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

DE-FOA-0001235
FE0026423

•**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**

USC VITERBI SCHOOL OF ENGINEERING

UCLA ENGINEERING Chemical and Biomolecular Engineering

2019 *Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review* (David L. Lawrence Convention Center, Pittsburgh, PA, USA; August 26-30, 2019)

Presentation Outline

- **Project Overview**
- **Technology Background**
- **Technical Approach/Project Scope**
- **Project Technical Progress and Key Accomplishments and Findings**
- **Appendix – Technical Publications**

Project Overview

Performance Period: 10-01-2015 – 3-31-2019

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

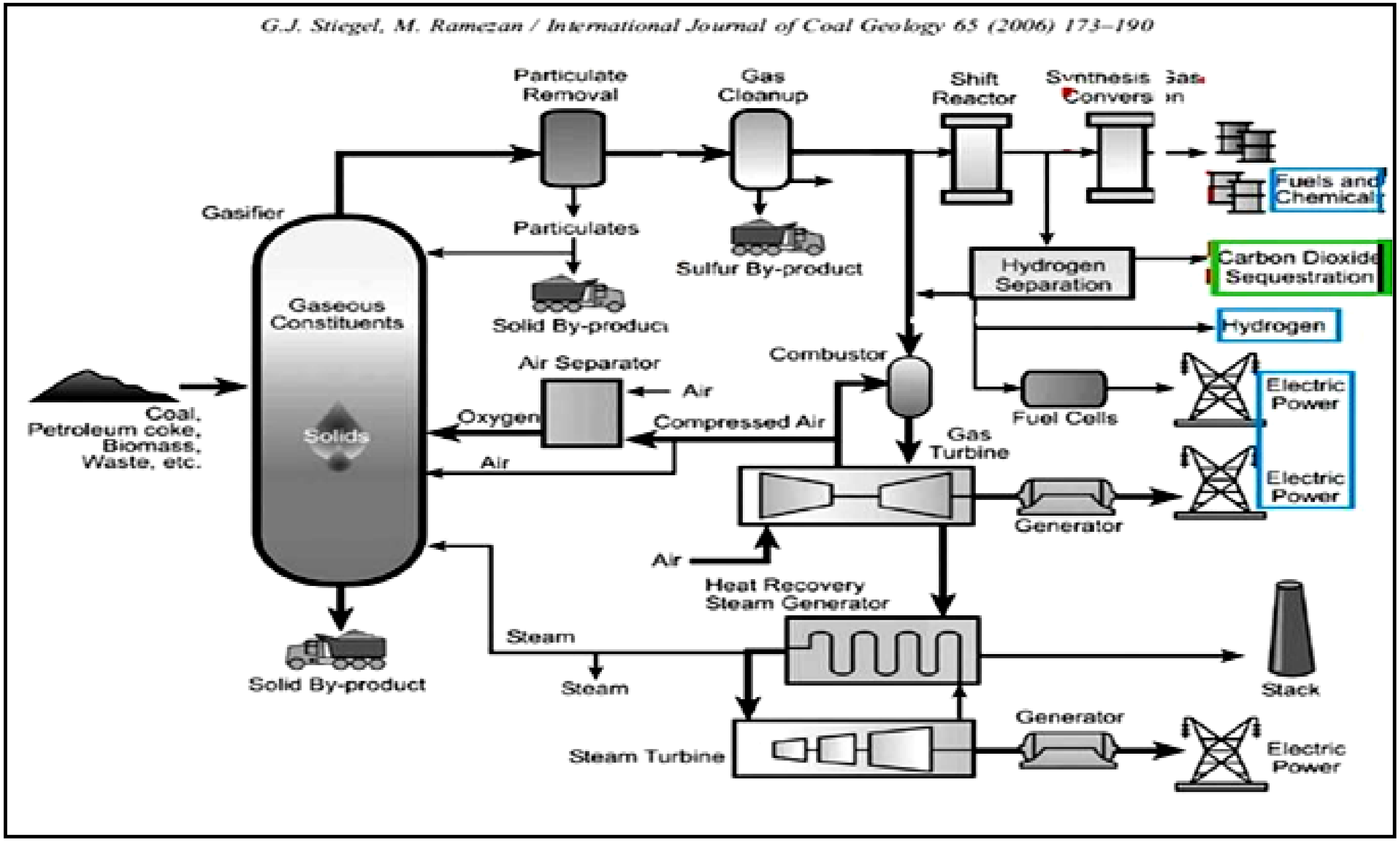
Overall Project Objectives:

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.*

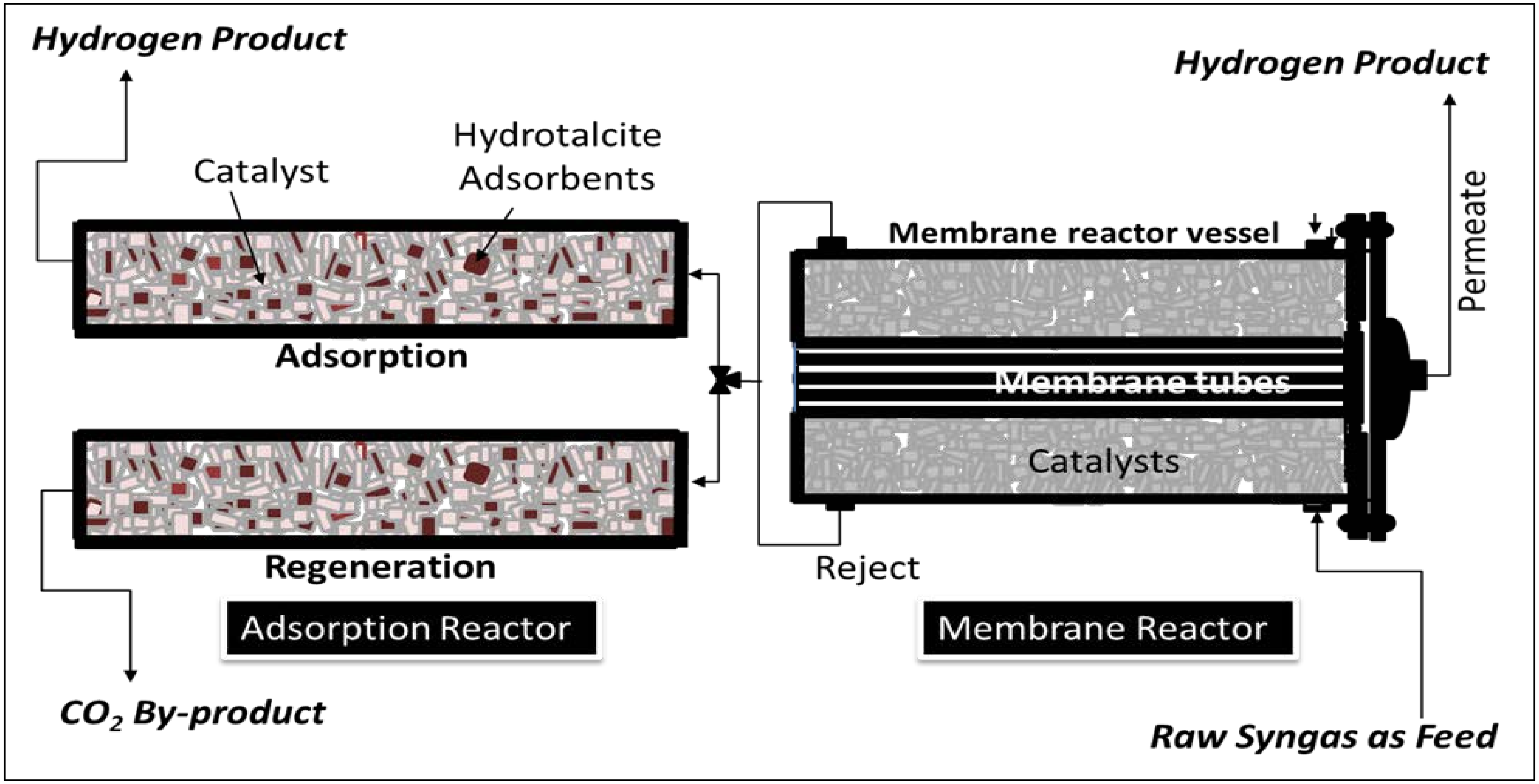
Key Project Tasks/Participants:

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. .**----- M&PT, UCLA, USC***

Conventional IGCC Power Plant



MR-AR Process Scheme



- Use of Partial Pressure Swing Adsorption based regeneration allows CO_2 recovery 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.

MR-AR Process Scheme – Advantages over 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.*

