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

DE-FOA-0001235

•Professor Theo Tsotsis, University of Southern California, Los Angeles, CA
•Professor Vasilios Manousiouthakis, University of California, Los Angeles, CA
•Dr. Rich Ciora, Media and Process Technology Inc., Pittsburgh, PA

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

<u>Performance Period</u>: 10-01-2015 – 9-31-2018

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

<u>Overall Project Objectives</u>:

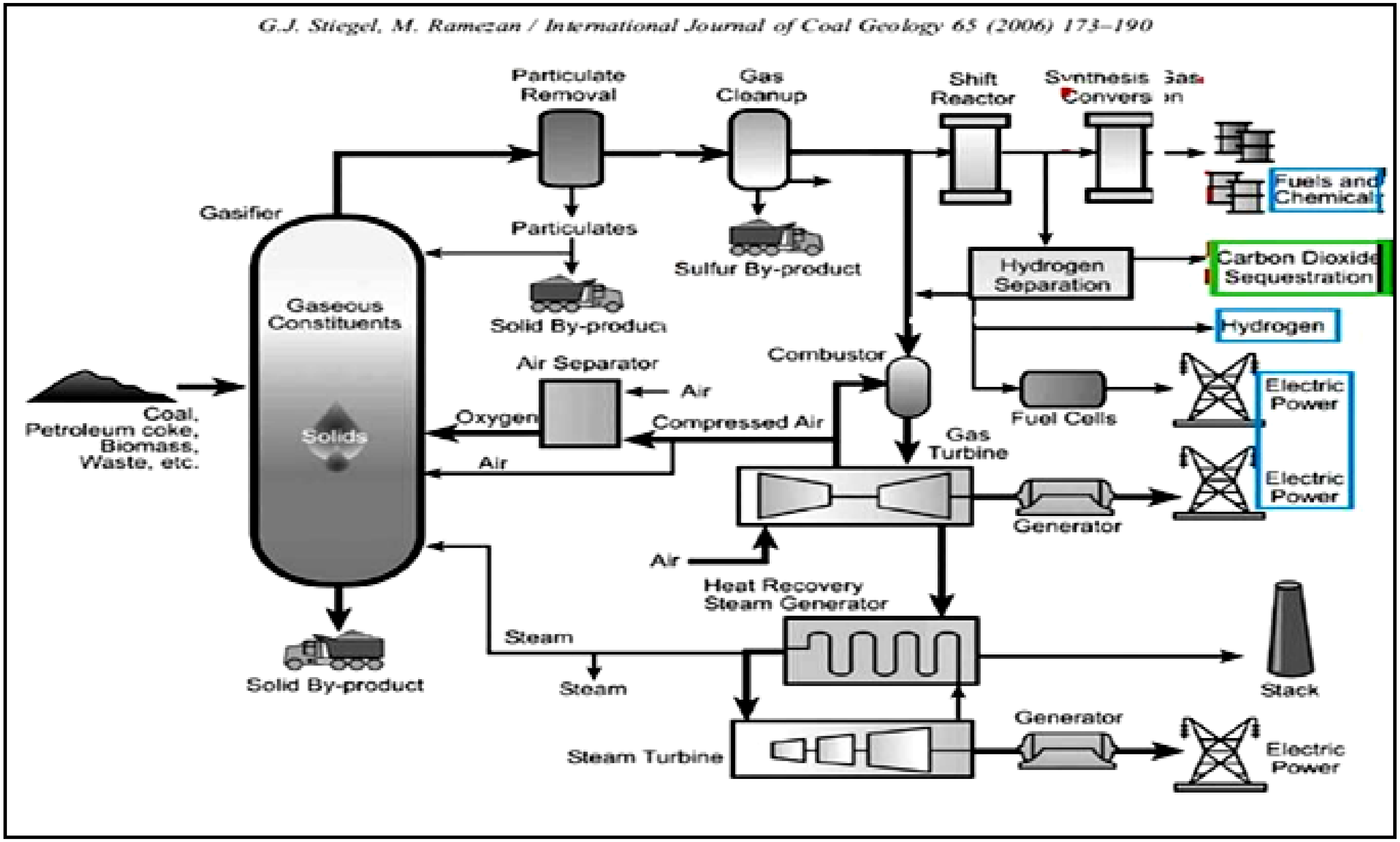
1. *Prove the technical feasibility of the membrane- and adsorption-enhanced water gas shift (WGS) process.*
2. *Achieve the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity of 30% less than baseline capture approaches.*

<u>Key Project Tasks/Participants</u>:

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***

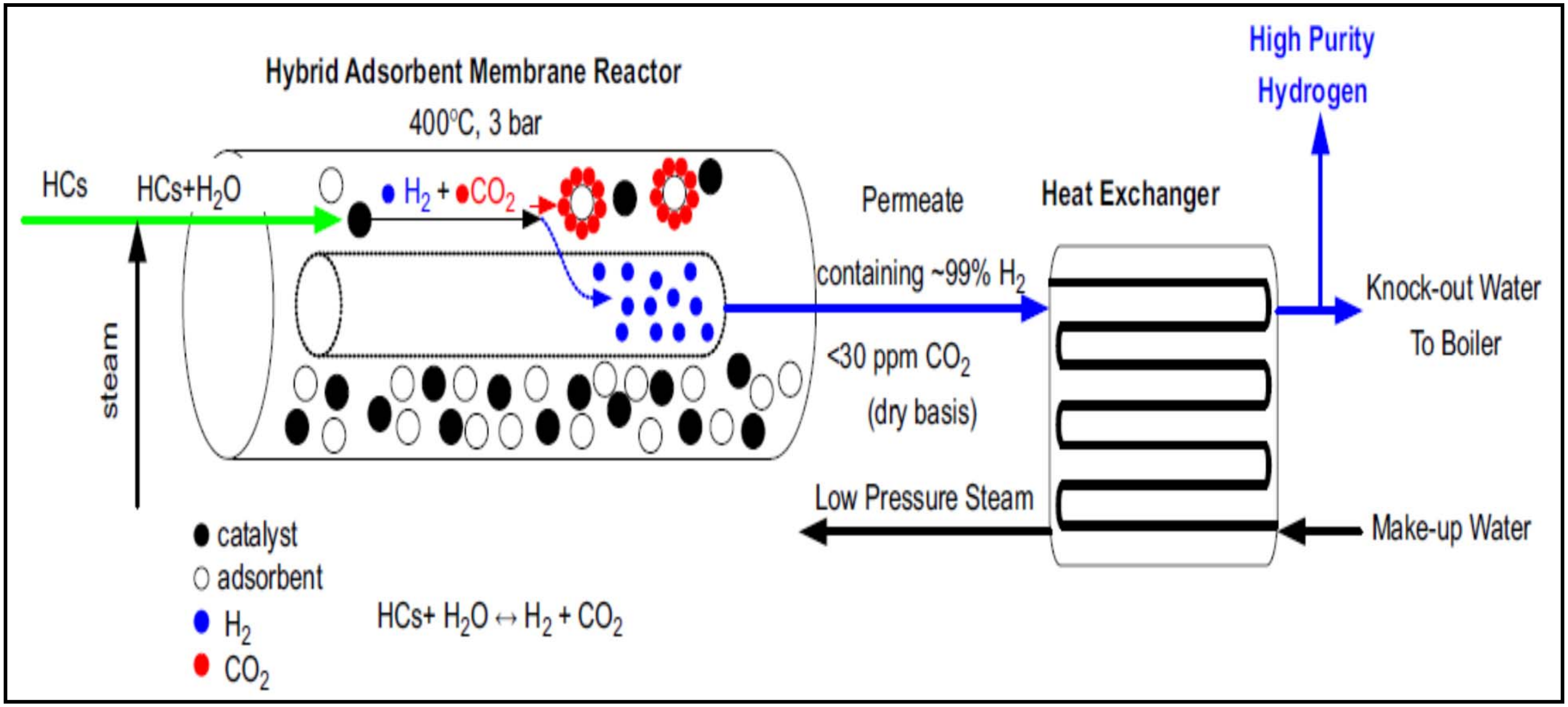
Technology Background

Conventional IGCC Power Plant



Technology Background, cont.

Hybrid Adsorbent Membrane Reactor (HAMR)



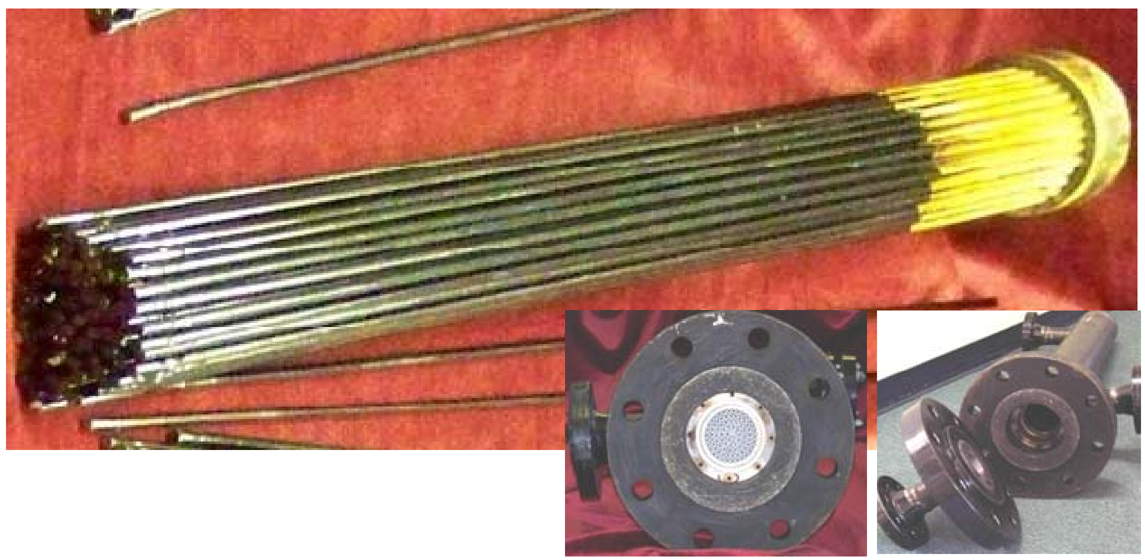
- The HAMR combines adsorbent, catalyst and membrane functions in the same unit. Previously tested for methane steam reforming (MSR) and the WGS reaction.
- The simultaneous in situ removal of H_2 and CO_2 from the reactor significantly enhances reactor yield and H_2 purity. CO_2 stream ready for sequestration.

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

<u>Hydrotalcite Adsorbent:</u>

- *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.%.*

<u>Co/Mo-Based Sour Shift Catalyst:</u>

- *A 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.

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.*

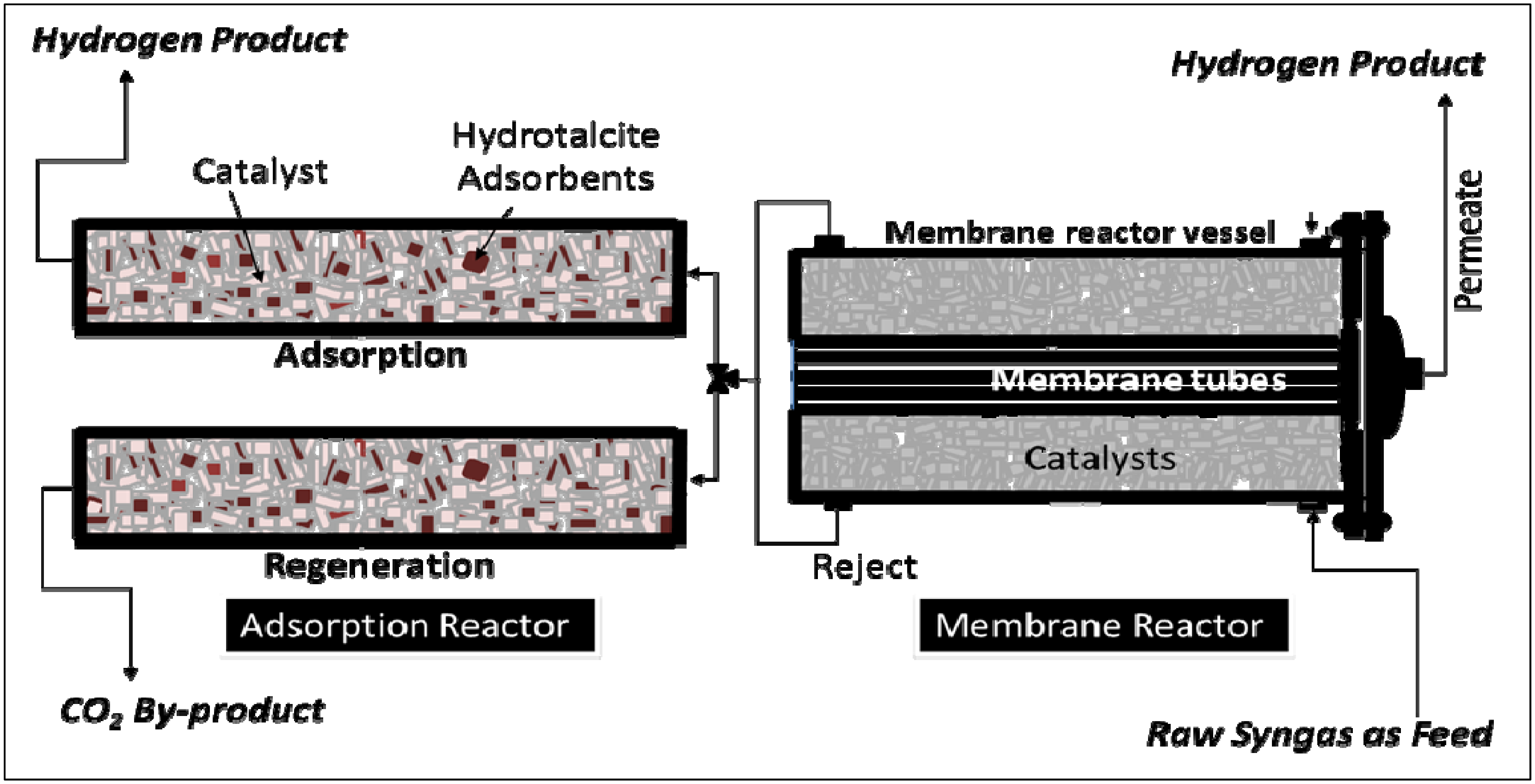
Technology Background, cont.

Key Technical Objectives and Focus in 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.*
- *Complete the construction of the 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 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

	Start Date	End Date	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
			Budget Period 1 10 1 2015 - 3 31 2017						Budget Period 2 4 1 2017 - 9 30 2018					
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 Modeling 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 –BP1

Title/Description	Planned Completion Date	Actual Completion Date	Verification Method	Comments (progress for achieving milestone, explanation from deviation, etc.)
Updated PMP submitted	10/31/2015	10/29/2015	PMP document	Milestone achieved
Kick-off meeting convened	12/31/2015	11/16/2015	Presentation file/report documents	Milestone achieved
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	Milestone achieved
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	Milestone achieved
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	Milestone achieved
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	This milestone is >80% achieved. To be completely achieved by 3/31/2017
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	This milestone is >80% achieved. To be completely achieved by 3/31/2017
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	This milestone is >90% achieved. To be completely achieved by 3/31/2017

Technical Approach/Project Scope, cont.

Project Success Criteria –BP1

Success Criteria for BP1	Status/Comments
Successful completion of all work proposed in Budget Period 1 (up to 12/31/2016).	Achieved
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). Target range for H_2 permeance 1-1.5 m^3/m^2.hr.bar; Target range for H_2/CO selectivity 80-100	Achieved, see Table 5 for IDs of Parts meeting the targets in H_2 permeance and H_2/CO selectivity
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%	Achieved for Mg-Al-CO_3 LDH with a Mg:Al ratio of 3:1 (working capacity 9.61 wt% at 17.5 bar)/Measurement of catalytic kinetics continuing until 3/31/2017.
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.	Achieved/Experimental studies of AR and MR individual units continuing until 3/31/2017
Completion of simulations of the MR-AR system that indicate its ability to meet the targets for CO conversion >95%, for H_2 purity >95%, for H_2 recovery >90%, for CO_2 purity >95%, for CO_2 recovery >90%.	Achieved (see Table 26)

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

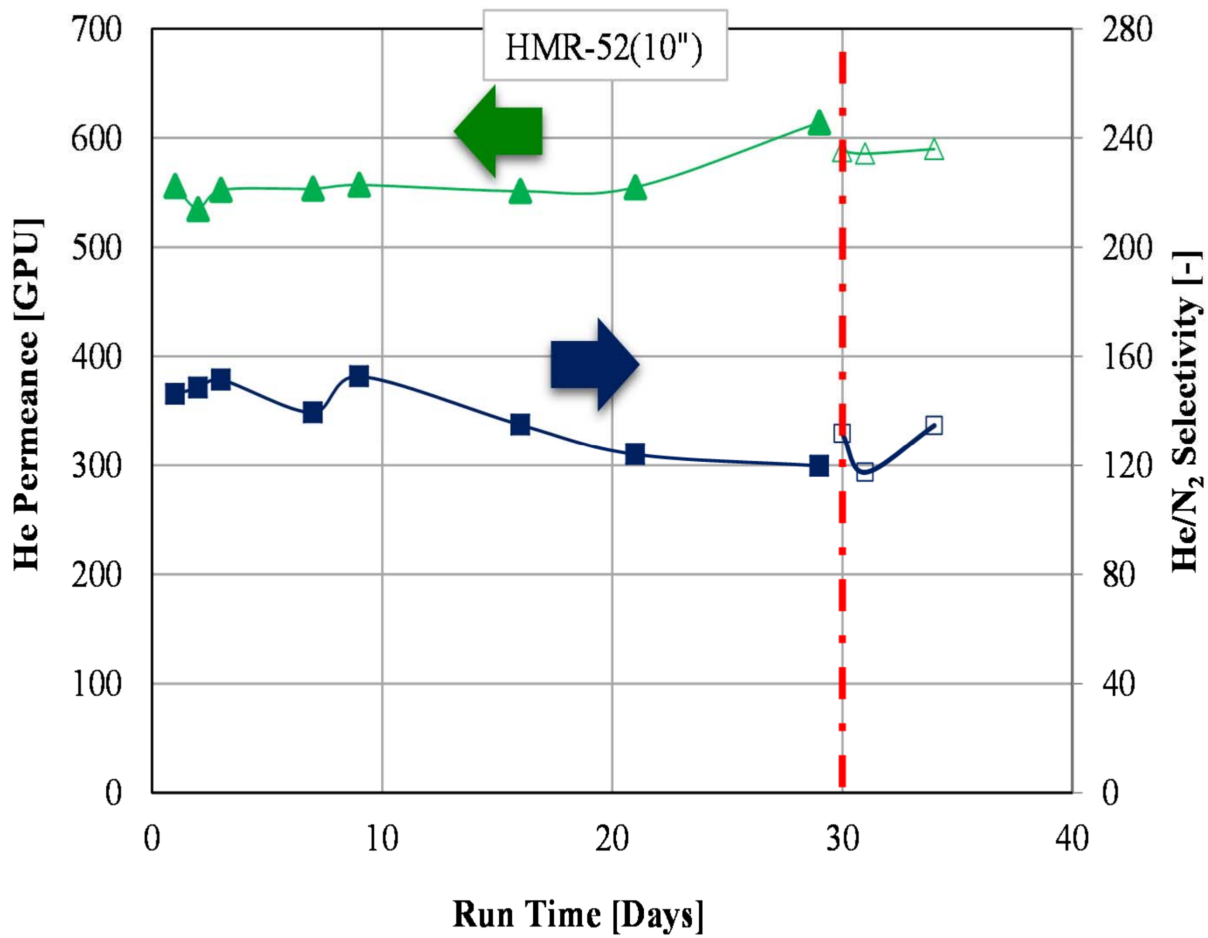
Performance of Selected CMS Membranes at 250^{o}C

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.

