A High Efficiency, Ultra-Compact Process For Pre-Combustion CO_2 Capture

DE-FOA-0001235

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U.S. Department of Energy
National Energy Technology Laboratory
Office of Fossil Energy
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Presentation Outline

- Project Overview
- Technology Background
- Technical Approach/Project Scope
- Progress and Current Status of Project
- Plans for future testing/development/commercialization

Project Overview

Performance Period: 10-01-2015 – 9-31-2018

Project Budget: Total/$1,909,018; DOE Share/$1,520,546; Cost-Share/$388,472

Overall Project Objectives:

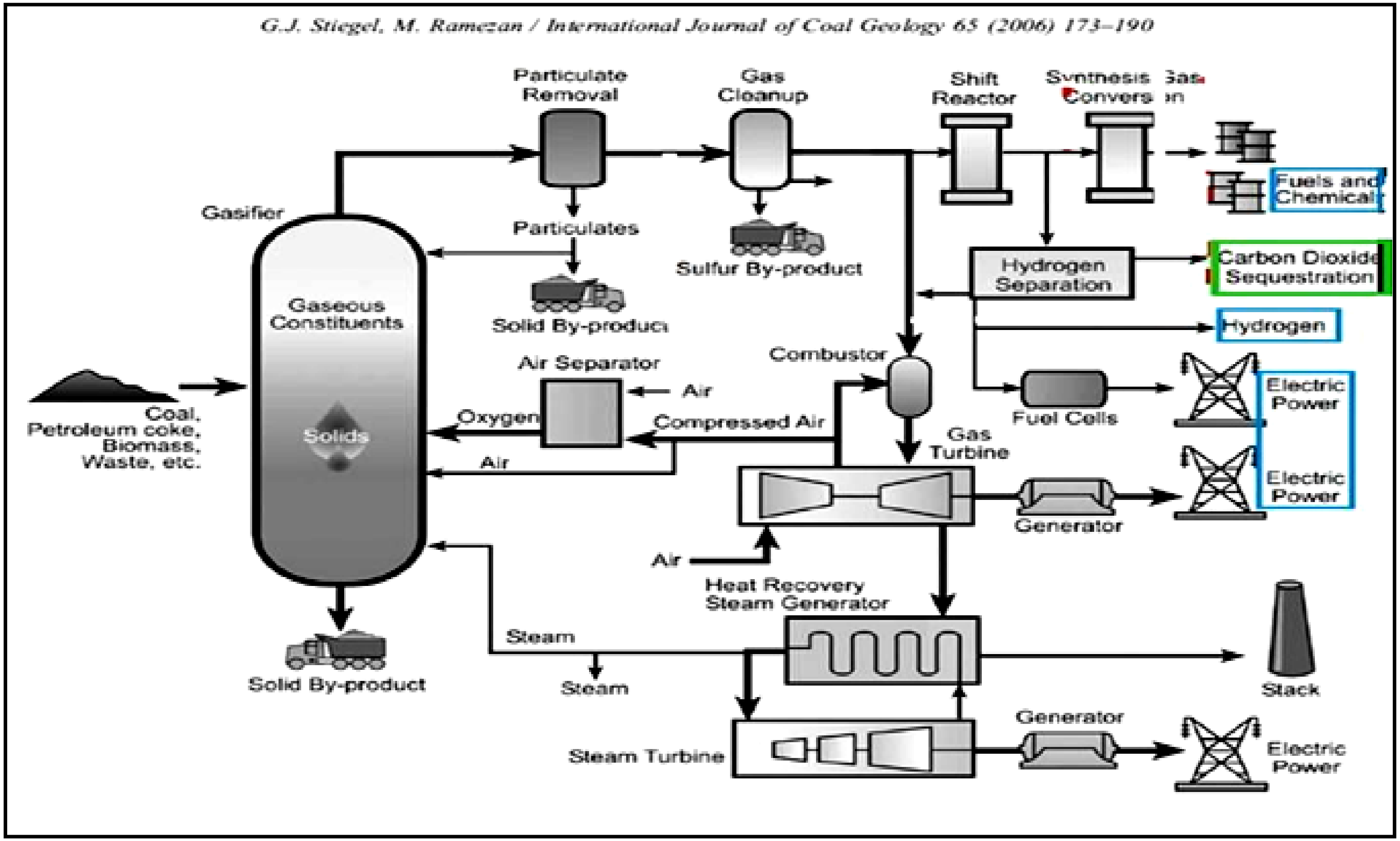
1. *Prove the technical feasibility of the membrane- and adsorption-enhanced water gas shift (WGS) process.*
2. *Achieve the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity of 30% less than baseline capture approaches.*

Key Project Tasks/Participants:

1. *Design, construct and test the lab-scale experimental MR-AR system.**-----USC***
2. *Select and characterize appropriate membranes, adsorbents and catalysts.**-----M&PT, USC***
3. *Develop and experimentally validate mathematical model.**-----UCLA, USC***
4. *Experimentally test the proposed novel process in the lab-scale apparatus, and complete the initial technical and economic feasibility study. **(Budget Period 2)**.**----- M&PT, UCLA, USC***

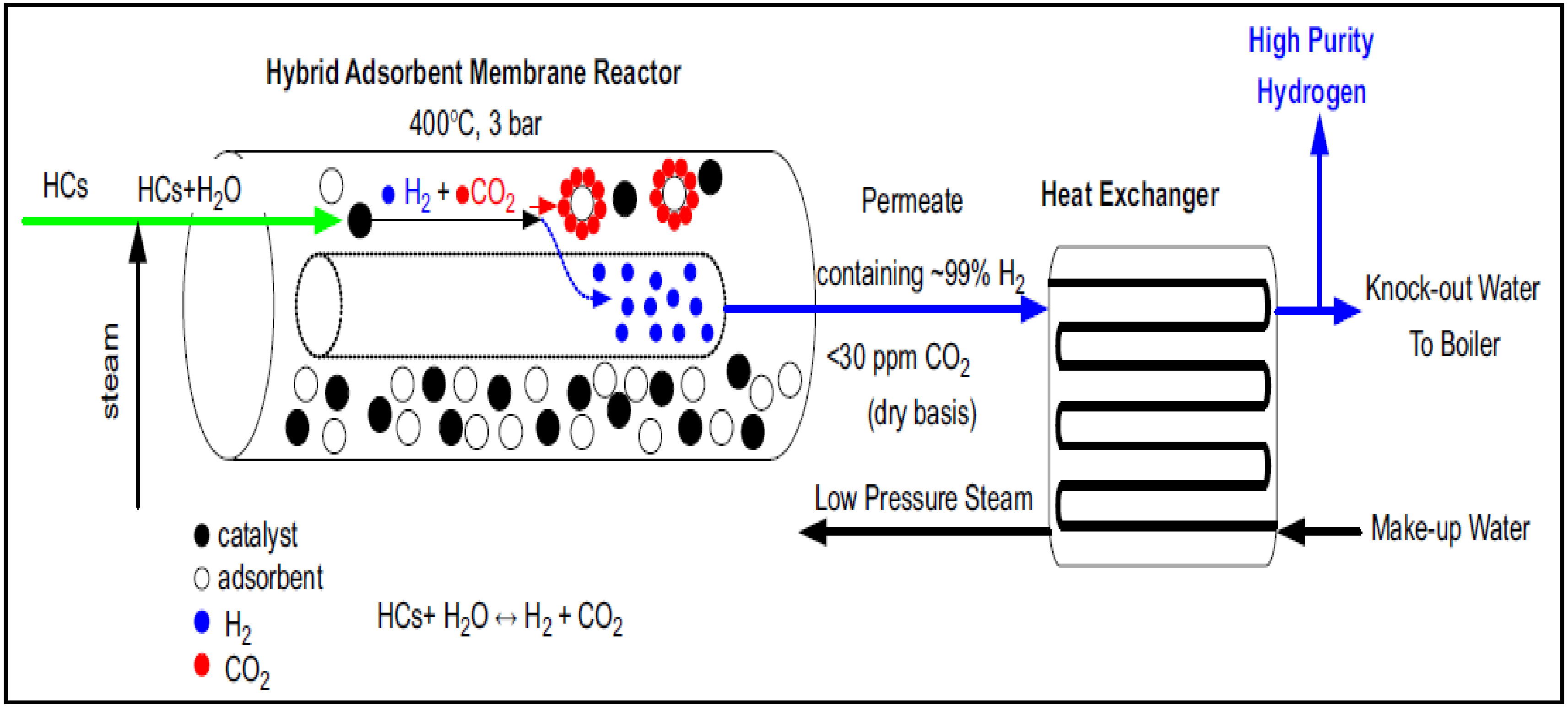
Technology Background

Conventional IGCC Power Plant



Technology Background, cont.

