Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

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DOE Award:

DE-FE0026435

NETL CO_2 Capture Technology Meeting

August 10, 2016

Pittsburgh, Penn

Overview

Timeline

- Project start date:
  Oct.1, 2015
- Project end date:
  Sept.30, 2018
- Budget Periods:
  I: 10/1/2015-3/31/2017
  II: 4/1/2017-9/31/2018

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
- University of Cincinnati
- Media and Process Technology, Inc
- Nexant, Inc.

Project Objectives

To demonstrate a bench-scale zeolite membrane reactor for WGS reaction of coal gasification gas for hydrogen production at capacity equivalent to 10 kW 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.

Technical Background

Approach

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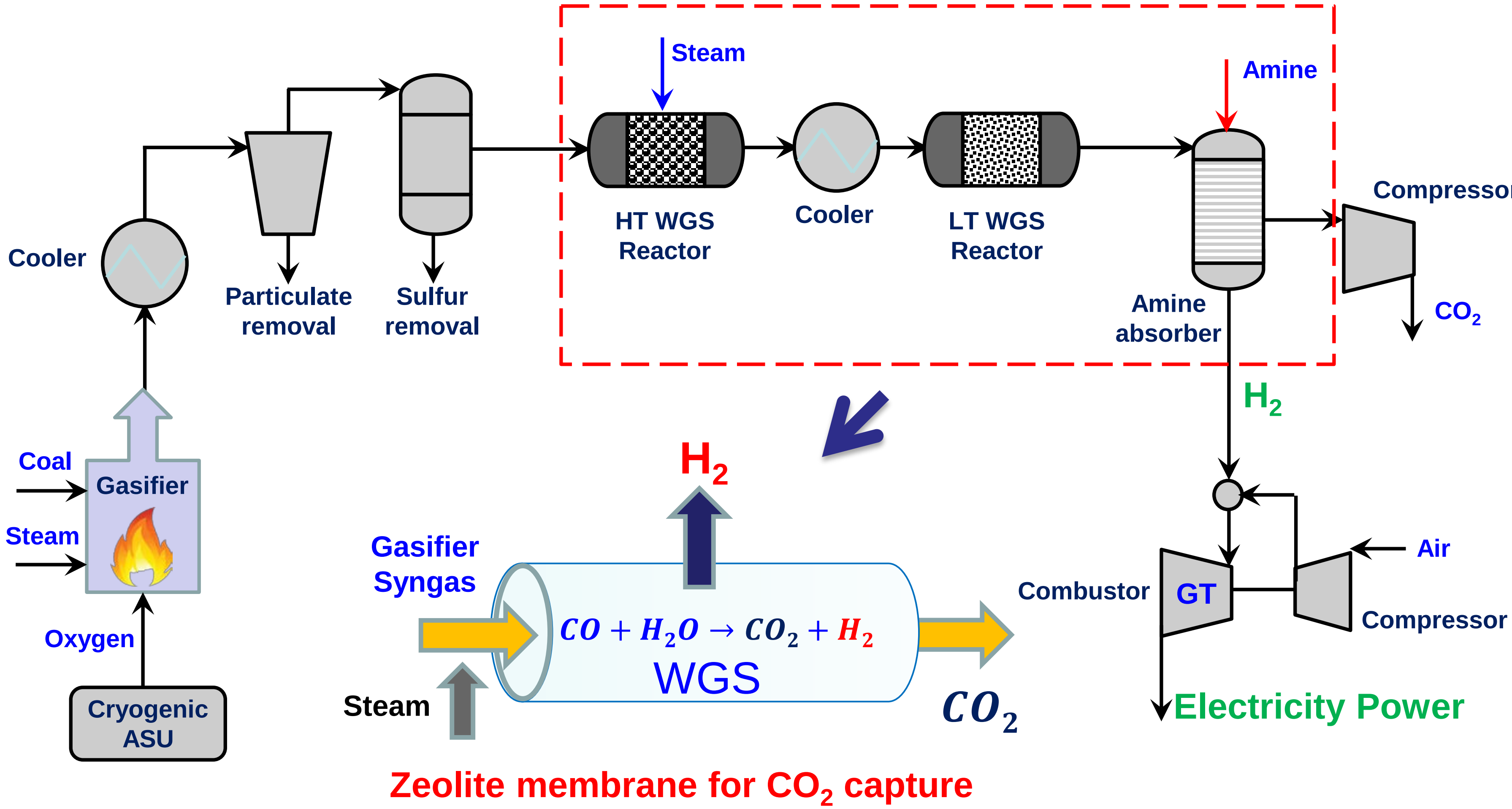
Scope of Work

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

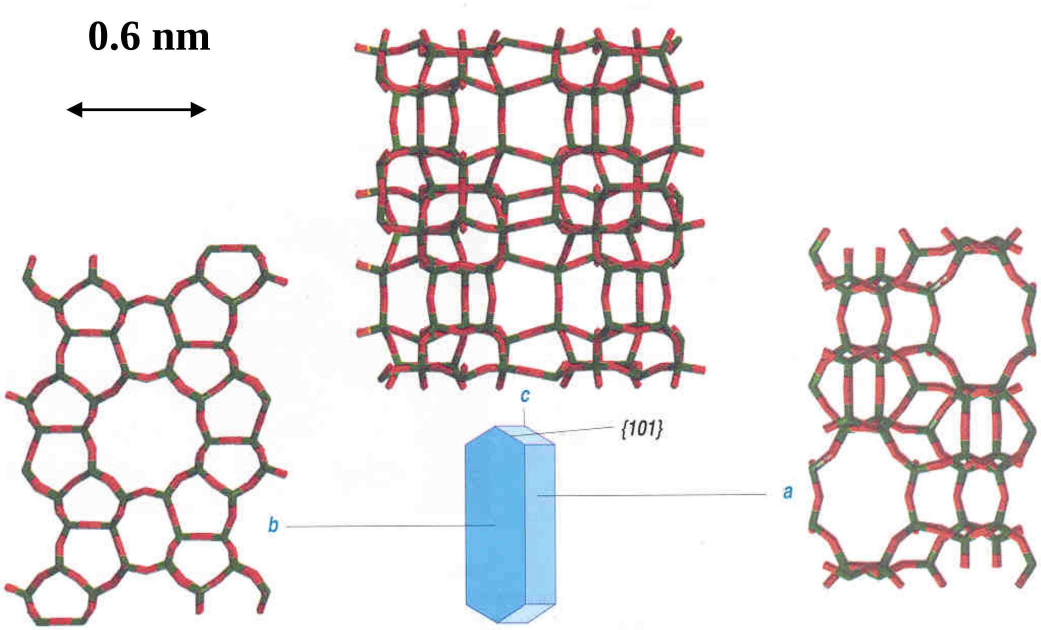


Zeolite Membrane Requirements:

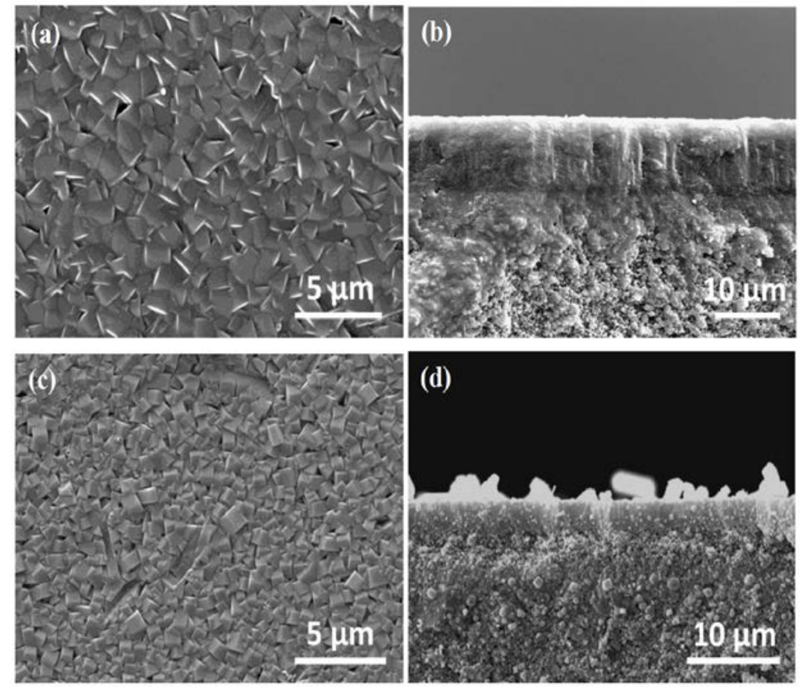
- Operate at 350-550°C
- Chemically stable in H_2S, thermally stable at ~400°C
- Hydrogen permeance ~ 2×10^{-7} mol/m^2.s.Pa (600 GPU)
- Hydrogen selectivity ~ 50