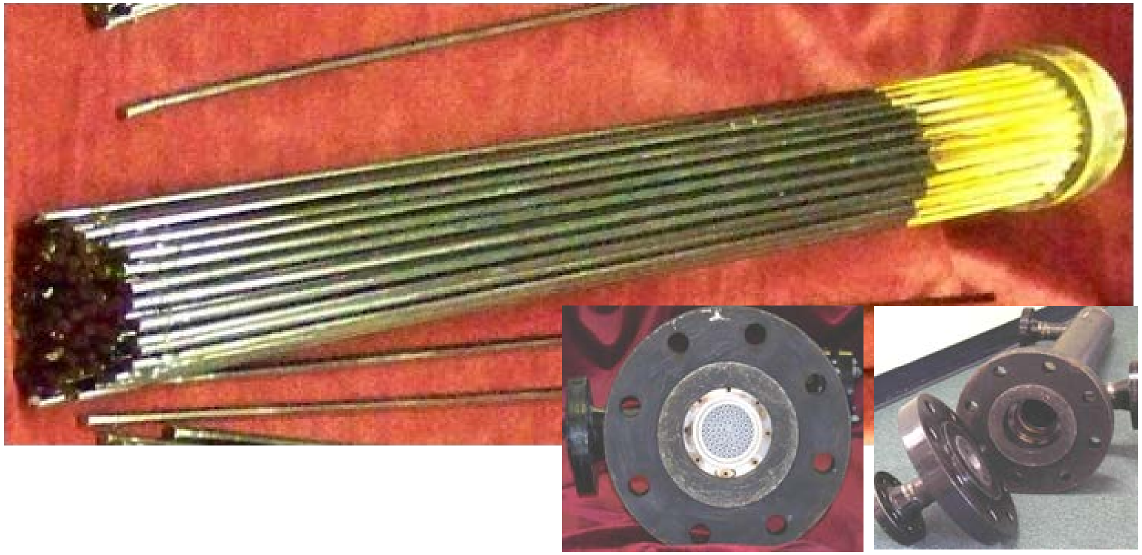
Unique Advantages:

