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

DE-FOA-0001235
FE0026423

•P.I.: Professor Theo Tsotsis, University of Southern California (USC), Los Angeles, CA
•Co-P.I.: Professor Vasilios Manousiouthakis, University of California (UCLA), Los Angeles, CA
•Co-P.I.: Dr. Rich Ciora, Media and Process Technology Inc. (M&PT), Pittsburgh, PA

U.S. Department of Energy National Energy Technology Laboratory (NETL)
2017 NETL CO_2 Capture Technology Project Review Meeting
August 22, 2017

Presentation Outline

- Project Overview
- Technology Background
- Technical Approach/Project Scope
- Project Progress and Current Status
- Future Plans

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

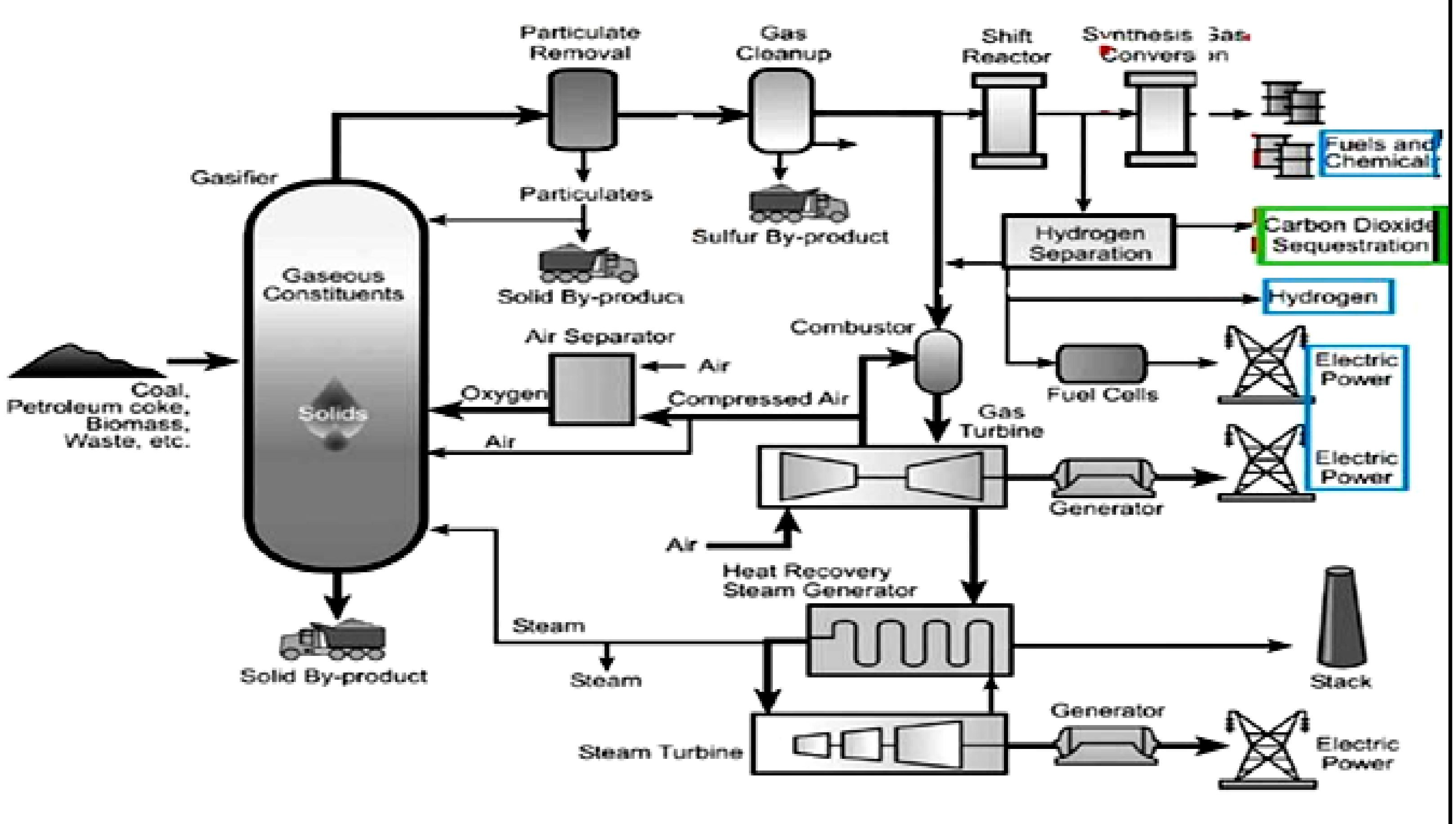
Key Project Tasks/Participants:

1. Design, construct and test the lab-scale experimental MR-AR system. **(USC)**
2. Select and characterize appropriate membranes/adsorbents/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. **(M&PT/UCLA/USC)**

Technology Background

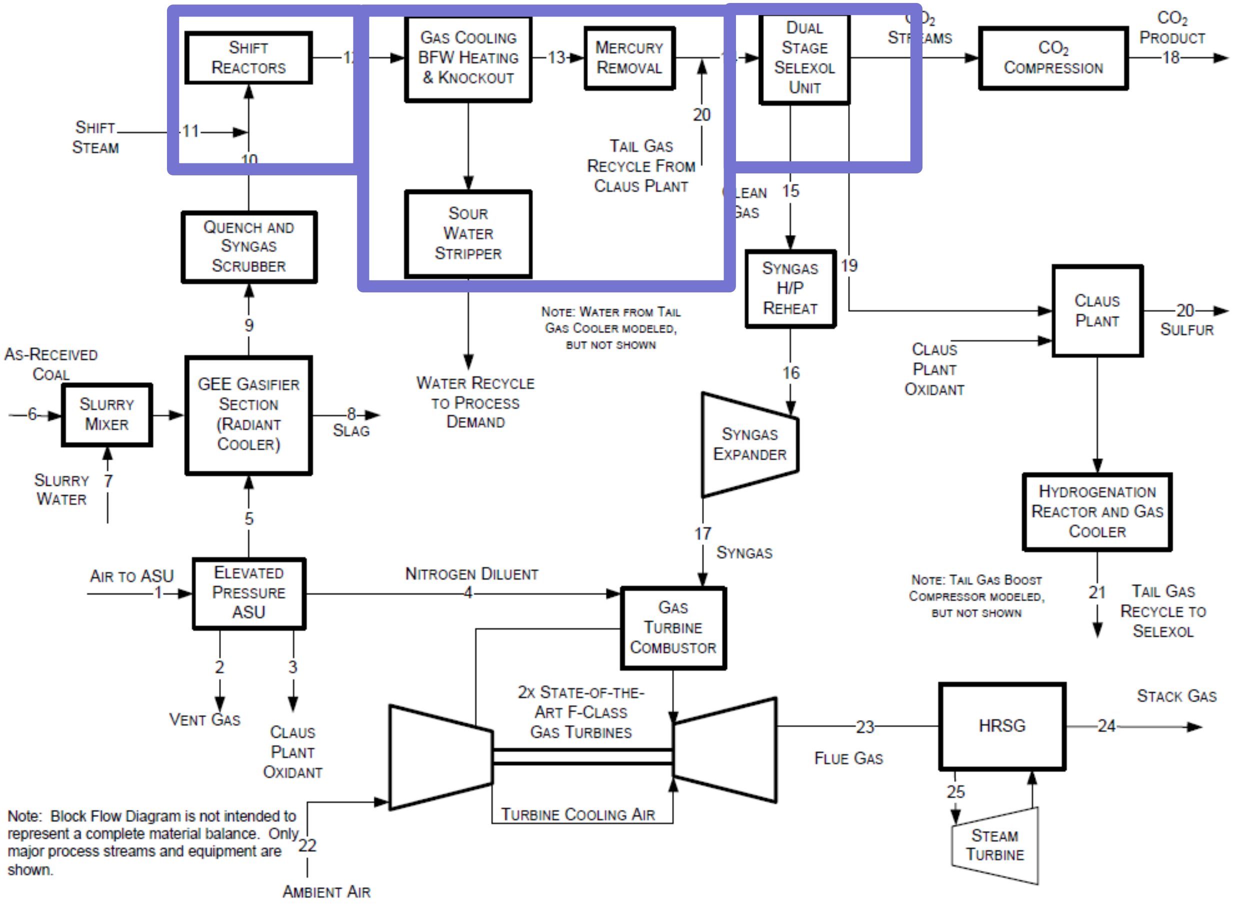
Conventional IGCC Power Plant

G.J. Stiegel, M. Ramezan / International Journal of Coal Geology 65 (2006) 173–190



Technology Background Cont'd

Baseline IGCC Power Plant

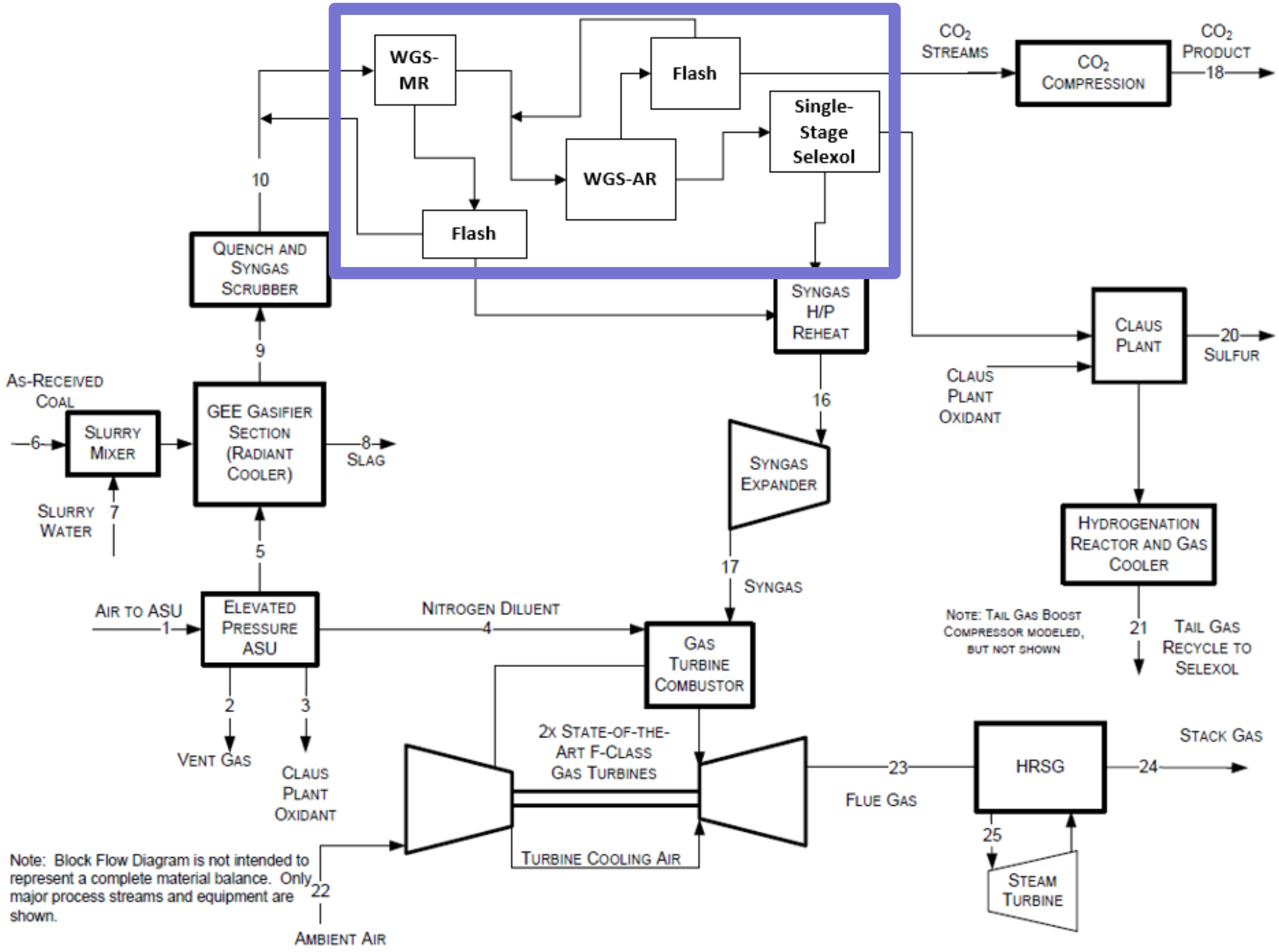


Source: NETL

*Picture: DOE/NETL-2015/1727 NETL SHELL IGCC CASE B5B

Technology Background Cont'd

Proposed IGCC Power Plant



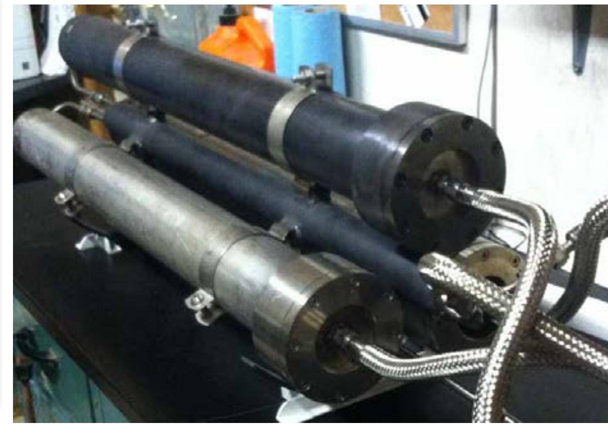
*Original Picture: DOE/NETL-2015/1727 NETL SHELL IGCC CASE B5B