MFI Type Zeolite

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



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



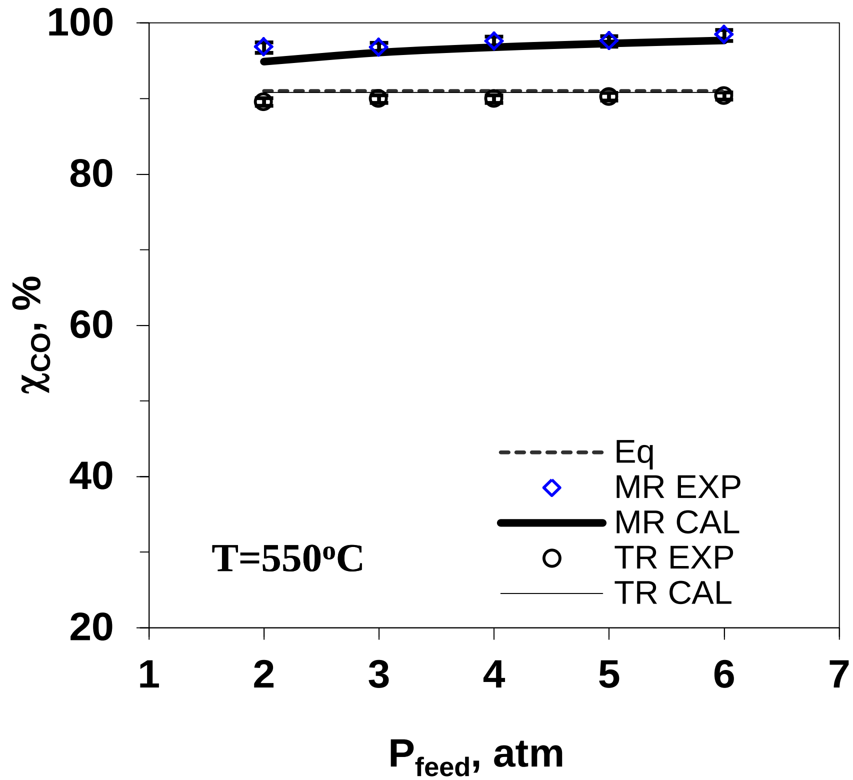
Surface and cross-section SEM images of (a, b) templated synthesized random oriented MFI membrane, (c, d) template-free synthesized random oriented MFI membranes (from Lin lab)

Properties of Lab-Scale CVD Modified MFI Zeolite Membranes

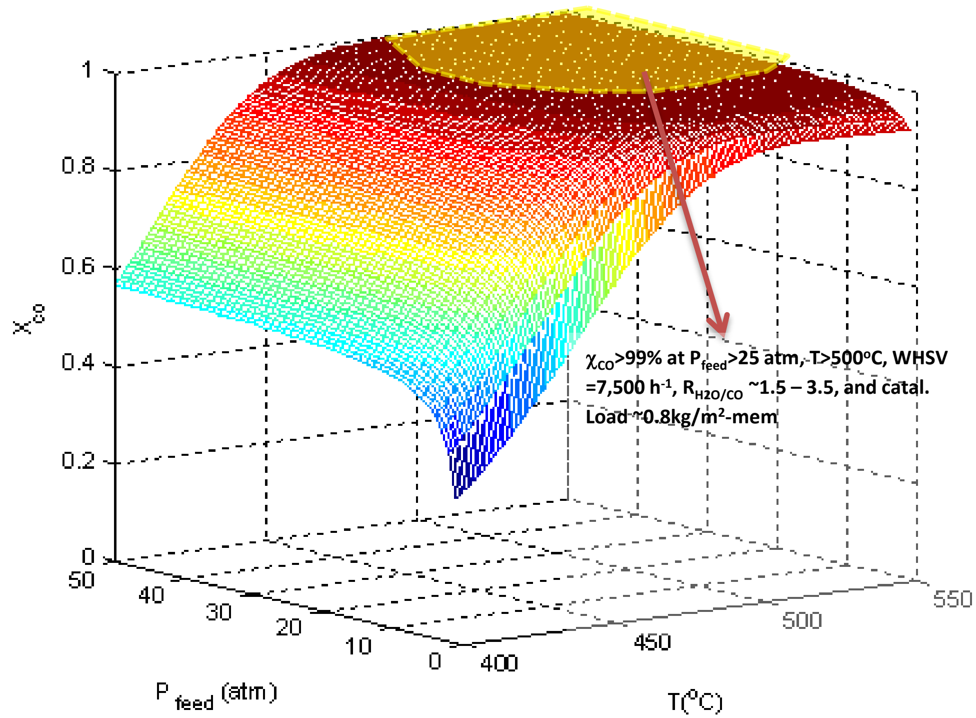
Parameter	Value
H_2 Permeance in (mol/m^2.s.Pa)	$1\text{-}4 \times 10^{-7}$
H_2 Permeance in GPU	300-1200
H_2/CO_2 selectivity	20-140
H_2/CO selectivity	50-200
H_2/H_2O selectivity	120-180
H_2/H_2S selectivity	100-180
Tested stability hours in syngas stream at 400 ppm H_2S at 500^{o}C	600

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

WGS in Lab Scale Tubular Membrane Reactor



*Experimental and simulated CO conversion (χ_{CO}) of the zeolite membrane reactor (**MR**) and traditional fixed-bed reactor (**TR**) (WHSV=7,500 h^{-1}, $R_{H2O/CO}$=3.4, Sweep(N_2)= 20 cm^3/min; $P_{permeate}$= 1 bar, T=550°C (from Dong Lab)*



Modeling of lab-scale zeolite membrane reactor for CO conversion as a function of reaction temperature and pressuring using the experimentally determined parameters (from Lin Lab)

Proposed Bench-Scale Zeolite Membrane Rectors for WGS

	Unit	Measured	Projected Performance
Materials Properties			
Materials of Fabrication for Selective Layer		Modified MFI zeolite	
Materials of Fabrication for Support Layer (if applicable)		Macroporous alumina with or without a macroporous yttria stabilized zirconia layer	
Nominal Thickness of Selective Layer	µm	5-10	1-5
Membrane Geometry		disk and tube	Small OD tube
Max Trans-Membrane Pressure	bar	7	30
Hours tested without significant degradation		600 hours with 400ppm H_2S	1000
Membrane Performance			
Temperature	°C	≥500	≥500
Pressure Normalized Flux for Permeate (CO_2 or H_2)	GPU or equivalent	1000	1200
CO_2/H_2O Selectivity	-	/	
CO_2/N_2 Selectivity	-	/	
CO_2/SO_2 Selectivity	-	/	
CO_2/H_2 Selectivity	-	/	
H_2/CO_2 Selectivity	-	140	140
H_2/H_2O Selectivity	-	100	100
H_2/H_2S Selectivity	-	180	180
Type of Measurement (Ideal or mixed gas)	-	mixture	mixture
Proposed Module Design		Single tube	Multiple tubes
Flow Arrangement	-	Co-current flow	
Packing Density	m^2/m^3	40-60	
Shell-Side Fluid	-	Sweep with steam at 1 bar	

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: 70 zeolite membrane tubes of 3.5 ID, 5.7 OD and 25 cm L(active)
- A system producing H_2 at rate of about 10 kg/day, equivalent to a 10-kW_{th} IGCC power plant

Approaches/Tasks

Progress

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Current Status

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: 7 to 14 tube membrane module, and WGS reaction in the intermediate-scale reactor