- ***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.*

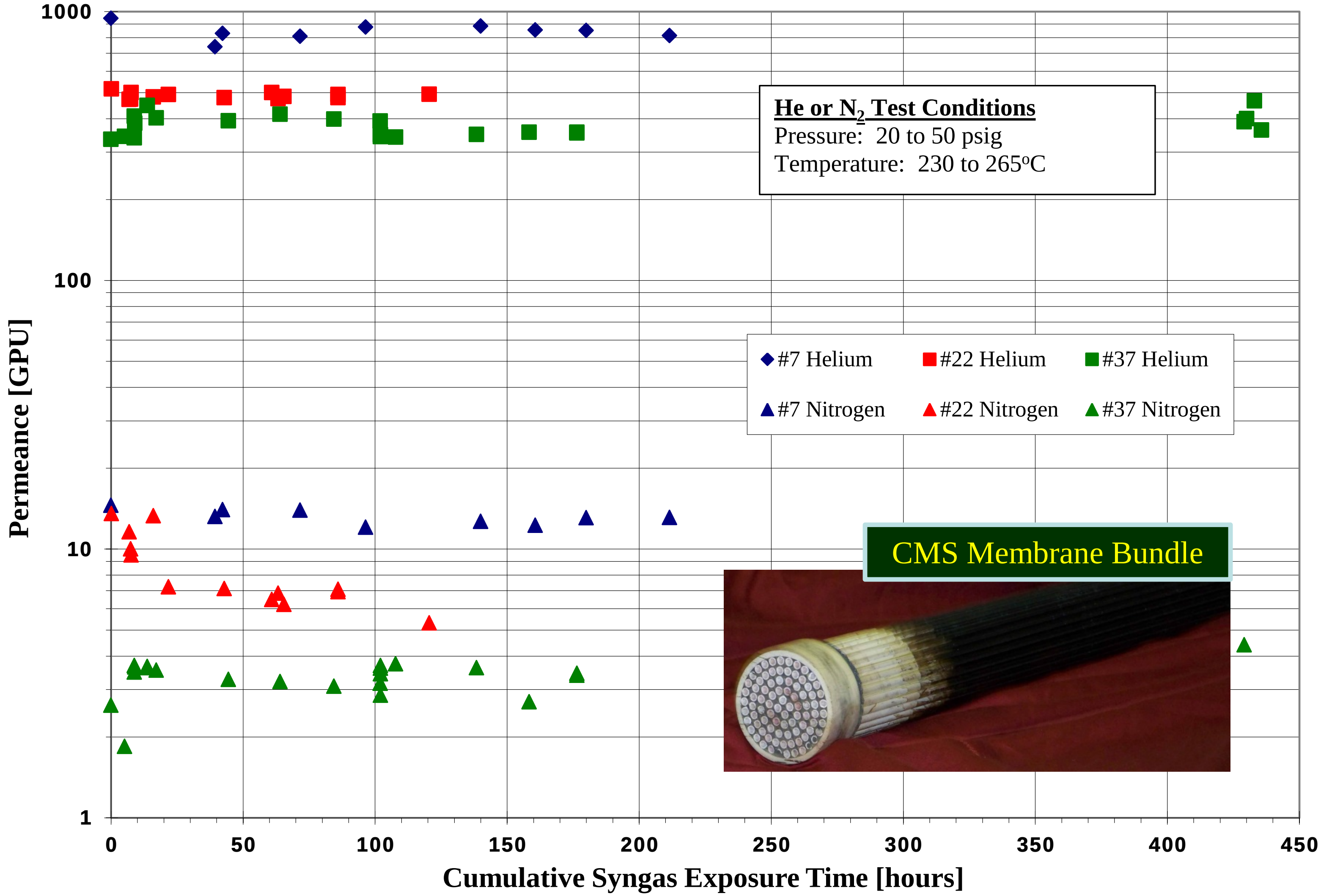
Field-Testing of CMS Membranes

M&PT test-unit at NCCC for hydrogen separation

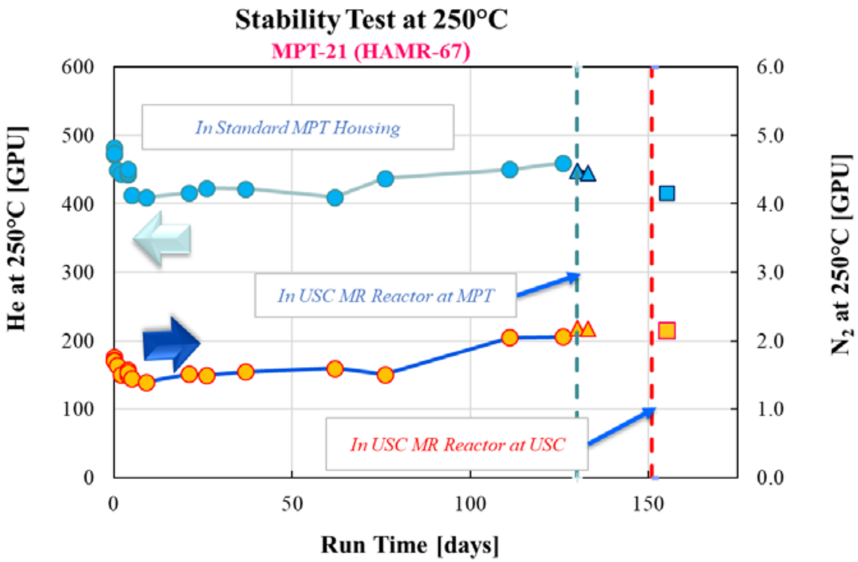
CMS membranes and modules



Long-Term Stability Testing in Gasifier Off-gas [NCCC]



A New Generation of CMS Membranes

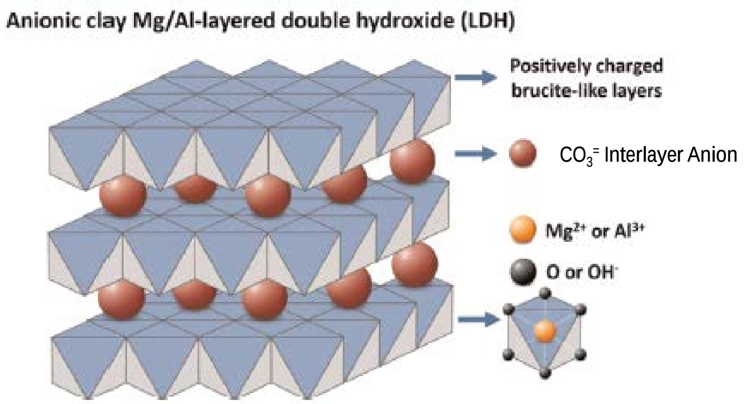


Original Project Targets:
H_2_Permeance (350 – 500 GPU);
$H_2/CO>80$ (Equivalent to $He/N_2>100$)

He/N_2 used as H_2/CO surrogates in routine permeation tests. He and H_2 permeances within 5-10% from each other (H_2, typically, faster). CO permeance, typically, 15-20% larger than N_2

Part ID	*He [GPU]*	*N_2 [GPU]*	*H_2 [GPU]*	*CO_2 [GPU]*	*H_2/N_2 [-]*	*H_2/CO_2 [-]*
HMR-61	578	2.5	550	1.0	219	558
HMR-67	450	1.6	581	2.8	354	211
HMR-68	591	3.0	675	2.7	227	248
MR-70	445	1.5	502	0.7	344	738
HMR-72	500	1.7	602	2.5	359	246
HMR-104	542	1.5	540	2.0	361	270