Technology Background Cont'd

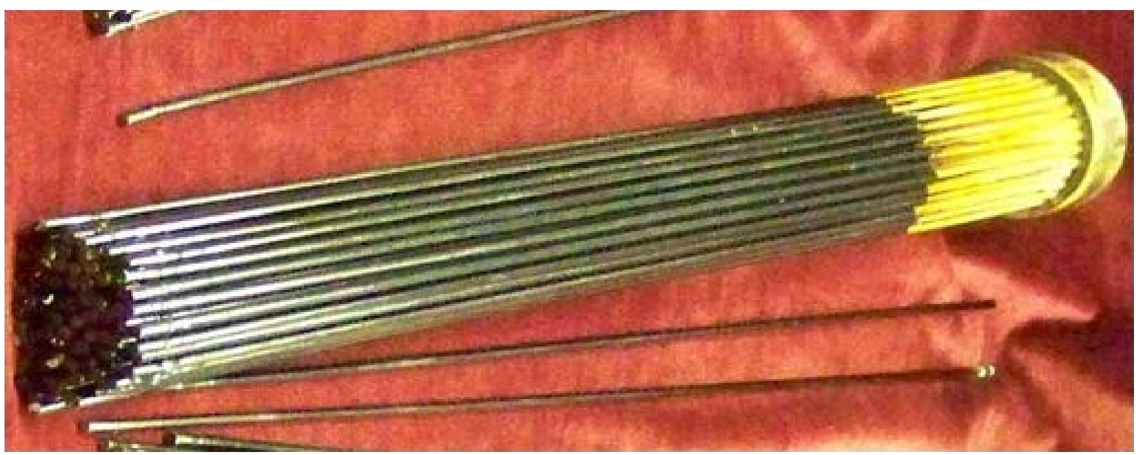
Ceramic Membranes for Large-Scale Applications

Ceramic Membrane Tubes

Ceramic Membrane Containing High Pressure Vessel



Ceramic Membrane Bundle



Technology Background Cont'd

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

Hydrotalcite (HT) Adsorbent:

- HT adsorbent shown to have a working CO_2 capacity of 3-4 wt.% during past (HAMR) MSR, WGS reaction studies. Theoretical capacity >16 wt.%.

Co/Mo-Based Sour Shift Catalyst:

- Commercial Co/Mo-based sour shift catalyst has been used in our past and ongoing lab-scale MR studies with simulated coal-derived and biomass-derived syngas. Shown to have stable performance for >1000 hr of continuous operation.

Technology Background Cont'd

Proposed Process Advantages vs. SOTA

Key Innovation:

- Highly-efficient, low-temperature, membrane/adsorptive reactor process for the water-gas-shift reaction of coal-gasifier syngas for pre-combustion CO_2 capture

Unique Advantages:

- **No syngas pretreatment required:** Ceramic membranes proven stable in past/ongoing studies to all gas contaminants present in coal-derived syngas.
- **Improved WGS Efficiency:** Enhanced reactor yield and selectivity via removal of both H_2 and CO_2 from the reacting phase.
- **Significantly reduced catalyst weight usage requirements:** Reaction rate enhancement (over conventional WGSR), due to removal of both products, potentially allows one to operate at lower W/F_{CO} (kg_{cat}/(mol/hr)).
- **Efficient H_2 production, and superior CO_2 recovery and purity:** The synergy of the MR and AR units makes the simultaneous satisfaction of the CO_2 recovery/purity, carbon utilization (CO conversion), and hydrogen recovery/purity goals, a potential reality.

Technology Background Cont'd

Key Technical Objectives and Focus

- Prepare and characterize membranes/adsorbents and validate their performance at the relevant experimental conditions.

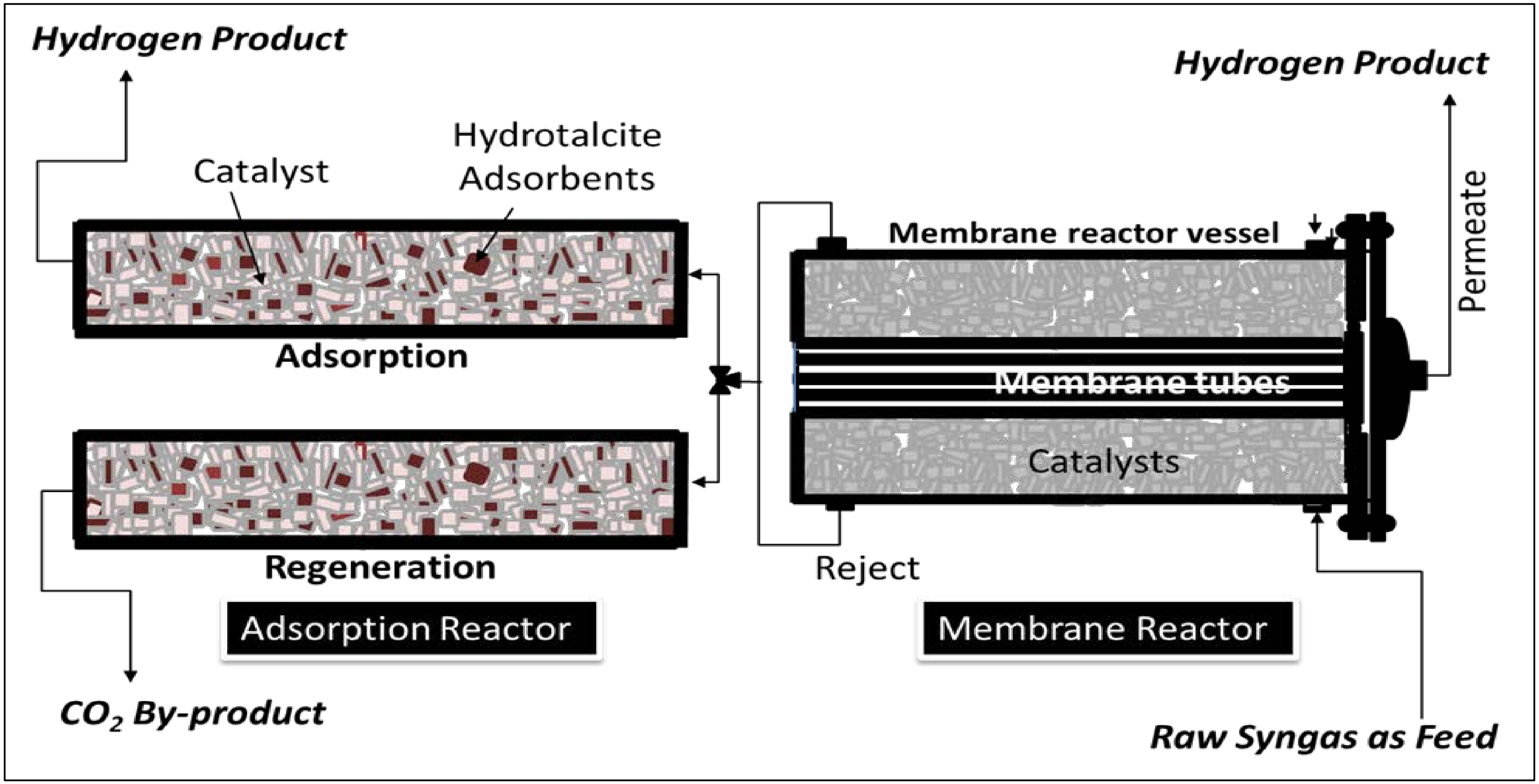
- Validate catalyst performance at the relevant pressure conditions. Verify applicability of global reaction kinetics.

- Complete construction of lab-scale MR-AR experimental system and test the individual MR and AR subsystems.

- Develop and experimentally validate mathematical model.

Technical Approach/Project Scope

Proposed MR-AR Process



- **Potential use of a TSA/PPSA regeneration scheme allows high pressure CO_2 recovery**
- **MR-AR process overcomes limitations of stand-alone systems (WGSR, WGS-MR, WGS-AR)**

Progress and Current Status of Project, Cont'd

Completed Project Tasks

Budget Period 1 (BP1):

Task 1.0 – Project Management and Planning

Task 2.0 – Materials Preparation and Characterization

Task 3.0 – Design and Construction of the Lab-Scale Experimental System

Task 4.0 – Initial Testing and Modeling of the Lab-Scale Experimental System

Progress and Current Status of Project, Cont'd

Current Project Tasks

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

Task 5.0 - Integrated Testing and Modeling of the Lab-Scale Experimental System.

Task 6.0 - Preliminary Process Design/Optimization and Economic Evaluation.

Technical Approach/Project Scope, Cont'd

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	12/31/2016	Results reported in the quarterly report

Technical Approach/Project Scope, Cont'd

Milestone Log

Budget Period	ID	Task	Description	Planned Completion Date	Actual Completion Date	Verification Method
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	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	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	3/31/2017	Results reported in the quarterly report

Technical Approach/Project Scope, Cont'd

Milestone Log

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

Technical Approach/Project Scope, Cont'd

Milestone Log

Budget Period	ID	Task	Description	Planned Completion Date	Actual Completion Date	Verification Method
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

Progress and Current Status of Project

Materials Preparation and Characterization

Carbon Molecular Sieve (CMS) Membrane Preparation, Characterization Performance Assessment

Project Targets for CMS Membranes

H_2 permeance at ≥ 550 GPU ; H_2/CO at ≥ 80 to 100

Performance of Selected CMS Membranes at 250ºC

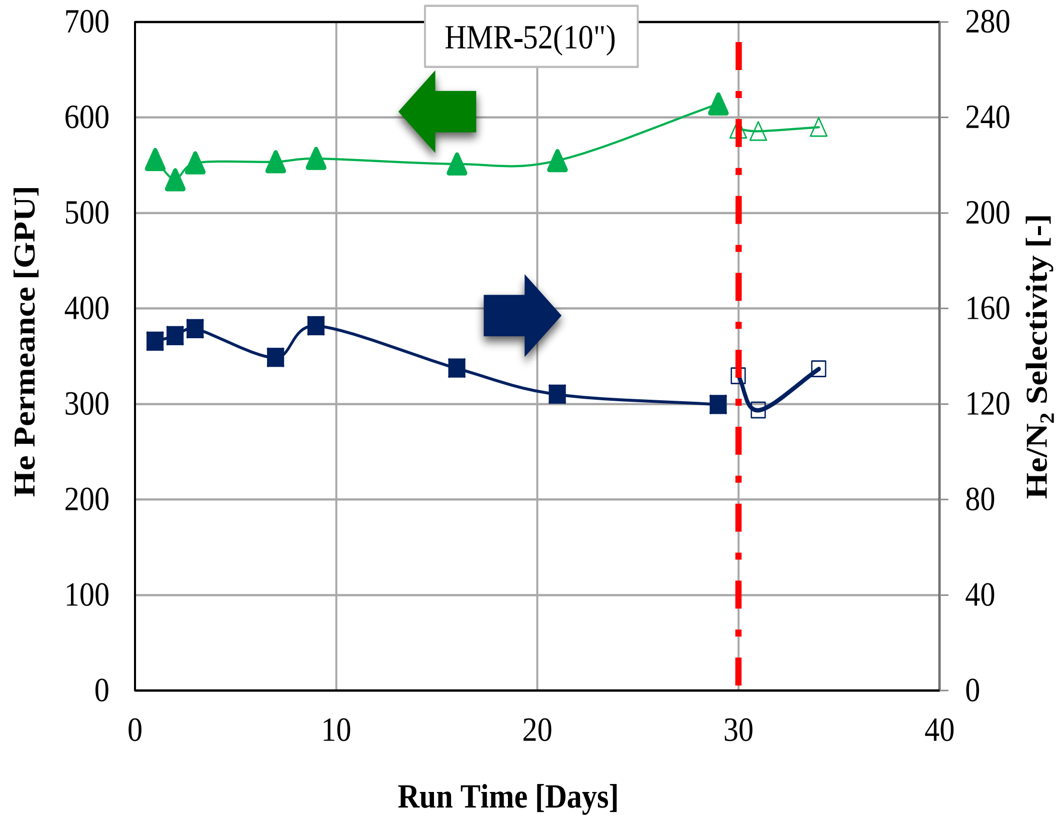
Part ID	*He [GPU]*	*N_2 [GPU]*	*H_2 [GPU]*	*CO_2 [GPU]*	*H_2/N_2 [-]*	*H_2/CO*	*H_2/CO_2 [-]*
HMR-41(10”)	482	5.7	367	5.7	145	121-126	65
HMR-44(10”)	645	4.2	722	11.3	172	143-150	64
HMR-45(10”)	366	0.85	400	3.2	471	392-410	126*
HMR-46(10”)	684	4.7	-	12.0	-		-
HMR-52(10”)	556	3.8	539	14.3	148	123-129	38
HMR-39(10”	381	4.4	-	-	86	72-75	-
HMR-47(10”)	846	4.5	819	4.9	179	149-156	167*
HMR-49(10”)	434	1.7	427	8.3	249	207-216	51
HMR-48(10”)	418	4.4	451	6.8	102	85-89	68
HMR-42(10”)	368	1.0	364	0.7	361	301-314	540*