Bench-scale membrane reactor: 70 tube membrane module, and WGS reaction in the bench-scale membrane reactor

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

Fabrication of Zeolite Membranes

In-situ synthesis of MFI film on multiple support tubes (35 cm long, 3.5 mm ID and 5.7 mm OD) on horizontally rotating synthesis reactor housing 61 tubes

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Formation of single and multiple tube zeolite membrane module

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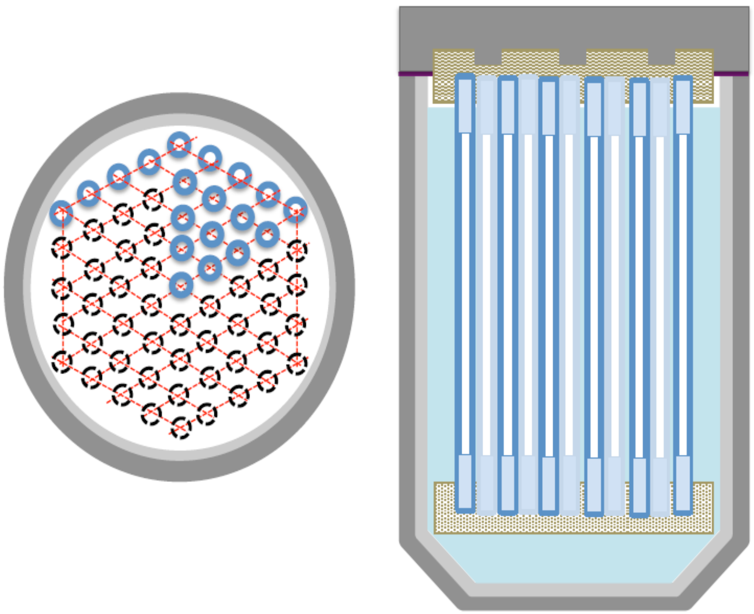
CVD modification of the single or multiple tube zeolite membrane in membrane modules with simultaneous measurement of H_2/CO_2 separation characteristics



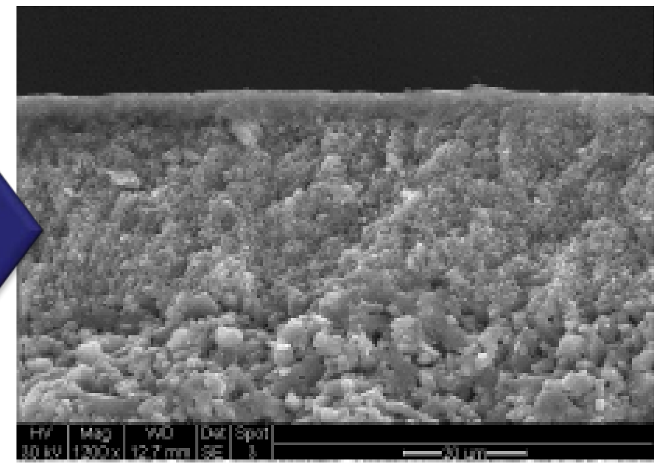
horizontally rotating multi-tube zeolite membrane synthesis reactor

Progress: Membrane Preparation and Scale-up

Ceramic Tube Extrusion

Intermediate Layer Deposition
+
Non-porous Tip and End Seals

Zeolite Layer Deposition
+
(Silica CCD Modification)



Package into Multiple Tube Bundle
+
(Silica CCD Modification)

MPT 57-tube Bundle
(Carbon Molecular Sieve Membrane)

Progress: Optimizing Tubule Support Fabrication

Substrate Tube Strength: Material Stability in Zeolite Synthesis Solution

***Challenge Conditions:** 1.4wt% NaOH; T = 180^{o}C; 6 and 48 hours*

***Post Challenge Strength Determination:** 3-Point Bend Test*

Other details:

- *Nominal tube wall thicknesses of 1, 1.45, and 1.75mm tested*
- *Target bend strength minimum ~ 40psi based upon commercial 1mm tube*

Test Condition	No Challenge Testing			1.4wt% NaOH, 6 hours			1.4wt% NaOH, 48 hours		
Part ID	Standard	TW#1	TW#2	Standard	TW#1	TW#2	Standard	TW#1	TW#2
OD	5.7mm	6.6mm	7.2mm	5.7mm	6.6mm	7.2mm	5.7mm	6.6mm	7.2mm
	Pre-Challenge Testing			Post Challenge Testing			Post Challenge Testing		
Strength [lb]	40	59	63	33	50	56	33	47	54
	41	56	82	36	44	56	32	44	57
	38	63	70	32	50	60	34	54	55
	40	59	81						
	40	58	71						
	40	60	72						
Average	39.8	59.2	73.2	33.7	48.0	57.3	33.2	48.3	55.3
% Loss from Original Part Strength				15.5%	18.9%	21.6%	16.7%	18.4%	24.4%

1. ***Target strength** required for finished zeolite membrane tube is based upon MPT commercial experience with the 1mm wall standard part.*

2. ***Post challenge testing strength** of the 1.45mm wall thickness tube is superior to the "unchallenged" MPT standard membrane.*

Progress: Optimizing Tubule Support Fabrication

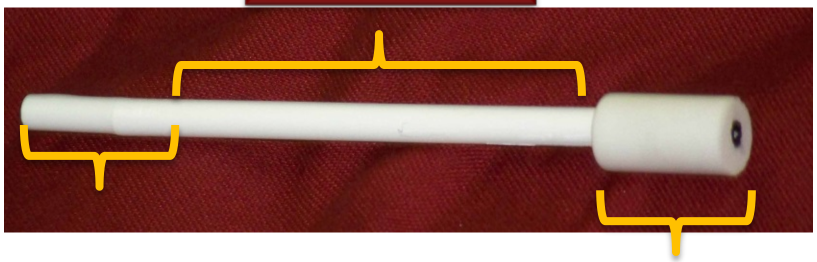
Hydrothermal Stability Testing of Membrane Scale-up Components

Proposed WGS Conditions: *T = 500°C; P = 300 psig; Steam = 30% (in N_2)*

Three Primary Scale-up Components

Impermeable End Seal

Ceramic Tip



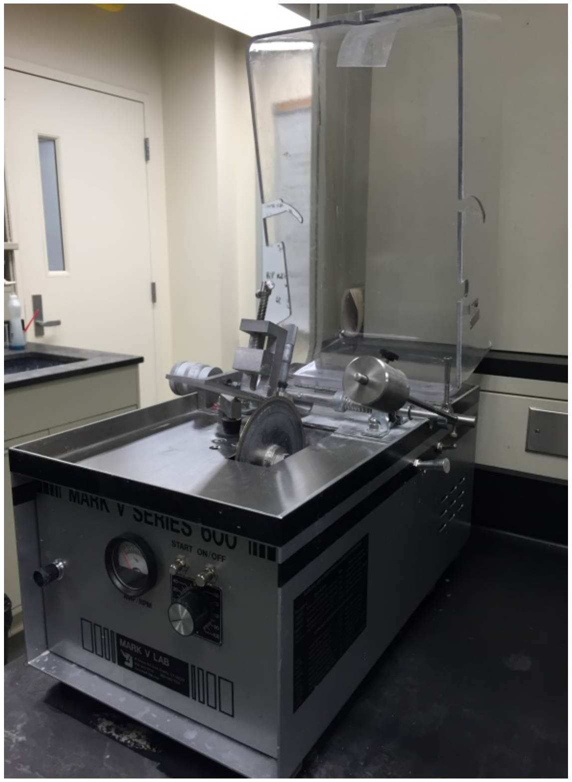
Ceramic Tube Sheet and Ceramic/Glass Potting