Hybrid Adsorbent Membrane Reactor (HAMR)



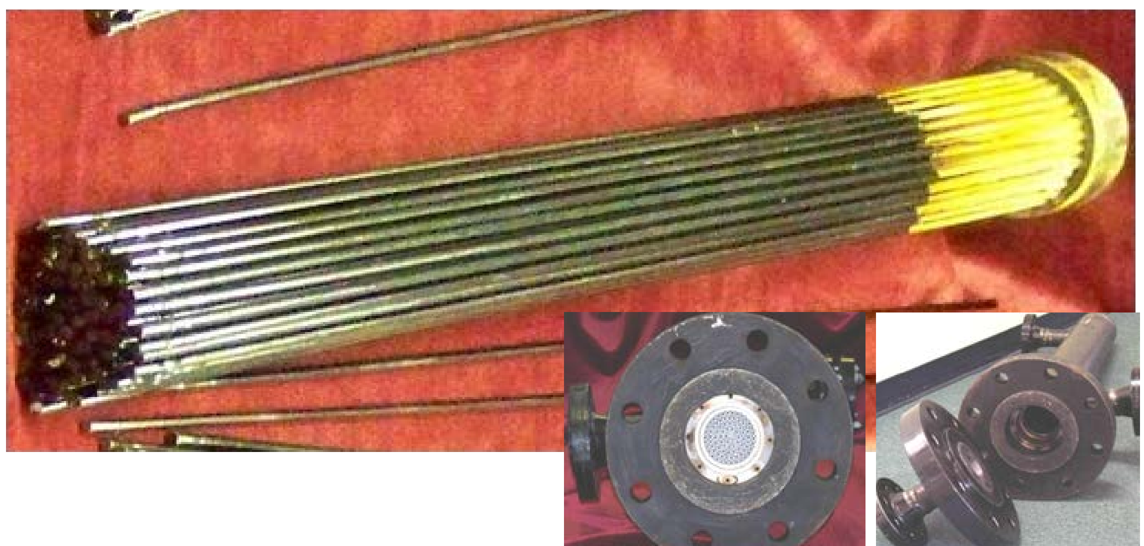
- **The HAMR combines adsorbent, catalyst and membrane functions in the same unit. Previously tested for methane steam reforming (MSR) and the WGS reaction.**
- **The simultaneous in situ removal of H_2 and CO_2 from the reactor significantly enhances reactor yield and H_2 purity. CO_2 stream ready for sequestration.**

Technology Background, cont.

CMS Membranes for Large-Scale Applications

M&PT test-unit at NCCC for hydrogen separation

CMS membranes and modules



Technology Background, cont.

Hydrotalcite (HT) Adsorbents & Co/Mo-Based Sour-Shift Catalysts

Hydrotalcite Adsorbent:

- *The HT adsorbents shown to have a working CO_2 capacity of 3-4 wt.% during the past HAMR studies with the MSR and WGS reactions. Theoretical capacity >16 wt.%.*

Co/Mo-Based Sour Shift Catalyst:

- *A commercial Co/Mo-based sour shift catalyst has been used in our past and ongoing lab-scale MR studies (P<15 bar) with simulated coal-derived and biomass-derived syngas. Shown to have stable performance for >1000 hr of continuous operation.*

Technology Background, cont.

Advantages--Our Proposed Process vs. SOTA

Key Innovation:

- *Highly-efficient, low-temperature reactor process for the WGS reaction of coal-gasifier syngas for pre-combustion CO_2 capture, using a unique adsorption-enhanced WGS membrane reactor (MR-AR) concept.*

Unique Advantages:

- ***No syngas pretreatment required:*** *CMS membranes proven stable in past/ongoing studies to all of the gas contaminants associated with coal-derived syngas.*

- ***Improved WGS Efficiency:*** *Enhanced reactor yield and selectivity via the simultaneous removal of H_2 and CO_2.*

- ***Significantly reduced catalyst weight usage requirements:*** *Reaction rate enhancement (over the conventional WGSR) that results from removing both products, potentially, allows one to operate at much lower W/F_{CO} (K_{gcat}/mol.hr).*

- ***Efficient H_2 production, and superior CO_2 recovery and purity:*** *The synergy created between the MR and AR units makes simultaneously meeting the CO_2 recovery/purity targets together with carbon utilization (CO conversion) and hydrogen recovery/purity goals a potential reality.*

Technology Background, cont.

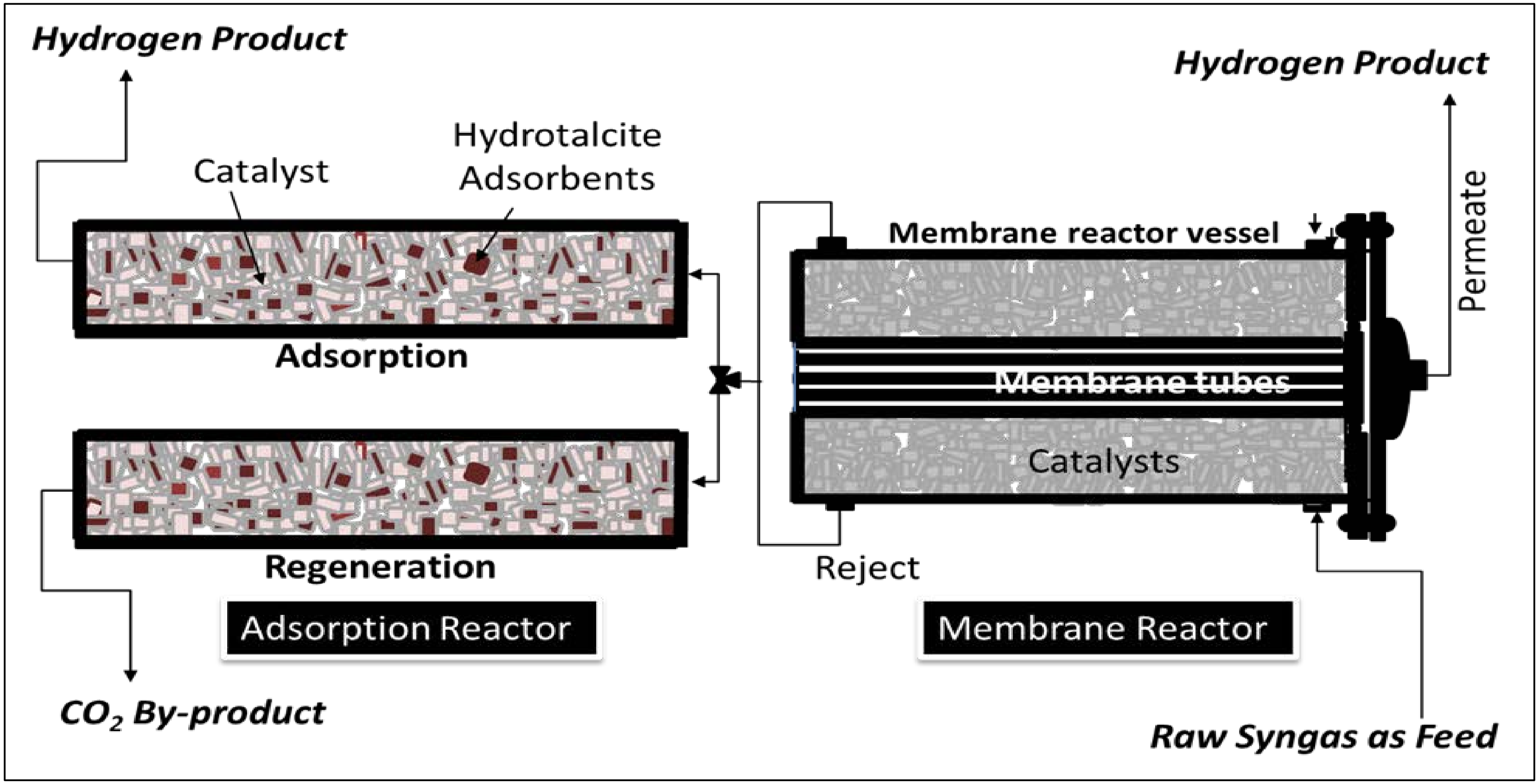
Challenges

Key Technical Challenges Ahead (BP1):

- *Prepare and characterize membranes/adsorbents and validate their performance at the relevant experimental conditions.*
- *Validate catalyst performance at the relevant pressure conditions. Verify applicability of global reaction kinetics.*
- *Develop and experimentally validate mathematical model.*

Technical Approach/Project Scope

Proposed MR-AR Process



- **Potential use of a TSA regeneration scheme allows the recovery of CO_2 at high pressures.**
- **The MR-AR process overcomes the limitations of competitive singular, stand-alone systems, such as the conventional WGSR, and the more advanced WGS-MR and WGS-AR technologies.**

Technical Approach/Project Scope, cont.