Materials Preparation and Characterization

Carbon Molecular Sieve Membrane Preparation & Characterization
Long-Term Stability Testing

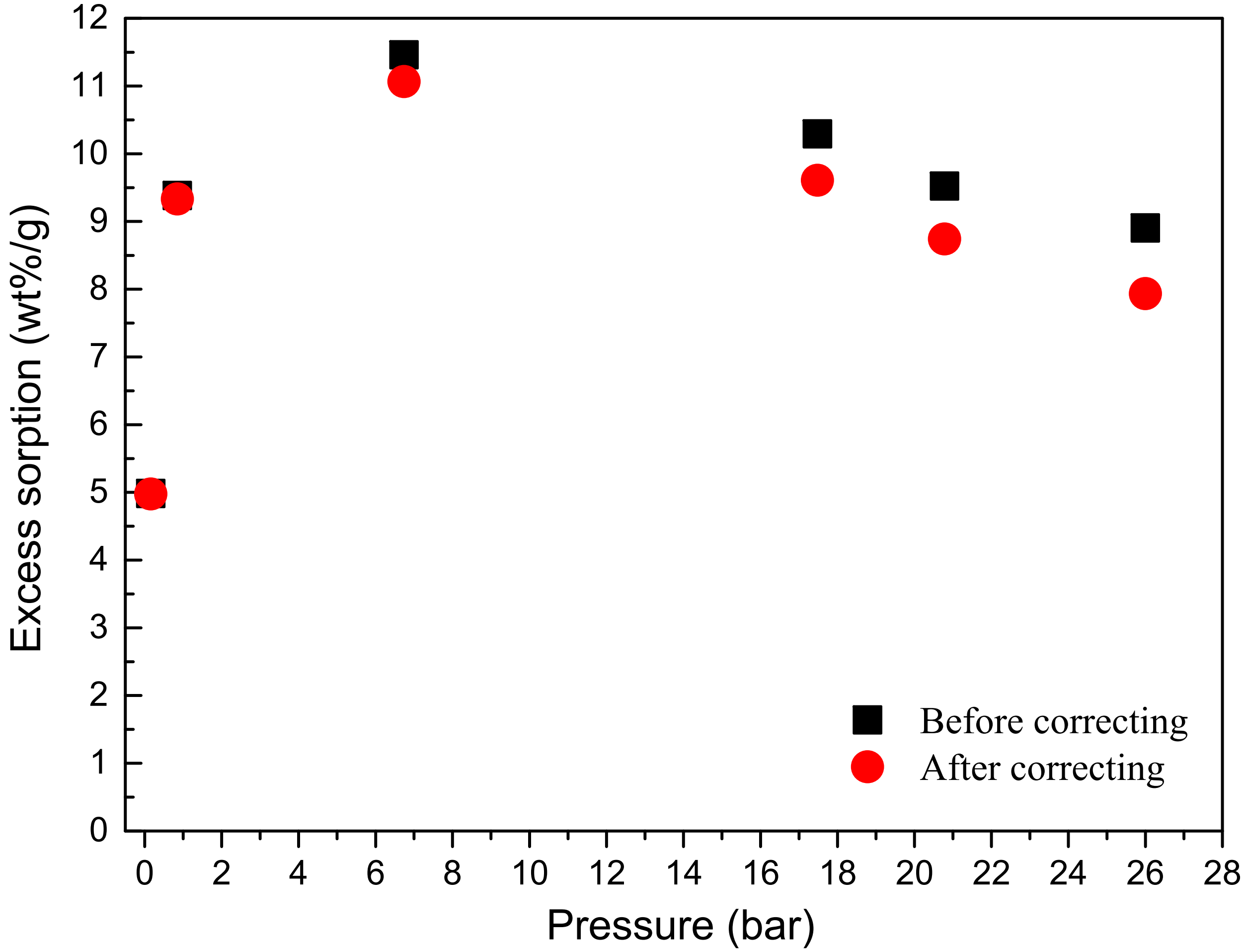


Progress and Current Status of Project, cont.

Materials Preparation and Characterization

Hydrotalcite Materials Preparation and Characterization

High-Pressure Adsorption Isotherm at 250°C

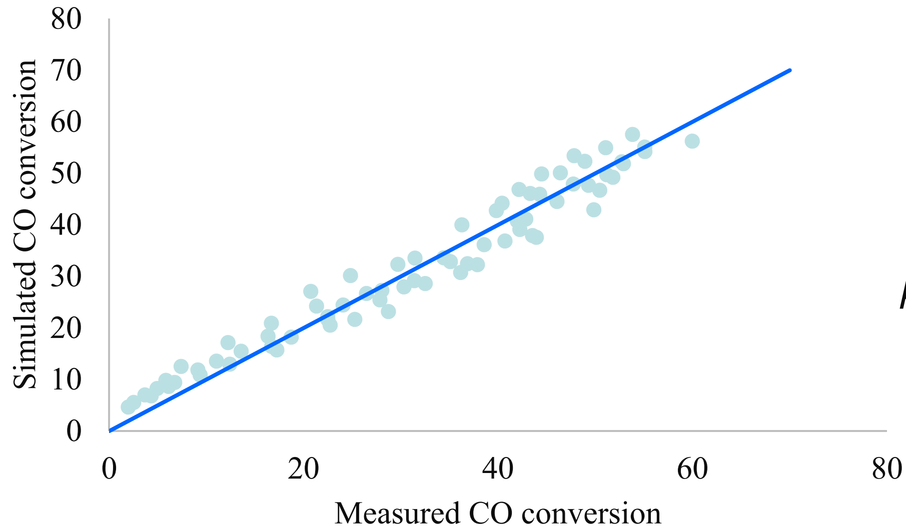


Progress and Current Status of Project, cont.

Materials Preparation and Characterization

Co-Mo/Al_2O_3 Sour-Shift Catalyst Characterization

Global Reaction Kinetics- Empirical Model and Comparison with Microkinetc Models



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

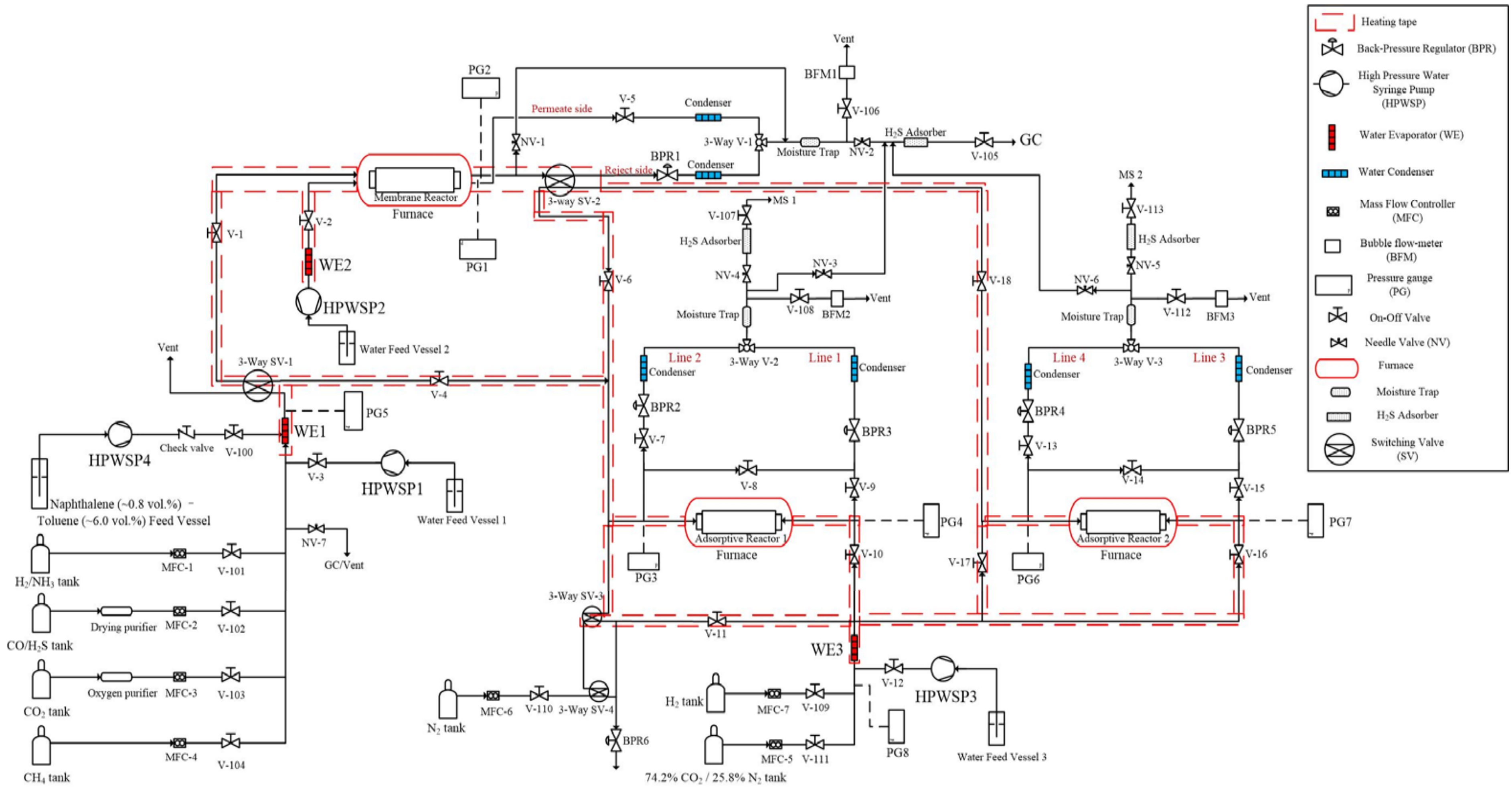
$$\beta = \frac{1}{K_{eq}} \frac{(P_{CO_2} . P_{H_2})}{(P_{CO} . P_{H_2O})} \quad K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

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

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

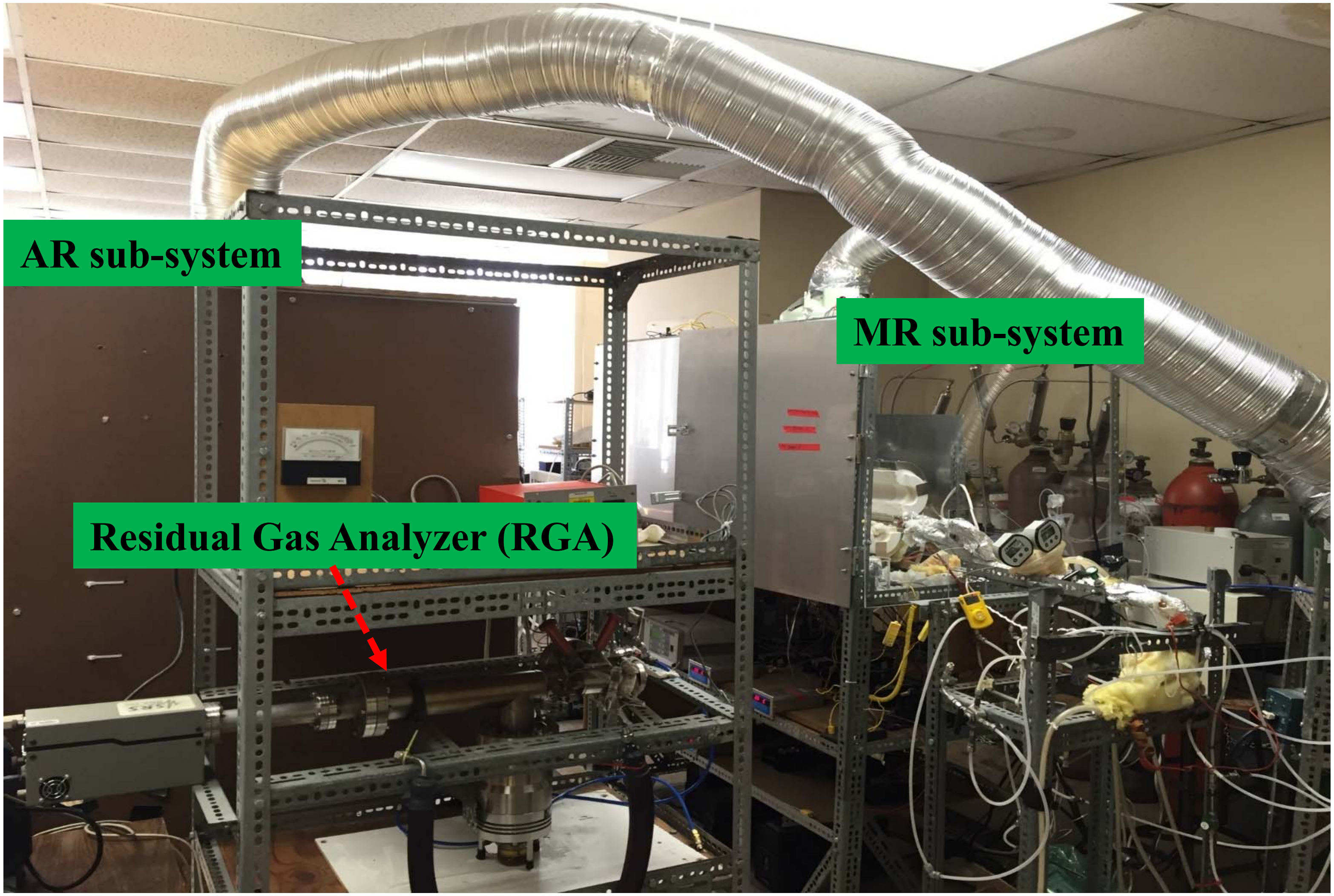
Progress and Current Status of Project, cont.

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



Progress and Current Status of Project, cont.

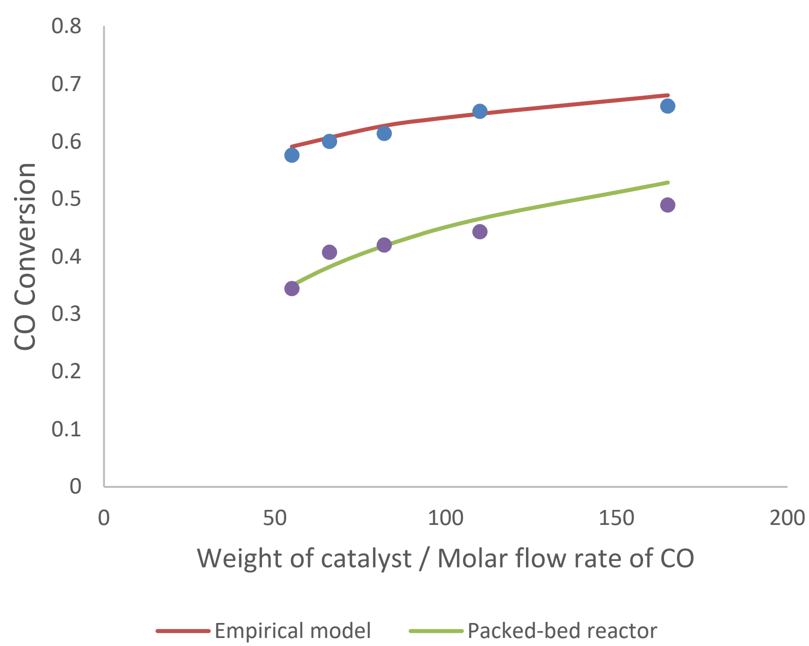
Design and Construction of the Lab-Scale Experimental System



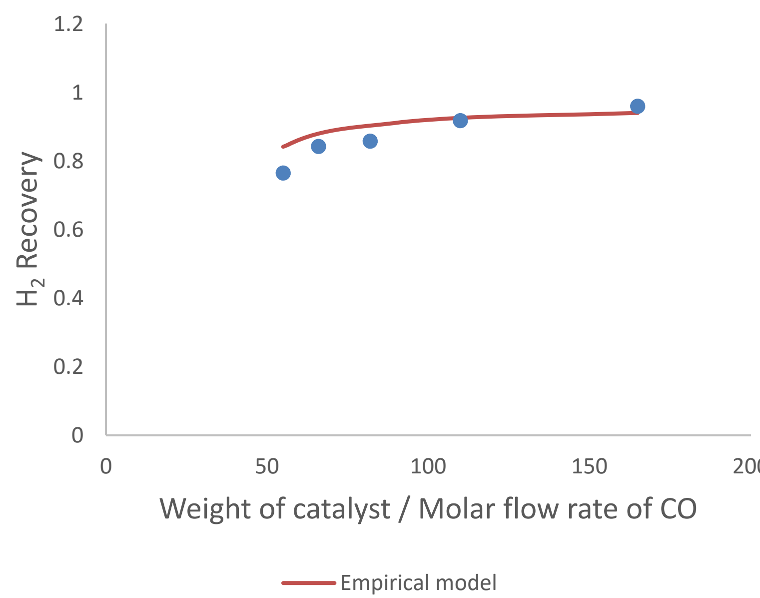
Progress and Current Status of Project, cont.