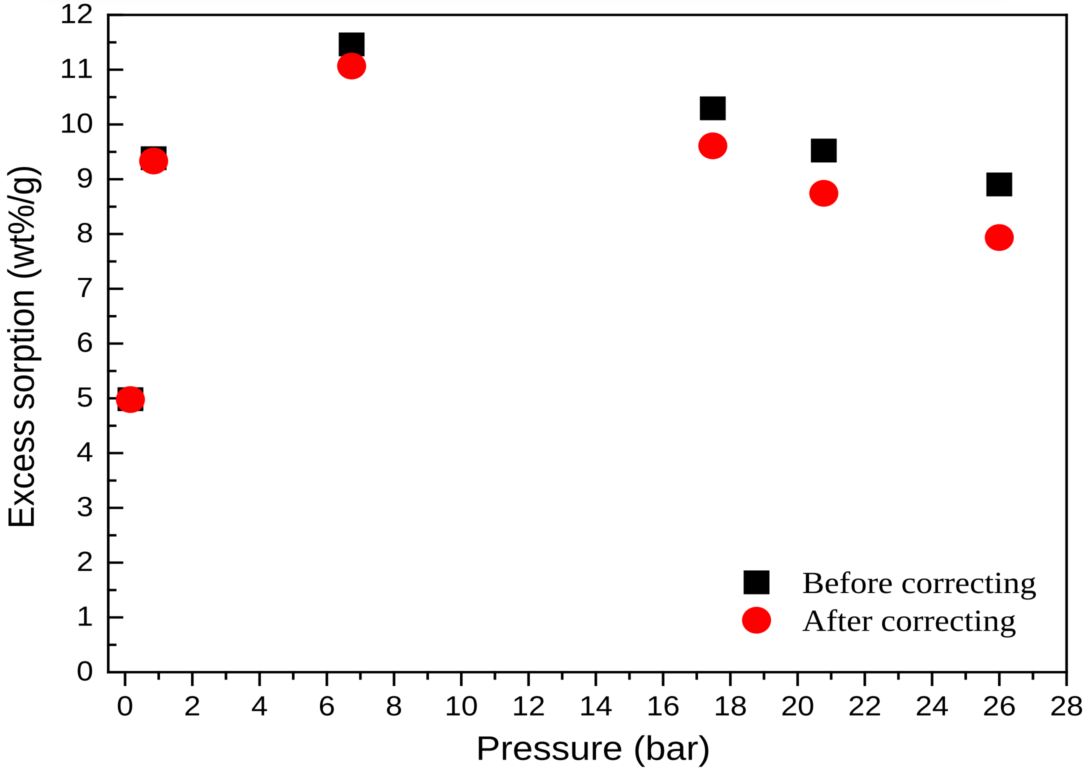
Adsorbent Preparation and Characterization



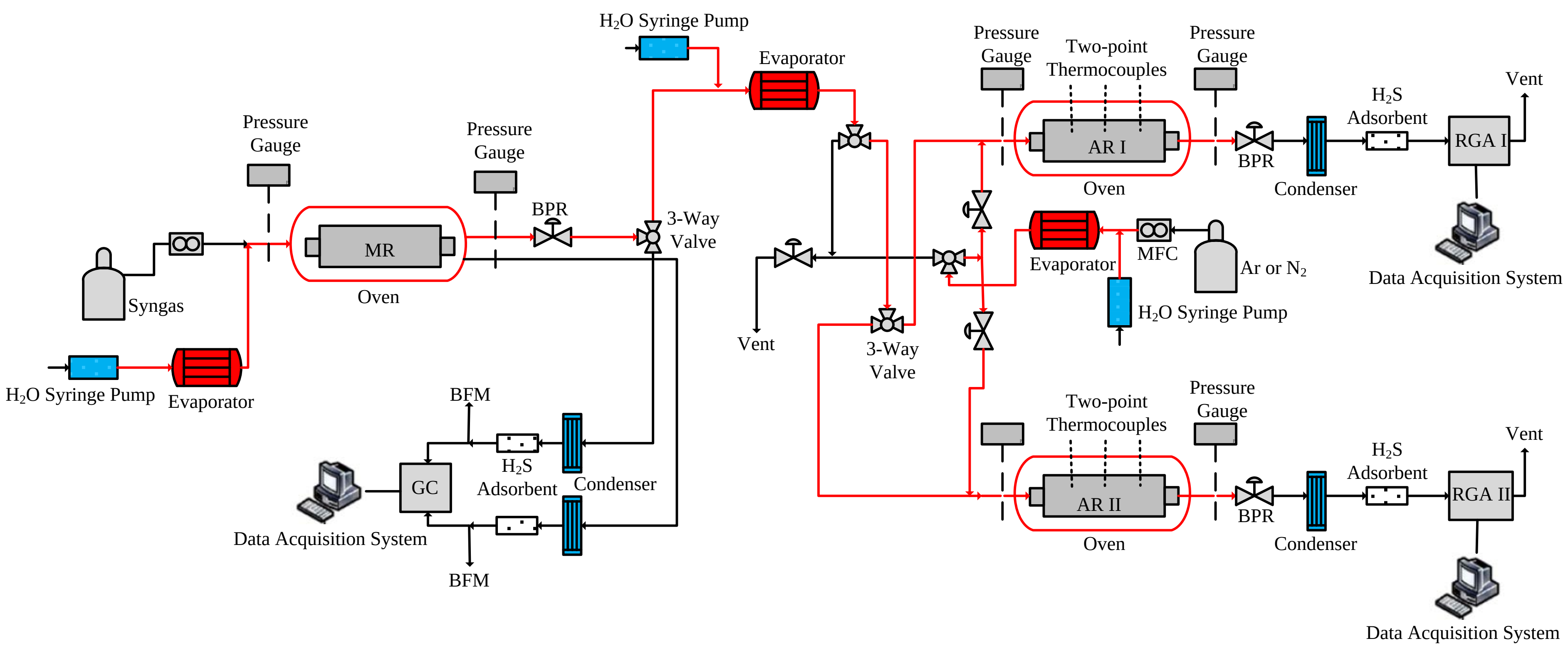
Hydrotalcite (HTC) Adsorbent

- ✓ ***High CO_2 capacity:*** *Over wide range of temperatures and pressures.*
- ✓ ***Simple Preparation:*** *Precipitation of Al/Mg from solution in $NaOH/Na_2CO_3$*
- ✓ ***Stable:*** *Unaffected by H_2S and simulated tars at the operating temperature.*