Hydrothermal Stability Testing System

Challenge Test Results

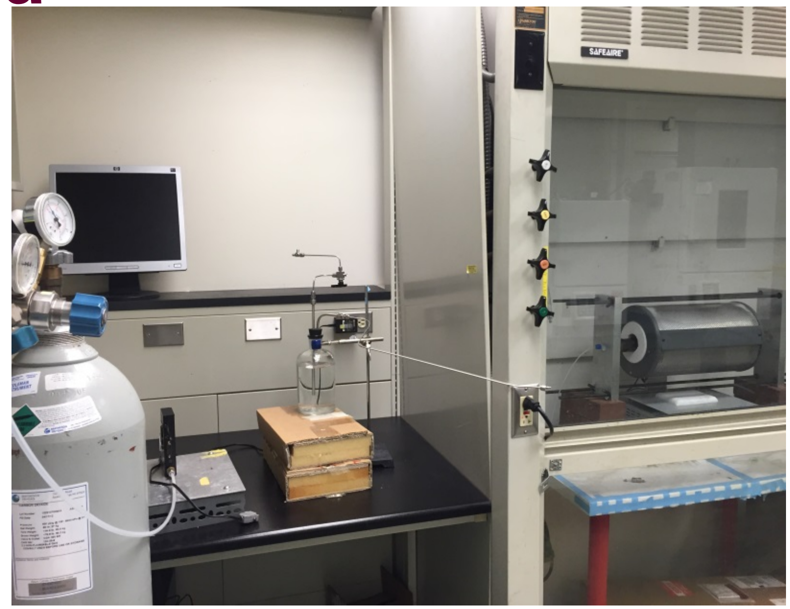
No leak development in the three major components was observed in over xxx hours of hydrothermal stability challenge testing.

Progress: Zeolite Membrane Growth Facility Established



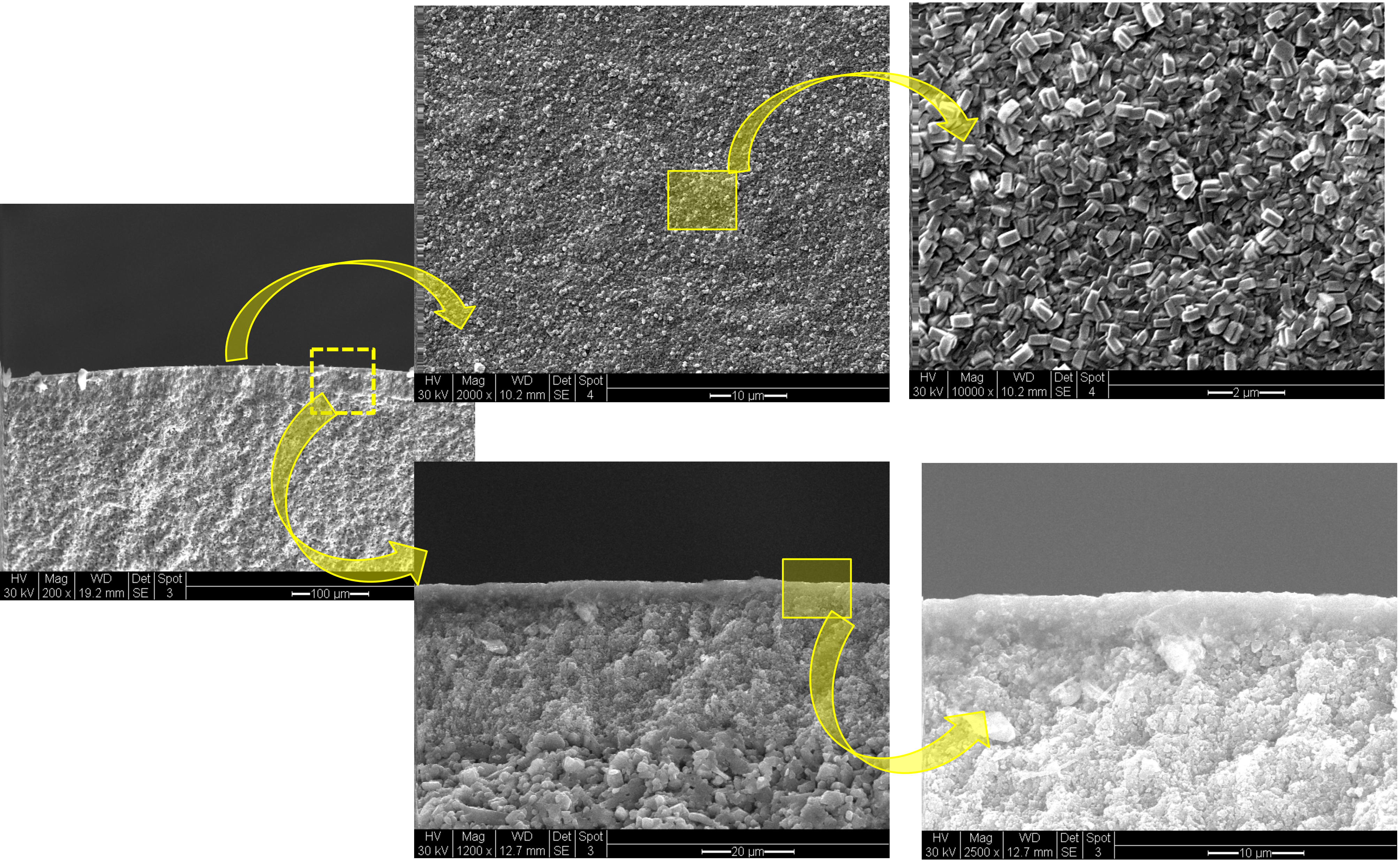
Tube cutter

Synthesis oven

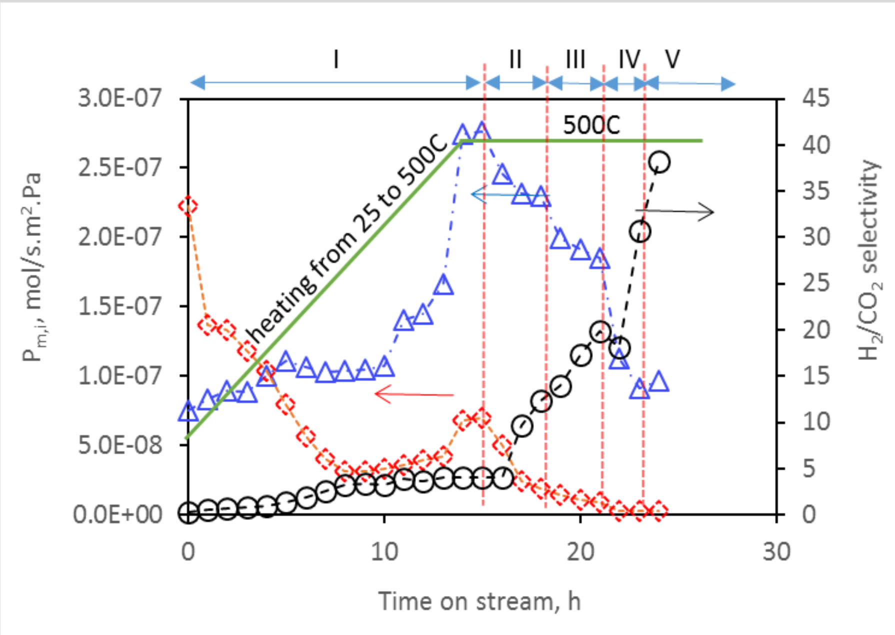


Stability testing system

Progress: Synthesis of MFI Zeolite Membranes on MPT Tubes



Progress: Properties of Modified Zeolite Membrane



Evolution of the H_2 and CO_2 ($P_{m,i}$) permeances and H_2/CO_2 separation factor ($\alpha_{H2/CO2}$) during the entire process of CCD modification of the tubular MFI zeolite membrane: (I) ramping up from 25 to 500°C and dwelling for 2 h at 500°C; (II) MDES vapor introduced; (III) MDES feed stopped; (IV) MDES vapor introduced for the second time; and (V) MDES vapor feed stopped – CCD modification completed.

