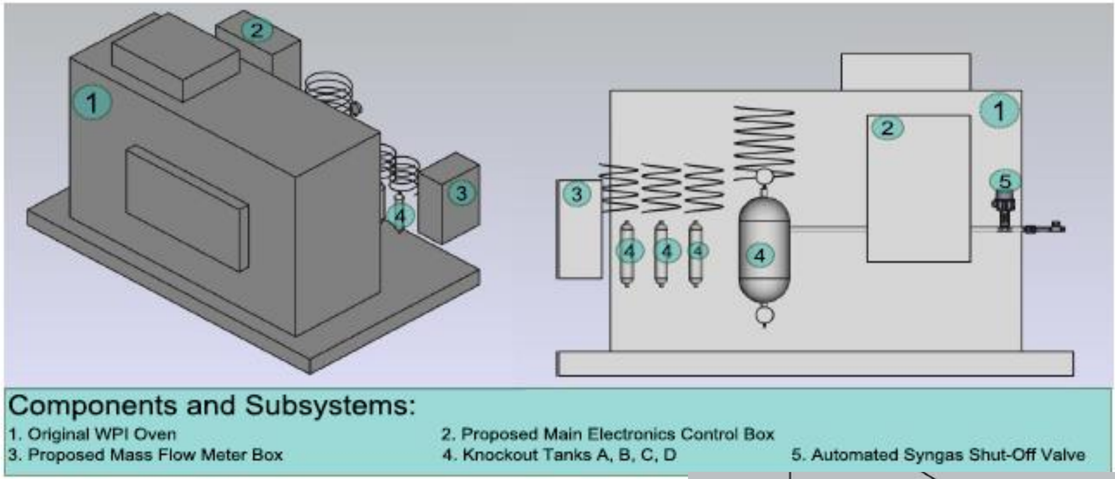


Testing Zeolite Tube Bundles under Gasifier Conditions Including Membrane Reactor Configuration (Task 8.0)

Modify NCCC Test Rig for Gasifier Off-gas Challenge Testing of Zeolite Membrane and Bundle Components and Seals Target Conditions: 450^{o}C and 300psig; no pretreatment (NCCC max operating conditions available); Single tube, 7-tube, and 21-tube bundles

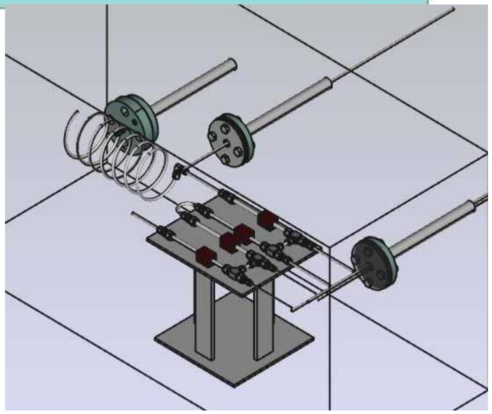
WPI/MTR skid: Oven and system components approved for use by NCCC under proposed operating conditions.

MPT Modifications: Target automated operation and remote monitoring for continuous long term testing of proposed membrane technology.



Interior dimensions
48w x 24h x 24 deep

MPT Modifications
Testing of several membrane bundles/modules simultaneously



Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology (Task 9.0)

ZMR Integration Methodology

- ***Reference Case IGCC - Case 2 (GE Gasifier with Selexol AGR and GE F-class gas turbines) in the 2013 DOE/NETL Report 1397 on "Bituminous Coal and Natural Gas to Electricity, Rev 2a"***
- ***IGCC Design to NETL's QGESS Guidelines***
- ***Cost Estimation and Financial Modeling Methodology***
  - ***For process systems associated with the ZMR WGS and CO_2 capture technologies, Nexant will carry out preliminary process design to establish system performances and develop major equipment-factored capital costs. Costs for proprietary equipment will be provided by technology licensors.***
  - ***For process and support systems that are unrelated to the ZMR WGS and CO2 capture technology, performances and capital costs will be scaled from the NETL Reference Case 2 according to capacity factors established by process H&MB, and by overall utility and commodity material balances.***