Resource-Loaded Schedule

			Budget Period 1 10/1/2015 - 3/31/2017						Budget Period 2 4/1/2017 - 9/30/2018					
	Start Date	End Date	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1.0 - Project Management and Planning	10/1/2015	9/30/2018	■	■	■	■	■	■	■	■	■	■	■	■
Subtask 1.1 - Project Management and Planning	10/1/2015	9/30/2018	■	■	■	■	■	■	■	■	■	■	■	■
Subtask 1.2 - Briefing and Reports	10/1/2015	9/30/2018	■	■	■	■	■	■	■	■	■	■	■	■
Milestones														
- a			◆											
- b			◆											
Task 2.0 - Materials Preparation and Characterization	10/1/2015	12/31/2016	■	■	■	■	■							
Subtask 2.1 - Preparation and Characterization of the CMS Membranes	10/1/2015	6/30/2016	■	■	■									
Subtask 2.2 - Preparation and Characterization of Adsorbents and Catalysts	1/1/2016	12/31/2016		■	■	■	■							
Milestones														
- d					◆									
- e							◆							
Task 3.0 - Design and Construction of the Lab-Scale Experimental System	10/1/2015	3/31/2016	■	■										
Milestones														
- c				◆										
Task 4.0 - Initial Testing and Modelng of the Lab-Scale Experimental System	10/1/2015	3/31/2017	■	■	■	■	■	■						
Subtask 4.1 - Unit Operation Testing	4/1/2016	3/31/2017			■	■	■	■						
Subtask 4.2 - Mathematical Model Development and Simulations	10/1/2015	3/31/2017	■	■	■	■	■	■						
Milestones														
- f								◆						
- g								◆						
- h								◆						
Task 5.0 - Integrated Testing and Modeling of the Lab-Scale Experimental System	4/1/2017	6/30/2018							■	■	■	■	■	
Subtask 5.1 - Materials Optimization and Scale-up	4/1/2017	3/31/2018							■	■	■	■		
Subtask 5.2 - Integrated Testing	4/1/2017	6/30/2018							■	■	■	■	■	
Subtask 5.3 - Model Simulation and Data Analysis	4/1/2017	3/31/2018							■	■	■	■		
Milestones														
- i										◆				
- j												◆		
- k												◆		
- l													◆	
- m													◆	
Task 6.0 - Preliminary Process Design/Optimization and Economic Evaluation	4/1/2018	9/30/2018											■	■
Subtask 6.1 - Process Design/Optimization	4/1/2018	9/30/2018											■	■
Subtask 6.2 - Sensitivity Analysis	7/1/2018	9/30/2018												■
Milestones														
- n														◆
- o														◆

Technical Approach/Project Scope, cont.

Milestone Log

Budget Period	ID	Task	Description	Planned Completion Date	Actual Completion Date	Verification Method
1	a	1	Updated PMP submitted	10/31/2015	10/29/2015	PMP document
1	b	1	Kick-off meeting convened	12/31/2015	11/16/2015	Presentation file/report documents
1	c	3	Construction of the lab-scale MR-AR experimental system (designed for pressures up to 25 bar) completed	3/31/2016	3/31/2016	Description and photographs provided in the quarterly report
1	d	2	Preparation/characterization of the CMS membranes at the anticipated process conditions (up to 300ºC and 25 bar total pressure) completed	6/30/2016	6/30/2016	Results reported in the quarterly report
1	e	2	Preparation/characterization of the HT-based adsorbents at the anticipated process conditions (300-450ºC and up to 25 bar total pressure) completed. Adsorbent working capacity, adsorption/desorption kinetics determined. Global rate expression for Co/Mo-based sour shift catalysts at the anticipated process conditions (up to 300ºC and 25 bar total pressure) generated	12/31/2016		Results reported in the quarterly report
1	f	4	MR subsystem testing and reporting of key parameters (permeance, selectivity, catalyst weight, temperature, pressures, residence time, CO conversion, effluent stream compositions, etc.) completed	3/31/2017		Results reported in the quarterly report
1	g	4	AR subsystem testing and reporting of key parameters (adsorbent and catalyst weight, temperatures, pressures, residence time, desorption mode, working capacity, energy demand, effluent stream compositions, etc.) completed	3/31/2017		Results reported in the quarterly report
1	h	4	Mathematical model modifications to simulate the hybrid MR-AR process and validate model using experimental MR and AR subsystem test results completed	3/31/2017		Results reported in the quarterly report

Budget Period	ID	Task	Description	Planned Completion Date	Actual Completion Date	Verification Method
2	i	5	Parametric testing of the integrated, lab-scale MR-AR system and identification of optimal operating conditions for long-term testing completed	9/30/2017		Results reported in the quarterly report
2	j	5	Short-term (24 hr for initial screening) and long-term (>100 hr) hydrothermal and chemical stability (e.g., NH_3, H_2S, H_2O, etc.) materials evaluations at the anticipated process conditions completed	3/31/2018		Results reported in the quarterly report
2	k	5	Integrated system modeling and data analysis completed	3/31/2018		Results reported in the quarterly report
2	l	5	Materials optimization with respect to membrane permeance/selectivity and adsorbent working capacity at the anticipated process conditions (up to 300ºC for membranes and 300-450ºC for adsorbents, and up to 25 bar total pressure) completed	6/30/2018		Results reported in the quarterly report
2	m	5	Operation of the integrated lab-scale MR-AR system for at least 500 hr at the optimal operating conditions to evaluate material stability and process operability completed	6/30/2018		Results reported in the quarterly report
2	n	6	Preliminary process design and optimization based on integrated MR-AR experimental results completed	9/30/2018		Results reported in Final Report
2	o	6	Initial technical and economic feasibility study and sensitivity analysis completed	9/30/2018		Results reported in Final Report
1,2	QR	1	Quarterly report	Each quarter		Quarterly Report files
2	FR	1	Draft Final report	10/31/2018		Draft Final Report file

Technical Approach/Project Scope, cont.

Project Success Criteria

Decision Point	Basis for Decision/Success Criteria
Completion of **Budget Period 1**	Successful completion of all work proposed in Budget Period 1.
	Measurements of membrane permeance for H_2, CH_4, CO, CO_2 both in the absence and presence of H_2O, NH_3, H_2S for full-range of operating temperatures (up to 300ºC) and total pressures (10-25 bar). Creation of Robeson (selectivity vs. permeance) plots. Target range for H_2 permeance 1-1.5 m^3/m^2.hr.bar; Target range for H_2/CO selectivity 80-100
	Measurement of adsorption/desorption kinetics and working capacity at relevant conditions (300˚C<T<450˚C, pressures up to 25 bar). Measurement of catalytic kinetics, and the development of global rate expression at relevant conditions (temperatures up to 300ºC and pressures up to 25 bar). Target for working capacity >3 wt%
	Complete fabrication of the lab-scale apparatus and testing of the individual units (MR or AR) at relevant experimental conditions. Measurements of CO conversion (%), H_2 recovery (%) and purity (%), CO_2 capture ratio/purity (%) and energy demand for regeneration (kJ/mol CO_2). Generation of experimental data sufficient to validate the model. Target for CO conversion >95%; Target for H_2 purity >95%; Target for H_2 recovery >90%; Target for CO_2 purity >95%; Target for CO_2 recovery >90%.
	Completion of simulations of the MR-AR system that indicate its ability to meet the 90% CO_2 capture and 95% CO_2 purity targets.
	Submission and approval of a Continuation Application in accordance with the terms and conditions of the award. The Continuation Application should include a detailed budget and budget justification for budget revisions or budget items not previously justified, including quotes and budget justification for service contractors and major equipment items
Completion of **Budget Period 2**	Successful completion of all work proposed in Budget Period 2.
	Completion of short-term (24 hr) and long-term (>100 hr) hydrothermal/chemical stability evaluations. Membranes/adsorbents are stable towards fuel gas constituents (e.g., NH_3, H_2S, H_2O) at the anticipated process operating conditions. Target <10% decline in performance over 100 hr of testing.
	Completion of integrated testing and system operated for >500 hr at optimal process conditions.
	Results of the initial technical and economic feasibility study show significant progress toward achievement of the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches
	Submission of updated membrane and adsorbent state-point data tables based on the results of integrated lab-scale MR-AR testing
	Submission of a Final Report

Technical Approach/Project Scope, cont.