Typical gas separation properties for "high quality" MFI zeolite membranes before and after CCD modifications

Stage of Fab-rication	T (°C)	$\alpha_{H2/CO2}$	$P_{m,H2}$ (10^{-7} mol/ m^2.s.Pa)	$P_{m,CO2}$ (10^{-7} mol/ m^2.s.Pa)
Before CCD	20	0.19 – 0.35	0.54 – 0.75	1.6 – 3.2
Before CCD	500	4.0 – 5.1	2.0 – 3.2	0.23 – 0.68
After 1st CCD	500	12 – 20	1.8 – 2.7	0.019 – 0.095
After 2nd CCD	500	20 – 45	1.0 – 1.9	0.011 – 0.025

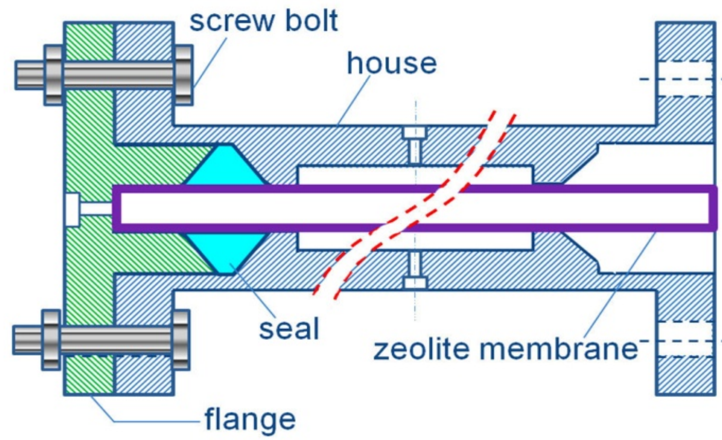
Experimental and Modeling Studies of WGS in Membrane Reactors at High Pressures

Design of reactor for longer tube (12.5 and 25 cm) and higher pressure (30 bar)

Synthesis of stable, H_2S and coking resistant ceria based WGS catalyst

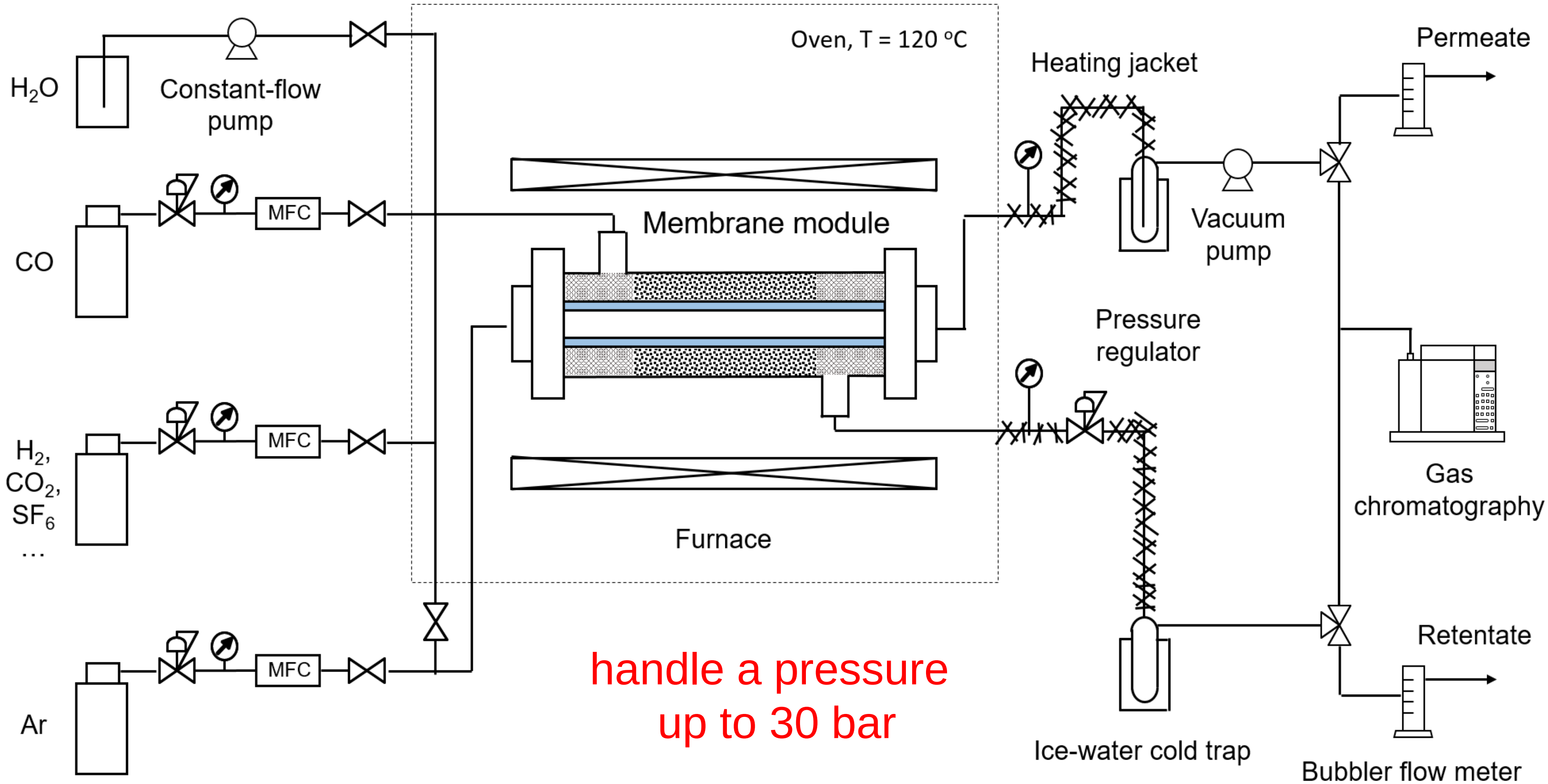
H_2 separation and WGS reaction experiments

Modeling H_2 separation and WGS reaction in single tube and multiple tube zeolite membrane reactor



Schematic illustration of the ends structure of the tubular membrane module to be used with radially compressed graphite seals (not to scale)