High-Pressure Adsorption Isotherm at 250 °C



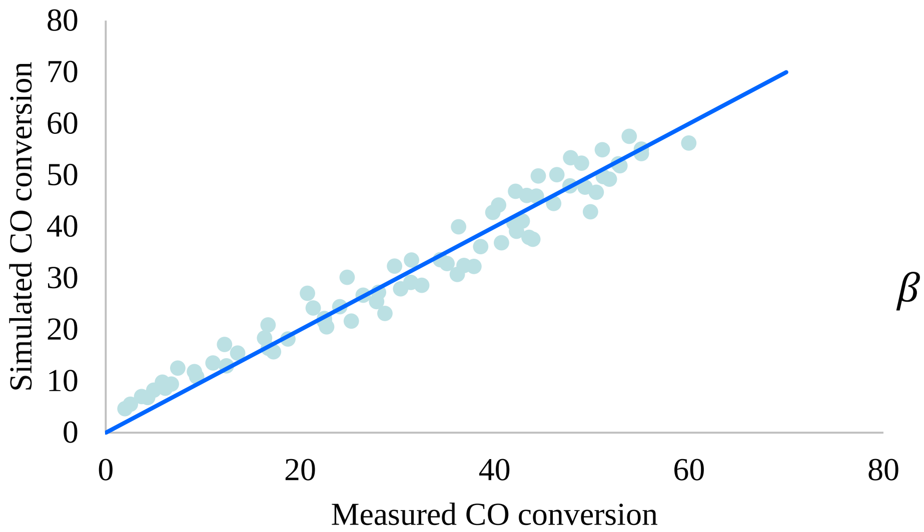
Lab-Scale Experimental Set-Up



Lab-Scale Experimental Results and Analysis

Co-Mo/Al_2O_3 Sour-Shift Catalyst Characterization

Global Reaction Kinetics- Empirical Model and Comparison with Microkinetic Models



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

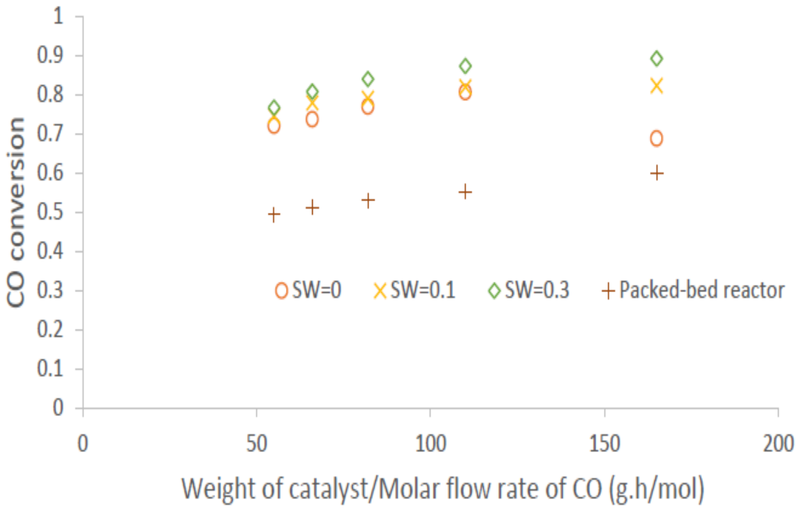
$$\beta = \frac{1}{K_{eq}} \frac{(P_{CO_2} . P_{H_2})}{(P_{CO} . P_{H_2O})} \quad K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