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

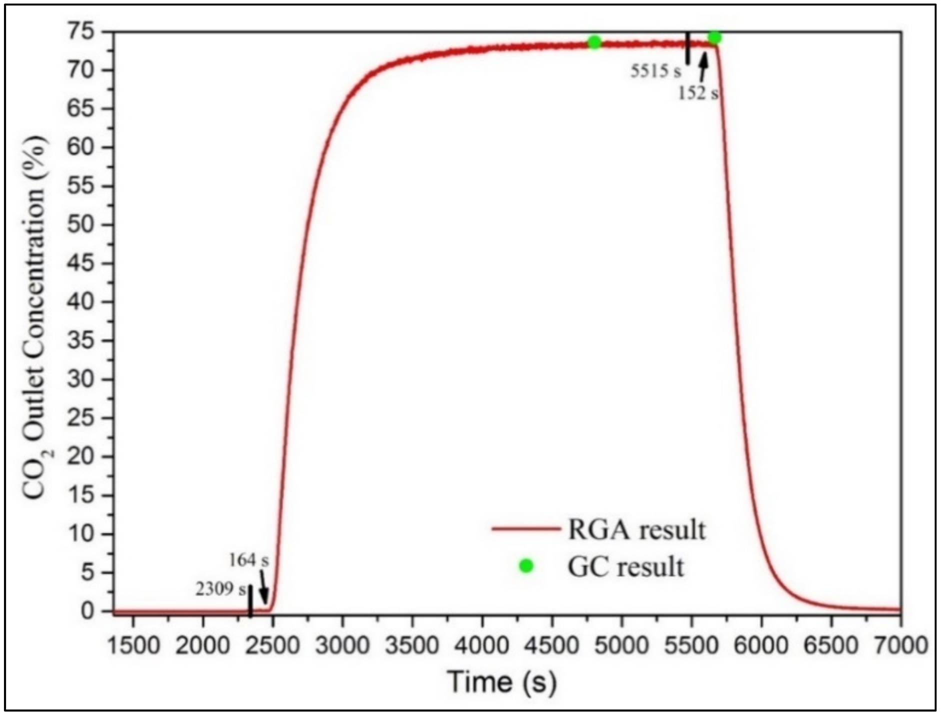


Progress and Current Status of Project, cont.

AR Sub-System Operation Testing

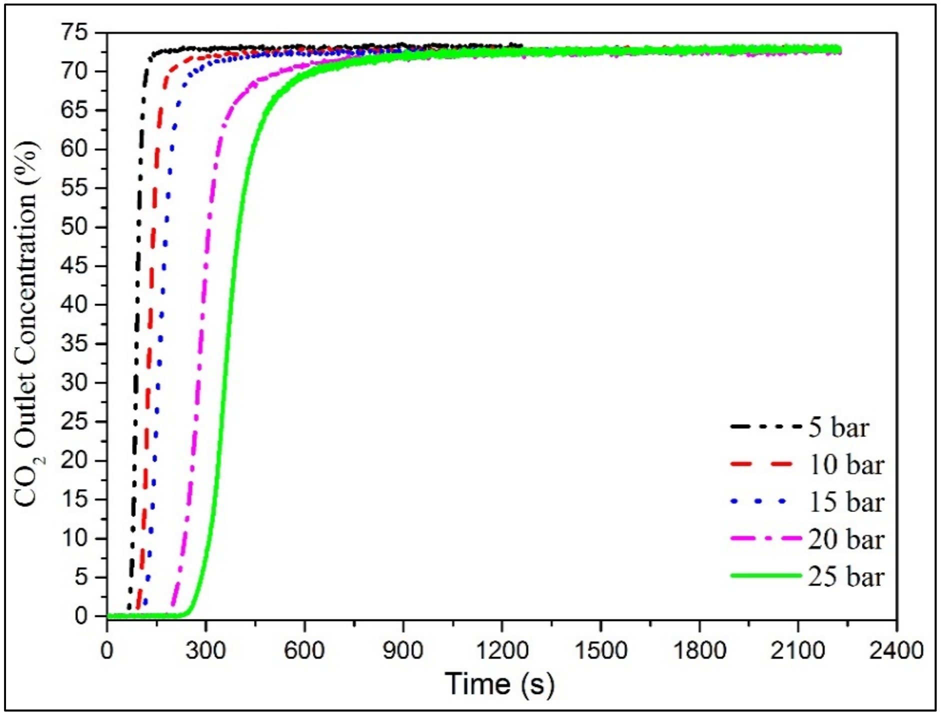
Empty Reactor Dynamics

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



Blank Experiments Using only Quartz

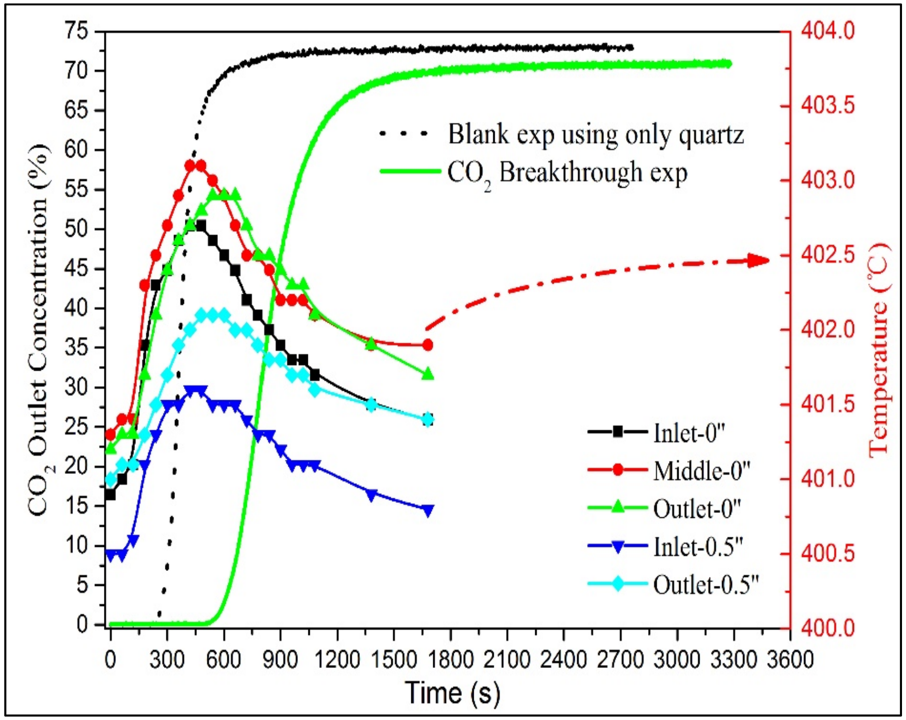
Reactor pressure = 5, 10, 15, 20, 25 bar, Oven temperature = 400°C, Flow rate=500 sccm



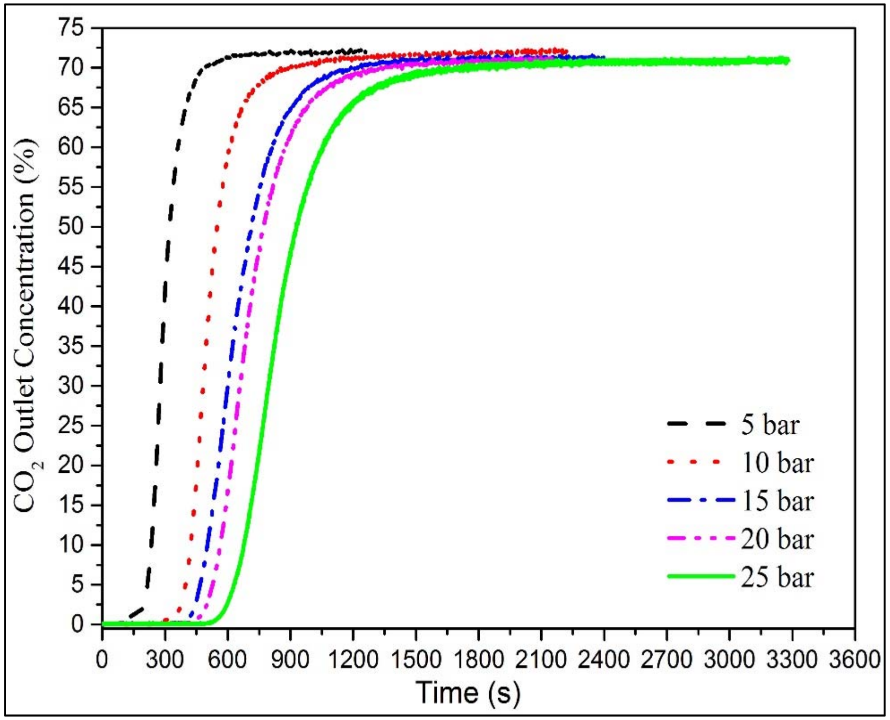
Progress and Current Status of Project, cont.

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

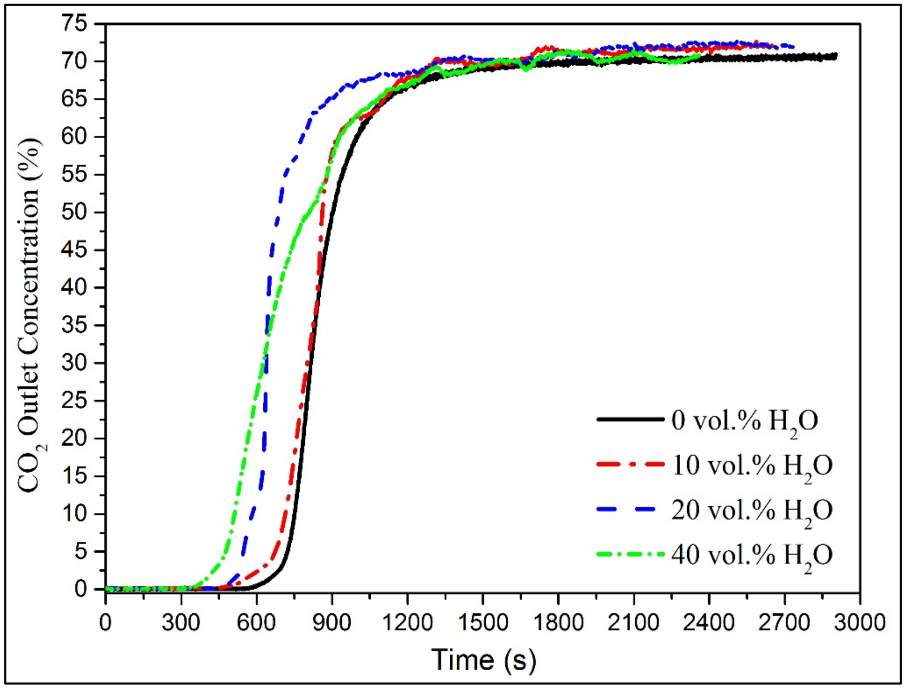


Progress and Current Status of Project, cont.