Progress and Current Status of Project, Cont'd

Materials Preparation and Characterization

Carbon Molecular Sieve Membrane Preparation & Characterization

Long-Term Stability Testing

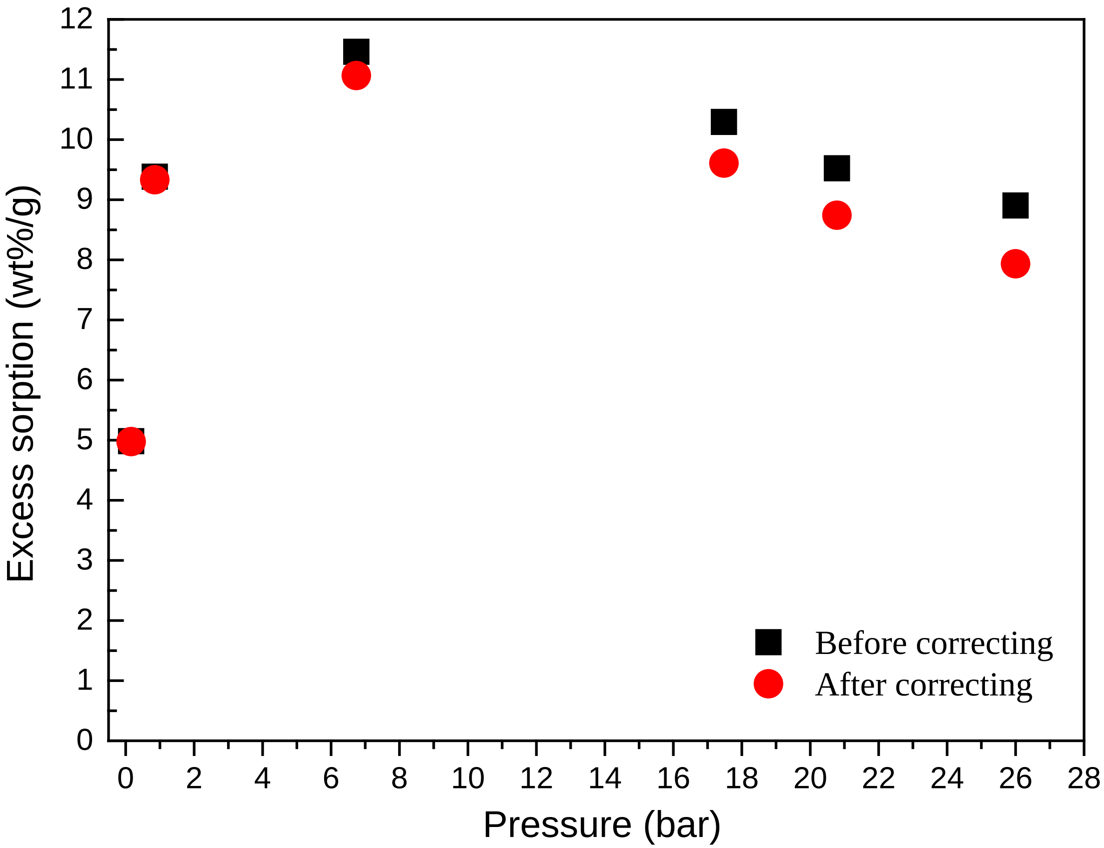


Progress and Current Status of Project, Cont'd

Materials Preparation and Characterization

Hydrotalcite Materials Preparation and Characterization

High-Pressure Adsorption Isotherm at 250°C



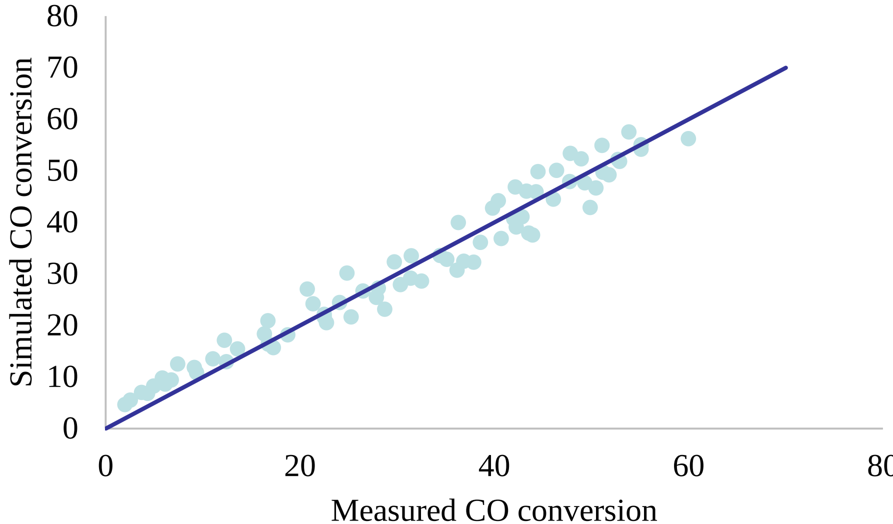
UCLA/USC/M&PT

Progress and Current Status of Project, Cont'd

Materials Preparation and Characterization

Co-Mo/Al_2O_3 Sour-Shift Catalyst Characterization

Global Reaction Kinetics- Empirical Model and Comparison with Microkinetc Models



$$-r_{co} = A\, e^{\frac{-E}{RT}}\, p_{co}^{a} p_{H_2O}^{b} p_{co_2}^{c} p_{H_2}^{d} \,(1-\beta)$$

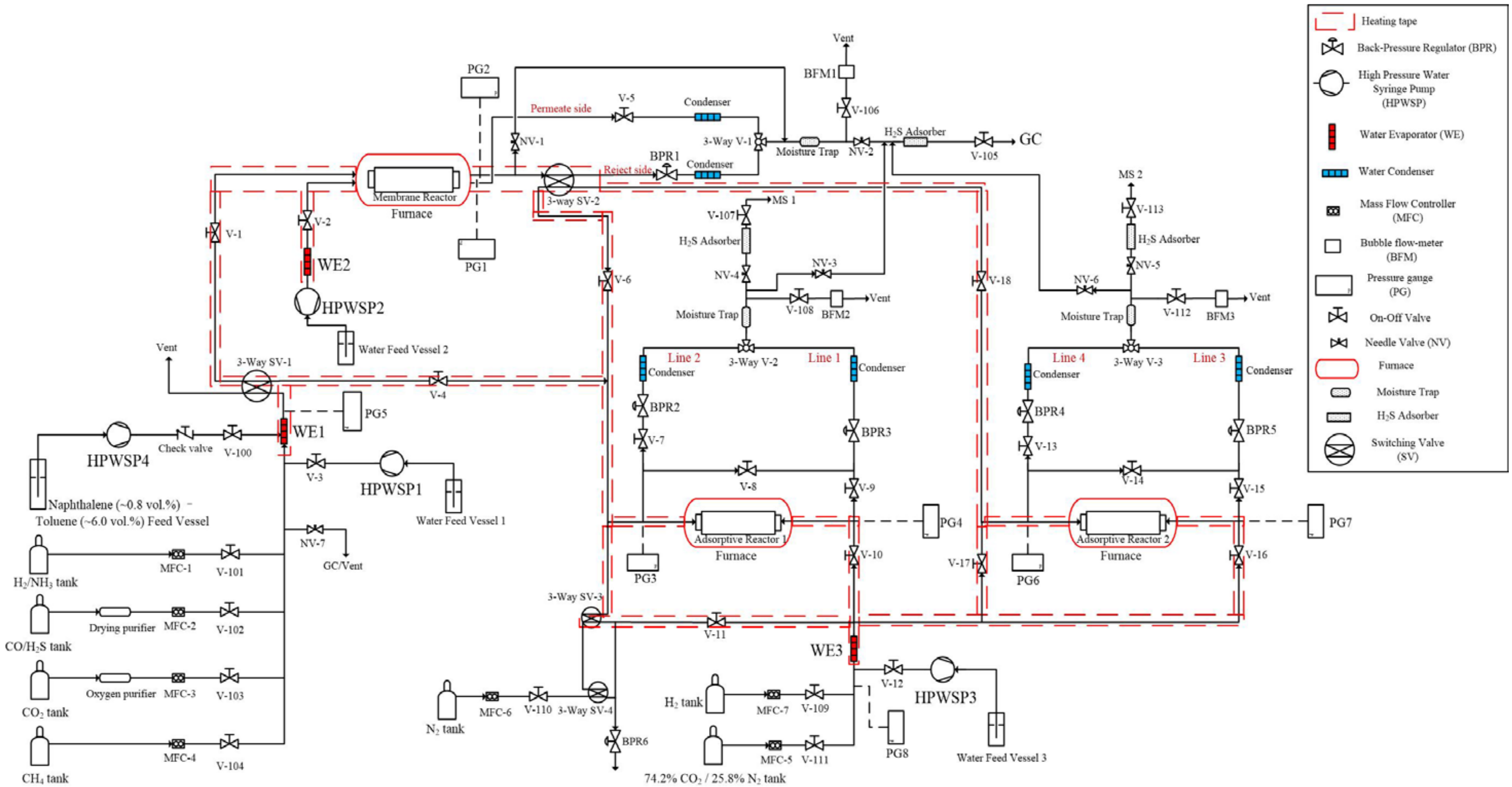
$$\beta = \frac{1}{K_{eq}} \frac{(P_{CO_2} . P_{H_2})}{(P_{CO} . P_{H_2O})} \quad K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

A[mol/(atm$^{(a+b+c+d)}$ · h · g)]	**18957**
E [J/mol]	58074
a	4
b	-1.46
c	0.13
d	-1.44

Root-Mean-Square Deviation (RMSD)	
Direct oxidation	3.38
Associative	5.12
Formate intermediate	8.04
Empirical model	3.32

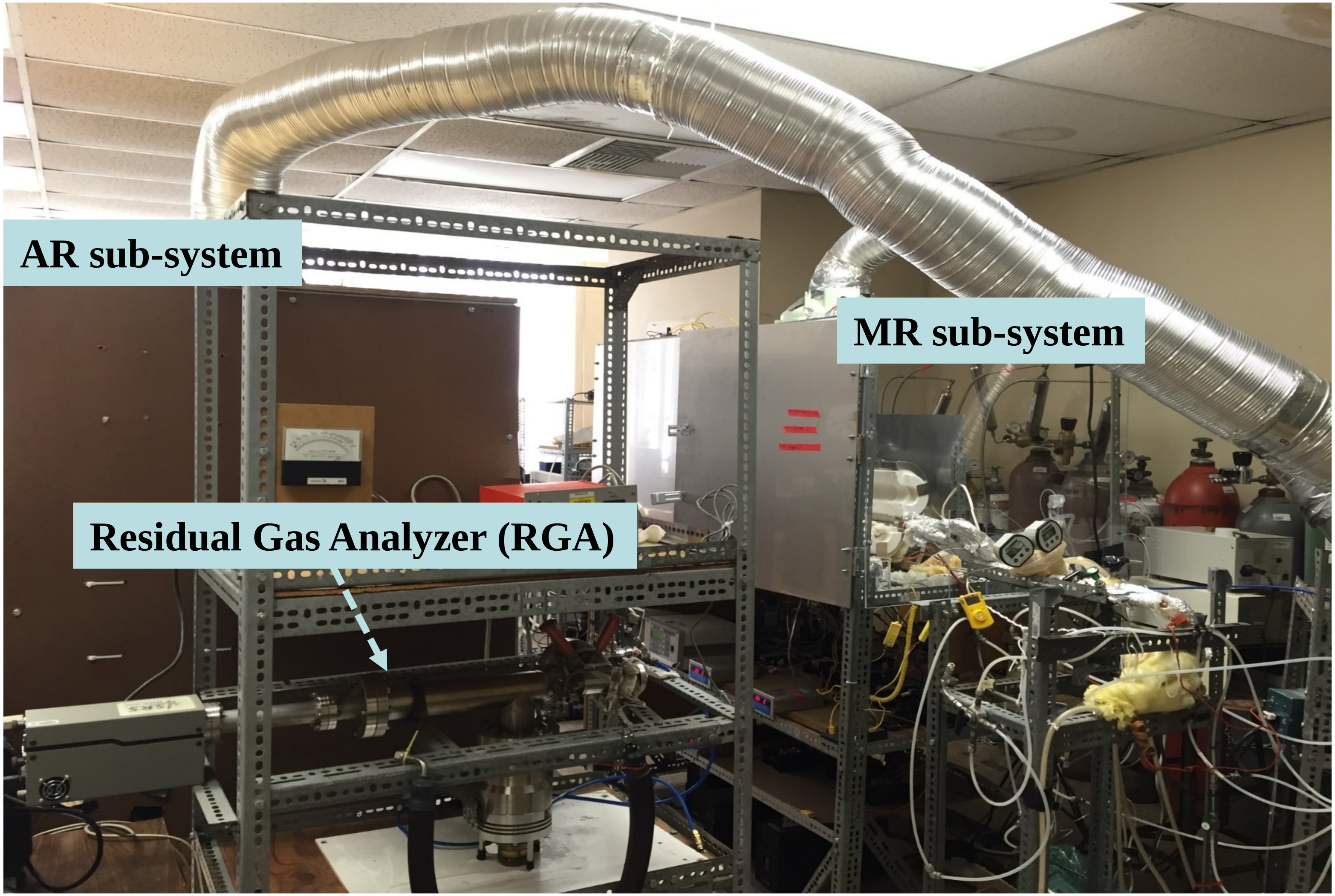
Progress and Current Status of Project, Cont'd