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

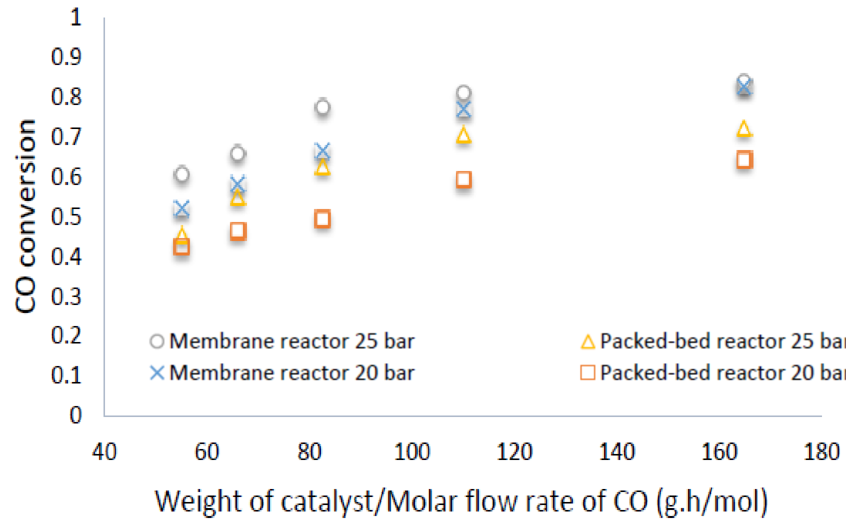
A[mol/(atm$^{(a+b+c+d)}$ · h · g)]	**18957**
E [J/mol]	58074
a	4
b	-1.46
c	0.13
d	-1.44

Lab-Scale Experimental Results and Analysis, Cont.

Experimental Conversion vs. W/F_{CO} for MR and PBR



Conversion of MR and PBR with three different steam sweep ratios (300 ºC, feed pressure of 15 bar, CMS#1)

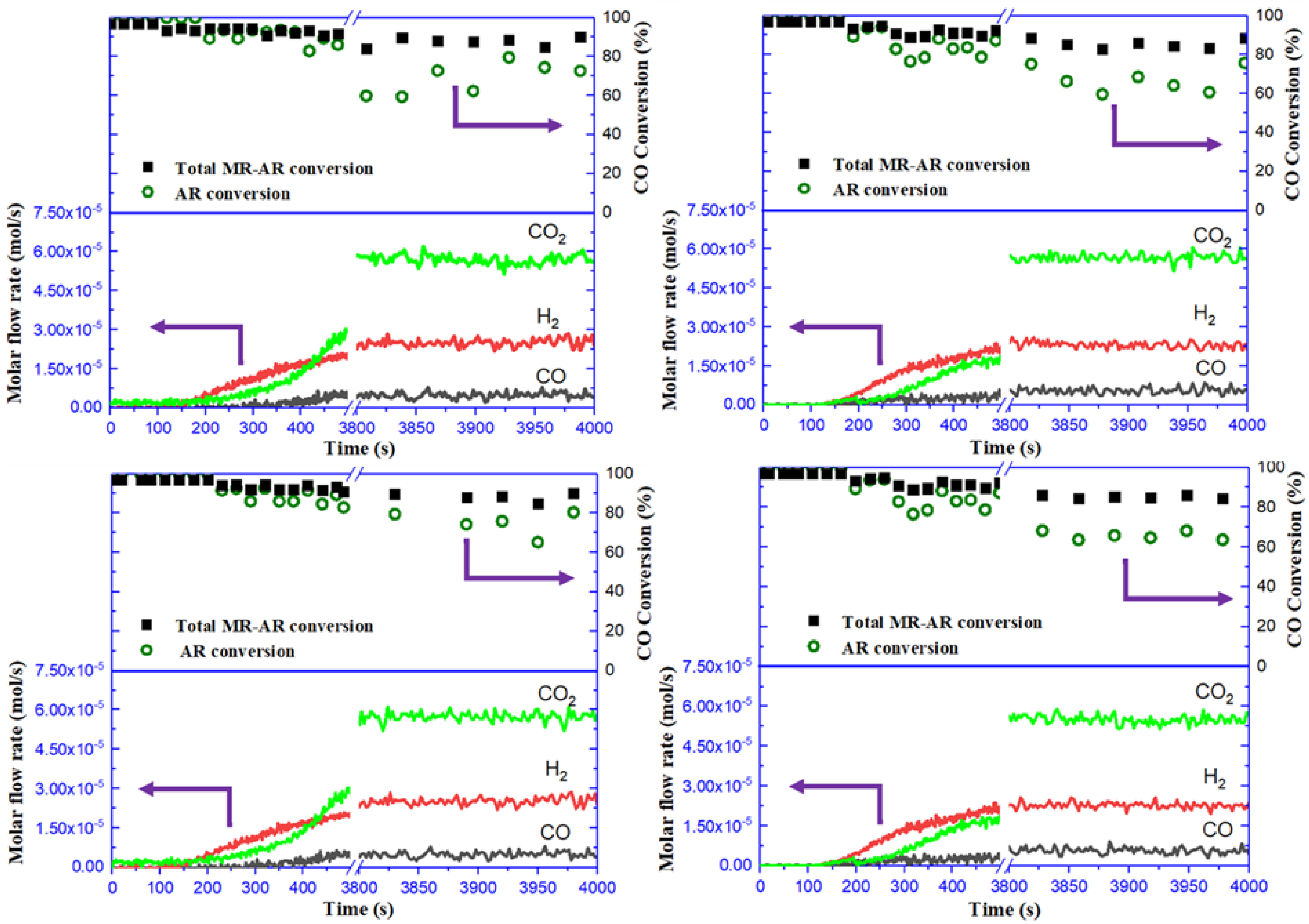


Conversion of MR and PBR with no sweep (250 ºC, feed pressure of 20 and 25 bar, CMS#2)

$$X_{CO} = \frac{n^F_{COo} - (n^F_{CO,exit} + n^P_{CO,exit})}{n^F_{COo}}$$

Lab-Scale Experimental Results and Analysis, Cont.