AR Sub-System Operation Testing

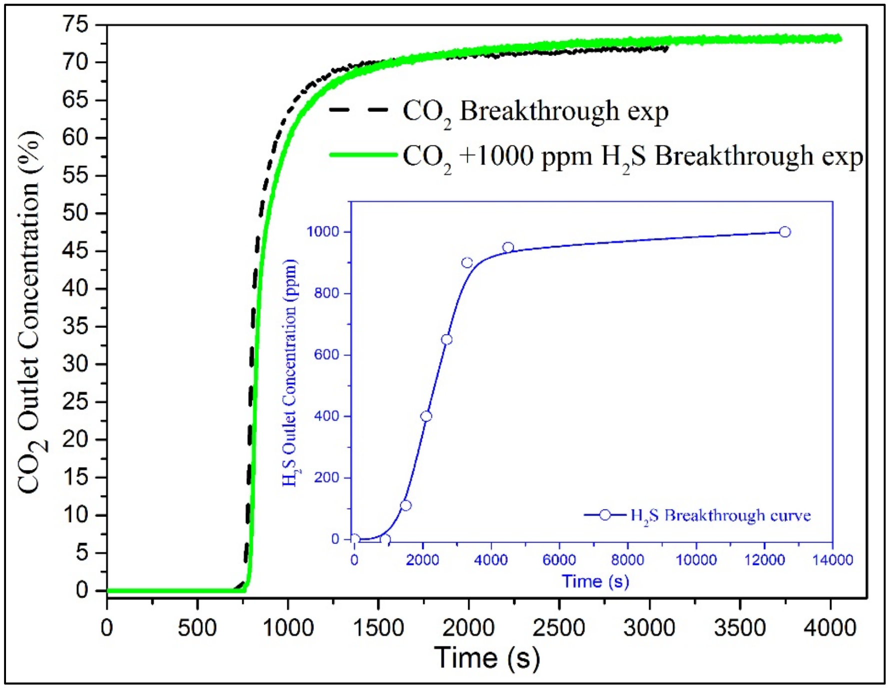
CO_2/ H_2O Breakthrough Experiments

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

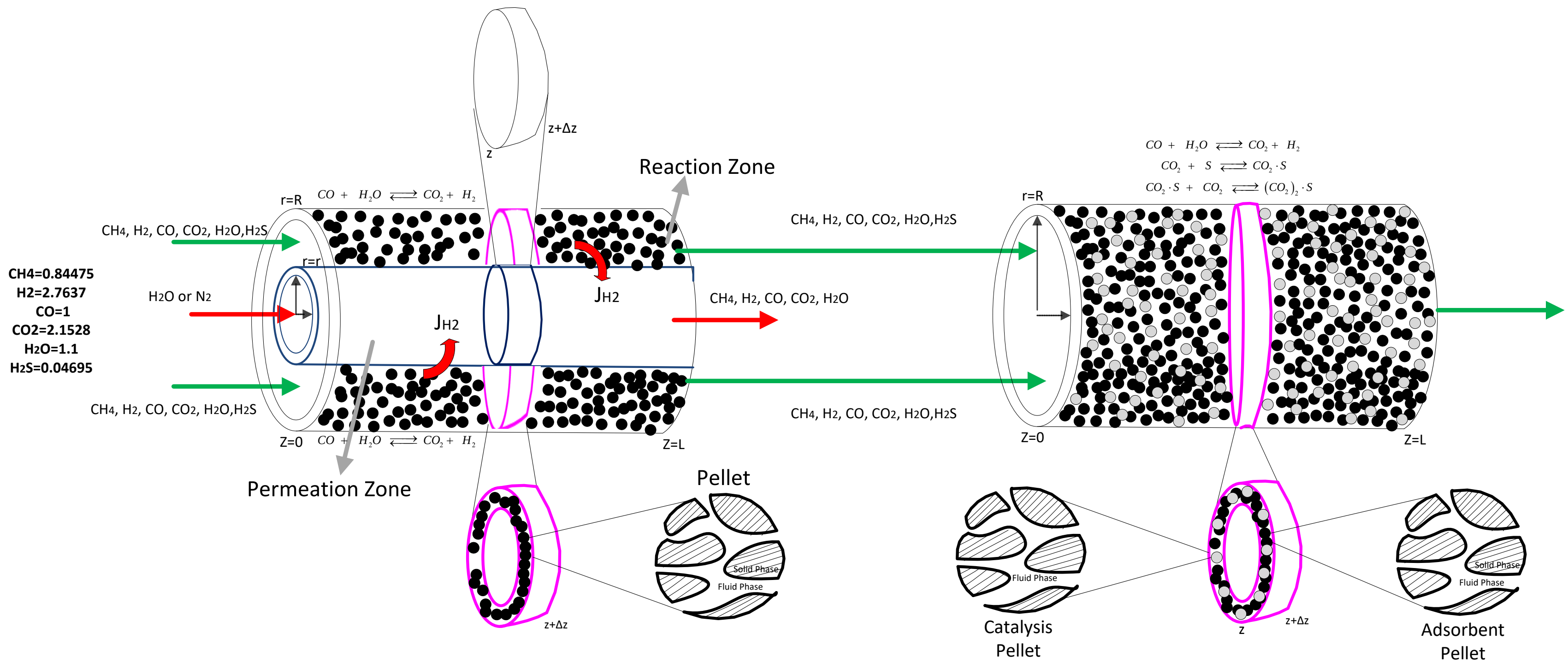


CO_2/ H_2S Breakthrough Experiments

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

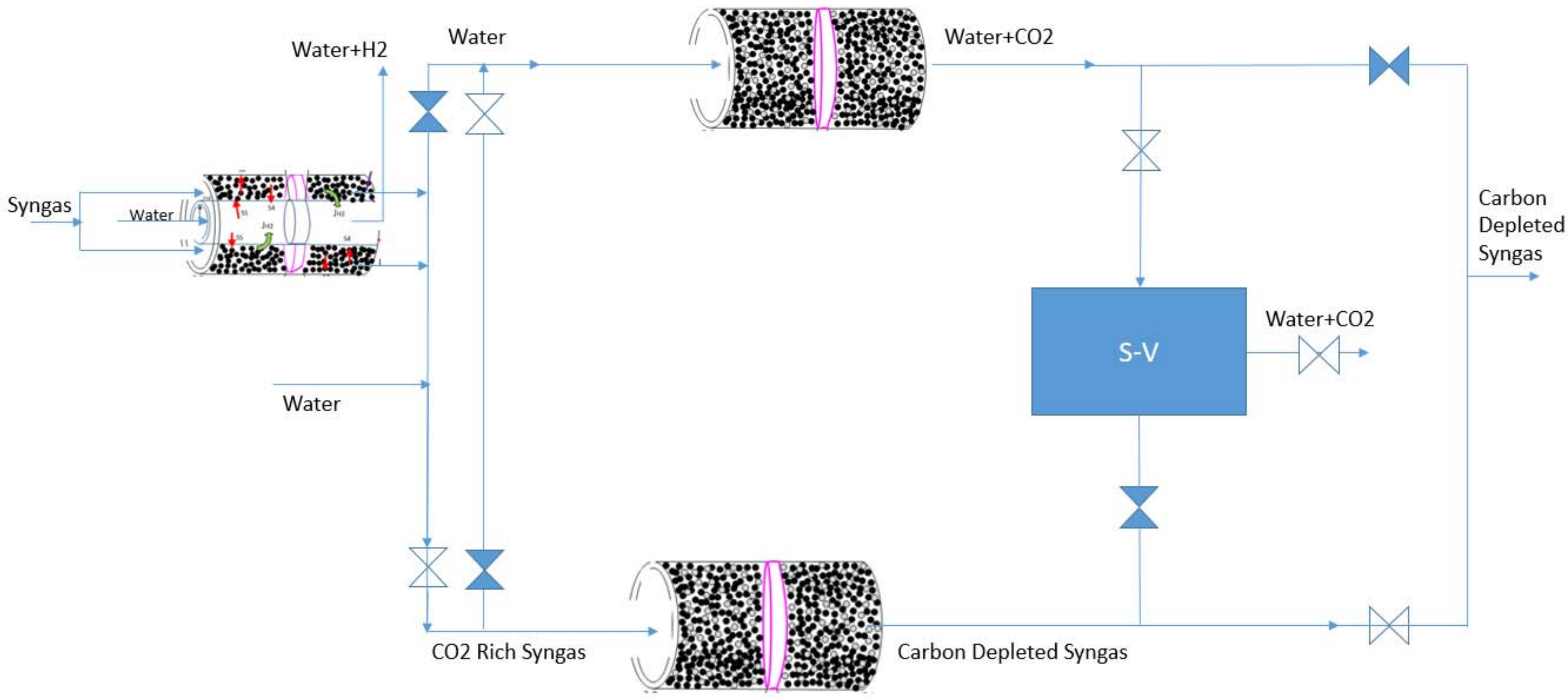


Membrane Reactor/Adsorptive Reactor Process

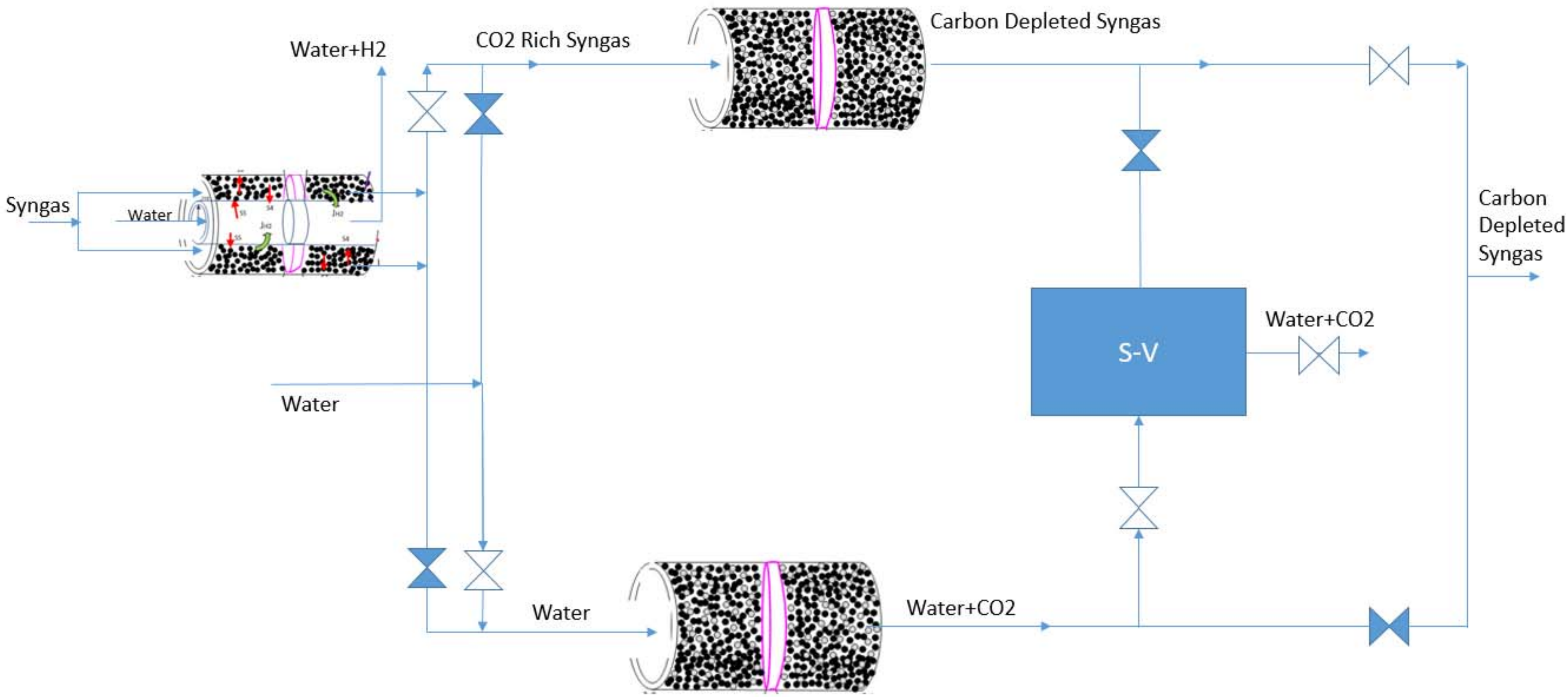


Combined MR + AR System

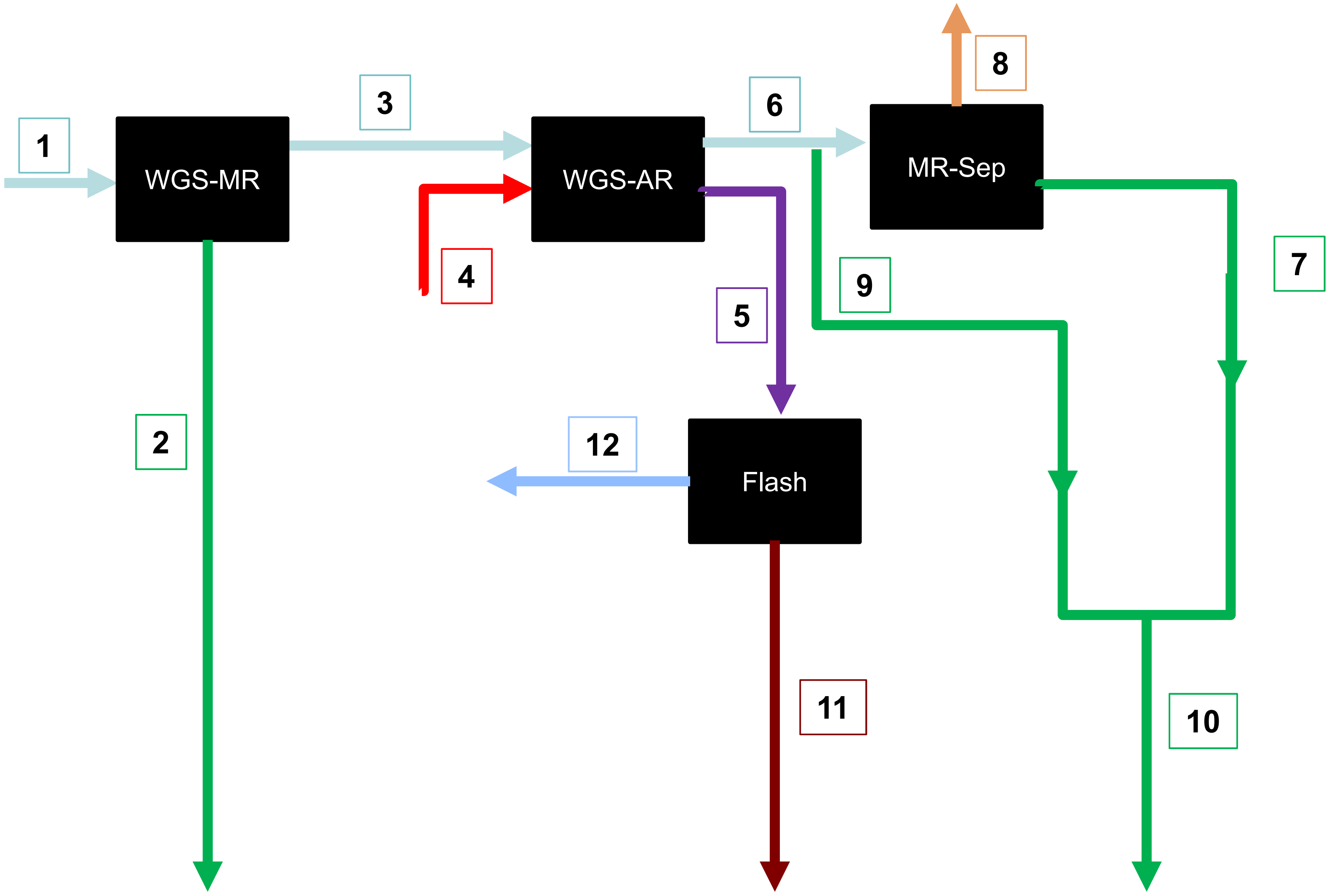
Membrane Reactor (MR)/Adsorptive Reactor (AR) Process



Membrane Reactor (MR)/Adsorptive Reactor (AR) Process



MR/AR Steady State Process



MR/AR Steady State Process

x=57.64, y=10, z=10, m=100						
	1	2	3	4	5	6
T (K)	573.15	600	591	723.15	723.15	523.15
P (bar)	14	14	1	14	14	14
x_inert	0.10746	0	1.39E-01	0	0	0.247362256
x_h2o	0.13993	0.04	1.32E-01	1	0.5	0.014131239
x_h2	0.35156	0.96	2.92E-01	0	0	0.738506505
x_co	0.12721	0	1.24E-01	0	0	0
x_co2	0.27385	0	3.14E-01	0	0.5	0
F(mol/s)	3.79E-04	6.23E-05	0.0002924	0.000127828	0.000255656	0.00016456
	7	8	9	10	11	12
T (K)	523.15	523.15	523.15	523.15	330	330
P (bar)	14	14	14	14	14	14
x_inert	0	0.996806	0.2473623	9.51E-03	0	0
x_h2o	0.018	0.0022886	0.0141312	1.77E-02	0.015	0.998
x_h2	0.982	0.0009054	0.7385065	0.972799	0	0
x_co	0	0	0	0	0	0
x_co2	0	0	0	0	0.985	0.002
F(mol/s)	0.000118948	3.58119E-05	0.0000049	0.000123848	0.000129248	0.000126408

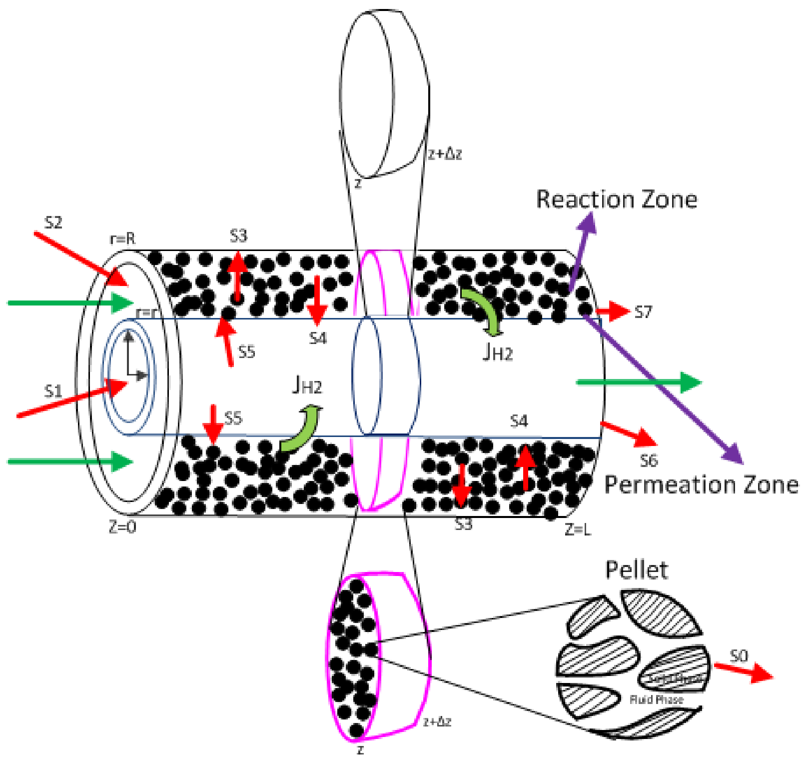
MR/AR Steady State Process

x=115.29, y=10, z=10, m=100						
	1	2	3	4	5	6
T (K)	573.15	600	591	723.15	723.15	523.15
P (bar)	14	14	1	14	14	14
x_inert	0.10746	0	0.1678438	0	0	0.303844885
x_h2o	0.13993	0.04	0.1138235	1	0.5	0.008224374
x_h2	0.35156	0.96	0.2707322	0	0	0.687930742
x_co	0.12721	0	0.1092804	0	0	0
x_co2	0.27385	0	0.3383201	0	0.5	0
F(mol/s)	3.79E-04	9.29E-05	0.0002425	0.000108553	0.000217106	0.000133969
	7	8	9	10	11	12
T (K)	523.15	523.15	523.15	523.15	330	330
P (bar)	14	14	14	14	14	14
x_inert	0	0.9943722	0.3038449	0.012467	0	0
x_h2o	0.01	0.0046718	0.0082244	9.93E-03	0.015	0.998
x_h2	0.99	0.000956	0.6879307	0.977606	0	0
x_co	0	0	0	0	0	0
x_co2	0	0	0	0	0.985	0.002
F(mol/s)	8.94902E-05	3.6479E-05	0.0000040	4.0479E-05	1.10E-04	1.07E-04

MR/AR Steady State Process

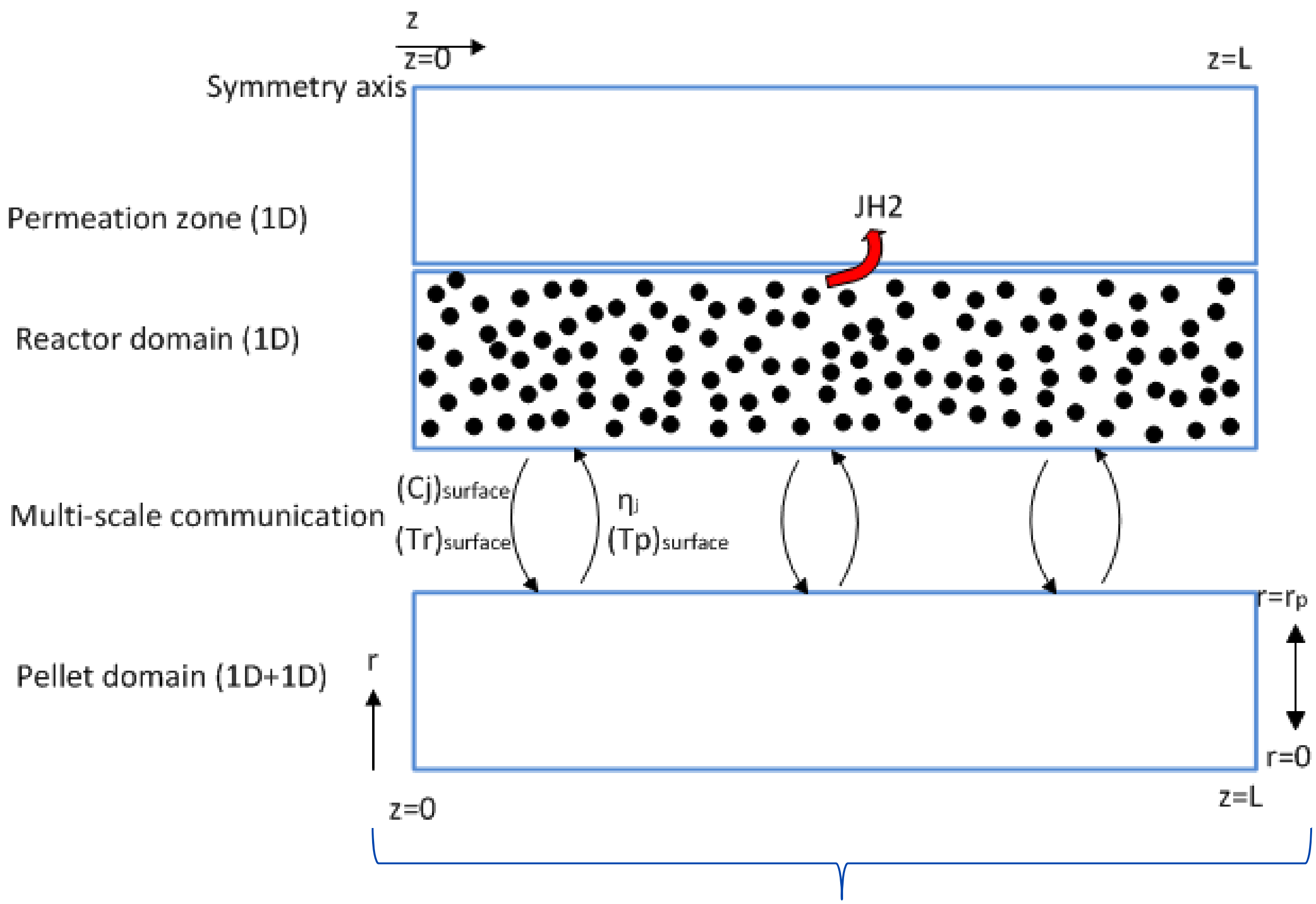
x=230.58, y=10, z=10, m=100						
	1	2	3	4	5	6
T (K)	573.15	600	591	723.15	723.15	523.15
P (bar)	14	14	1	14	14	14
x_inert	0.10746	0	0.2155852	0	0	0.39678791
x_h2o	0.13993	0.04	0.08082	1	0.5	0
x_h2	0.35156	0.96	0.2460744	0	0	0.60321209
x_co	0.12721	0	0.0816664	0	0	0
x_co2	0.27385	0	0.3758541	0	0.5	0
F(mol/s)	3.79E-04	0.0001888	1.24E-04	8.6387E-05	0.000172774	0.000102588
	7	8	9	10	11	12
T (K)	523.15	523.15	523.15	523.15	330	330
P (bar)	14	14	14	14	14	14
x_inert	0	0.999077	0.3967879	1.24E-02	0	0
x_h2o	0	0	0	0	0.015	0.9973
x_h2	1	0.000923	0.6032121	0.987587	0	0
x_co	0	0	0	0	0	0
x_co2	0	0	0	0	0.985	0.0017
F(mol/s)	6.16309E-05	4.03576E-05	0.0000003	6.19309E-05	8.73E-05	8.54E-05

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



1D Representation of control volumes in Membrane Reactor

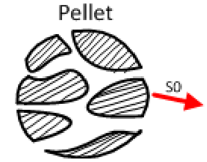
Membrane Reactor
Multi-scale (Pellet-Reactor Scale) Model



1D (pellet radial direction) pellet equations solved at each grid point of the discretized reactor domain (z axis).

Pellet-Scale Steady-State Model

Pellet-scale model equations.