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



Progress and Current Status of Project, Cont'd

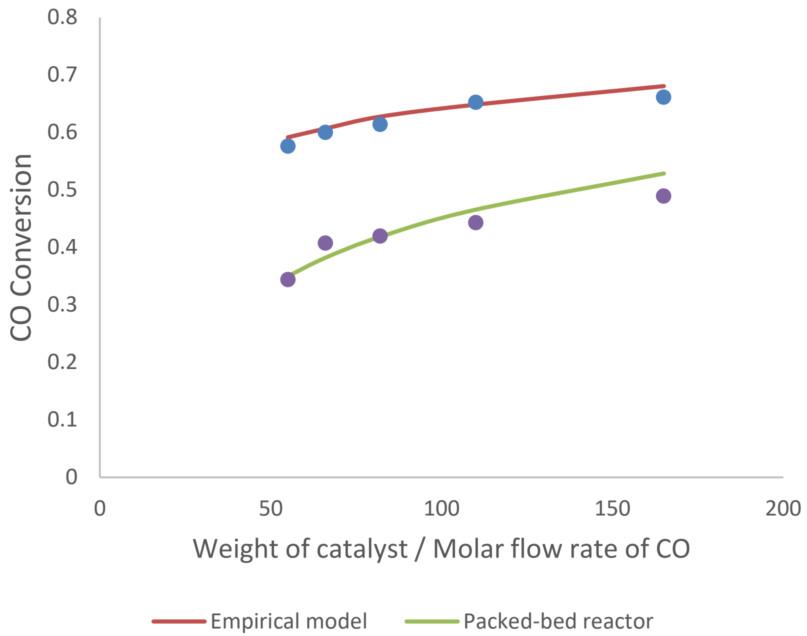
Design and Construction of Lab-Scale Experimental System



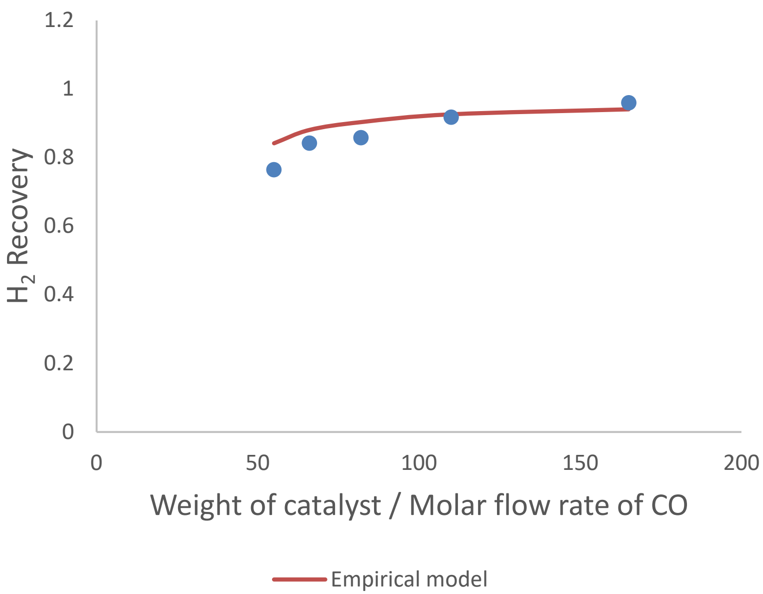
Progress and Current Status of Project, Cont'd

MR Sub-System Operation Testing

MR Perfomance – Membrane HMR-52 (10")
Reactor pressure = 14.5 bar, Reactor temperature = 250°C, H_2O:CO=1.1



MR Perfomance – Membrane HMR-52 (10")
Reactor pressure = 14.5 bar, Reactor temperature = 250°C, H_2O:CO=1.1