Project Risks and Mitigation Strategies

Description of Risk	Probability (low, moderate, high)	Impact (low, moderate, high)	Risk Management Mitigation and Response Strategies
Technical Risks:			
Adsorbent not chemically stable in presence of syngas components	Moderate	High	Explore the addition of a warm or cold gas clean-up step into the process design
Concerns with the adsorbent's physical integrity under the operating conditions	Moderate	Moderate	Reduce heating/cooling rates; improve physical strength during preparation via increased binder content. Replace TSA with PSA or hybrid TSA/PSA operation
Model does not fit experimental data	Low	Low	Investigate causes of poor fit. Re-evaluate intrinsic system parameters
Experimental difficulties with high-pressure reactor operation and temperature control	Moderate	Moderate	Identify and fix leaks; replace malfunctioning valves and high-pressure components; adjust control hardware/software
Resource Risks:			
Equipment malfunction	Moderate	Moderate	Use back-up systems, when available. Repair malfunctioning equipment
Personnel performance issues	Low	Moderate	Address/remedy performance issues. Replace personnel, if need arises
Delays in delivery of materials from M&PT to USC	Low	Moderate	Improve coordination between M&PT and USC
Budgetary issues, i.e., not enough funds to complete a certain Task	Low	Low	Seek DOE guidance and approval for shifting funds from less critical tasks and consolidating certain activities
Management Risks:			
Poor coordination among PI's	Low	High	Address communication/coordination issues. Increase frequency of meetings and data exchange and coordination
IP ownership issues develop	Low	Moderate	Face-to-face meetings among PIs and appropriate administrative people. Address/remedy issues and disagreements

Progress and Current Status of Project

Materials Preparation and Characterization

Carbon Molecular Sieve (CMS) Membrane Preparation & Characterization
Preliminary Performance Assessment

Project Targets for CMS Membranes

1. Extend operation to 300°C	***Standard Operation at 250°C***
2. Improve H_2/CO_2 to ≥ 65 (from 35)	***Move CO_2 capture to adsorption section***
3. Target H_2/CO at ≥ 80 to 100	***Standard performance at 250°C***
4. H_2 permeance at ≥ 550 GPU	***Standard performance at 250°C***

Preliminary Performance of Selected CMS Membranes at 300°C

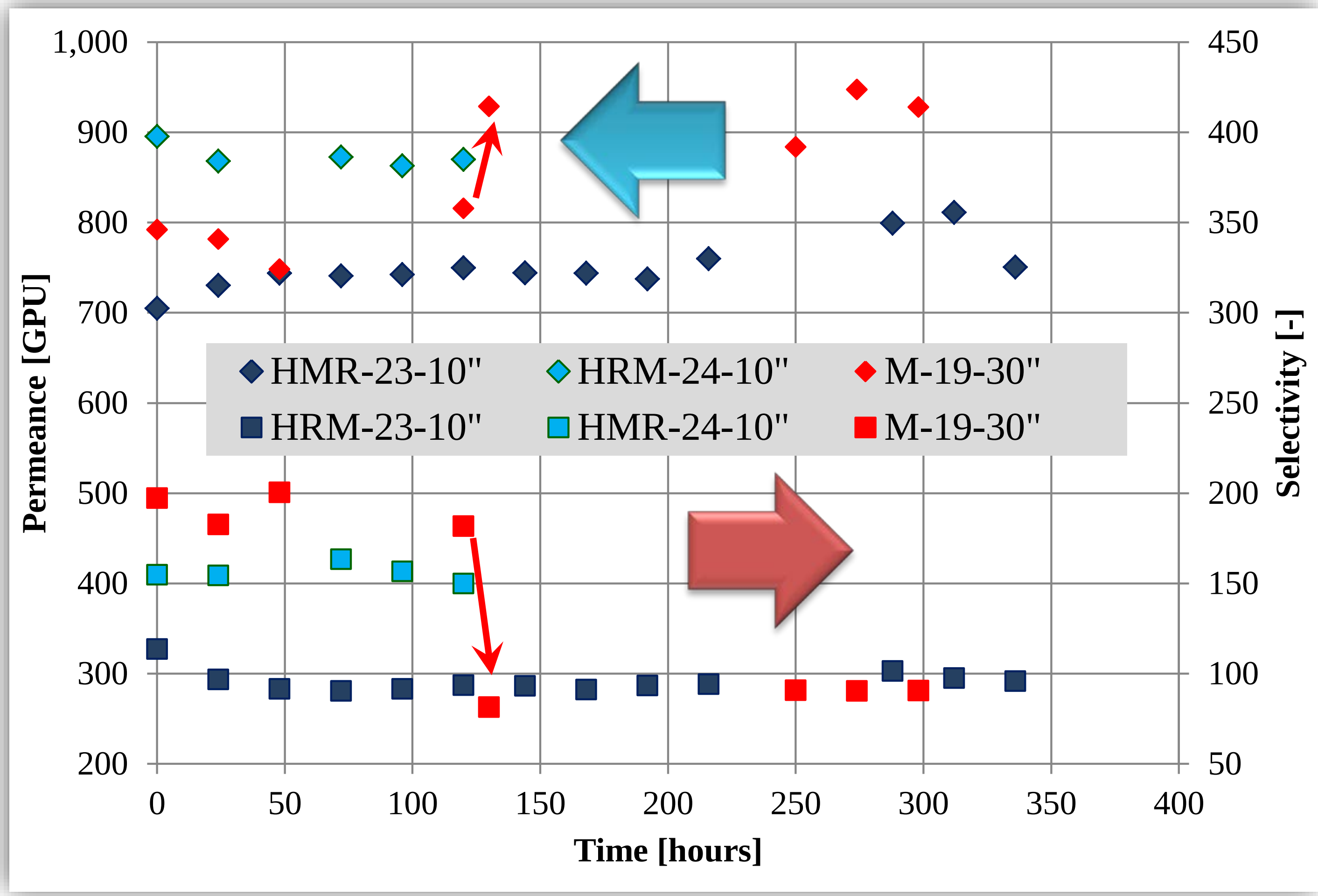
Part ID	He [GPU]	N_2 [GPU]	H_2 [GPU]	CO_2 [GPU]	H_2/N_2 [-]	H_2/CO_2 [-]	
M-8 (30")	573	5.5	624	16.1	113	39	
M-17 (30")	891	6.5	934	23.7	144	39	
M-19 (30")	792	4.0	781	12.4	195	63	
HMR-23 (10")	732	8.7	727	16.4	84	45	
HMR-24 (10")	871	5.6	780	9.5	154	81	

Progress and Current Status of Project, cont.