Constitutive laws

Continuity Equation:

$$\vec{\nabla}\cdot\left(\varepsilon_A^p c_f^p \overrightarrow{v_f^p}\right)=\sum_{j=1}^{n_s}\left(1-\varepsilon_v^p\right)\rho_s^p\sum_{k=1}^{n_R}R_k v_{jk}$$

Component mass conservation:

$$\vec{\nabla}\cdot\left(\varepsilon_A^p x_j^p c_f^p \overrightarrow{v_f^p}\right)+\vec{\nabla}\cdot\left(\varepsilon_A^p \overrightarrow{n_j^p}\right)=\left(1-\varepsilon_v^p\right)\rho_s^p\sum_{k=1}^{n_R}R_k v_{jk}$$

Energy conservation:

$$\left(\sum_{j=1}^{n_s}\varepsilon_A^p x_j^p c_f^p C_j^p\right)\overrightarrow{v_f^p}\cdot\left(\vec{\nabla}T^p\right)=\vec{\nabla}\cdot\left(\lambda\vec{\nabla}T^p\right)+\left(1-\varepsilon_v^p\right)\rho_s^p\left(\sum_{k=1}^{n_R}-\Delta H_{R,k}R_k\right)$$

Boundary Conditions:

$$\left.\begin{aligned}&\overrightarrow{n_j^p}=0\\&Q_r=-\lambda\vec{\nabla}T^p=0\\&\vec{\nabla}P^p=0\end{aligned}\right\}\ for\ r=0$$

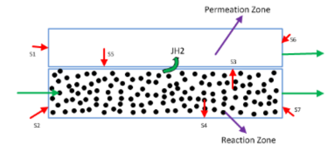
$$\left.\begin{aligned}&\left(1-\varepsilon_v^r\right)\eta_j\rho_s\sum_{k=1}^{n_s}R_k v_{jk}=\overrightarrow{n_j^p}+x_j^p c_f^p\overrightarrow{v_f^p}\\&-h\left(T^r-T^p\right)=Q_r+\left(\sum_{j=1}^{n_s}x_j^p c_f^p C_j^p\right)\overrightarrow{v_f^p}T^p\\&x_j^p=x_j^r\\&P^p=P^r\end{aligned}\right\}\ for\ r=r^p$$

DGM (Dusty Gas Model):

$$-\frac{1}{\sum_{j=1}^{N_s}c_j}\sum_{\substack{j=1\\j\neq i,p}}^{N_s}\left(\frac{c_j}{D_{ij}^{eff}}\overrightarrow{N_i}-\frac{c_j}{D_{ij}^{eff}}\overrightarrow{N_j}\right)-\frac{\overrightarrow{N_i}}{D_{iK}^{eff}}=\vec{\nabla}c_i+\frac{c_i}{\sum_{i=1}^{N_s}c_i RT}\left(1+\frac{P}{D_{iK}^{eff}}\frac{B_O}{\mu_f}\right)\vec{\nabla}P$$

$$\begin{bmatrix}\overrightarrow{N_1}\\\overrightarrow{N_2}\\\overrightarrow{N_3}\\\overrightarrow{N_4}\\\overrightarrow{N_5}\end{bmatrix}=-\begin{bmatrix}\left(\frac{\sum_{i=2}^{5}\frac{c_i}{D_{1i}^{eff}}}{\sum_{j=1}^{5}c_j}+\frac{1}{D_{1K}^{eff}}\right) & \frac{-c_1}{D_{12}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_1}{D_{13}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_1}{D_{14}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_1}{D_{15}^{eff}\sum_{j=1}^{5}c_j}\\ \frac{-c_2}{D_{21}^{eff}\sum_{j=1}^{5}c_j} & \left(\frac{\sum_{\substack{i=1\\i\neq 2}}^{5}\frac{c_i}{D_{2i}^{eff}}}{\sum_{j=1}^{5}c_j}+\frac{1}{D_{2K}^{eff}}\right) & \frac{-c_2}{D_{23}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_2}{D_{24}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_2}{D_{25}^{eff}\sum_{j=1}^{5}c_j}\\ \frac{-c_3}{D_{31}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_3}{D_{32}^{eff}\sum_{j=1}^{5}c_j} & \left(\frac{\sum_{\substack{i=1\\i\neq 3}}^{5}\frac{c_i}{D_{3i}^{eff}}}{\sum_{j=1}^{5}c_j}+\frac{1}{D_{3K}^{eff}}\right) & \frac{-c_3}{D_{34}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_3}{D_{35}^{eff}\sum_{j=1}^{5}c_j}\\ \frac{-c_4}{D_{41}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_4}{D_{42}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_4}{D_{43}^{eff}\sum_{j=1}^{5}c_j} & \left(\frac{\sum_{\substack{i=1\\i\neq 4}}^{5}\frac{c_i}{D_{4i}^{eff}}}{\sum_{j=1}^{5}c_j}+\frac{1}{D_{4K}^{eff}}\right) & \frac{-c_4}{D_{45}^{eff}\sum_{j=1}^{5}c_j}\\ \frac{-c_5}{D_{51}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_5}{D_{52}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_5}{D_{53}^{eff}\sum_{j=1}^{5}c_j} & \frac{-c_5}{D_{54}^{eff}\sum_{j=1}^{5}c_j} & \left(\frac{\sum_{\substack{i=1\\i\neq 5}}^{5}\frac{c_i}{D_{5i}^{eff}}}{\sum_{j=1}^{5}c_j}+\frac{1}{D_{5K}^{eff}}\right)\end{bmatrix}\cdot\underbrace{\begin{bmatrix}\vec{\nabla}c_1+\frac{c_1}{\sum_{j=1}^{N_s}c_j RT}\left(1+\frac{P}{D_{1K}^{eff}}\frac{B_O}{\mu_f}\right)\vec{\nabla}P\\\vec{\nabla}c_2+\frac{c_2}{\sum_{j=1}^{N_s}c_j RT}\left(1+\frac{P}{D_{2K}^{eff}}\frac{B_O}{\mu_f}\right)\vec{\nabla}P\\\vec{\nabla}c_3+\frac{c_3}{\sum_{j=1}^{N_s}c_j RT}\left(1+\frac{P}{D_{3K}^{eff}}\frac{B_O}{\mu_f}\right)\vec{\nabla}P\\\vec{\nabla}c_4+\frac{c_4}{\sum_{j=1}^{N_s}c_j RT}\left(1+\frac{P}{D_{4K}^{eff}}\frac{B_O}{\mu_f}\right)\vec{\nabla}P\\\vec{\nabla}c_5+\frac{c_5}{\sum_{j=1}^{N_s}c_j RT}\left(1+\frac{P}{D_{5K}^{eff}}\frac{B_O}{\mu_f}\right)\vec{\nabla}P\end{bmatrix}}_{\vec{\nabla}x}$$

Reactor-Scale Steady-state Model



MR-scale reaction zone model equations.

Bulk Gas Constitutive laws

Continuity Equation:

$$\vec{\nabla}\cdot\left(\varepsilon_A^r c_f^r \vec{v_f^r}\right) = \sum_{j=1}^{n_s}\beta_c\left(1-\varepsilon_v^r\right)\rho_s^r\sum_{k=1}^{n_R}R_k\nu_{jk} - \sum_{j=1}^{n_s}\frac{2}{R_{mem}}J_j$$

Component mass conservation:

$$\vec{\nabla}\cdot\left(\varepsilon_A^r x_j^r c_f^r \vec{v_f^r}\right) + \vec{\nabla}\cdot\left(\varepsilon_A^r \vec{n_j^r}\right) = \beta_c\left(1-\varepsilon_v^r\right)\eta_j\rho_s^r\sum_{k=1}^{n_R}R_k\nu_{jk} - \frac{2}{R_{mem}}J_j$$

Energy conservation:

$$\left(\varepsilon_A^r\sum_{j=1}^{n_s}x_j^r c_j^r C_j^r\right)\vec{v_f^r}\cdot\left(\vec{\nabla}T^r\right) = \left\{\begin{array}{l}\vec{\nabla}\cdot\left(\lambda'\vec{\nabla}T^r\right) + \varepsilon_p^r h_p\left(T^r-\left(T^p\right)^s\right) + \varepsilon_q^r h_q\left(T^r-\left(T^q\right)^s\right) \\ -\frac{A^{SM}U'}{V^r}\left(T^r - T^{perm}\right) + \frac{4U}{d_t}\left(T_{fur}-T^r\right)\end{array}\right\}$$

MR-scale reaction zone boundary conditions.

Boundary Conditions:

$$\left.\begin{array}{l}\vec{v_f^r} = \left(\vec{v_f^r}\right)_{in} \\ P^r = P_{in}^r \\ \vec{x_f^r} = \left(\vec{x_f^r}\right)_{in} \\ T^r = T_{in}^r\end{array}\right\} for\ z = 0$$

$$\left.\begin{array}{l}\vec{\nabla}T^r = 0 \\ \vec{n_j^r} = 0 \\ \vec{\nabla}P^r = 0\end{array}\right\} for\ z = L$$

Momentum Equation (Ergun Equation)

$$\vec{\nabla}P^r = -K_D\vec{v_f^r} - K_v\vec{v_f^r}^2 = \vec{\nabla}P^r = \left(-150\frac{\left(1-\varepsilon_V^r\right)^2}{\left(\varepsilon_V^r\right)^3 d_p^2} - \mu_f^r 1.75\frac{\left(1-\varepsilon_V^r\right)}{\left(\varepsilon_V^r\right)^3 d_p}\rho_f^r\left|\vec{v_f^r}\right|\right)\vec{v_f^r}$$

Stefan-Maxwell Equation

$$\vec{\nabla}x_i = \sum_{j=1}^{N_s}\frac{x_i\, x_j}{D_{ij}^{eff}}\left(\frac{1}{\rho_j}\vec{J_j} - \frac{1}{\rho_i}\vec{J_i}\right) + \left(w_i - x_i\right)\left(\frac{\vec{\nabla}P}{P}\right) + \sum_{j=1}^{N_s}\frac{x_i\, x_j}{\rho_f D_{ij}^{eff}}\left(\frac{D_j^T}{w_j} - \frac{D_i^T}{w_i}\right)\left(\frac{\vec{\nabla}T}{T}\right)$$

Steady-State Permeation Zone Model

MR-scale permeation zone model equations.

Bulk Gas Constitutive laws

Continuity Equation:

$$\vec{\nabla}\cdot\left(c_f^{perm}\overrightarrow{v_f^{perm}}\right)=\sum_{j=1}^{n_s}\frac{2}{R_{mem}}J_j$$

Component mass conservation:

$$\vec{\nabla}\cdot\left(x_j^{perm}c_f^{perm}\overrightarrow{v_f^{perm}}\right)=\frac{2}{R_{mem}}J_j$$

Energy conservation:

$$\left\{\begin{array}{l}\left(\sum_{j=1}^{n_s}x_j^{perm}c_f^{perm}C_j^{perm}\right)\overrightarrow{v_f^{perm}}\cdot\left(\vec{\nabla}T^{perm}\right)=\\ =\vec{\nabla}\cdot\left(\lambda''\vec{\nabla}T^{perm}\right)+\frac{A^{SM}U'}{V^{perm}}\left(T^r-T^{perm}\right)+\sum_{j=1}^{n_s}\frac{A^{SM}}{V^{perm}}J_j\left(h_j^r-h_j^{perm}\right)\end{array}\right\}$$

MR-scale reaction zone boundary conditions.

Boundary Conditions:

$$\left.\begin{array}{l}\overrightarrow{v_f^{perm}}=\left(\overrightarrow{v_f^{perm}}\right)_{in}\\ P^{perm}=P_{in}^{perm}\\ \overrightarrow{x_f^r}=\left(\overrightarrow{x_f^r}\right)_{in}\\ T^r=T_{in}^{perm}\end{array}\right\}\ for\ z=0$$

$$\left.\begin{array}{l}\vec{\nabla}T^{perm}=0\\ \vec{\nabla}P^{perm}=0\end{array}\right\}\ for\ z=L$$

Constitutive law and other property defining equations

Gas Law:

$$c_{TOT}^r=\frac{P}{ZRT}$$

Definitions:

$$\sum_{j=1}^{n_s}x_j=1,\ c_{tot}^p=\sum_{j=1}^{n_s}c_j^r,\ P=\sum_{j=1}^{n_s}P_i,\ \beta_{cat}+\varphi_{qua}=1$$

Heat Flux (Fourier's Law):

$$Q=-\lambda\nabla T$$

Dimensionless Groups :

$$Nu=\frac{hd_p}{\lambda_g},\ Re_p=\frac{\overrightarrow{v_f}\rho_g d_p}{\mu_g},\ Pr=\frac{C_{p,g}\mu_g}{\lambda_g}$$

Viscosity of Gas Mixture :

$$\mu_g=\sum_{i=1}^{N_s}\frac{x_i\mu_i}{\sum_{j=1}^{N_s}x_i\phi_{ij}},\qquad \phi_{ij}=\frac{\left[1+\left(\mu_i/\mu_j\right)^{1/2}\left(M_j/M_i\right)^{1/4}\right]^2}{8\left(1+\left(M_i/M_j\right)\right)^{1/2}}$$

Thermal Conductivity:

$$\lambda'=\left(1-\varepsilon_v^r\right)\beta_{cat}\lambda_{cat}+\left(1-\varepsilon_v^r\right)\varphi_{qua}\lambda_{ad}+\varepsilon_v^r\lambda_g$$

Thermal Conductivity of Pure Gases:

$$\lambda_i=A_i+B_iT+C_iT^2+D_iT^3$$

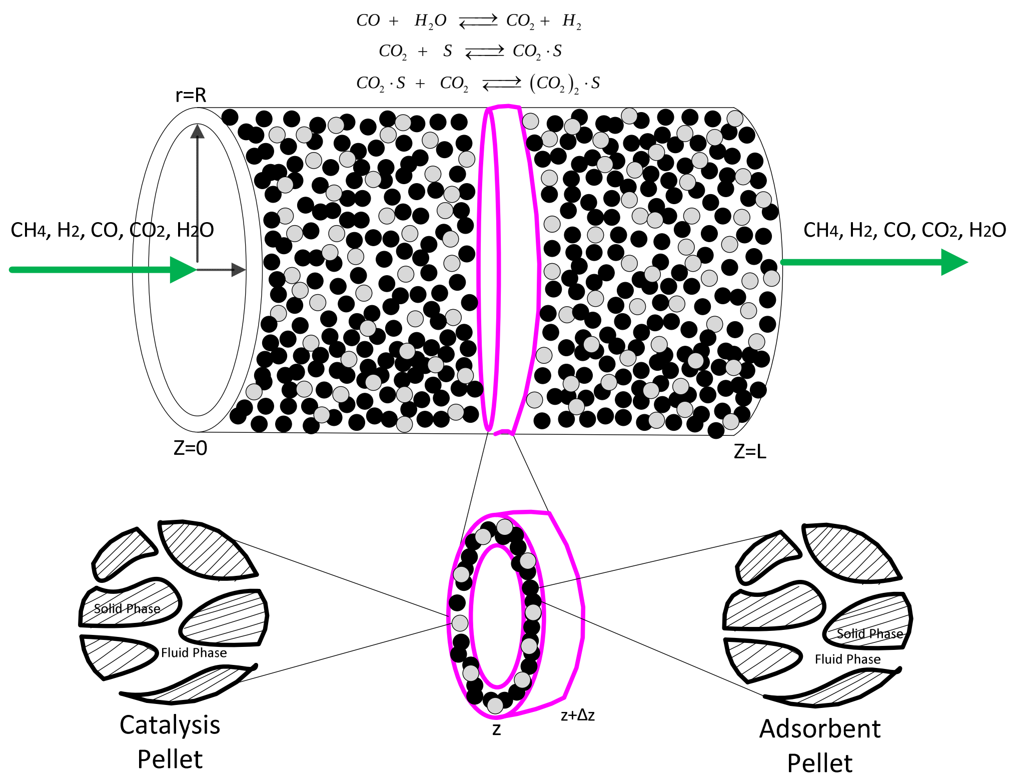
Thermal Conductivity of Gas Mixture:

$$\lambda_g=\sum_{i=1}^{N_s}\frac{x_i\lambda_i}{\sum_{j=1}^{N_s}x_i\phi_{ij}},\qquad \phi_{ij}=\frac{\left[1+\left(\mu_i/\mu_j\right)^{1/2}\left(M_j/M_i\right)^{1/4}\right]^2}{8\left(1+\left(M_i/M_j\right)\right)^{1/2}}$$

Specific Heat Capacity of Pure Gases:

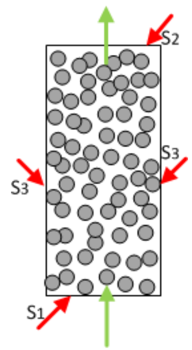
$$C_i=a_{0,i}+a_{1,i}t+a_{2,i}t^2+a_{3,i}t^3+a_{4,i}/t^2,\quad t=\left(T/1000\right)$$

Adsorptive Reactor (AR) Model



1D Representation of control volumes in AR

Adsorptive Reactor (AR) Model



Component Mass Balances

$$\frac{\partial}{\partial t}\left(\varepsilon^r_{tot.gas} c^r_j\right) + \vec{\nabla}\cdot\left(\overrightarrow{v^r_f} c^r_j\right) = \varepsilon_{gas\cdot bed}\vec{\nabla} D_{z,i}\left(\vec{\nabla} c^r_j\right) + \left(1-\varepsilon_{gas\cdot bed}\right)\eta_j \beta_{cat}\rho_{cat} R_j - \left(1-\varepsilon_{gas\cdot bed}\right)\phi_{ad}\rho_{ad} R_{ad}$$

$$\beta_{cat} + \phi_{ad} + \varphi_{qua} = 1$$

Energy balance:

$$\left\{\begin{array}{l} \left\{\begin{array}{l} \left(\left(1-\varepsilon_{gas\cdot bed}\right)\beta_{cat}\rho^r_c C^r_c + \left(1-\varepsilon_{gas\cdot bed}\right)\phi_{ad}\rho^r_{ad} C^r_{ad} + \left(1-\varepsilon_{gas\cdot bed}\right)\varphi_{qua}\rho^r_{qua} C^r_{qua} + \sum_{j=1}^{n_s}\varepsilon^r_{tot.gas} c^r_j C^r_j\right)\frac{\partial T^r}{\partial t} + \\ \left(\varepsilon^r_A \sum_{j=1}^{n_s} c^r_j C^r_j\right)\overrightarrow{v^r_f}\cdot\left(\vec{\nabla} T^r\right) \end{array}\right\} = \\ = \vec{\nabla}\cdot\left(\lambda' \vec{\nabla} T^r\right) + \left(1-\varepsilon_{gas\cdot bed}\right)\eta_j \beta_{cat}\rho_{cat}\sum_{j=1}^{n_s} H_j R_j - \left(1-\varepsilon_{gas\cdot bed}\right)\phi_{ad}\rho_{ad}\Delta H_{ad} R_{ad} + \frac{4h_w}{d_t}\left(T_w - T^r\right) \end{array}\right\}$$

$$\left\{\begin{array}{l} \rho_w C_w \frac{\partial T_w}{\partial t} = \frac{d_t}{\left(w_{thick}\left(d_t + w_{thick}\right)\right)} h_w\left(T_w - T^r\right) - \frac{U\left(T_w - T_{fur}\right)}{\left(d_t + w_{thick}\right)\cdot \ln\left(\frac{\left(d_t + w_{thick}\right)}{d_t}\right)} \\ \frac{\lambda_z}{\lambda_g} = \frac{\lambda^0_z}{\lambda_g} + 0.75\cdot Pr\cdot Re_p \\ \frac{\lambda^0_z}{\lambda_g} = \varepsilon^r_{tot.gas} + \frac{1-\varepsilon^r_{tot.gas}}{0.139\varepsilon_{gas\cdot bed} - 0.0339 + 2/3\left(\lambda_g/\lambda_p\right)} \\ \frac{h_w d_t}{\lambda_g} = 2.03\cdot Re_p exp\left(-\frac{d_p}{d_t}\right) \end{array}\right\}$$

Momentum balance:

$$\vec{\nabla} P^r = -K_D \overrightarrow{v^r_f} - K_v \overrightarrow{v^r_f}^2 = \vec{\nabla} P^r = \left(-150\frac{\left(1-\varepsilon_{gas\cdot bed}\right)^2}{\left(\varepsilon_{gas\cdot bed}\right)^3 d_p^{\ 2}} - \mu^r_f 1.75\frac{\left(1-\varepsilon_{gas\cdot bed}\right)}{\left(\varepsilon_{gas\cdot bed}\right)^3 d_p}\rho^r_f\left|\overrightarrow{v^r_f}\right|\right)\overrightarrow{v^r_f}$$

Adsorptive Reactor (AR) Model

Initial and boundary conditions for the AR model.