Plan for Budget Period 2 Work

Budget Period 2 Project Tasks & Schedule

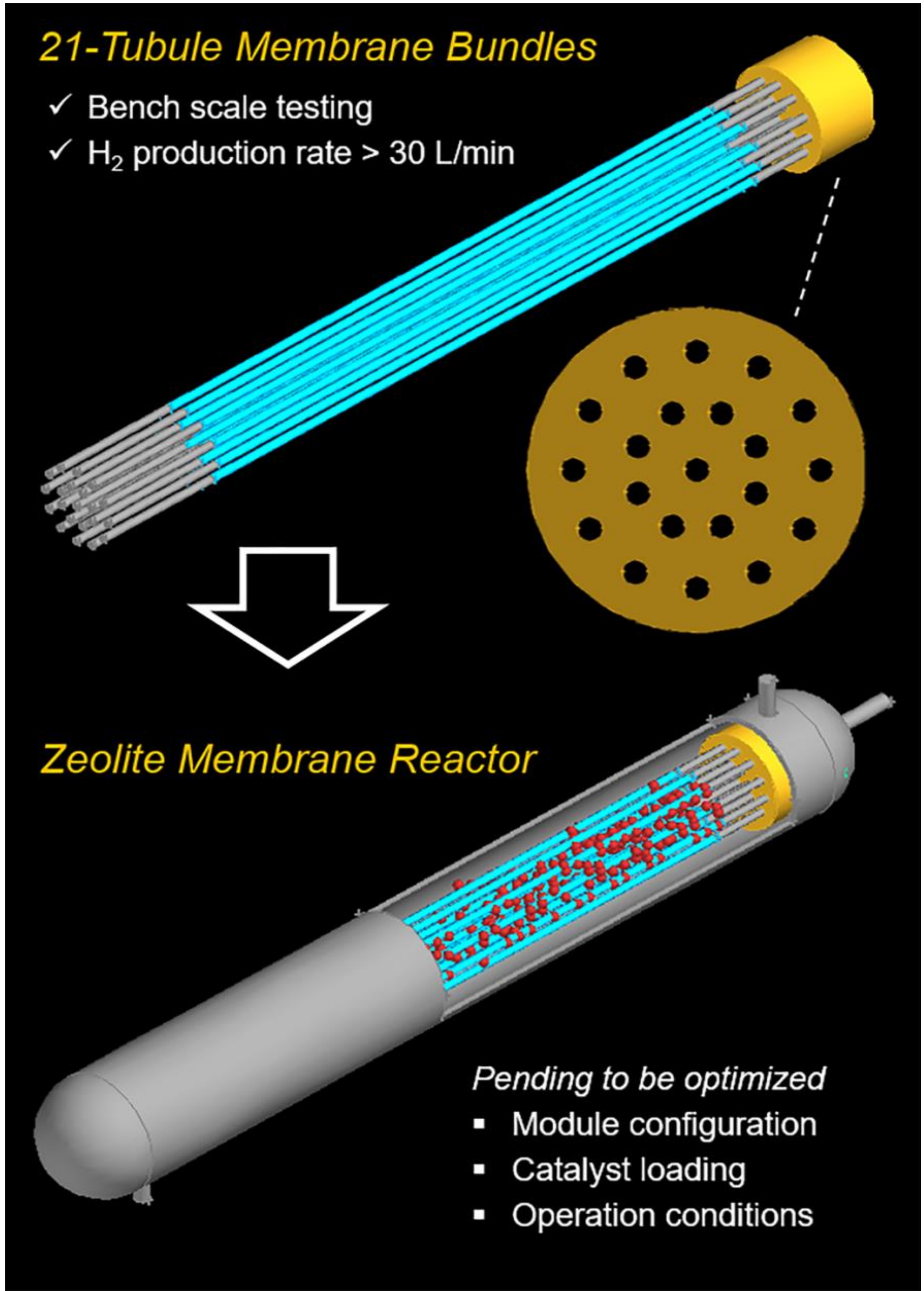
Task	Quarter 1	2	3	4	5	6
Task 10.0 Modeling and Analysis of WGS in Bench Scale Zeolite Membrane Modules for WGS (ASU)	■	■	■	■		
Subtask 10.1 Modeling and analysis of WGS in multi-tube membrane reactor module	■	■				
Subtask 10.2 Optimization of operation conditions for WGS in zeolite membrane module			■	■		
Task 11.0. Fabrication of Large Quality Tubular Supports (MPT)	■	■				
Task 12.0 Preparation of Large Quantity MFI Zeolite Tube Membranes for Bench-Scale Module (UC)	■	■	■	■		
Subtask 12.1 Identifying conditions for fabrication of large quantity of zeolite membrane tubes	■	■				
Subtask 12.2 Fabrication of 200-300 zeolite membrane tubules with desired quality			■	■		
Task 13.0 Design and Fabrication of Bench-Scale Zeolite Membrane Module Housing with Seals (MPT/UC/ASU)	■	■				