Materials Preparation and Characterization

<u>Carbon Molecular Sieve Membrane Preparation & Characterization</u>

Long-Term Stability Testing at Target 300°C

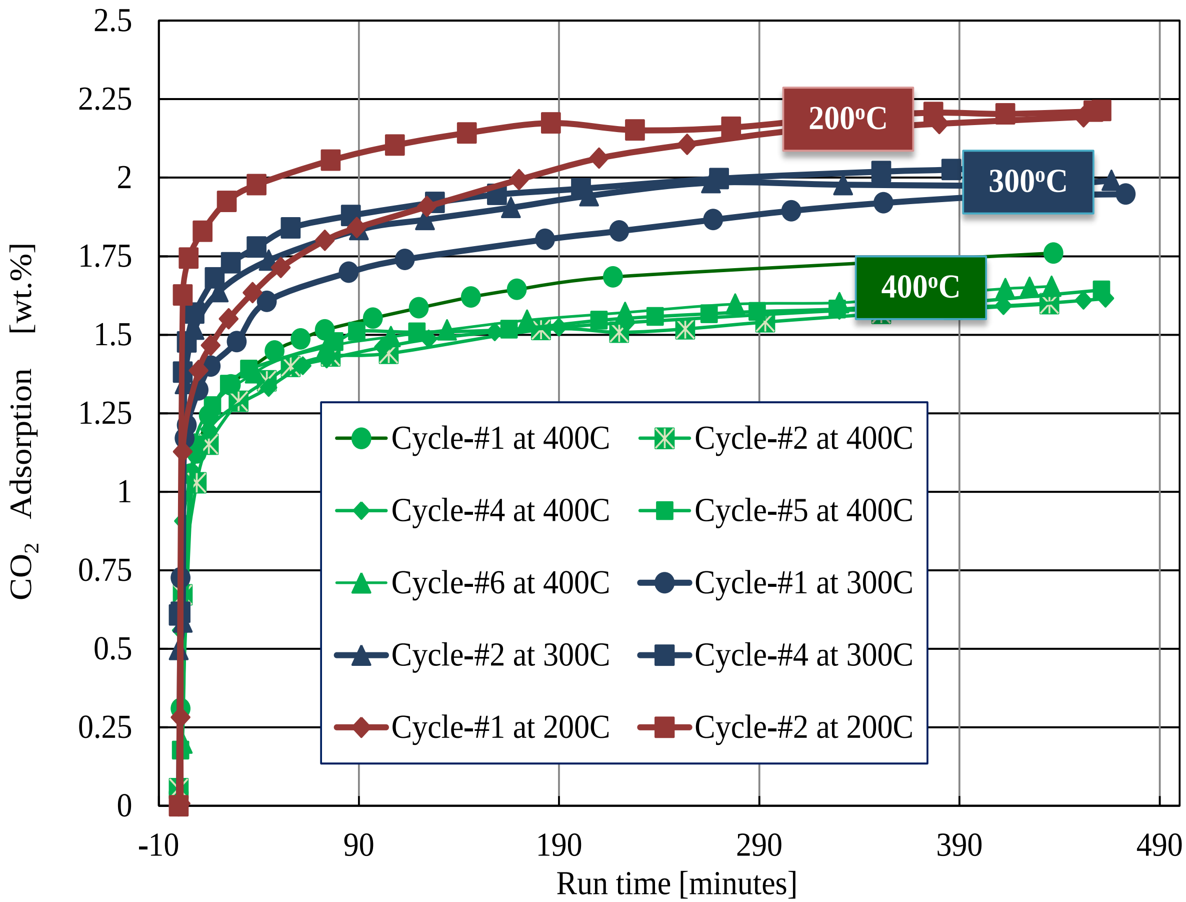


Progress and Current Status of Project, cont.

Materials Preparation and Characterization

Hydrotalcite Materials Preparation and Characterization

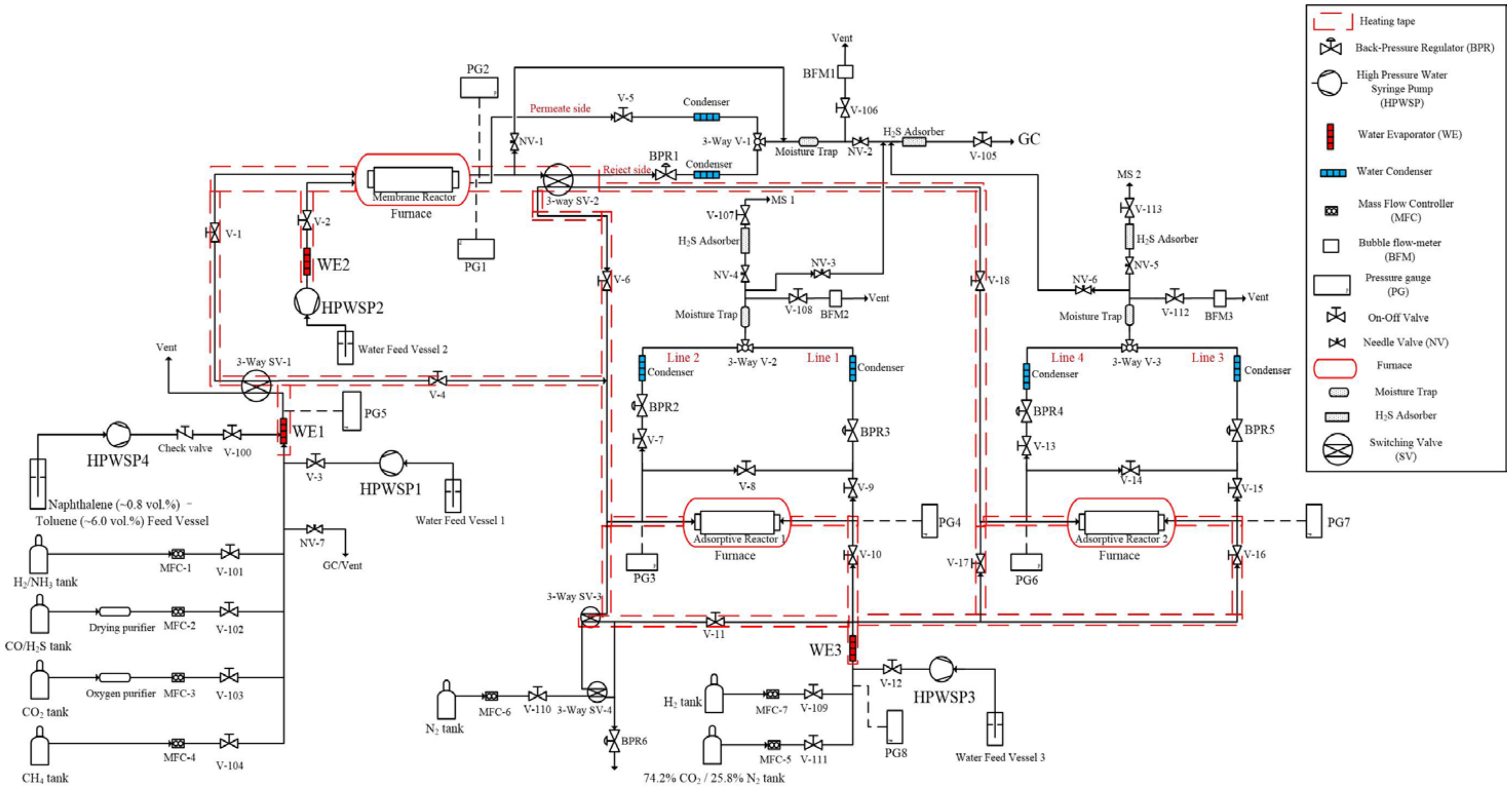
Cyclic Adsorption/Desorption Testing at WGS Temperatures



Sample ID: HT-3MgAl-G20-#1
Adsorption: CO_2, atmospheric pressure
Desorption: N_2, atmospheric pressure at run temperature

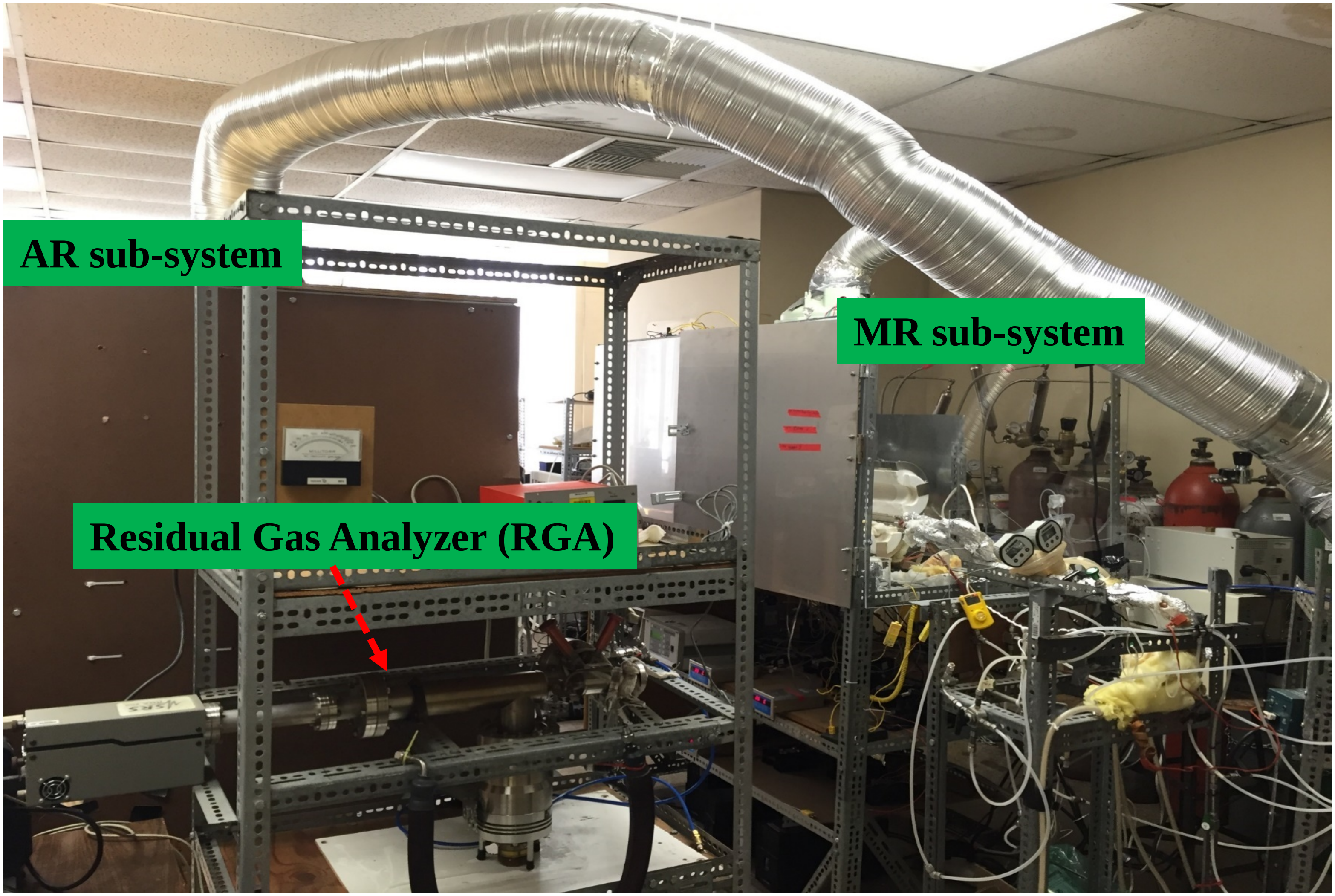
Progress and Current Status of Project, cont.