Initial Conditions:	***Boundary Conditions:***
$\left.\begin{aligned} c_j^r &= 0 \\ T^r &= T_{in}^r \\ P^r &= P_{in}^r \end{aligned}\right\} \text{for } t=0,\ \forall z$	$\left.\begin{aligned} \vec{v_f^r} &= \left(\vec{v_f^r}\right)_{in} \\ P^r &= P_{in}^r \\ \vec{c_j^r} &= \left(\vec{c_j^r}\right)_{in} \\ T^r &= T_{in}^r \end{aligned}\right\} \text{for } z=0$ $\left.\begin{aligned} \vec{\nabla} T^r &= 0 \\ \vec{n_j^r} &= 0 \\ \vec{\nabla} P^r &= 0 \end{aligned}\right\} \text{for } z=L$

Constitutive laws and other property equations.

Gas Law:

$$c_{TOT}^r = \frac{P}{ZRT}$$

Definitions:

$$\sum_{j=1}^{n_s} x_j = 1,\ c_{tot}^p = \sum_{j=1}^{n_s} c_j^r,\ P = \sum_{j=1}^{n_s} P_i,\ \beta_{cat} + \phi_{ad} + \varphi_{qua} = 1$$

Heat Flux (Fourier's Law):

$$Q = -\lambda \nabla T$$

Dimensionless Groups :

$$Nu = \frac{hd_p}{\lambda_g},\ Re_p = \frac{\vec{v_f} \rho_g d_p}{\mu_g},\ Pr = \frac{C_{p,g}\mu_g}{\lambda_g}$$

Viscosity of Gas Mixture :

$$\mu_g = \sum_{i=1}^{N_s} \frac{x_i \mu_i}{\sum_{j=1}^{N_s} x_i \phi_{ij}}, \qquad \phi_{ij} = \frac{\left[1 + \left(\mu_i/\mu_j\right)^{1/2} \left(M_j/M_i\right)^{1/4}\right]^2}{8\left(1 + \left(M_i/M_j\right)\right)^{1/2}}$$

Thermal Conductivity:

$$\lambda' = \left(1-\varepsilon_v^r\right)\beta_{cat}\lambda_{cat} + \left(1-\varepsilon_v^r\right)\varphi_{qua}\lambda_{qua} + \left(1-\varepsilon_v^r\right)\phi_{ad}\lambda_{qua} + \varepsilon_v^r \lambda_g$$

Thermal Conductivity of Pure Gases:

$$\lambda_i = A_i + B_i T + C_i T^2 + D_i T^3$$

Thermal Conductivity of Gas Mixture:

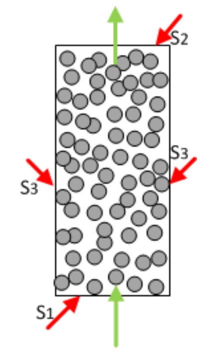
$$\lambda_g = \sum_{i=1}^{N_s} \frac{x_i \lambda_i}{\sum_{j=1}^{N_s} x_i \phi_{ij}}, \qquad \phi_{ij} = \frac{\left[1 + \left(\mu_i/\mu_j\right)^{1/2} \left(M_j/M_i\right)^{1/4}\right]^2}{8\left(1 + \left(M_i/M_j\right)\right)^{1/2}}$$

Specific Heat Capacity of Pure Gases:

$$C_i = a_{0,i} + a_{1,i} t + a_{2,i} t^2 + a_{3,i} t^3 + a_{4,i}/t^2,\quad t = \left(T/1000\right)$$

Specific Heat Capacity of Gas Mixture:

$$C_{p,g} = \sum_{i=1}^{N_s} \frac{x_i M_i C_{p,i}}{\sum_{j=1}^{N_s} x_i M_i}$$



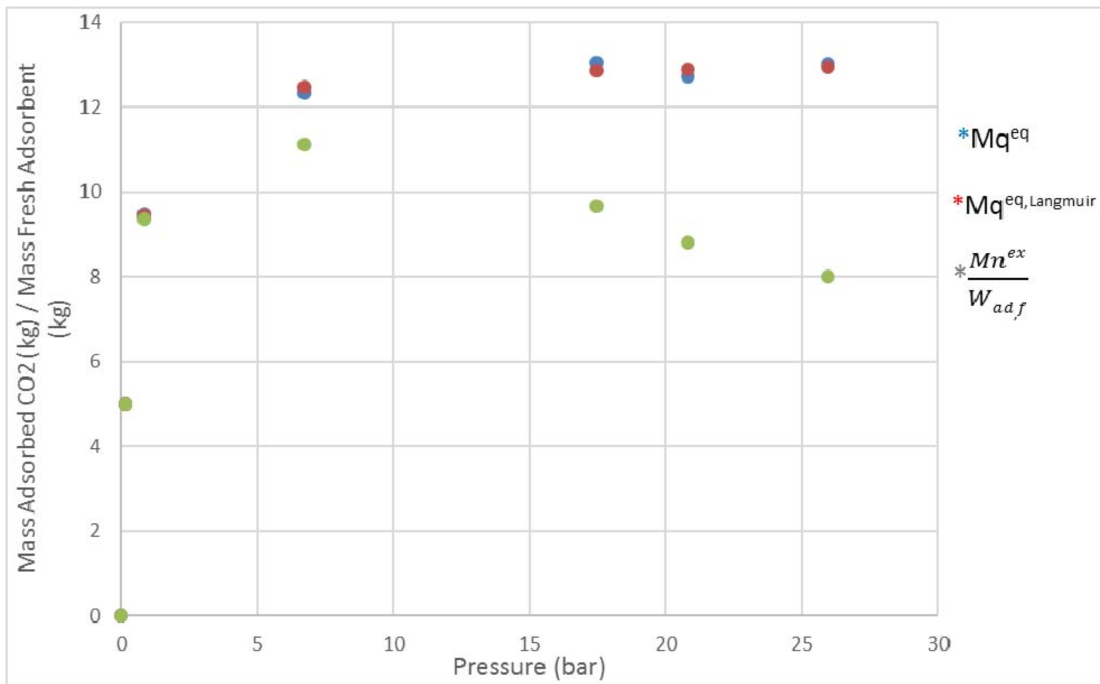
AR (Batch Adsorber/Static System) Model

$$n_{CO_2}^{ex}(t) - n_{CO_2}^{ex}(0) = \left[\left(\frac{P_{CO_2}(0)}{Z\left(T, P_{CO_2}(0)\right)RT} - \frac{P_{CO_2}(t)}{Z\left(T, P_{CO_2}(t)\right)RT} \right) \left[V^T - V^s(0) \right] - \int_0^t \dot{n}_l \left(P_{CO_2}(t') \right) dt' \right]$$

The Langmuir Isotherm:

$$q^{eq} = \frac{m_{CO_2} b_{CO_2} P_{CO2}}{1 + b_{CO_2} P_{CO2}}$$

m_{CO2} (mol/kg)	b (1/bar)
2.952592	3.690865



Model/Experimental Validation

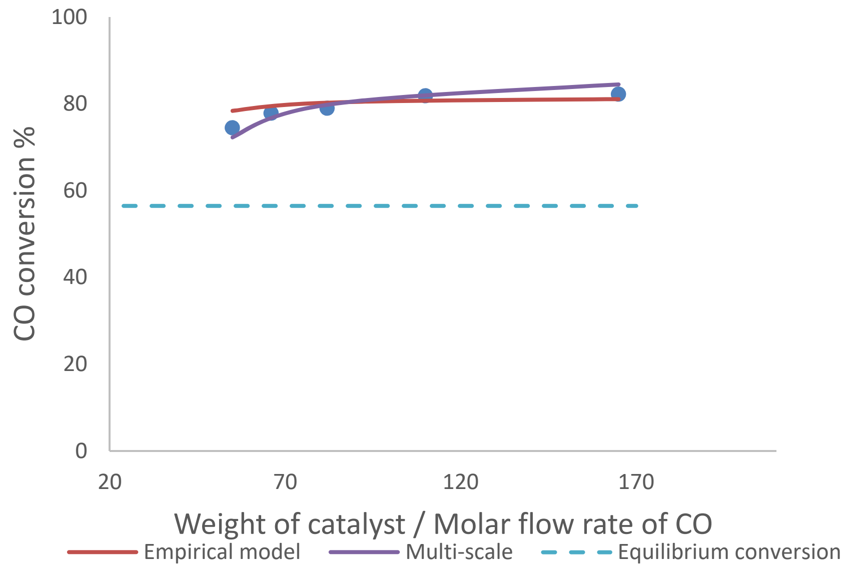
MR model simulation parameters.

Parameter	Value	Dimension
Density of catalyst	592.68	kg/m^3
Pellet void fraction	0.35561	-
Pellet radius	0.00035	m
Surface area of catalyst	160-220*10^3	m^2/g
Pore volume of catalyst	0.55-0.65*10^{-6}	m^3/g
Tortuosity	2.8121	-
Mean pore diameter	6.3*10^{-9}	m
Heat capacity of solid	1000	$J/kg \cdot K$
Inlet pressure	5-30	bar
Inlet temperature	523-573	K
Reactor diameter	0.03175	m
Inner dimeter of membrane	0.0035	m
Outer dimeter of membrane	0.0057	m
Reactor length	0.254	m
Reactor void fraction	0.7	-
Catalyst fraction	0.2886113	-
Inlet velocity	0.002-0.0005	m/s
Inlet mole fractions		
CH_4	0.101485	-
CO	0.1272	-
CO_2	0.27385	-
H_2	0.35156	-
H_2O	0.13993	-
H_2S	0.0059723	-
Chemical model parameters		
l	4	-
m	-1.46	-
n	0.13	-
q	-1.44	-
k_0	18957	$mol / atm^{l+m+n+q} \cdot h \cdot g$
E_a	58074	J / mol
Gas Permeance		$m^3 / m^2 \cdot h \cdot bar$
CO	0.036	$m^3 / m^2 \cdot h \cdot bar$
CO_2	0.056	$m^3 / m^2 \cdot h \cdot bar$
H_2	1.39	$m^3 / m^2 \cdot h \cdot bar$
H_2O	0.1985	$m^3 / m^2 \cdot h \cdot bar$

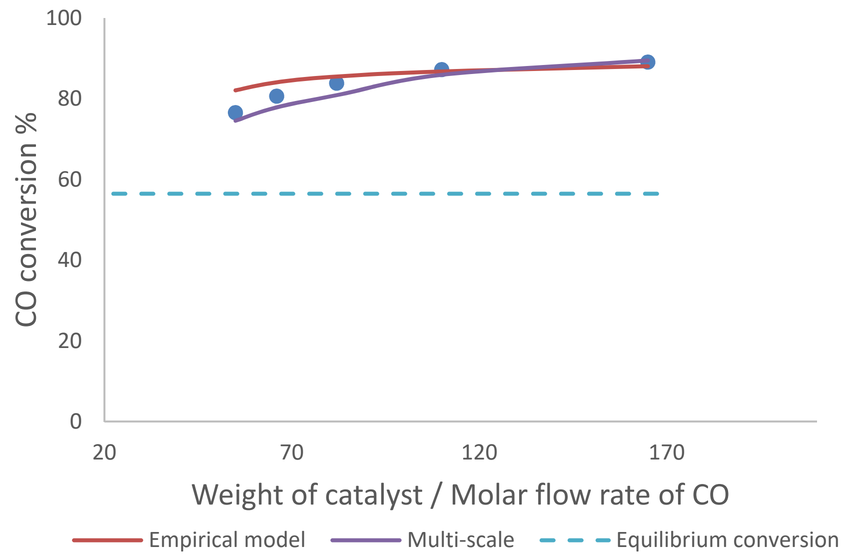
AR model simulation parameters.

Parameter	Value	Dimension
Density of catalyst	592.68	kg/m^3
Density of adsorbent	1481.13	kg/m^3
Catalyst void fraction	0.35561	-
Adsorbent void fraction	0.536	-
Pellet radius	0.00035	m
Surface area of catalyst	160-220*10^3	m^2/g
Pore volume of catalyst	0.55-0.65*10^{-6}	m^3/g
Tortuosity of catalyst	2.8121	-
Mean pore diameter of catalyst	6.3*10^{-9}	m
Heat capacity of solid	1000	$J/kg \cdot K$
Inlet pressure	5-30	bar
Inlet temperature	523-573	K
Reactor diameter	0.03175	m
Reactor length	0.1397	m
Reactor void fraction	0.40574	-

Membrane Reactor Model Experimental Validation



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



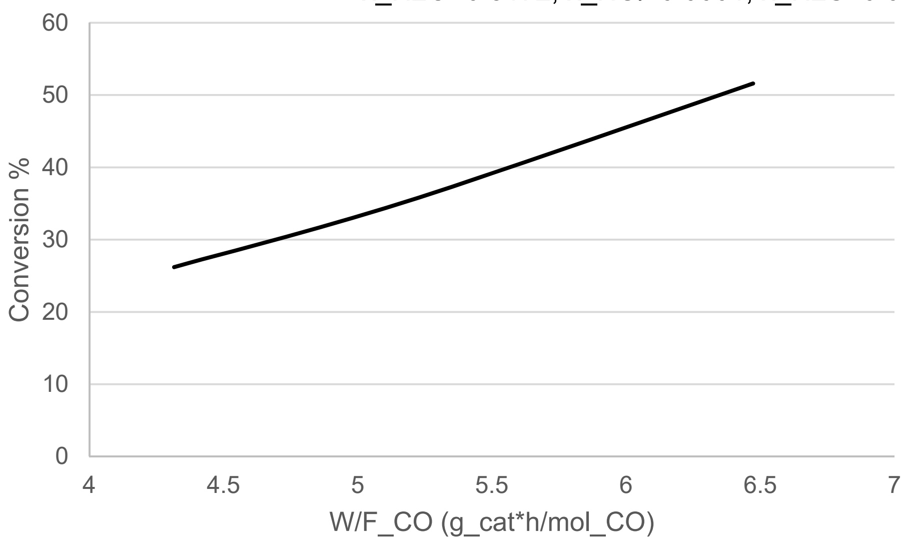
Conversion vs. W/F_{CO} for MR (feed pressure 14.1 bar, reactor temperature 300ºC, sweep ratio = 0.3).

Membrane Reactor Parametric Study

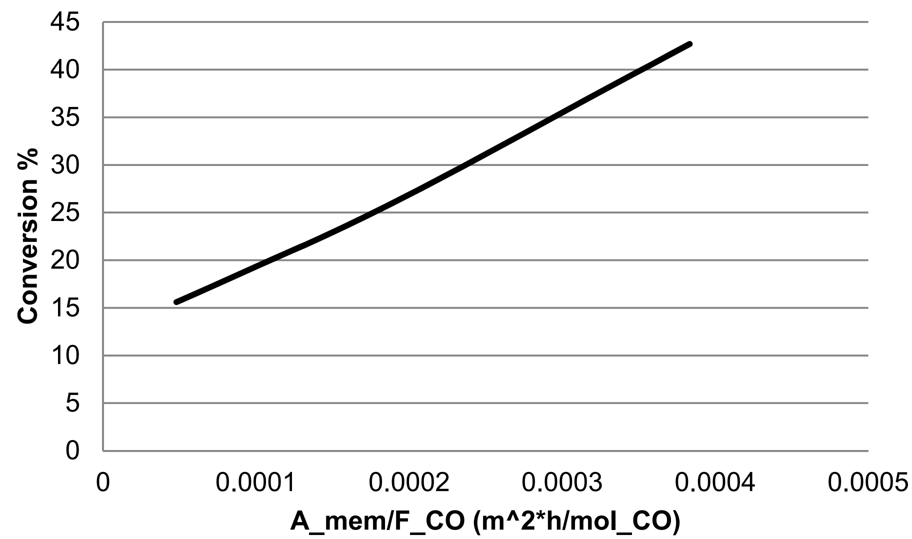
NETL Case Study Feed

Feed Pressure 39.6 bar, Feed Temperature 217ºC

x_Ar=0.0047, x_CH4=0.003, x_CO=0.2873, x_CO2=0.00070, x_COS=0.0003, x_H2=0.1491, x_H2O=0.5172, x_HCl=0.0001, x_H2S=0.0040, x_N2=0.0281, x_NH3=0.0019



Conversion vs. W/F_{CO} for MR (feed pressure 39.6 bar, feed temperature 217ºC).



Conversion vs. A/F_{CO} for MR (feed pressure 39.6 bar, feed temperature 217º).