Project Tasks and Schedule (Cont'd)

Task	Quarter ⇨ 1	2	3	4	5	6
Task 14.0 Building Bench-Scale Zeolite Membrane Reactors (MPT/ASU/UC)						
Subtask 14.1 Fabrication and evaluation of WGS catalyst for bench-scale WGS reaction (ASU)						
Subtask 14.2 Assembling and testing bench-scale zeolite membrane reactor (MPT/UC/ASU)						
Subtask 14.3. Modification and installation of the membrane reactor testing skid (MPT/ASU)						
Task 15.0 Testing WGS in Bench-Scale Membrane Reactor (MPT)						
Task 16.0 Process Design, Techno-Economic and EH&S Analyses (MPT)						
Subtask 16.1 Design of Commercial Scale WGS Zeolite Membrane Reactor and Process (MPT/Nexant)						
Subtask 16.2 Techno-Economic Analysis (TEA) of IGCC Plant (Nexant)						
Subtask 16.3 Preliminary Technology EH & S Assessment (MPT)						

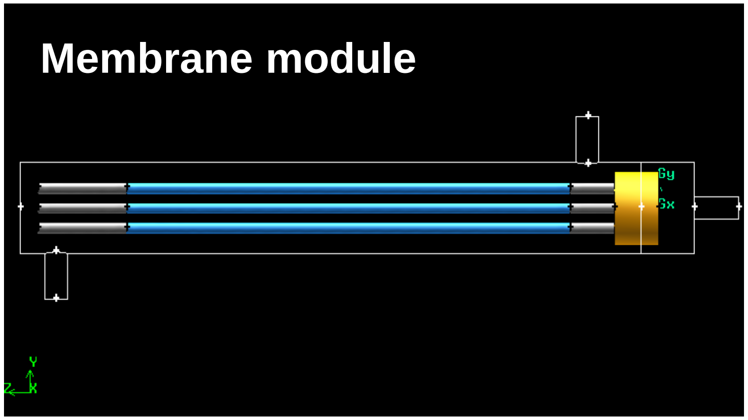
Bench-Scale Zeolite Membrane Reactors

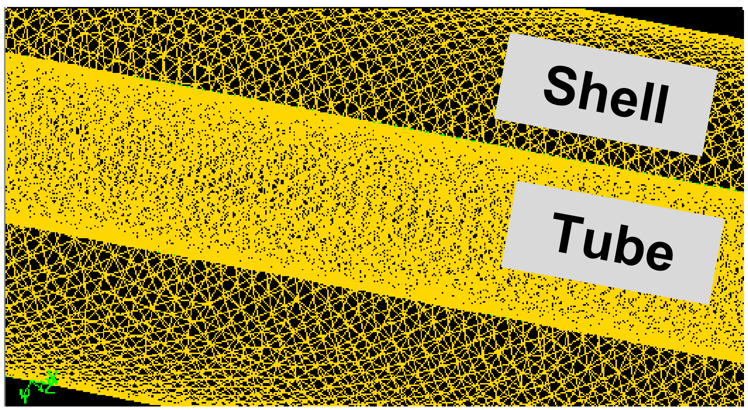
21 Tube, H_2 Production Rate 1-10 kg/Day