Design and Construction of the Lab-Scale MR-AR System.



Progress and Current Status of Project, cont.

Design and Construction of the Lab-Scale Experimental System

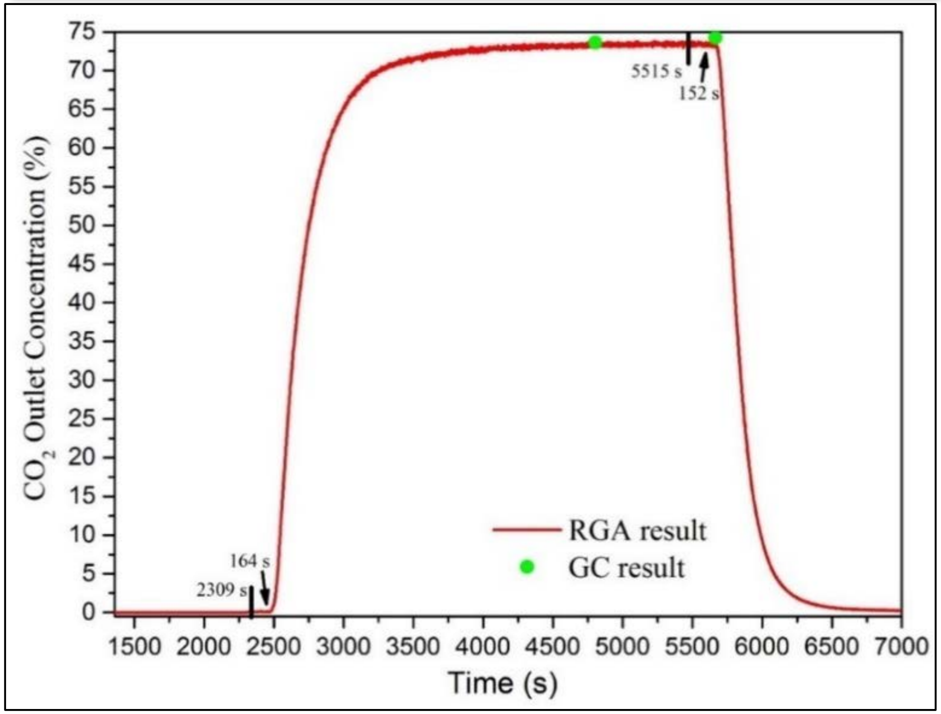


Progress and Current Status of Project, cont.

AR Sub-System Operation Testing

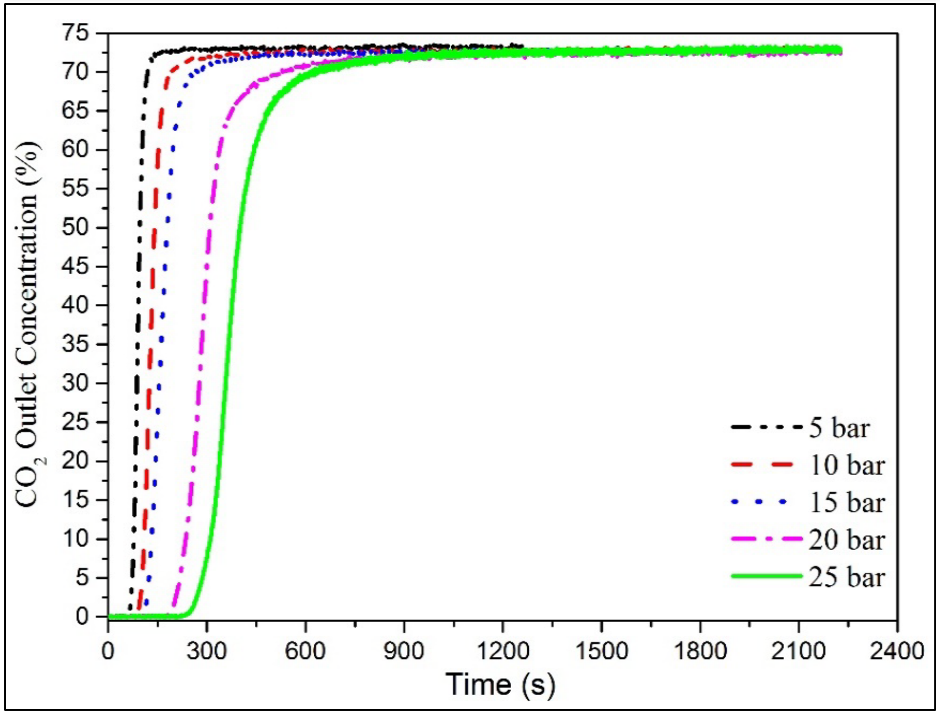
Empty reactor dynamics

Reactor pressure = 25 bar, Oven temperature = 400 °C, Flow rate=500 sccm



Blank experiments using only quartz

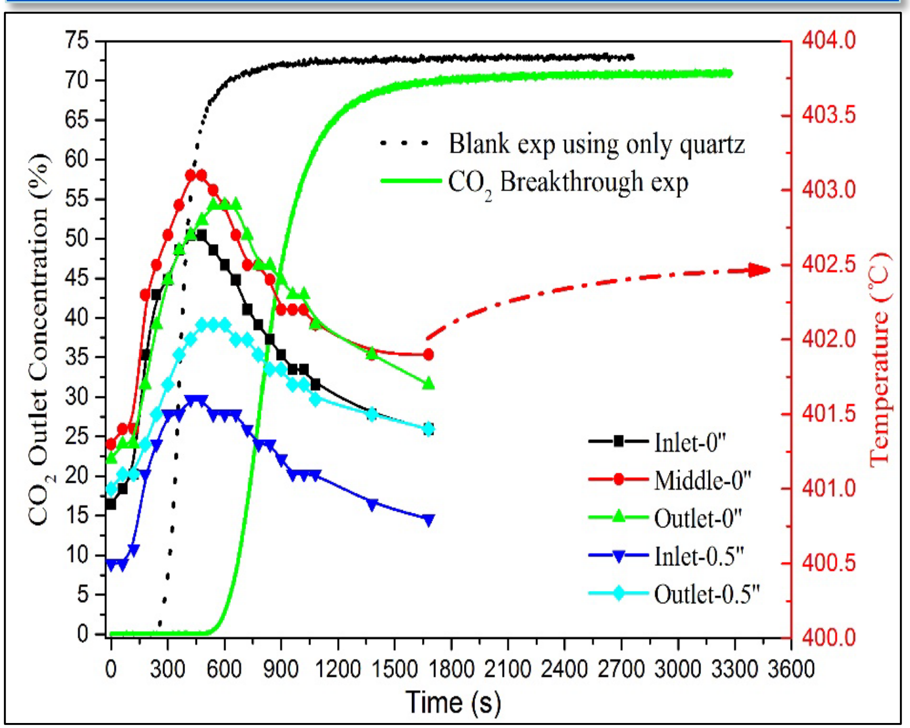
Reactor pressure = 5, 10, 15, 20, 25 bar, Oven temperature = 400 °C, Flow rate=500 sccm