Membrane Reactor Parametric Study

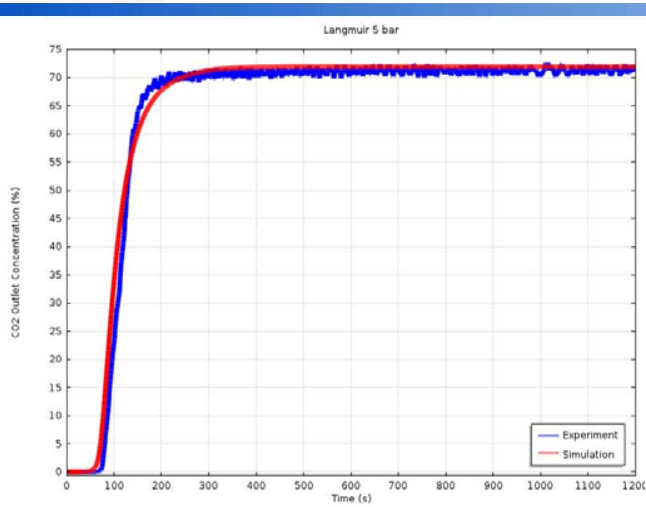
NETL Case Study Feed

Feed Pressure 39.6 bar, Feed Temperature 217ºC

x_Ar=0.0047, x_CH4=0.003, x_CO=0.2873, x_CO2=0.00070, x_COS=0.0003, x_H2=0.1491, x_H2O=0.5172, x_HCl=0.0001, x_H2S=0.0040, x_N2=0.0281, x_NH3=0.0019

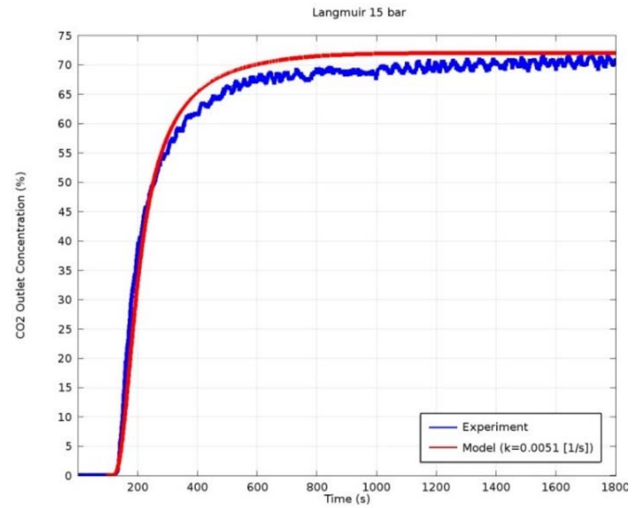
W/F_CO (g_cat hr/mol_CO)	A/F_CO (m^2 hr/mol_CO)	Conversion %	Total Catalyst (kg)	Total Membrane Surface Area (m^2)
4.32	0.000196	26.20	46845	2131
5.18	0.000236	35.25	56215	2557
6.47	0.000294	51.60	70267	3196
4.21	4.79E-05	15.60	45743	520
4.21	9.58E-05	19.04	45743	1040
4.21	0.000192	26.20	45743	2081
4.21	0.000383	42.70	45743	4161
5.02	5.71E-05	20.20	54490	620
5.02	0.000114	24.80	54490	1239
5.02	0.000228	35.25	54490	2478
5.02	0.000457	59.50	54490	4957
6.28	0.000143	35.30	68160	1550
6.28	0.000286	52.60	68160	3100
6.28	0.000571	78.00	68160	6200

Adsorptive Separator Model Experimental Validation



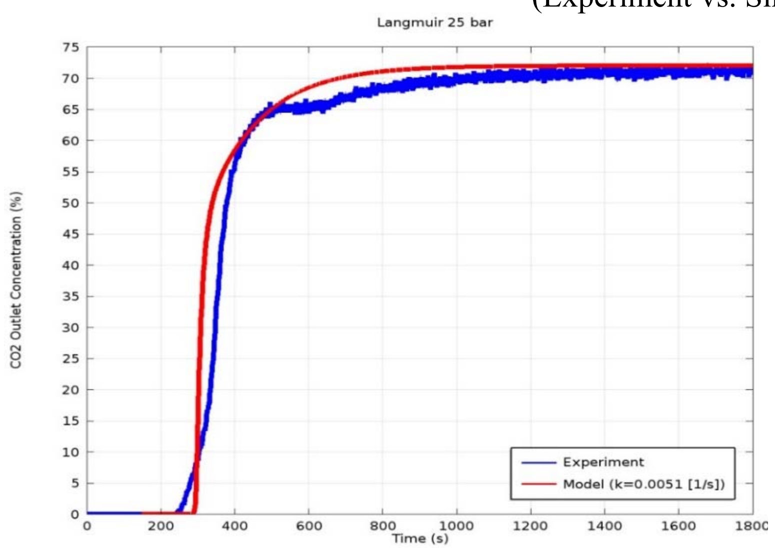
CO_2 outlet concentration at the exit of the adsorber

(Experiment vs. Simulation). Temp.= 523.15 K, Pressure = 5 bar.



CO_2 outlet concentration at the exit of the adsorber

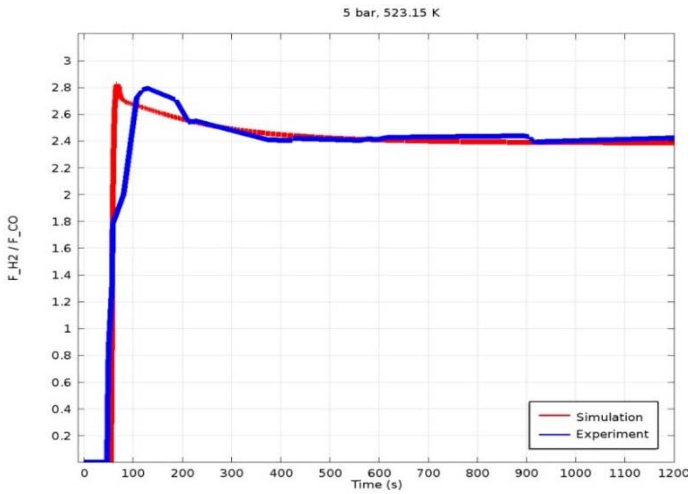
(Experiment vs. Simulation). Temp.= 523.15 K, Pressure = 15 bar.



CO_2 outlet concentration at the exit of the adsorber

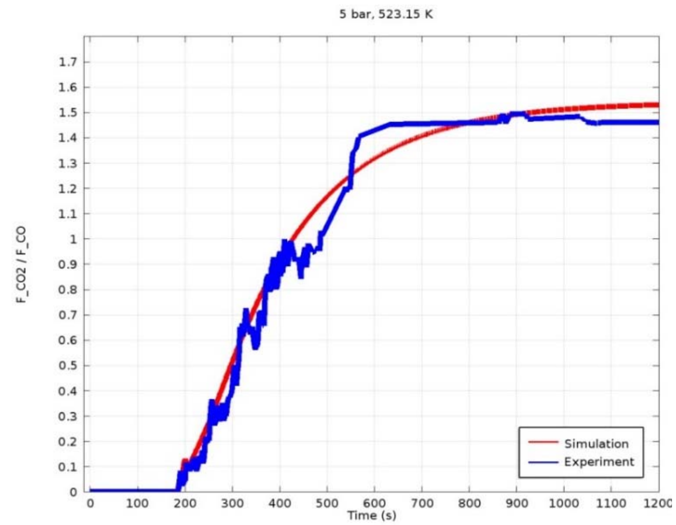
(Experiment vs. Simulation). Temp.= 523.15 K, Pressure = 25 bar.

AR Model Experimental Validation



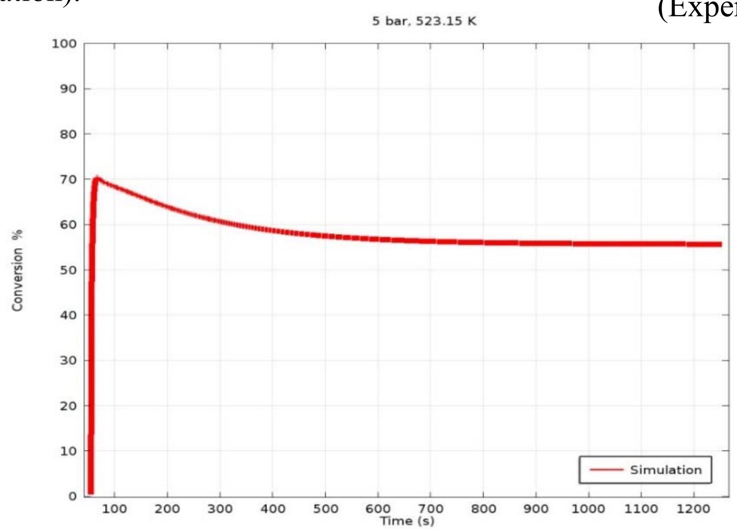
Molar ratio of H_2/CO at the AR outlet.

(Experiment vs. Simulation).



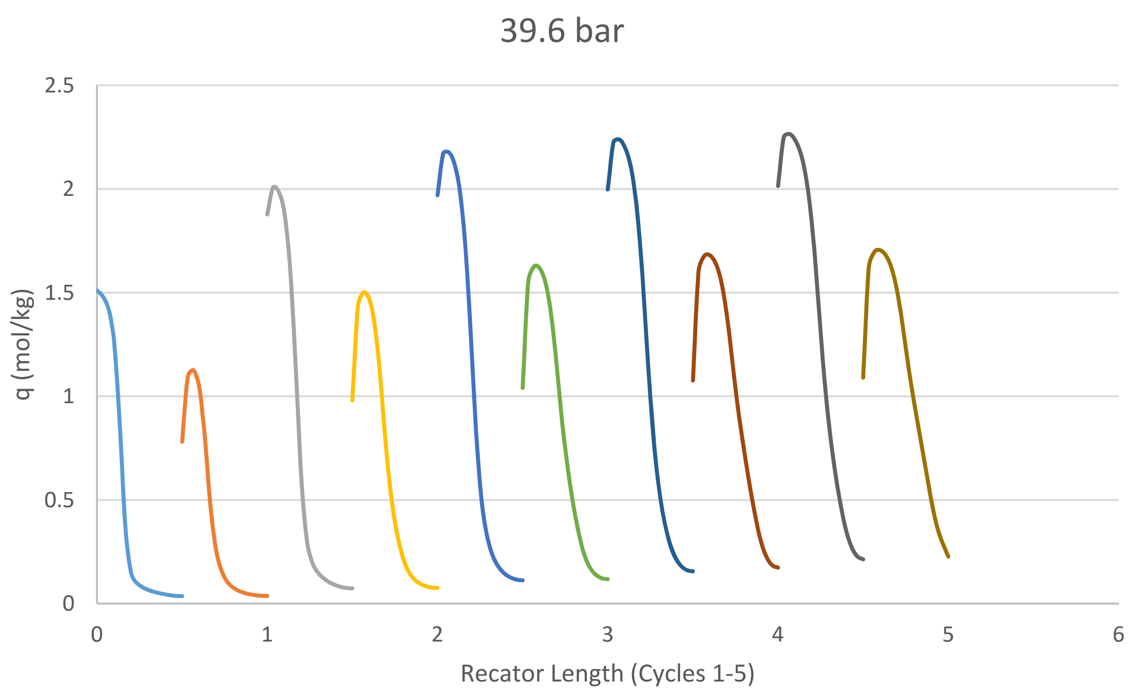
Molar ratio of CO_2/CO at the AR outlet.

(Experiment vs Simulation).



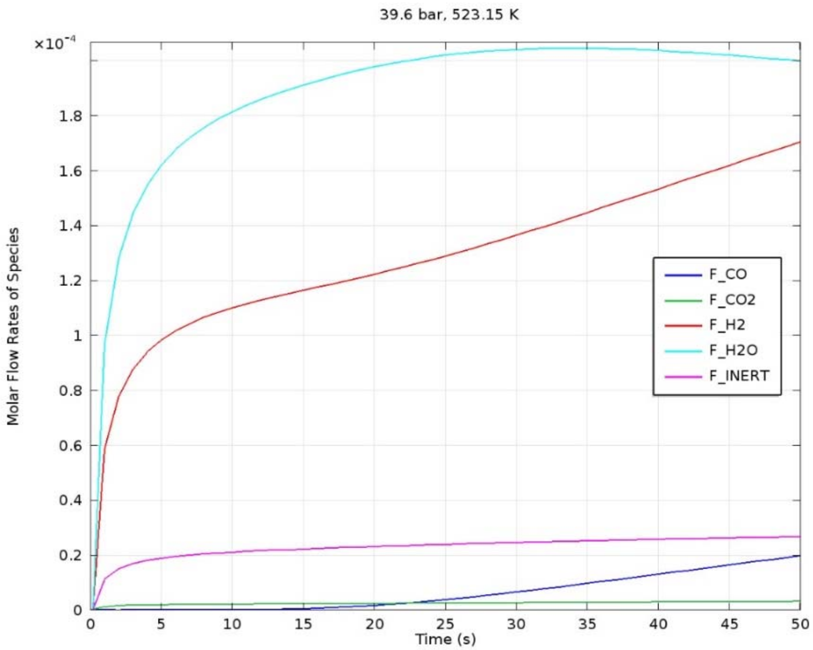
Percent CO conversion at the AR outlet.

Adsorption/Desorption Periodic Operation



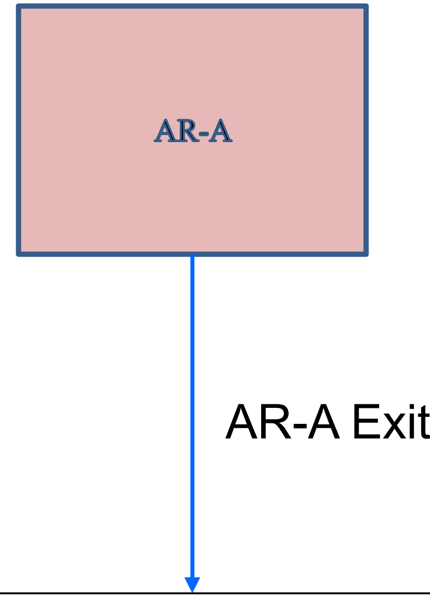
ADSORPTION/DESORPTION Cycles (q profile along the reactor from fresh to fifth cycle)

Adsorption Step for Fifth Cycle



Species Molar Flow Rate at the exit of the adsorber

Temp.= 523.15 K, Pressure = 39.6 bar.



F_CO_AVERAGE (mol/s)=**5.7876E-6 % 1.89**

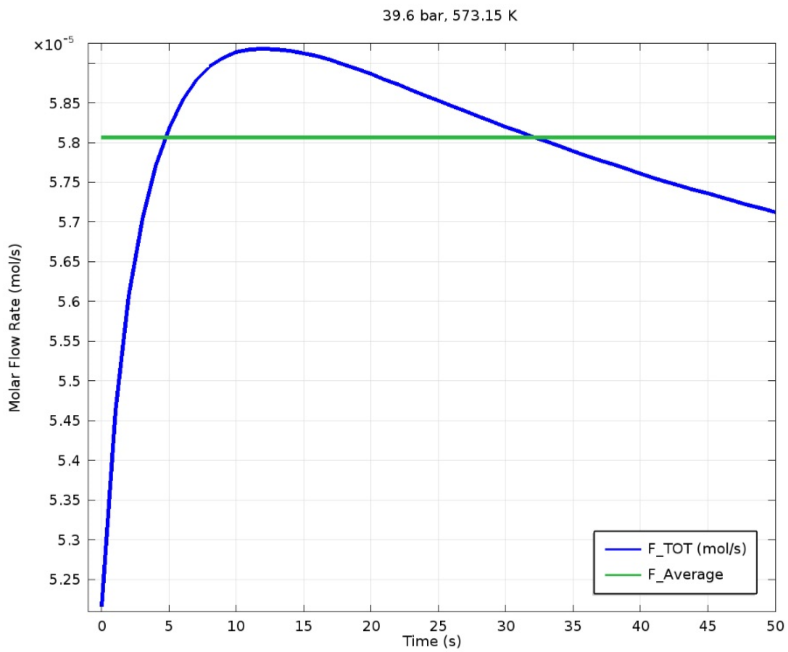
F_CO2_AVERAGE(mol/s)=**2.459E-6 % 0.803**

F_H2_AVERAGE (mol/s)=**8.704E-5 % 28.427**

F_H2O_AVERAGE (mol/s)=**1.877E-4 % 61.3**

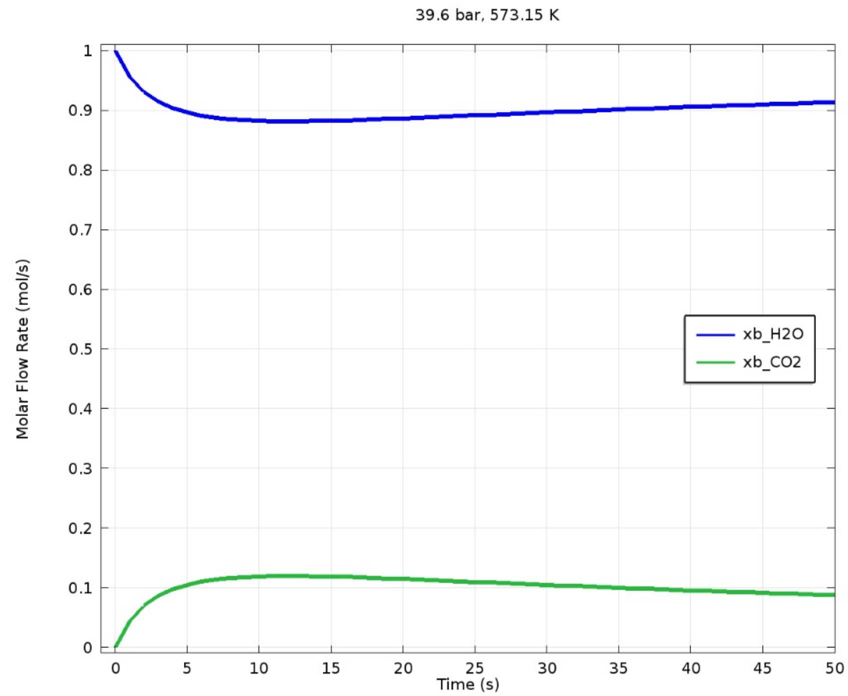
F_INERT_AVERAGE (mol/s)=**2.321E-5 % 7.58**

Desorption Step for Fifth Cycle

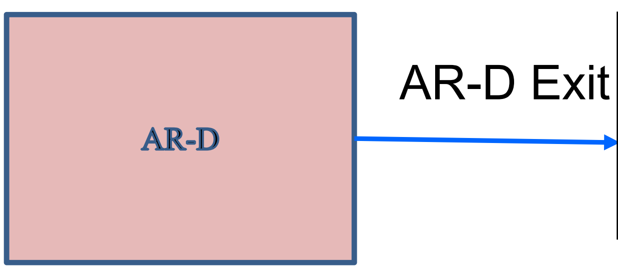


Species Molar Flow Rate at the exit of the reactor

Desorption, Temp.= 523.15 K, Pressure = 39.6 bar.