Progress: Lab-scale High-pressure WGS Membrane Reactor

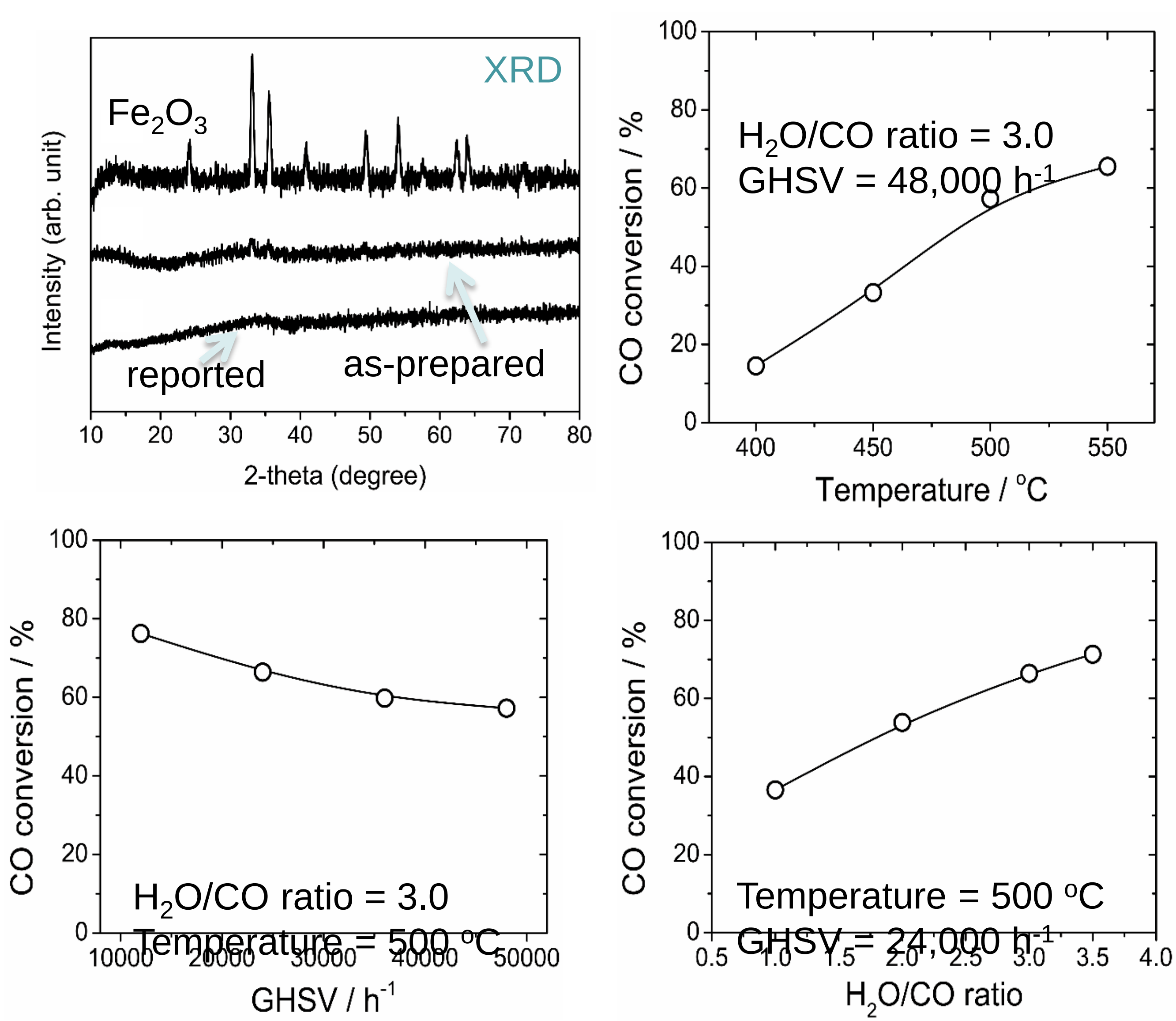


handle a pressure up to 30 bar

- Membrane module followed the design of tube-shell heat exchanger
- Combined fixed-bed reactor, disk/single tube/multiple tube membrane reactor

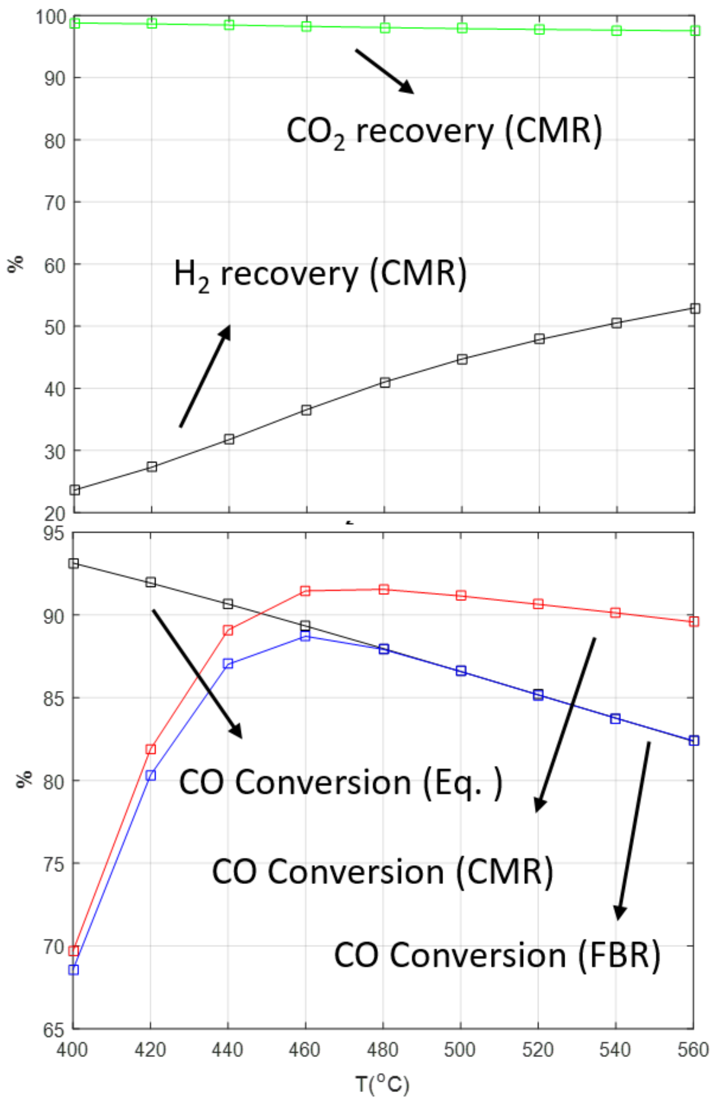
Progress: Synthesis of WGS Catalyst and Experimental Study on WGS

Subtask 2.2 Evaluating performance of WGS catalyst

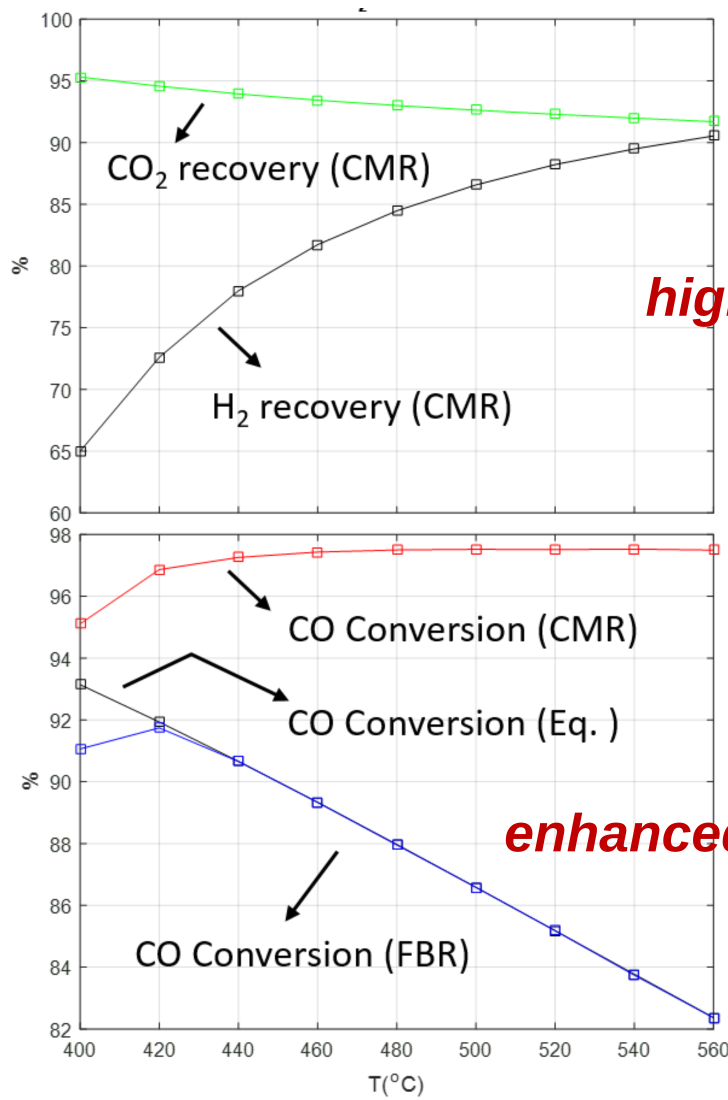


- Fe/Ce/Cr oxide based catalyst
- prepared by an ammonia assisted co-precipitation
- Reaction pressure: 1 bar
- CO conversion reached 76.2% at 500 °C, GHSV = 12,000 h^{-1} and H_2O/CO ratio = 3.0