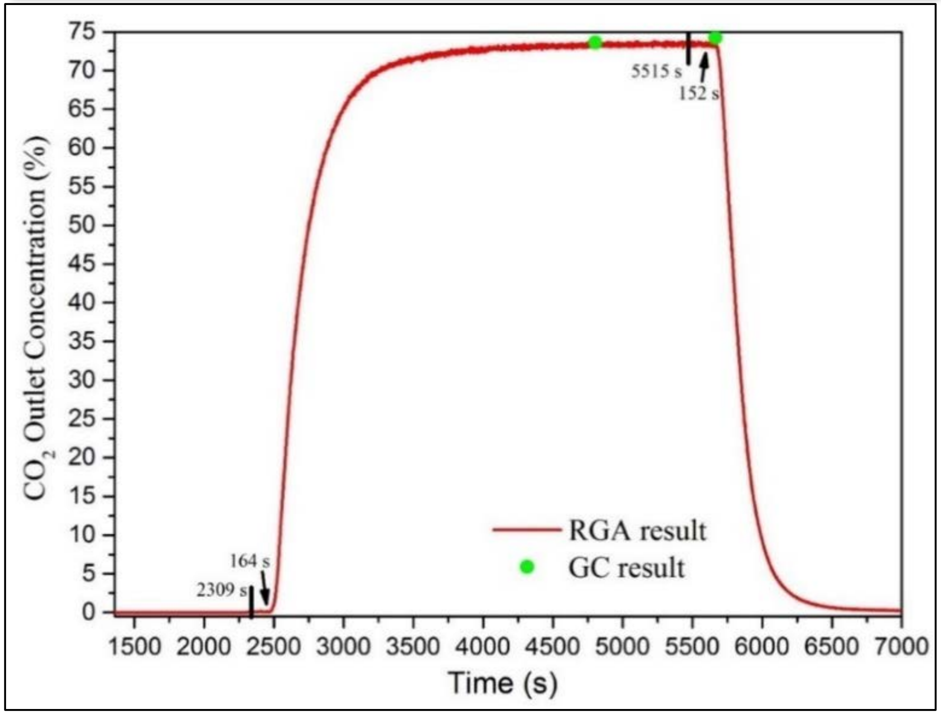


Progress and Current Status of Project, Cont'd

AR Sub-System Operation Testing

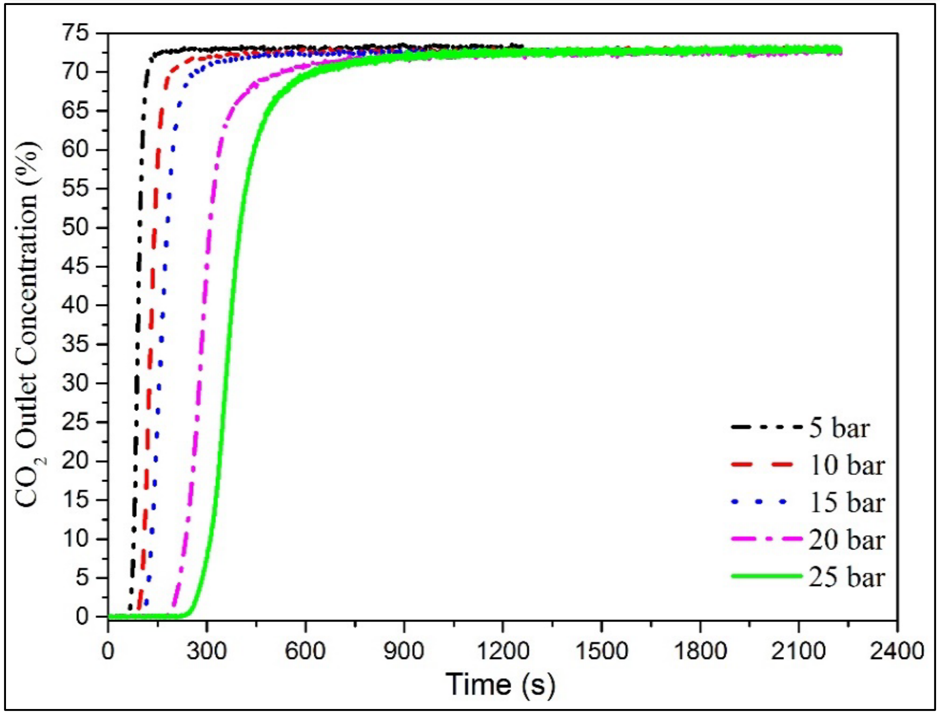
Empty Reactor Dynamics

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

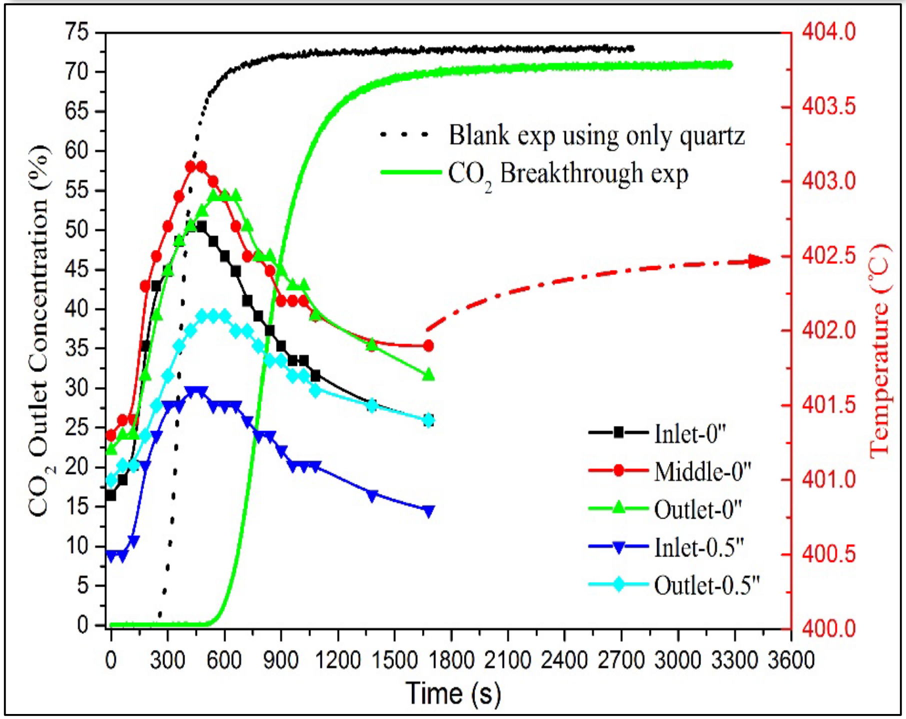


Progress and Current Status of Project, Cont'd

AR Sub-System Operation Testing

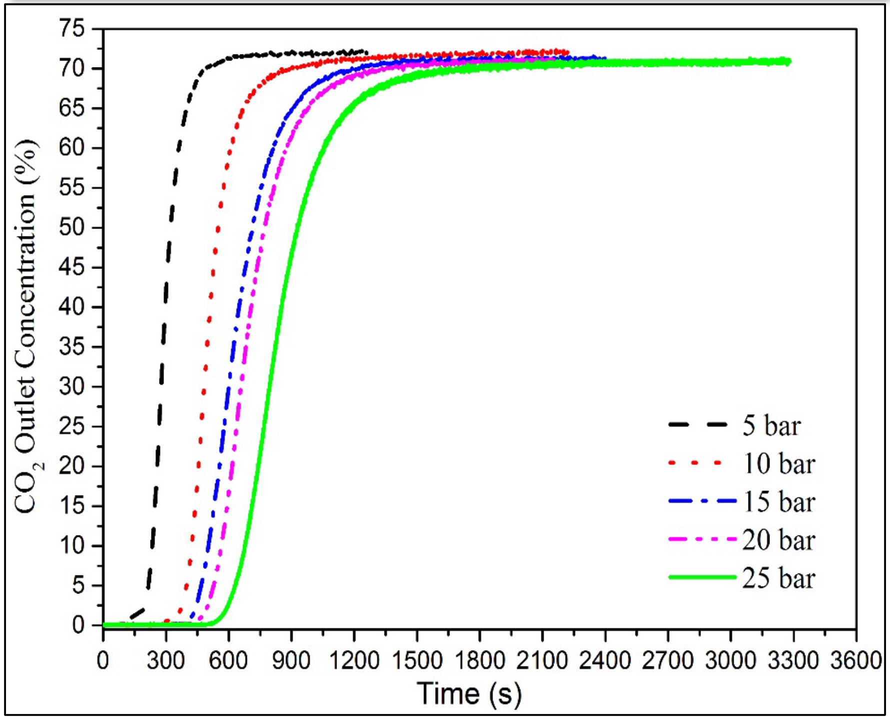
CO_2 Breakthrough Experiments

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

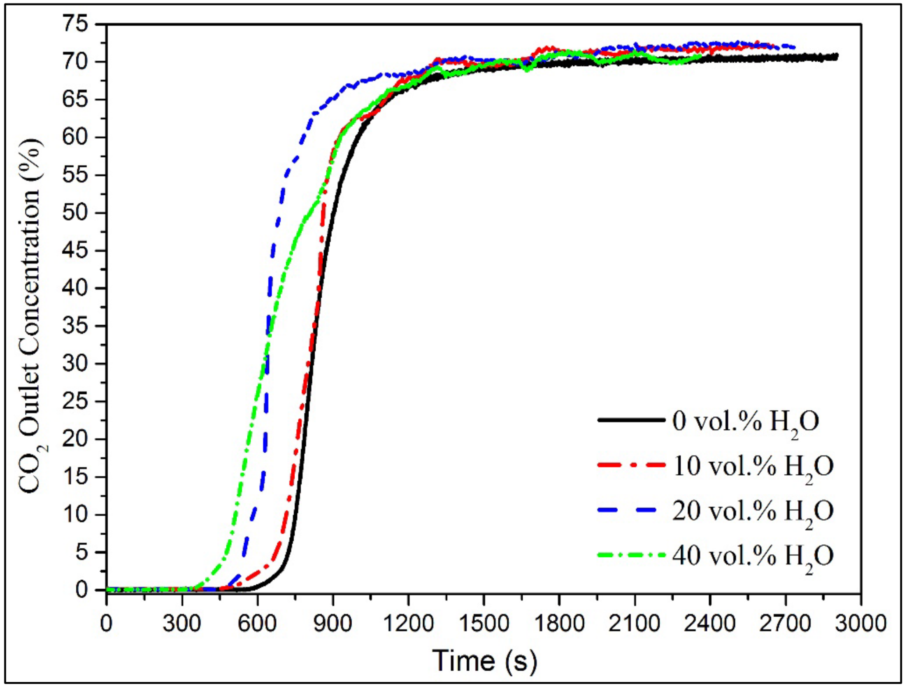


Progress and Current Status of Project, Cont'd

AR Sub-System Operation Testing

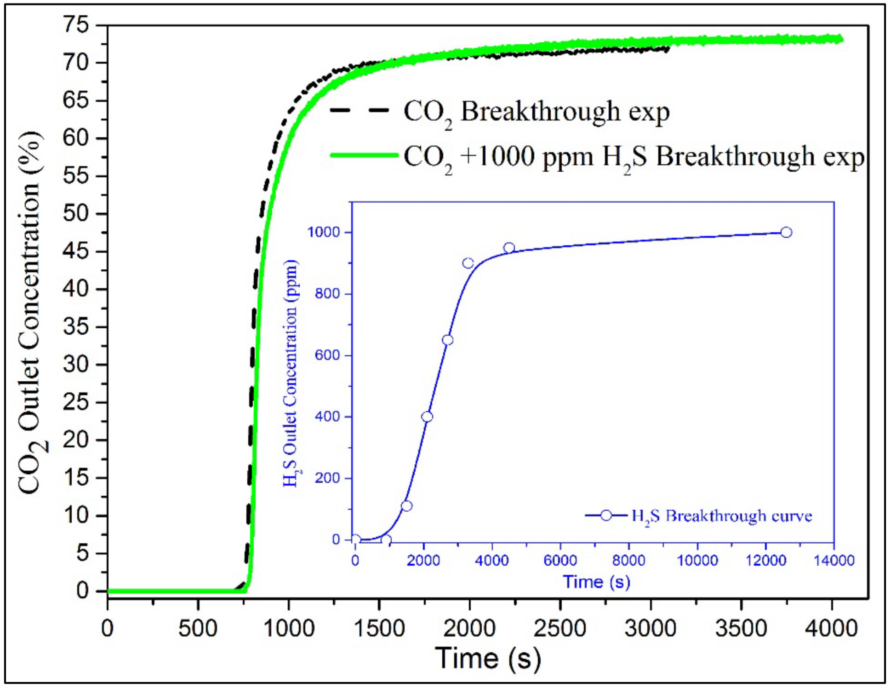
CO_2/ H_2O Breakthrough Experiments

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

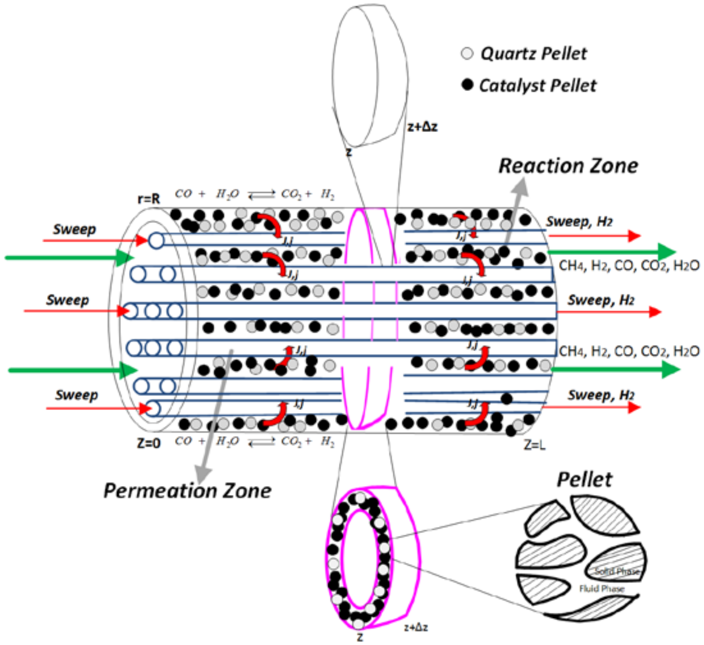
Reactor pressure = 25 bar, Oven temperature = 300°C, Total flow rate=500 sccm, H_2S concentration (0, 1000 ppm)



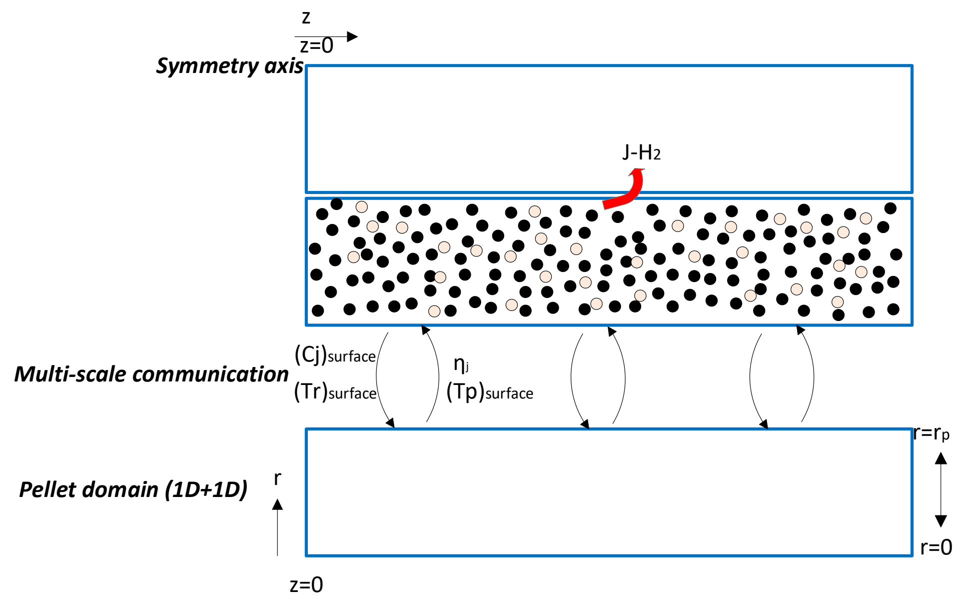
Progress and Current Status of Project, Cont'd

Membrane Reactor (MR) and Multi-scale Modeling Approach

Membrane Reactor Depiction



Multi-scale Modeling Approach



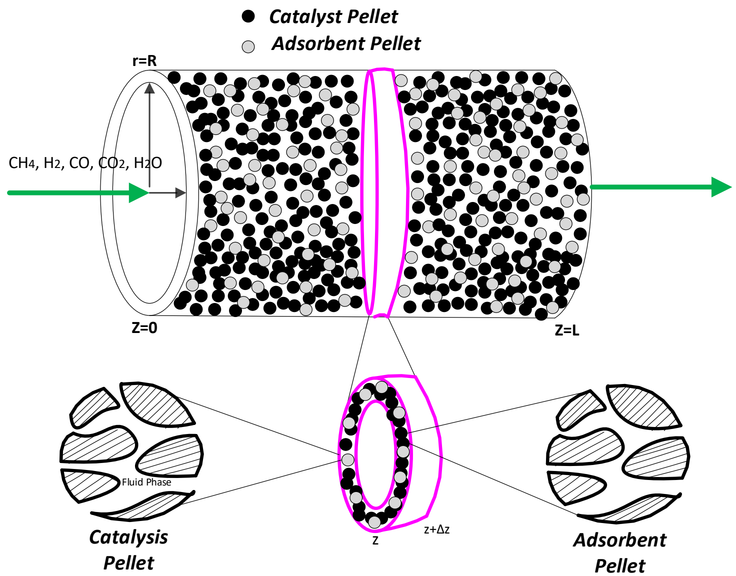
Advantages:

- ***In-situ removal of H_2 significantly enhances CO conversion and H_2 purity.***
- ***Eliminates the need for excess steam in the reaction.***
- ***Minimizes the need for downstream hydrogen purification.***
- ***Reduces the amount of catalyst for a desired conversion level.***
- ***Operates at lower reaction temperatures, reduces material costs, and increases operation safety.***

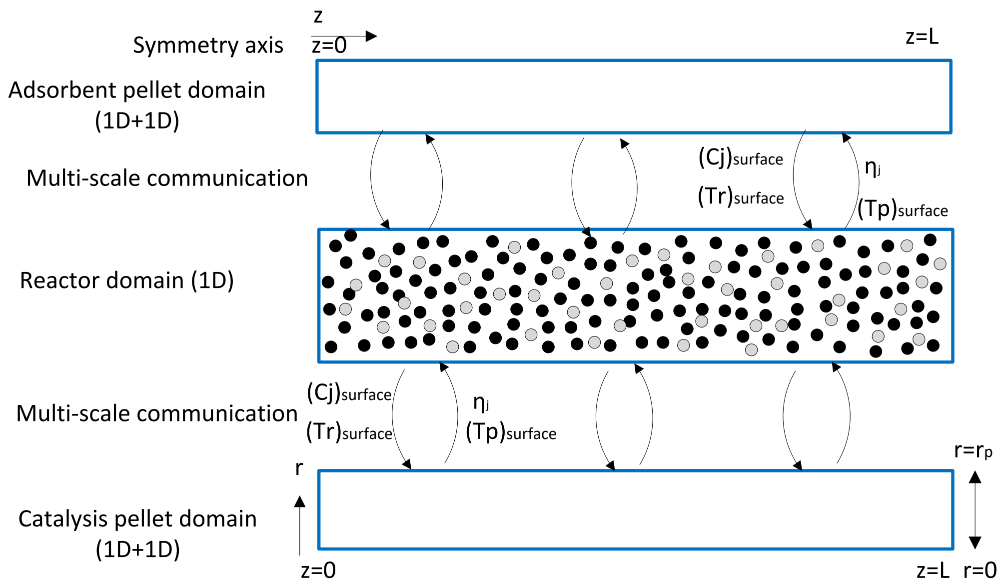
Progress and Current Status of Project, Cont'd

Adsorptive Reactor (AR) and Multi-scale Modeling Approach

Adsorptive Reactor Depiction



Multi-scale Modeling Approach



Advantages:

- ***In-situ removal of CO_2 significantly enhance CO conversion and CO_2 purity.***
- ***Eliminates the need for excess steam in the reaction.***
- ***Minimizes the need for downstream CO_2 purification.***
- ***Reduces the amount of catalyst for a desired conversion level.***
- ***Operates at lower reaction temperatures, reduces material costs, and increases operation safety.***

Progress and Current Status of Project, Cont'd

Multi-scale MR/AR Model: Catalyst/Adsorbent Pellet-scale

$$Operation = \begin{cases} steady-state \;\; if \; MR \\ dynamic \;\; if \;\; AR \end{cases}$$

$$Domain\ \alpha = \begin{cases} c & catalyst\ pellet\ \ if\ MR \\ c/a & catalyst/adsorbent\ pellet\ \ if\ AR \end{cases}$$

- ***Component mass conservation***
- ***Energy conservation***
- ***Diffusion Flux (Dusty Gas Model) DGM***

Progress and Current Status of Project, Cont'd

Multi-scale MR/AR Model: Reactor-scale, Reaction-domain

$$Operation = \left\{ \begin{array}{l} steady-state \;\; if \;\; MR \\ dynamic \;\; if \;\; AR \end{array} \right\}$$

$$Domain \; \alpha = \left\{ \begin{array}{ll} c & catalyst \; pellet \;\; if \; MR \\ c/a & catalyst/adsorbent \; pellet \;\; if \;\; AR \\ r & reaction \; zone \; if \; MR/AR \end{array} \right\}$$

- ***Component mass conservation***
- ***Energy conservation***
- ***Momentum conservation (Ergun Equation)***
- ***Diffusion Flux (Stefan-Maxwell Model) SMM***

Progress and Current Status of Project, Cont'd

Multi-scale MR Model: Reactor-scale, Permeation Zone

$$Operation = \{steady - state \;\; (MR)\}$$

$$Domain \;\; \alpha = \begin{Bmatrix} r & reaction \;\; zone \\ per & permeation \; zone \end{Bmatrix}$$

- ***Component mass conservation***
- ***Energy conservation***
- ***Momentum conservation***

Progress and Current Status of Project, Cont'd

Pseudo-homogeneous AR Model: Reactor-scale

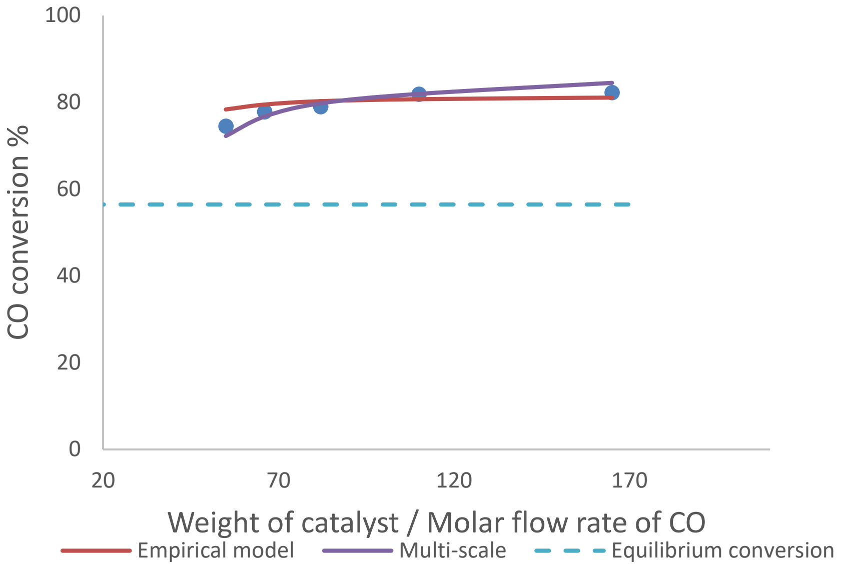
$$Operation = \{dynamic \ (AR)\}$$

$$Domain \ \alpha = \{r \qquad reaction \ zone\}$$

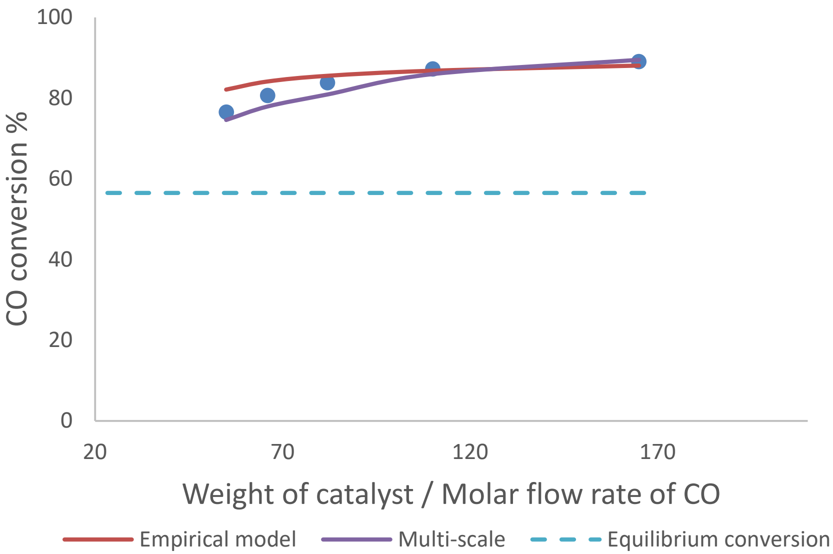
- ***Component mass conservation***
- ***Energy conservation***
- ***Momentum conservation***

Progress and Current Status of Project, Cont'd

Membrane Reactor Model Experimental Validation



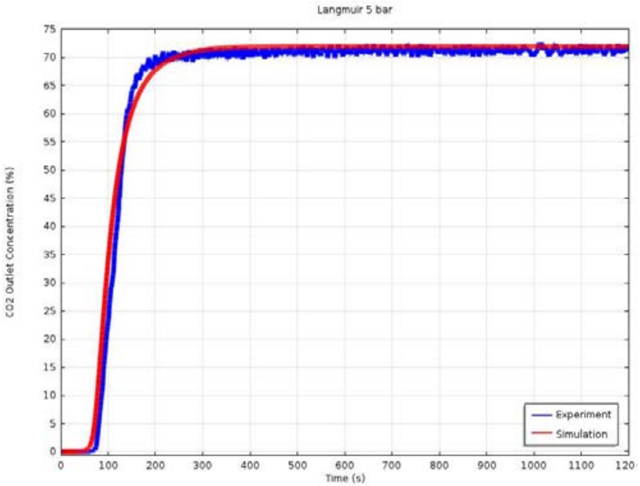
Conversion vs. W/F_{CO} for MR (feed pressure 14.1 bar, reactor temperature 300ºC, sweep ratio = 0.1).



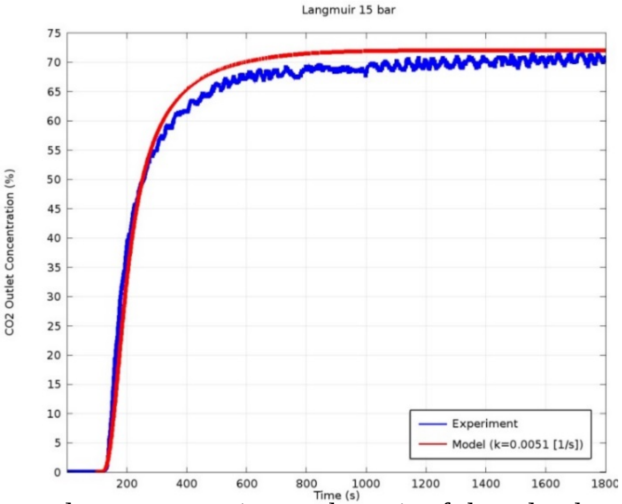
Conversion vs. W/F_{CO} for MR (feed pressure 14.1 bar, reactor temperature 300ºC, sweep ratio = 0.3).

Progress and Current Status of Project, Cont'd

Adsorptive Separator (AS) Model Experimental Validation

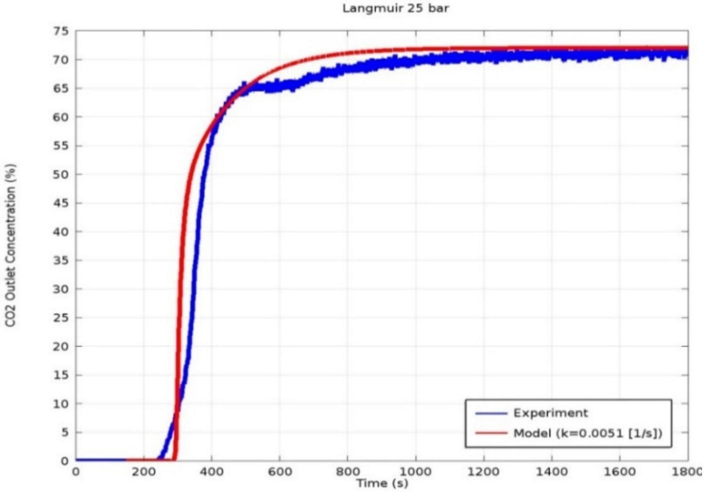


CO_2 outlet concentration at the exit of the adsorber (Experiment vs. Simulation). Temp.= 523.15 K, Pressure = 5 bar.



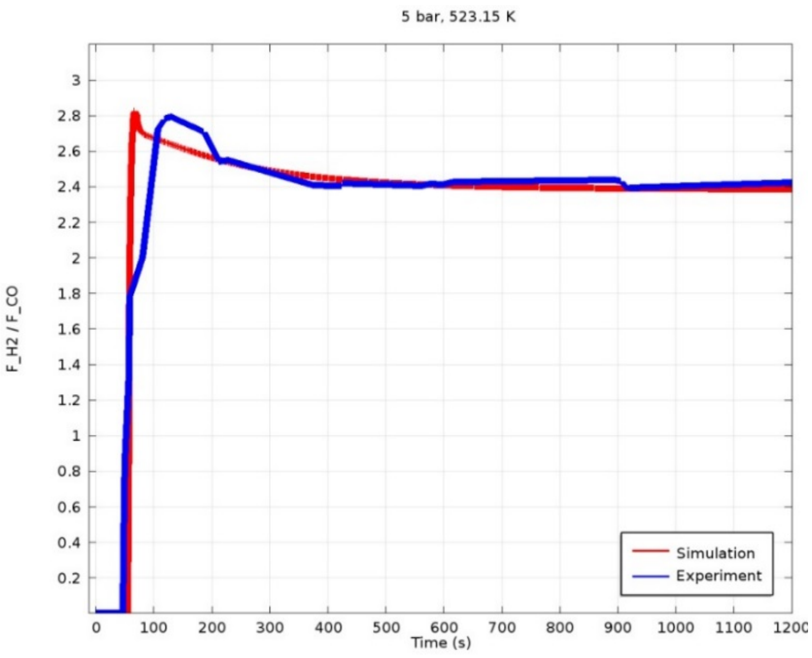
CO_2 outlet concentration at the exit of the adsorber (Experiment vs. Simulation). Temp.= 523.15 K, Pressure = 15 bar.

CO_2 outlet concentration at the exit of the adsorber (Experiment vs. Simulation). Temp.= 523.15 K, Pressure = 25 bar.



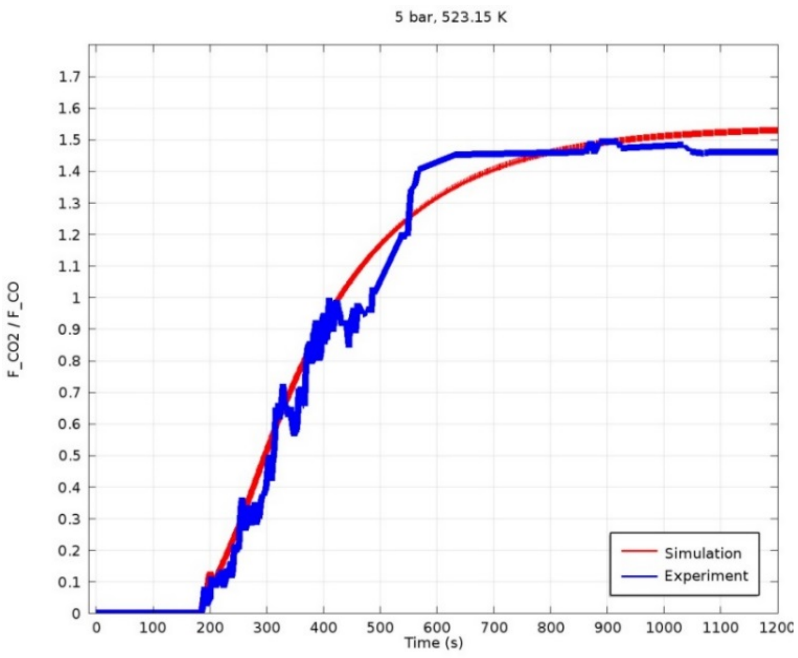
Progress and Current Status of Project, Cont'd

Adsorptive Reactor (AR) Model Experimental Validation



Molar ratio of H_2/CO at the AR outlet.