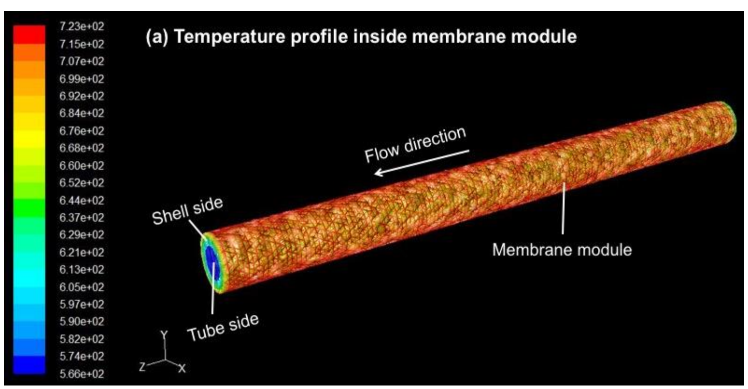


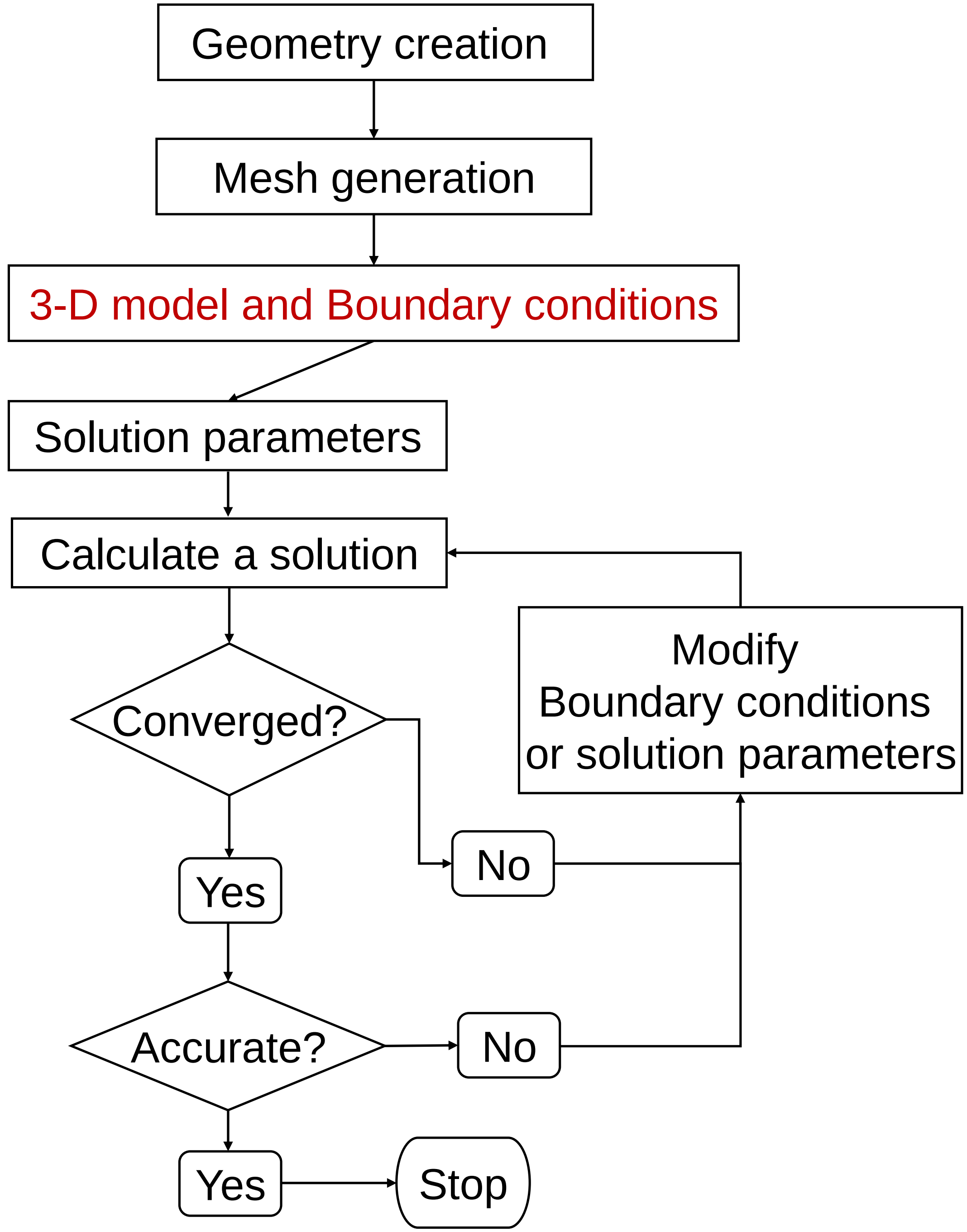
Modeling of 21 Tube Bench-Scale ZMR: 3-D CFD Simulation Approach

Software: *ANSYS Fluent*









Conclusions

- Zeolite membranes fabricated on cost-effective industrial alumina substrates
- CCD modified MFI zeolite membrane synthesis scaled up to longer alumina subtrates
- High pressure and temperature intermediate scale zeolite membrane modules built and tested
- WGS catalysts studied and model for WGS zeolite membrane reactors established
- TEA model for zeolite membrane reactor –IGCC process established
- The project positioned to move to the second phase (Budget Period 2).


THANK YOU
ASU
Palm
Walk