Progress: Modeling of WGS reaction in Fixed-bed and Membrane reactors



Feed pressure: **10 bar**



Feed pressure: **30 bar**

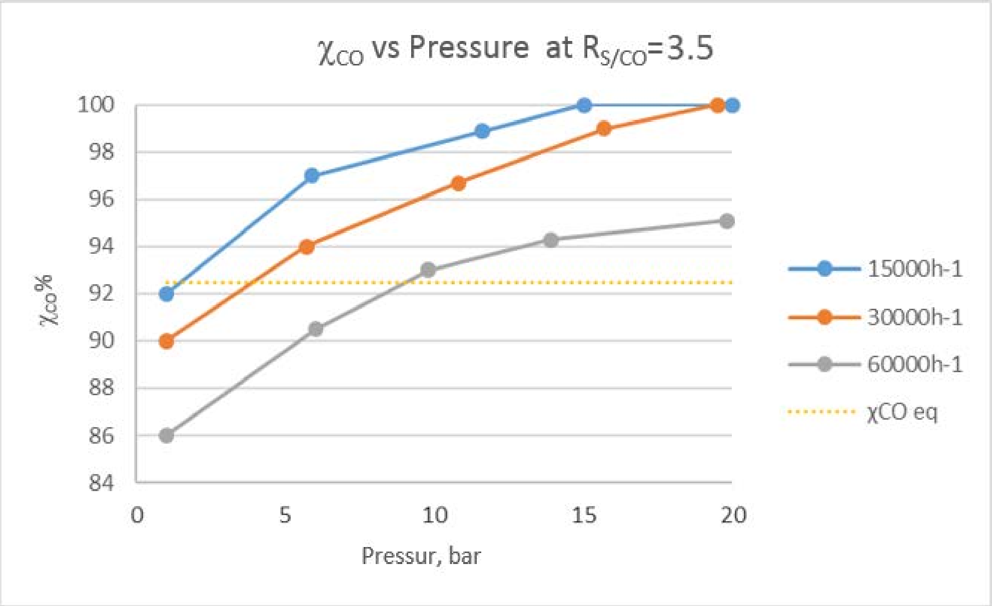
higher H_2 recovery

enhanced CO conversion

$H_2O/CO = 3$ and $F_{CO} = 40$ ml/min

Progress: Preliminary Experimental Results of High Pressure WGS in Tubular Zeolite Membrane Reactor

Flow configuration in Membrane Reactor: Counter-current
Temperature: 500°C

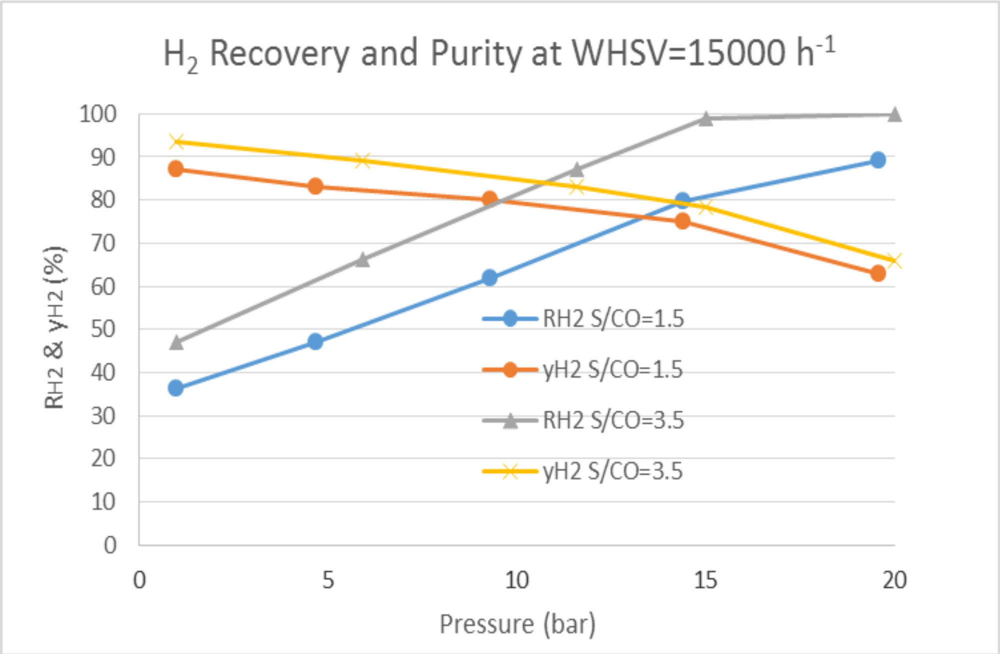


CO conversion in the MR as a function of reaction pressure with various WHSV:

1. χ_{CO} ~ 100% at >15 bar with WHSV of 15,000h^{-1}
2. χ_{CO} ~ 100% at >20 bar with WHSV of 30,000h^{-1}

H_2 recovery and purity as functions of reaction pressure at WHSV of 15000 h^{-1}:

1. R_{H2} ~ 100% at >15 bar with $R_{S/CO}$ of 3.5
2. H_2 purity in this case is low (<78%)



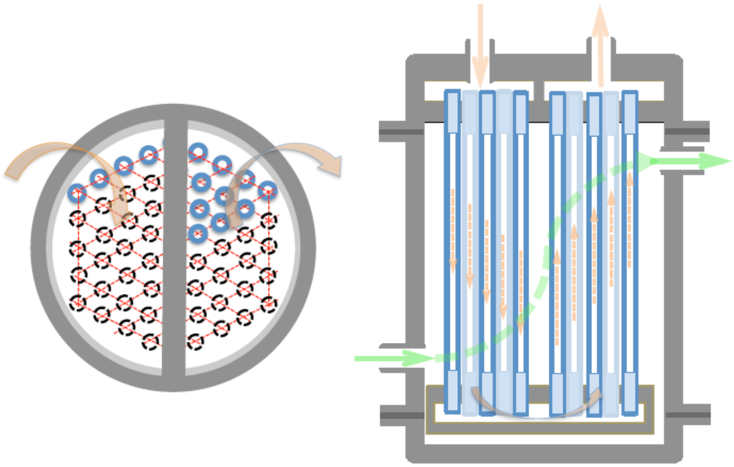
Design, Fabrication and Testing of Bench Scale Membrane Modules

A-Module Design and Fabrication

MPT's multiple tube bundle with full ceramic potting and tube sheet and stainless steel housing

Thorough re-rating and possible redesign of the module to confirm its potential for safe operation at the desired temperature up to 600°C and pressure up to a potential of 55 bar

Alternative free-end membrane module to handle thermal stress



Design, Fabrication and Testing of Bench Scale Membrane Modules (Cont'd)

B- Modeling WGS and H_2/CO_2 Separation in the Membrane Modules

Modeling WGS in multiple channel membrane reactor using permeation and kinetic data obtained in the single-tube reactor

C-Preliminary WGS Membrane Reactor Testing with Multiple-Tube Bundles

Testing H_2 separation at high pressure and temperature on the intermediate-scale zeolite membrane module (7-14 tubes)

WGS catalyst fabrication (up to 6 kg)

Catalyst packing, gas and pressure handling and separation performance of bench-scale zeolite membrane module

Membrane and WGS-Reactor Testing at National Carbon Capture Center

Composition and conditions of syngas at NCCC Site

Composition or Temperature and pressure	NCCC Raw Syngas	Desired syngas for this project
H_2	5-7%	26%
CO	9-11%	27%
CO_2	9-11%	14%
N_2	69-74%	0
CH_4	0.9-1.2%	0
H_2O	~0	34%
H_2S	400 ppm	50 ppm (0.56%)#
Pressure	180-190 psig	285 psig (20 bar)
Temperature	500-550 F	350-550^{o}C