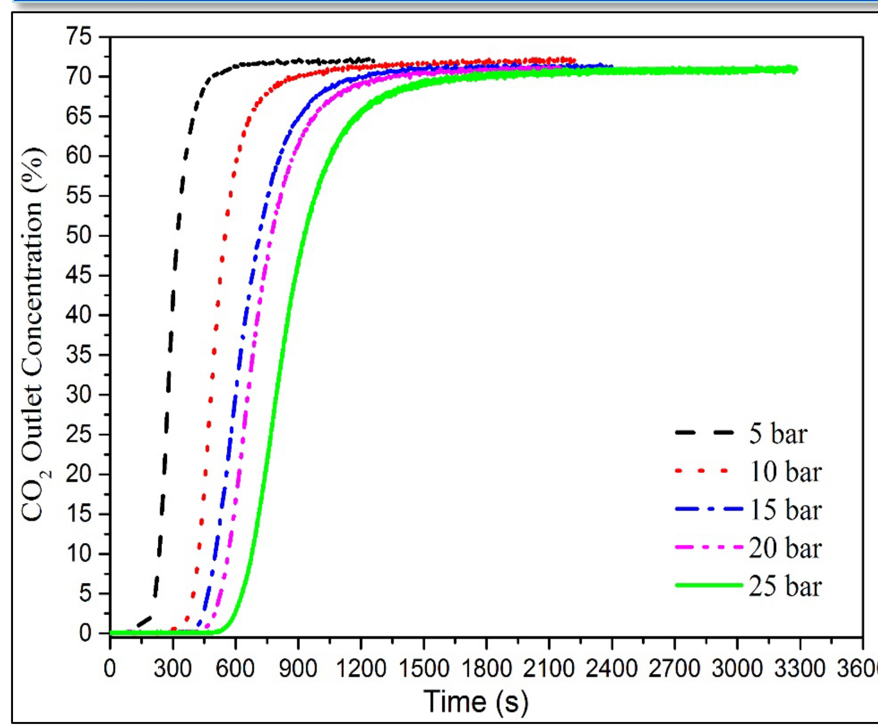
Progress and Current Status of Project, cont.

AR Sub-System Operation Testing

CO_2 breakthrough experiments
Reactor pressure = 25 bar, Oven temperature = 400 °C, Flow rate=500 sccm



CO_2 breakthrough experiments
Reactor pressure = 5, 10, 15, 20, 25 bar, Oven temperature = 400 °C, Flow rate=500 sccm



Progress and Current Status of Project, cont.

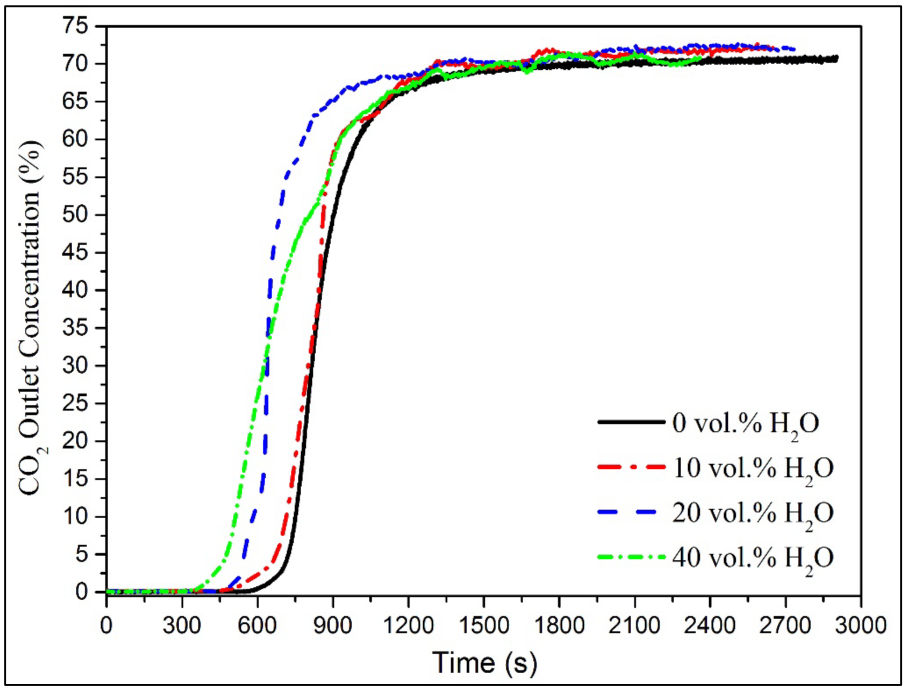
AR Sub-System Operation Testing

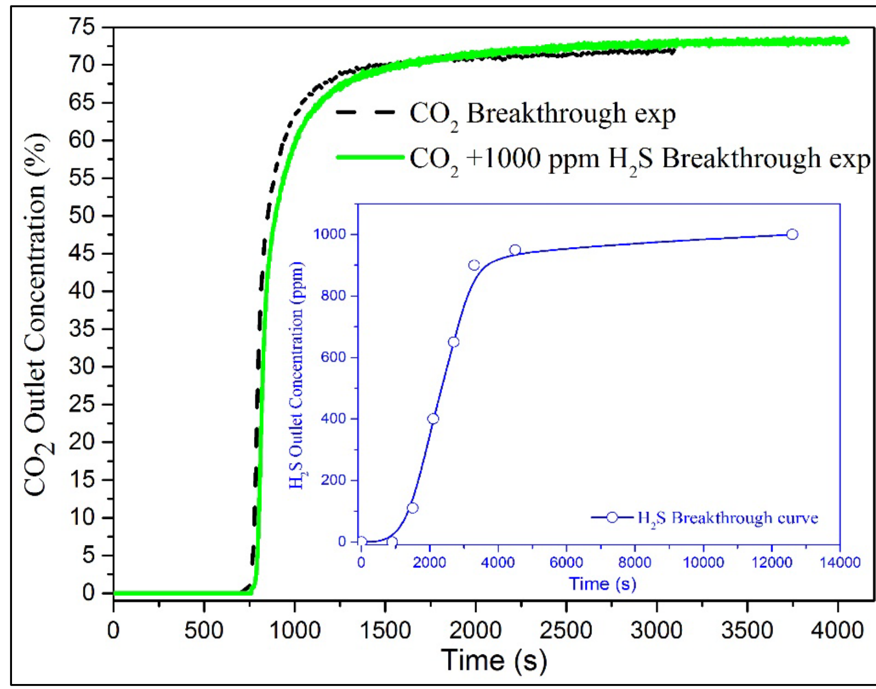
CO_2/ H_2O breakthrough experiments

Reactor pressure = 25 bar, Oven temperature = 300 °C, Total flow rate=500 sccm, Various steam concentration (0, 10, 20, 40 vol.%)

CO_2/ H_2S breakthrough experiments

Reactor pressure = 25 bar, Oven temperature = 300 °C, Total flow rate=500 sccm, H_2S concentration (0, 1000 ppm)





Progress and Current Status of Project, cont.

Mathematical Model Development and Simulations

Membrane Reactor (MR) Multi-Scale Model (Pellet Scale)

Accomplishments:

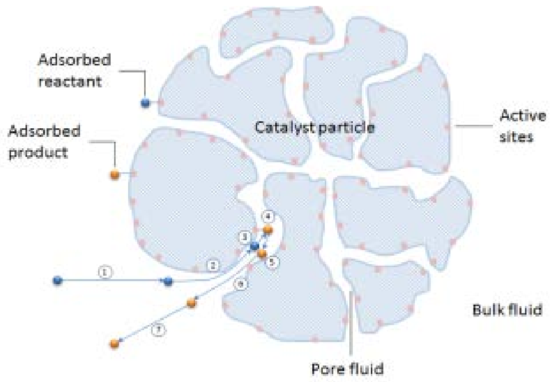
- o Developed spherical catalyst pellet, isothermal/non-isothermal, steady-state model.

Model Features:

- Captures species' reaction and transport through convection/diffusion, and energy transport through solid/gas conduction and gas enthalpic convection.
- Species transport captured by Dusty Gas Model (continuum/viscous/Knudsen diffusion).
- Finite Element based simulation method (COMSOL).

Outcomes:

- ❖ Concentration, temperature and pressure radial profiles.
- ❖ Effectiveness factor calculations.
- ❖ Knudsen diffusion established as the dominant species' transport mechanism.