Desorption, Temp.= 523.15 K, Pressure = 39.6 bar.



F_AVERAGE(mol/s)=**5.8065E-5**

xb_H2O_AVERAGE=**0.89836**

xb_CO2_AVERAGE=**0.10164**

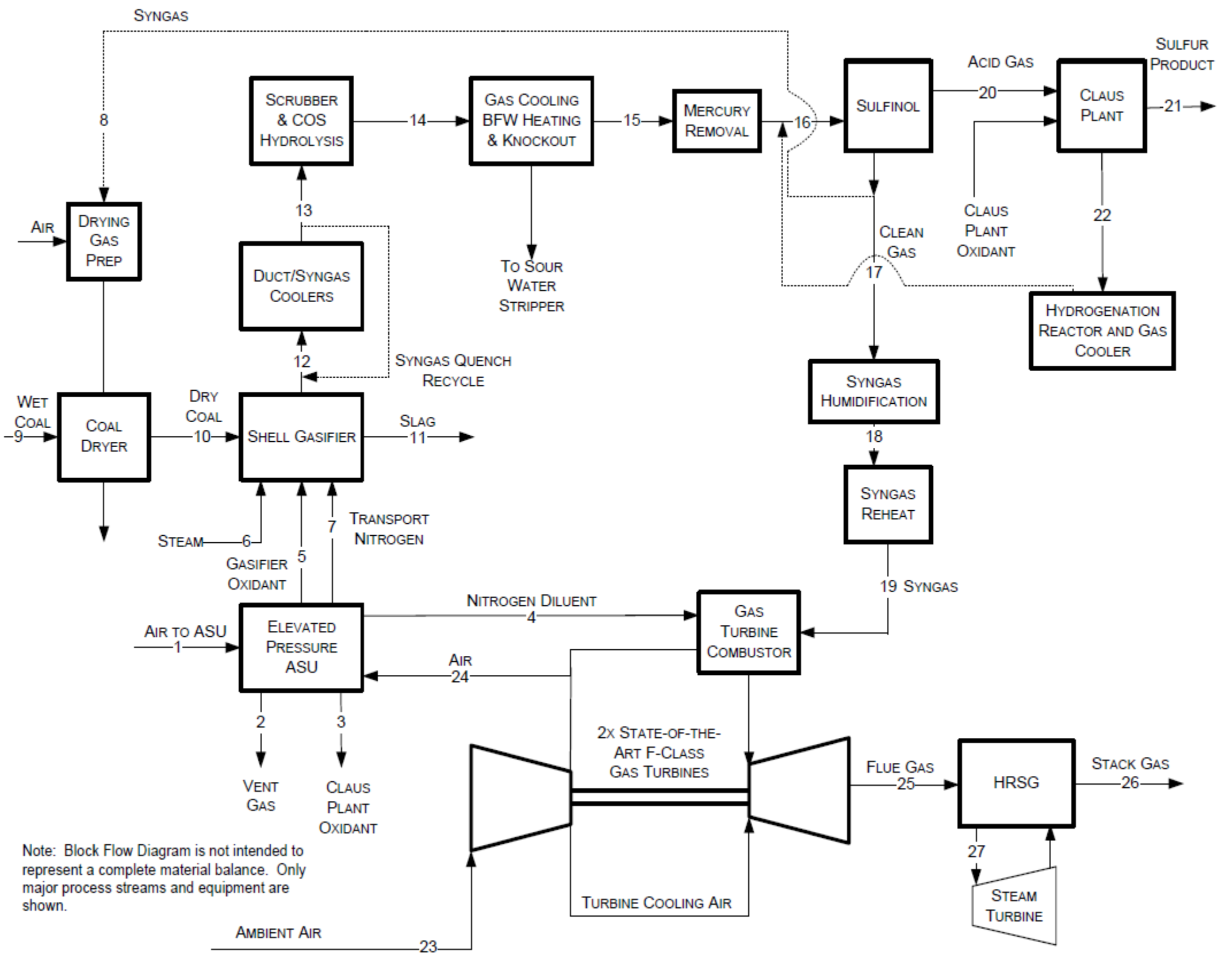
Combined MR-AR System: Success Criteria Satisfaction

		% CO Conversion	% H_2 Purity	% H_2 Recovery	% CO_2 Purity	% CO_2 Recovery
Target		<95	<95	<90	<95	<90
MR-AR Attainability	x=57.64 y=10 z=10 m=100	100	96.9	99.9	98.451	99.83
	x=115.29 y=10 z=10 m=100	100	96.9	99.9	98.451	99.8
	x=230.58 y=10 z=10 m=100	100	96.9	99.9	98.451	99.8

$x = W_{cat}/F_{CO}$(g_cat*h/CO_mol) in MR
y=Catalyst amount (gr) in MR
z=Catalyst amount (gr) in AR
m= Adsorbent amount (gr) in AR

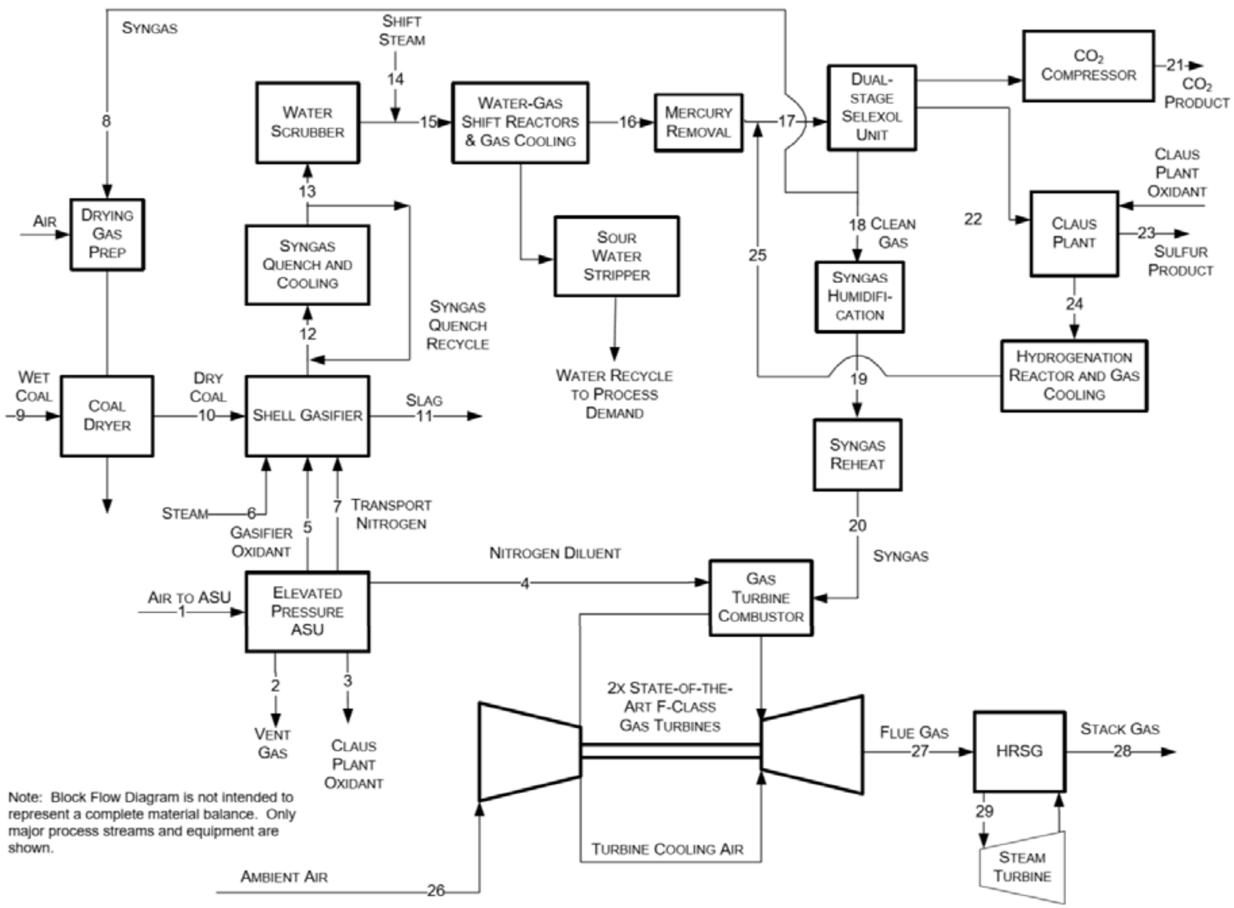
NETL Shell IGCC w/o CCS (Case B1A)

Exhibit 3-8 Case B1A block flow diagram, Shell IGCC without CO_2 capture



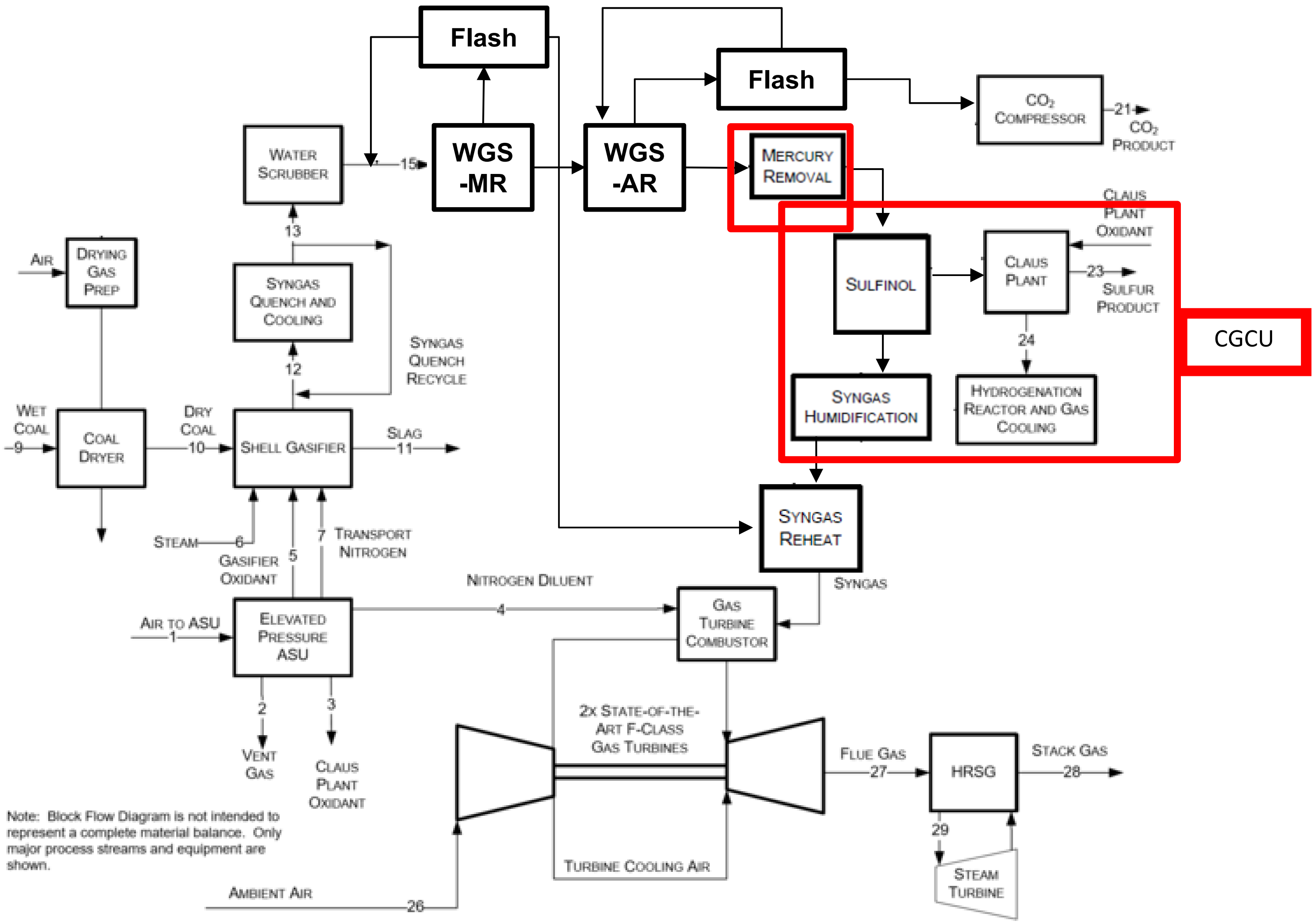
NETL Shell IGCC w/ CCS (Case B1B)

Exhibit 3-26 Case B1B block flow diagram, Shell IGCC with CO_2 capture

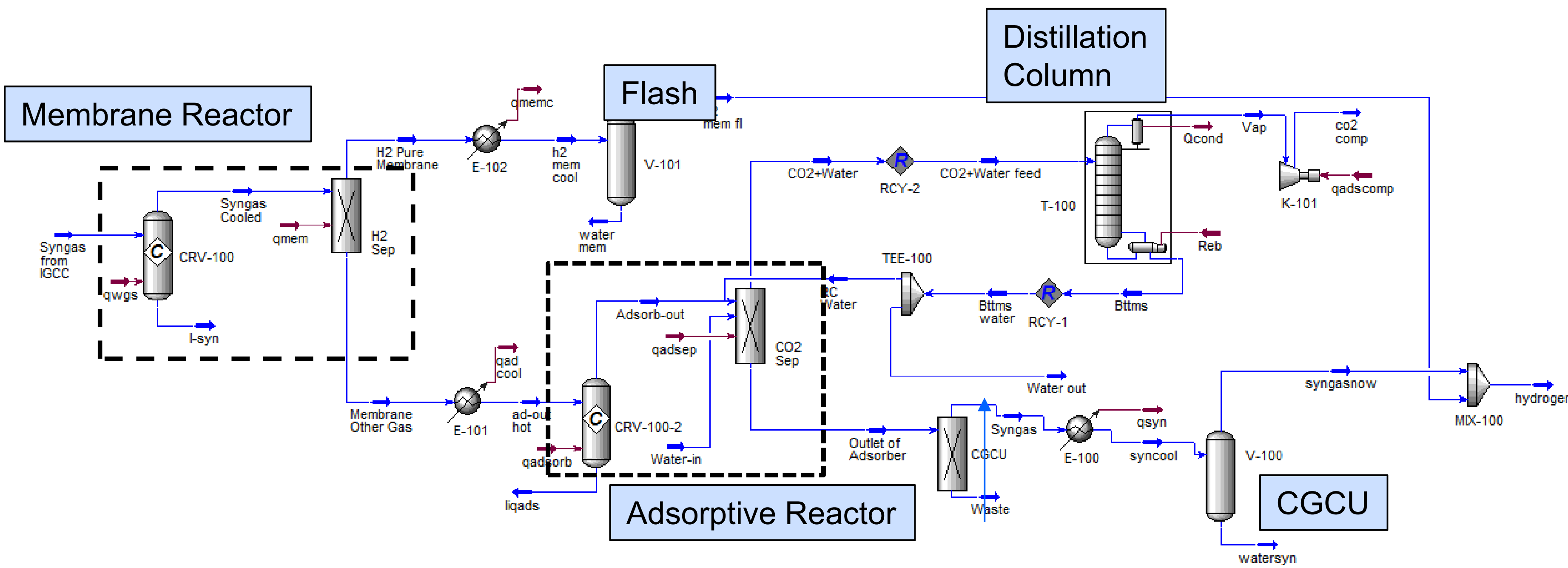


Source: NETL

Proposed Process Scheme Integration



Proposed Process Scheme



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

Designs	Net Power Production (Mwh/Ton)	CO2 Capture (%)
Shell IGCC w/o CCS - Sulfinol	4.68	0
Shell IGCC w/ CCS– 2 Stage Selexol	3.69	90
Shell IGCC w/ CCS- Membrane Reactor and Adsorptive Reactor	3.91	96

	% CO Conversion	% H_2 Purity	% H_2 Recovery	% CO_2 Purity	% CO_2 Recovery
Target	<95	<95	<90	<95	<90
MR-AR Realization	98	*91.8	96	99.5	95

* **Maximum attainable purity based on composition of utilized Syngas**

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

Designs	Total Gross Power (MWe)	Total Compression Power (kWe)	Acid Gas Removal (kWe)	Claus Plant Rec Comp (kWe)	Net Power (MWe)
Shell IGCC w/o CCS - Sulfinol	737	0	620	1140	629
Shell IGCC w/ CCS– 2 Stage Selexol	673	30210	18650	2080	497
Shell IGCC w/ CCS- Membrane Reactor and Adsorptive Reactor	677	23,300	992	1674	526

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

MR-AR Process (Equipment Cost)	
WGS Membrane Reactor (Tube)	$13,889,811.72
WGS Membrane Reactor (Membrane)	$12,893,975.68
Adsorption Reactor (Tube)	$15,736,899.56
Sulfinol System	$46,130,000.00
Distillation Column	$21,885,722.77
Flash Separator (Syngas)	$416,488.67
Flash Separator (H2)	$24,506.44
Flash Mem Cooler	$32,567.48
Ads Cooler	$34,927.84
Flash Ads Cooler	$146,936.36
Total Equipment Cost	**$111,191,836.51**

NETL w/ CCS:
Double Stage Selexol
Equipment Cost: $162,818,000

Compact Process Advantages

- ***Simultaneous CO conversion and H_2 and CO_2 separation***
- ***MR-AR Compression Work:*** <50% of IGCC w/ CCS compression work
- ***Equipment Capital Cost*:** <65% of IGCC w/ CCS dual-stage selexol unit equipment cost .
- ***Catalyst Amount*:** <70% of IGCC w/ CCS catalyst amount
- ***High Purity Hydrogen Produced***

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.*

Plans for Future Testing/Development/Commercialization

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

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

Subtask 4.1 - Unit Operation Testing - Continue and complete the testing of the individual MR and AR subsystems.

Subtask 4.2 - Mathematical Model Development and Simulations - Continue and complete the development of the mathematical models and their validation with the available experimental data.

<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.

Technical Approach/Project Scope, cont.

Project Success Criteria –BP2

Basis for Decision/Success Criteria
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.

Milestone Log –BP2

Title/Description	Planned Completion Date	Actual Completion Date	Verification Method	Comments (progress for achieving milestone, explanation from deviation, etc.)
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	
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	
Integrated system modeling and data analysis completed	3/31/2018		Results reported in the quarterly report	
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	
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	
Preliminary process design and optimization based on integrated MR-AR experimental results completed	9/30/2018		Results reported in Final Report	
Initial technical and economic feasibility study and sensitivity analysis completed	9/30/2018		Results reported in 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

Acknowledgement

The financial support of the US Department of Energy and the technical guidance and assistance of our Project Manager Andrew Jones are gratefully acknowledged.