(Experiment vs. Simulation).

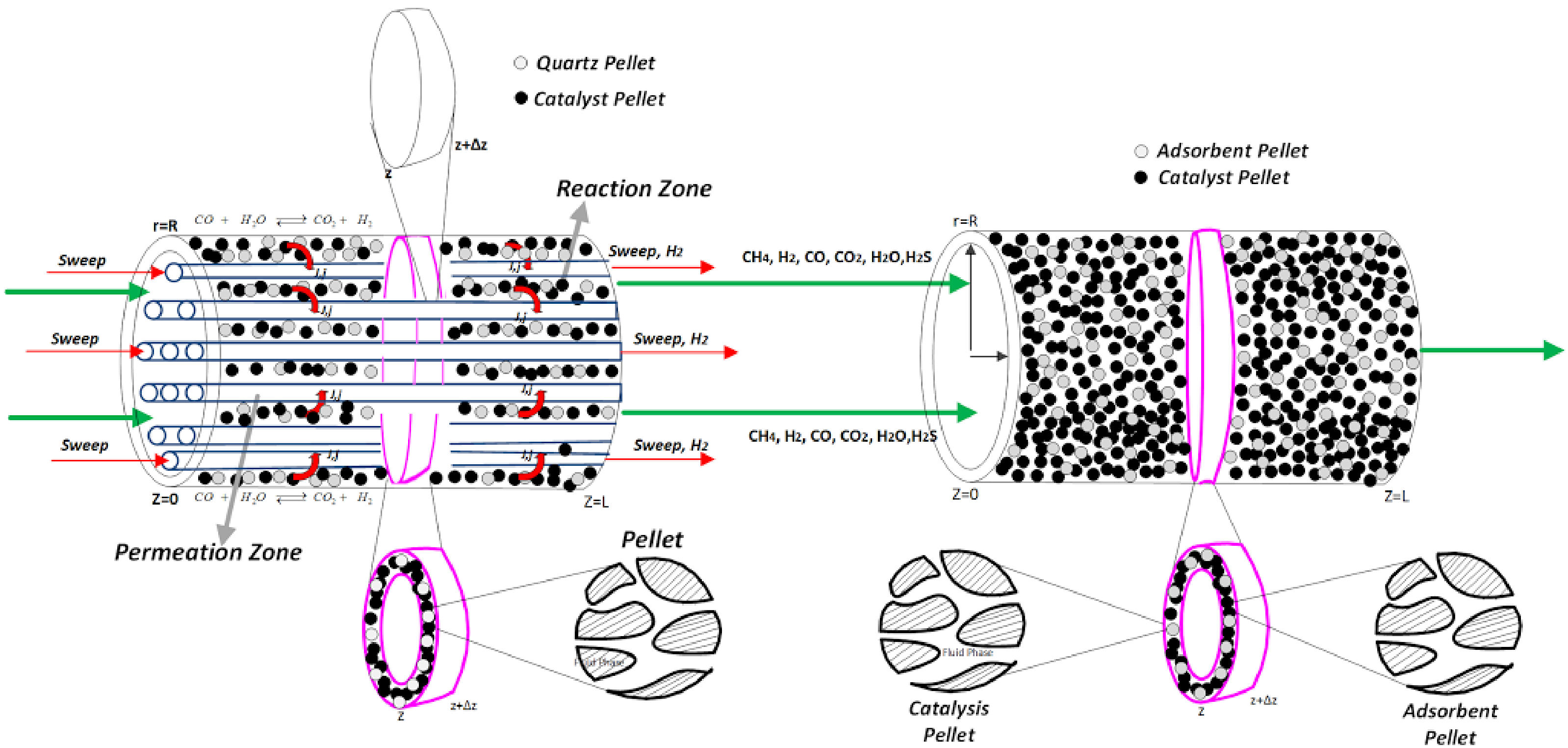


Molar ratio of CO_2/CO at the AR outlet.

(Experiment vs Simulation).

Progress and Current Status of Project, Cont'd

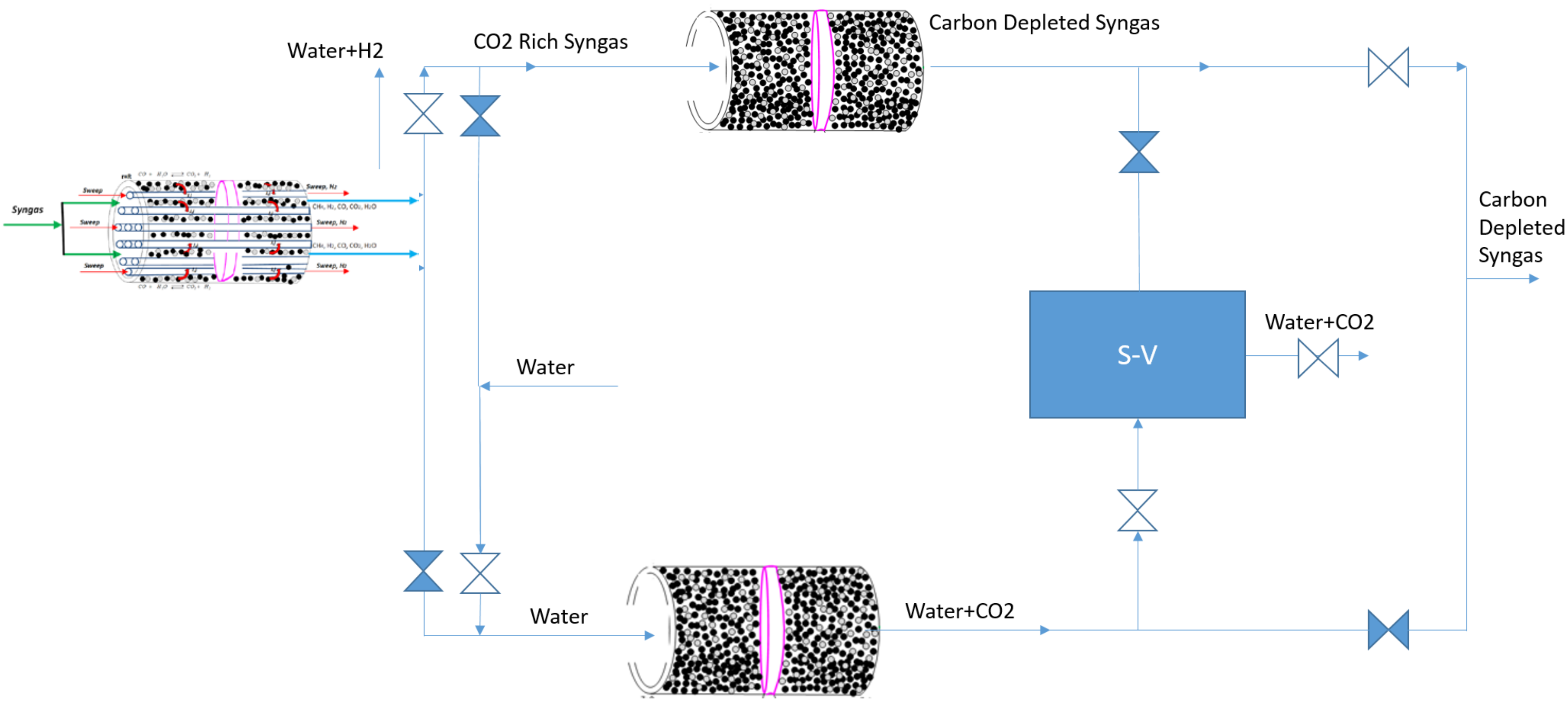
Membrane Reactor/Adsorptive Reactor Process



Combined MR + AR System

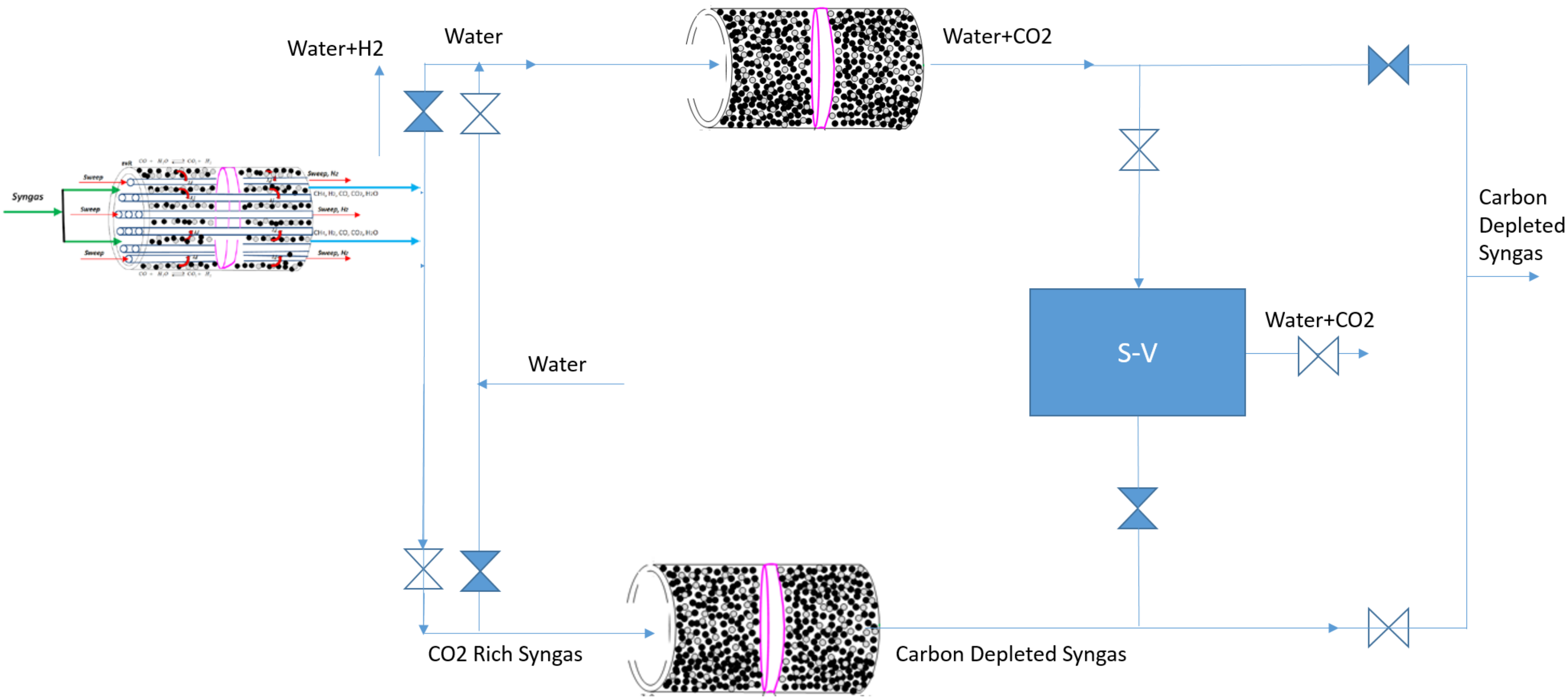
Progress and Current Status of Project, Cont'd

Membrane Reactor/Adsorptive Reactor Process



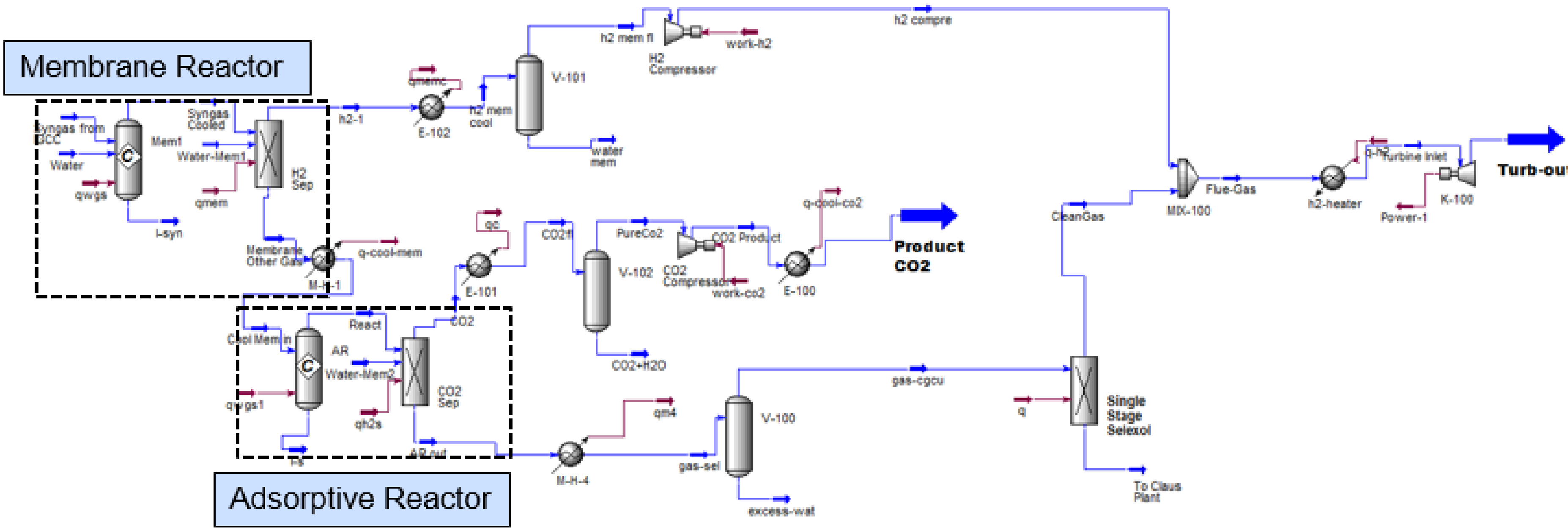
Progress and Current Status of Project, Cont'd