- ❖ 2016 AIChE Presentation (Upcoming): Modeling and Simulation of Transport Effects to a Single Reactor Pellet

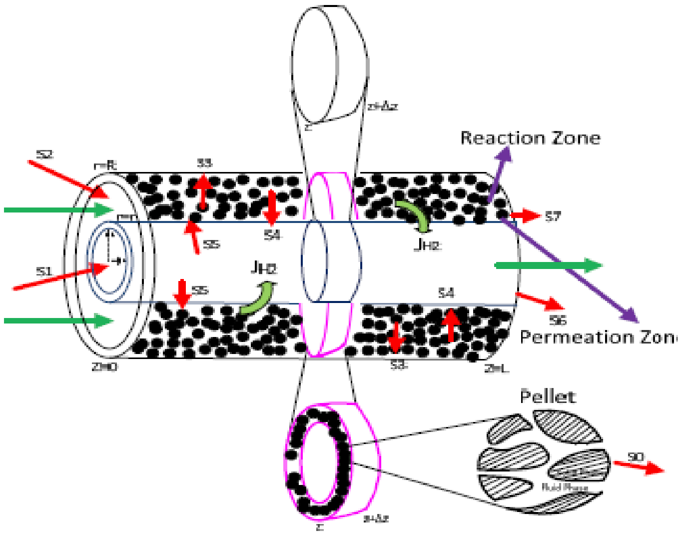
Progress and Current Status of Project, cont.

Mathematical Model Development and Simulations

Membrane Reactor (MR) Multi-Scale Model (Reactor Scale)

Accomplishments:

- Developed multi-phase, multi-scale, steady-state, isothermal, packed-bed reactor model, coupled with pellet model.
- Reacting zone coupled with permeation zone to create full membrane reactor (MR) model.



Model Features:

- Captures species' reaction, and transport through convection/diffusion (Stefan Maxwell Equations), and energy transport through gas conduction/enthalpic convection.
- Pressure drop calculated by the Ergun Equation.
- Pellet and reactor scale models coupled through species/energy fluxes at pellet radius.

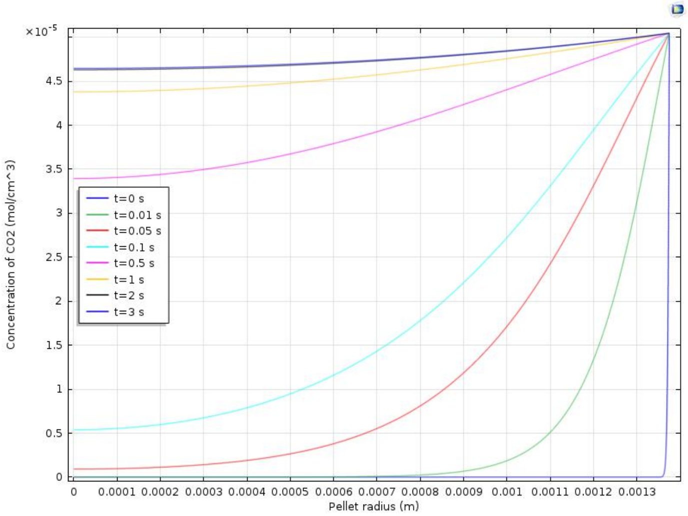
Outcomes:

- ❖ Concentration, temperature, and pressure radial (axial) profiles at pellet (reactor) scales.
- ❖ 2016 AIChE Presentation (Upcoming): Multi-Scale (Pellet-Reactor Scale) Membrane Reactor Modeling and Simulation: Low Temperature and High Pressure Water-Gas Shift Reaction

Progress and Current Status of Project, cont.

Mathematical Model Development and Simulations

Adsorptive Reactor (AR) Multi-Scale Model (Catalyst /Adsorbent)



Accomplishments:

- Developed spherical adsorbent pellet, isothermal/non-isothermal, dynamic model.

Model Features:

- Incorporates species/energy accumulation terms, and captures species' reaction and transport through convection/diffusion, and energy transport through solid/gas conduction and gas enthalpic convection.
- Species transport captured by Dusty Gas Model (continuum/viscous/Knudsen diffusion).
- Employs variety of adsorption models (Langmuir isotherm, one-step/two-step reaction).

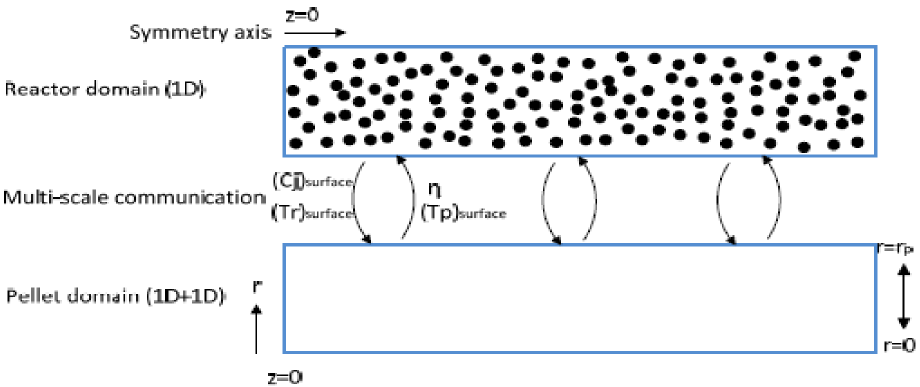
Outcomes:

- ❖ Time-dependent concentration, temperature, and pressure radial profiles.

Progress and Current Status of Project, cont.

Mathematical Model Development and Simulations

Adsorptive Reactor (AR) Multi-Scale Model (Reactor Scale)



Accomplishments:

- o Developed multiphase, multi-scale, isothermal, dynamic reactor model.
- o Catalyst and adsorbent pellet models coupled with packed bed reactor model to form a hybrid multi-scale Adsorptive Reactor (AR) model.

Model Features:

- Incorporates species/energy accumulation terms, captures species' reactions, and transport through convection/diffusion (Stefan Maxwell Equation), and energy transport through gas conduction/enthalpic convection.
- Pressure drop calculated by Ergun Equation.
- Catalyst/Adsorbent Pellet and reactor scale models coupled through species/energy fluxes at pellet radius.

Outcomes:

- ❖ Dynamic concentration/temperature/pressure radial (axial) profiles at pellet (reactor) scales.
- ❖ 2016 AIChE Presentation (Upcoming): Study of Adsorptive Reactor (AR): Dynamic Multi-Scale (Catalyst /Adsorbent/Reactor Scale) Modeling and Simulation

Mathematical Model Development and Simulations

CO_2 Adsorption on Hydrotalcite

Accomplishments:

- Proposed a novel two step reaction scheme for CO_2 adsorption on Hydrotalcite.
- Developed associated mathematical model and proposed analytical solution.
- Developed one to one and onto mapping between parameters identifiable from experimental adsorption data and the reaction scheme's kinetic constants.

Model Features:

- Two adsorption site types.
- Set of 2 linear time-invariant ODE's.
- Resulting mathematical model is analytically solvable.

$$\left\{\begin{array}{ll} CO_2(g) + V\cdot S \underset{k_2}{\overset{k_1}{\rightleftarrows}} CO_2\cdot S & R1 \\ CO_2(g) + CO_2\cdot S \underset{k_4}{\overset{k_3}{\rightleftarrows}} (CO_2)_2\cdot S & R2 \end{array}\right\}$$

Outcomes:

- Identified locally optimal kinetic constants from experimental adsorption data.
- Developing novel method for globally optimal kinetic constant identification.
- 2016 AIChE Presentation (Upcoming): Experimental and Theoretical Studies of CO_2 Adsorption on Hydrotalcite

Summary of Technical Accomplishments To Date

- *CMS membranes prepared and characterized at relevant process conditions.*
- *Hydrotalcite materials prepared and characterized via TGA and under relevant flow conditions in the AR subsystem.*
- *Lab-scale experimental system refurbished and AR subsystem tested.*
- *Mathematical model for the MR and AR subsystems developed. TGA sorption data analyzed via a 2-step adsorption model.*

Plans for Future Testing/Development/Commercialization

<u>Budget Period 1(BP1):</u>

Task 2.0 - Materials Preparation and Characterization. -----M&PT, USC

Subtask 2.1- Preparation and Characterization of the CMS Membranes at the anticipated process conditions.

Subtask 2.2- Preparation and Characterization of Adsorbents and Catalysts.

Task 4.0 - Initial Testing and Modeling of the Lab-Scale Experimental System. -----USC, UCLA

Subtask 4.1 - Unit Operation Testing.

Subtask 4.2 - Mathematical Model Development and Simulations.

<u>Budget Period 2 (BP2):</u>

Task 5.0 - Integrated Testing and Modeling of the Lab-Scale Experimental System. -----M&PT, USC

Subtask 5.1 - Materials Optimization and Scale-up.

Subtask 5.2 - Integrated Testing.

Subtask 5.3 - Model Simulations and Data Analysis.

Task 6.0 - Preliminary Process Design/Optimization and Economic Evaluation. -----UCLA, M&PT, USC

Subtask 6.1 - Process Design/Optimization.

Subtask 6.2 - Sensitivity Analysis.

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