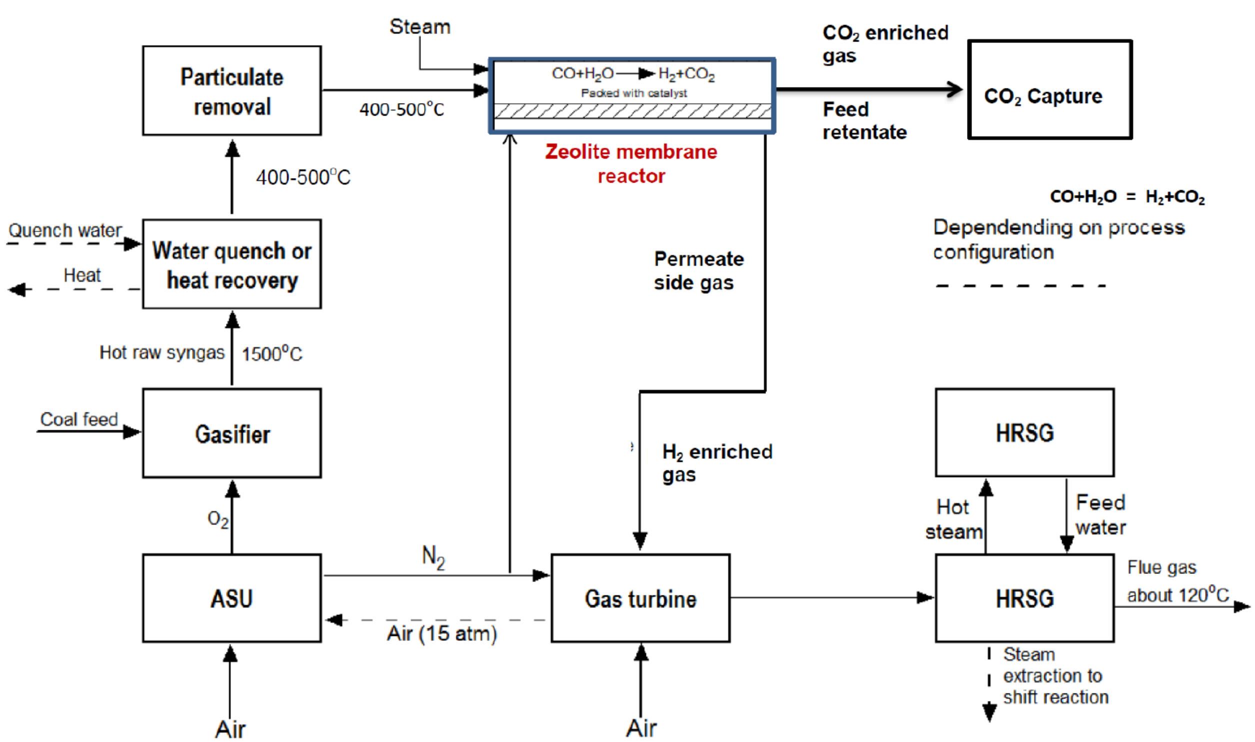
Picture of an MPT membrane test skid at NCCC for testing hydrogen separation by carbon molecular sieve membrane modules with shifted syngas.

Process Design, Economical Analysis and EH&S Risk Assessment

Conditions for Cost Estimation of Membrane Reactor (550 MW Coal-Burning IGCC Power Plant)

Parameters	Conditions
Coal type	Illinois 6#
Coal feed	slurry
Gasifier type	GE gasifier
Coal Consumption Rate	220,904 kg/hr
Carbon Content in Coal (dry basis)	0.70
Rate of CO in Syngas	2,296mol/s
Rate of H_2 in Syngas	2,187 mol/s
Pressure of coal gas to WGS reactor	3 MPa
Temperature of coal gas to WGS reactor	400-550ºC

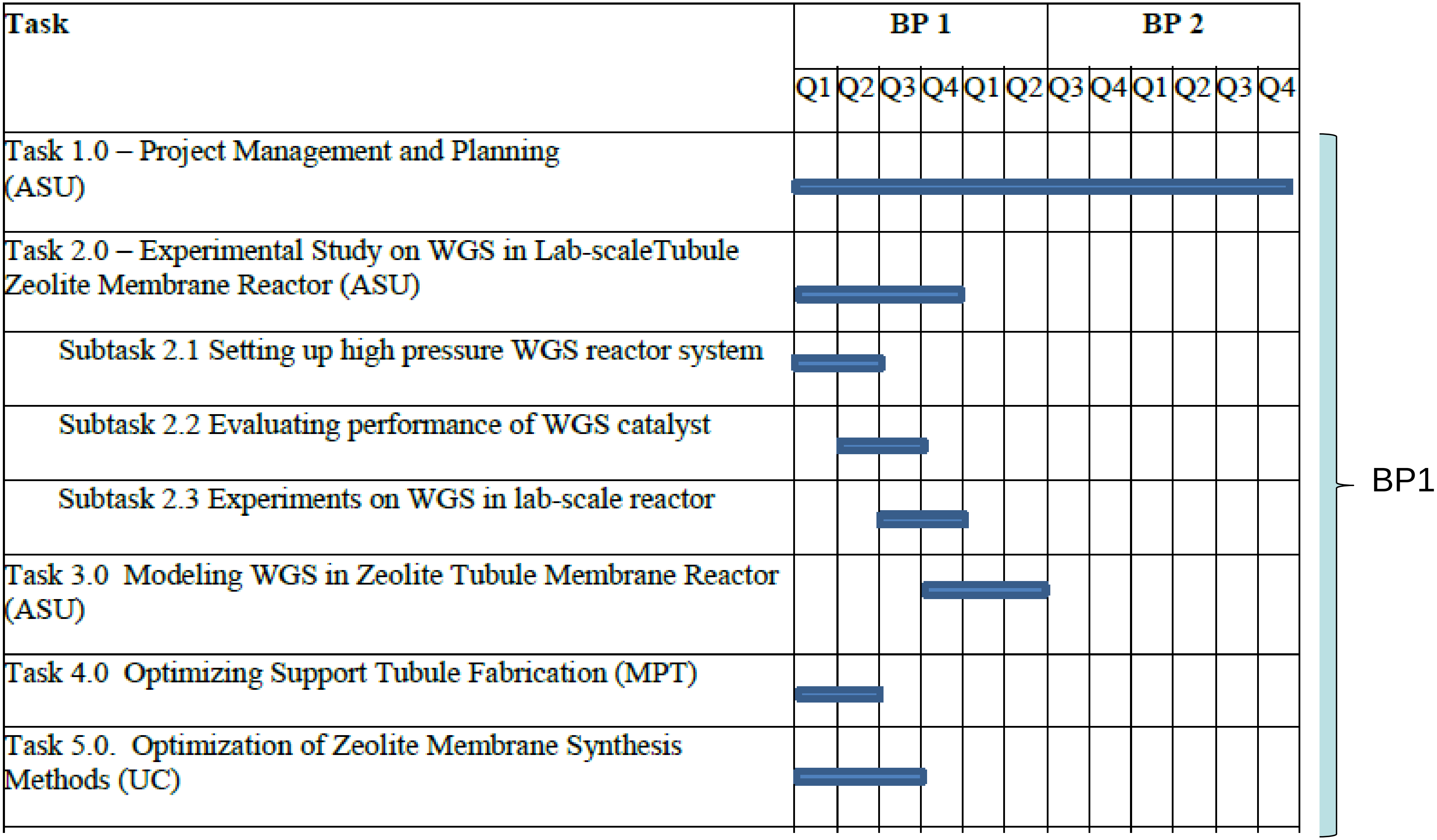
Preliminary Proposed IGCC Process with H_2 Separation using MFI Zeolite Membrane and Carbon Dioxide Capture



Success Criteria at Decision Point

Decision Point	Date	Success Criteria
End of Budget Period 1 (end of first18 months)	3/31/217	Success in testing WGS in 7 to14-tube intermediate scale WGS zeolite membrane module with membranes having H_2/CO_2 selectivity >45 H_2 permeance >600 GPU and operational at feed pressure up to 30 bar in 400-550^oC; WGS membrane reactor achieves CO conversion >99%, CO_2 capture/ recovery >90% and CO_2 purity >95%.

Project Schedule



Project Schedule (Cont'd)

Task
Task 6.0 Scaling up Synthesis of High Quality Zeolite Membranes (UC)
Subtask 6.1 Identifying condition to make 9 zeolite membrane tubes in one batch
Subtask 6.2 Preparing 20-30 zeolite membrane tubes Intermediate-scale membrane reactor module
Task 7.0 Design and Fabrication of Intermediate-Scale Zeolite Membrane Module (MPT)
Task 8.0. Testing Intermediate-Scale Membrane Reactors (MPT)
Subtask 8.1 Design and modifying the membrane reactor testing skids (MPT)
Subtask 8.2 Assembling and Testing Intermediate-Scale Zeolite Membrane Reactor (MPT/ASU)
Task 9.0. Establishing Conceptual Process Design, Performance Model and Preliminary Techno-Economic Analysis of WGS Zeolite Membrane Reactor Technology

BP1

Project Schedule (Cont'd)

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)

BP2

Project Schedule (Cont'd)

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)

BP2


ASU
THANK YOU
Palm
Walk