Membrane Reactor/Adsorptive Reactor Process



Progress and Current Status of Project, Cont’d

Proposed Process Scheme – UNISIM Implementation



Progress and Current Status of Project, Cont'd

Membrane Reactor Components

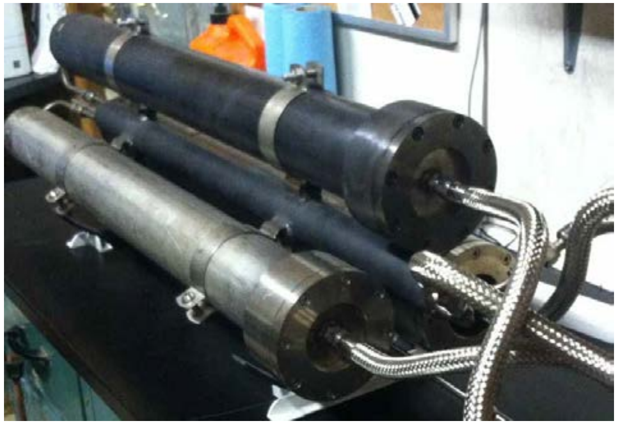
Membrane Reactors are composed of several components

- Ceramic membrane tubes
- Bundles typically containing 85-100 ceramic membrane tubes
- Pressure Vessel typically containing 1500-3000 bundles

Ceramic Tube

Bundle

Pressure Vessel



Progress and Current Status of Project, Cont'd

Membrane Reactor Operating Modes

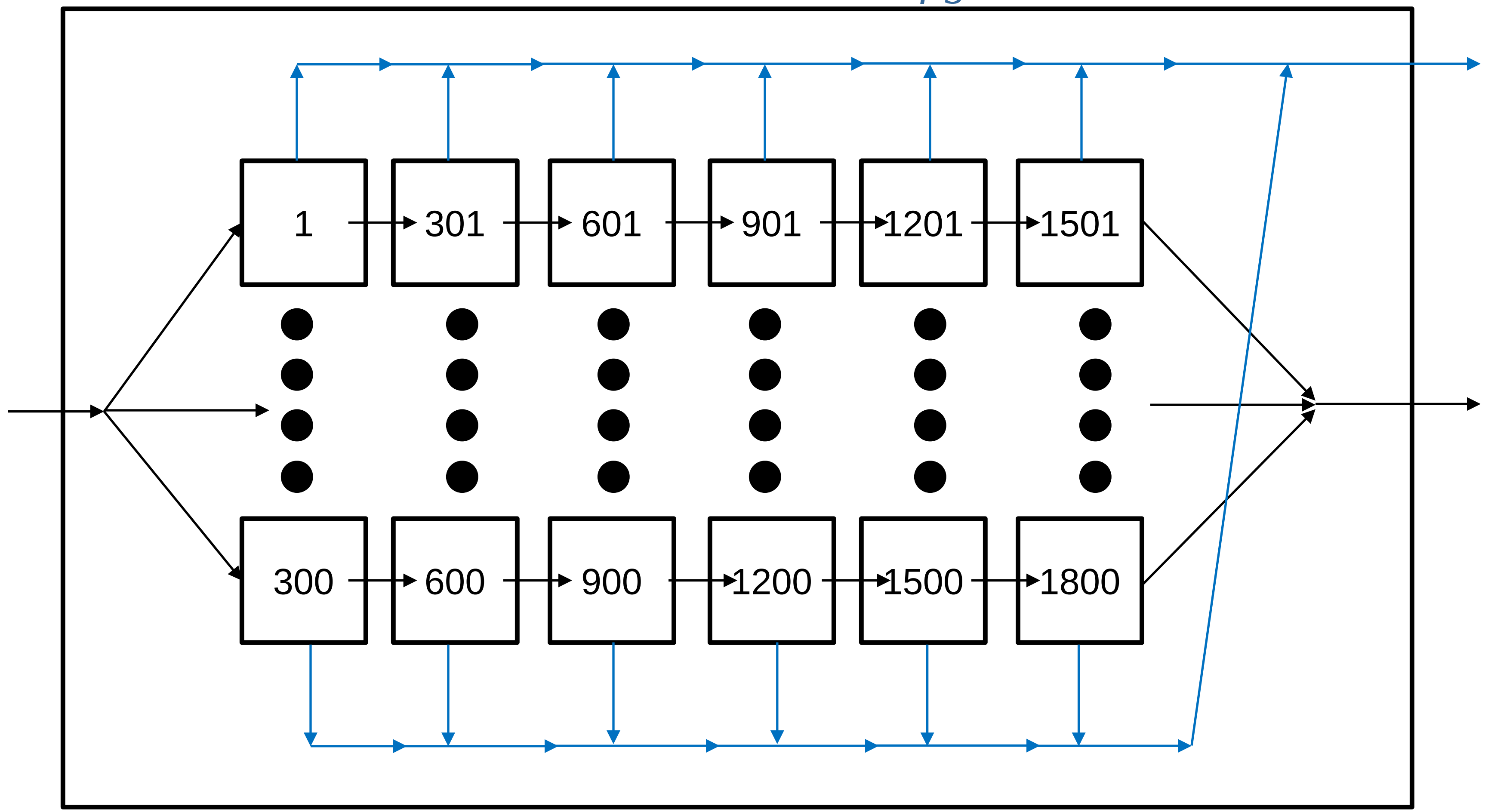
- Membrane tube inner/outer flow pattern
  - Countercurrent
  - Co-current
- Bundle configuration in Pressure Vessels
  - Bundles in series
  - Bundles in parallel
  - Bundles networked

Membrane Reactor Operating Mode Used in TEA:

- Membrane tubes are operated countercurrently
- Bundles are configured in 300 parallel bundle series, each of which consists of 6 bundles

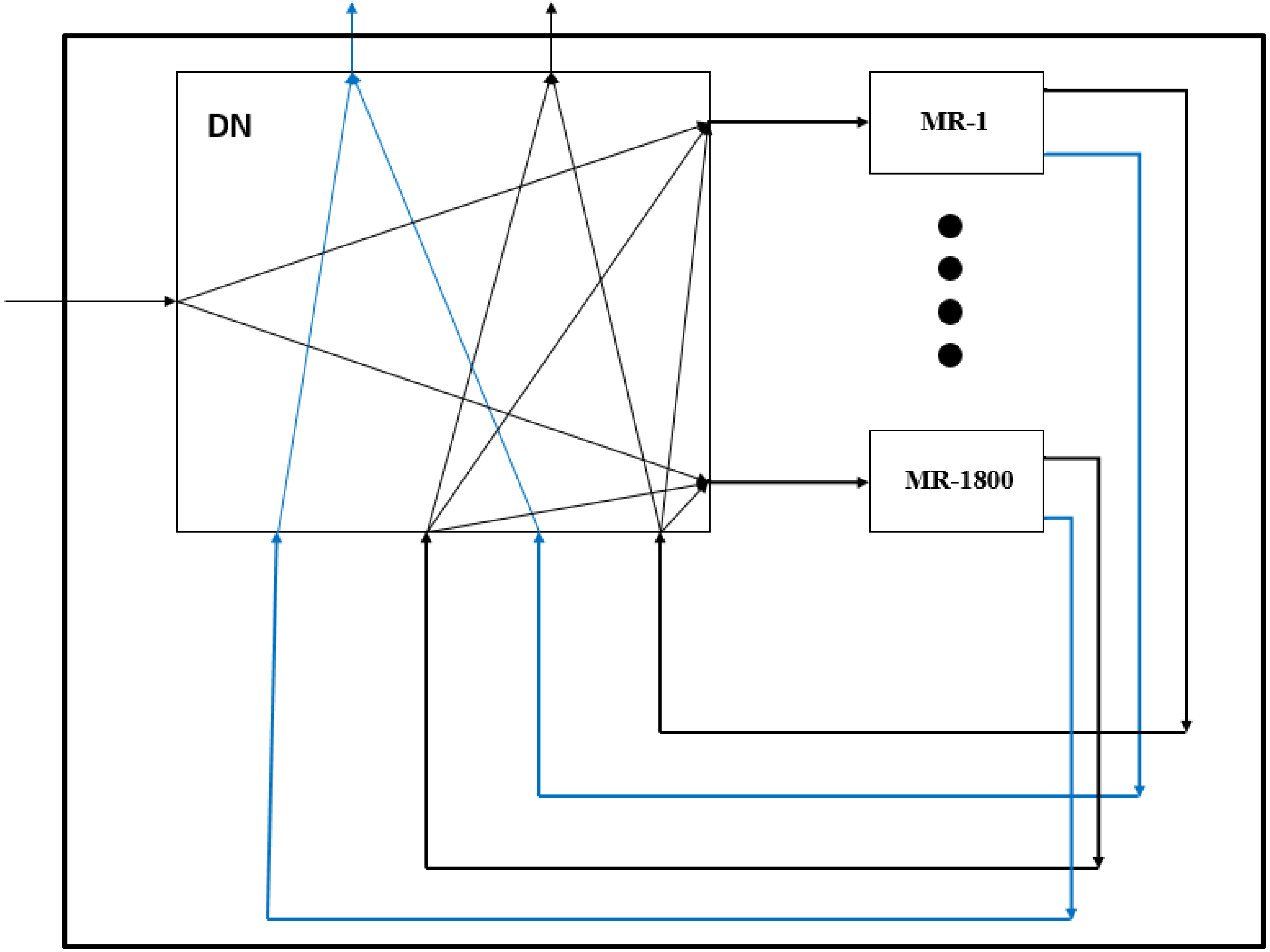
Progress and Current Status of Project, Cont'd

Membrane Reactor Vessel: Configuration 1



Progress and Current Status of Project, Cont'd

Membrane Reactor Vessel: Configuration 2



Progress and Current Status of Project, Cont'd

Preliminary Technical-Economic Analysis (TEA) for MR-AR Technology (NETL Case Study)

Designs	Net Power Production (MWe)	CO_2 Capture (%)
Shell IGCC w/o CCS – 1-Stage Selexol	622	0
Shell IGCC w/ CCS– 2 Stage Selexol	543	90
MR-AR IGCC Plant	566	93.5

Progress and Current Status of Project, Cont'd

Preliminary Technical-Economic Analysis (TEA) for MR-AR Technology (NETL Case Study)

	Conversion	Catalyst Amount (ft^3)	Adsorbent (kg)	Water Input (kmol/hr)
MR-AR Combined System	98%	2,800	3830,000	0 (no excess water need be inputted)
IGCC WGS Reactor	97%	6,200	0	7,200

	% CO Conversion	% H_2 Purity	% H_2 Recovery	% CO_2 Purity	% CO_2 Recovery
Target	>95	>95	>90	>95	>90
MR-AR Realization	98.2	95.6	99	99.7	93.5

Progress and Current Status of Project, Cont'd

MR-AR Process Advantages

- ***Simultaneous CO conversion and H_2 and CO_2 separation***
- ***MR-AR Compression Work:*** <20% of IGCC w/ CCS compression work
- ***Catalyst Amount*:** <50% of IGCC w/ CCS catalyst amount
- ***High Purity Hydrogen Produced:*** *95.6% Hydrogen Purity*

Progress and Current Status of Project, Cont'd

Summary of Technical Accomplishments To Date

- Completed the construction of the lab-scale MR-AR experimental system.
- Prepared and characterized CMS membranes at the anticipated process conditions.
- Prepared and characterized adsorbents at the anticipated process conditions, and generated global rate expressions for the catalyst.
- Began testing of the individual MR and AR subsystems.
- Developed mathematical models and began validating their ability to fit the experimental data.

Progress and Current Status of Project, Cont'd

Future Plans

Budget Period 2 (BP2):

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.

Acknowledgements

Financial support by US Department of Energy

(DE-FOA-0001235 FE0026423)

and the technical guidance and assistance of our

Project Manager Andrew Jones

are gratefully acknowledged.