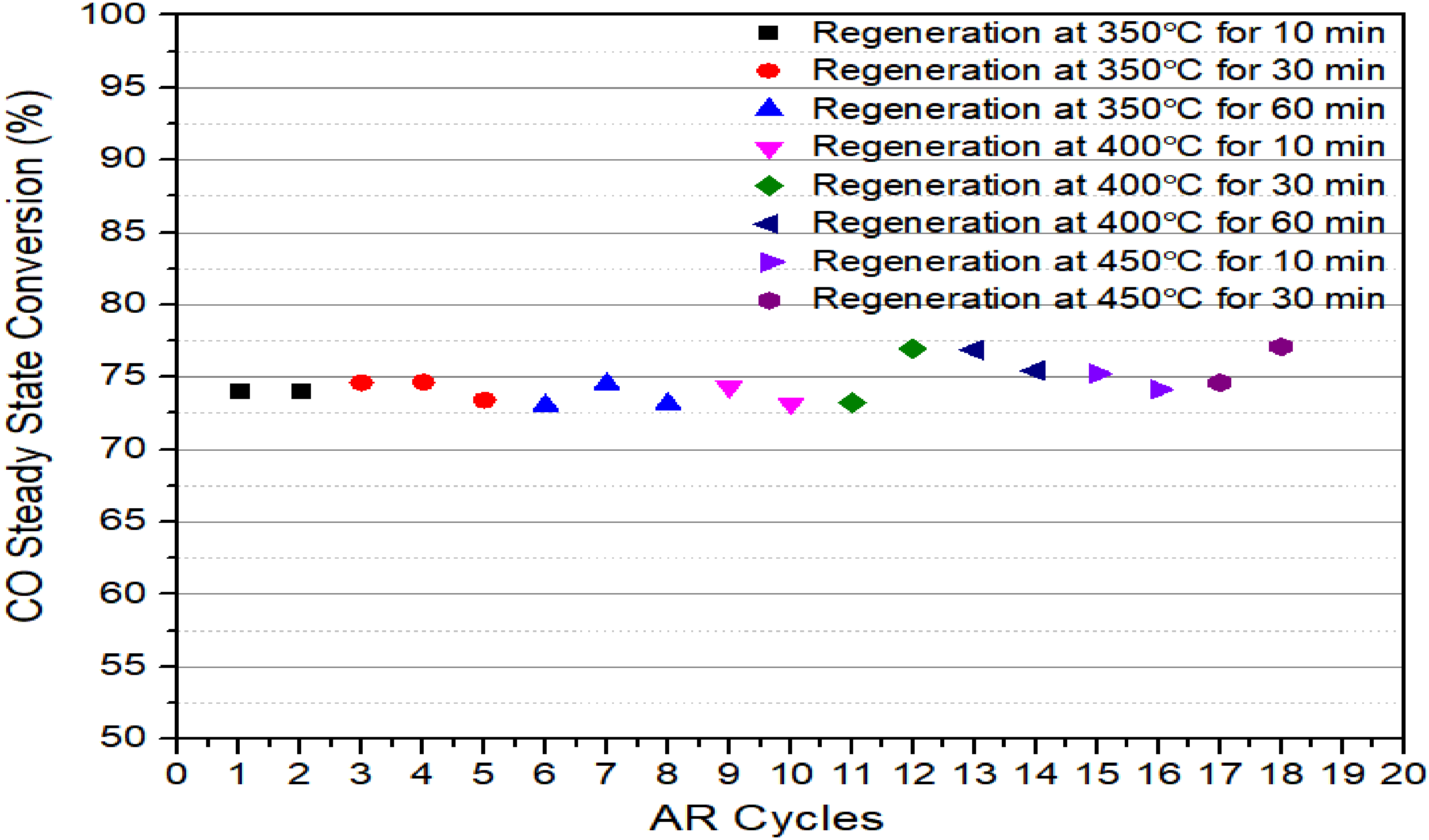
Experimental Results of MR-AR Performance



CO in the AR and total MR-AR conversion, and species molar flow rates. (Left Top) AR I, first cycle, (Right Top) AR II, first cycle, (Left Bottom) AR I, second cycle, (Right Bottom) AR II, second cycle. Temp.=250 °C, pressure=25 bar, H_2O/CO ratio=2.8, W/F_{CO}=55 g·h/mol.

Lab-Scale Experimental Results and Analysis, Cont.

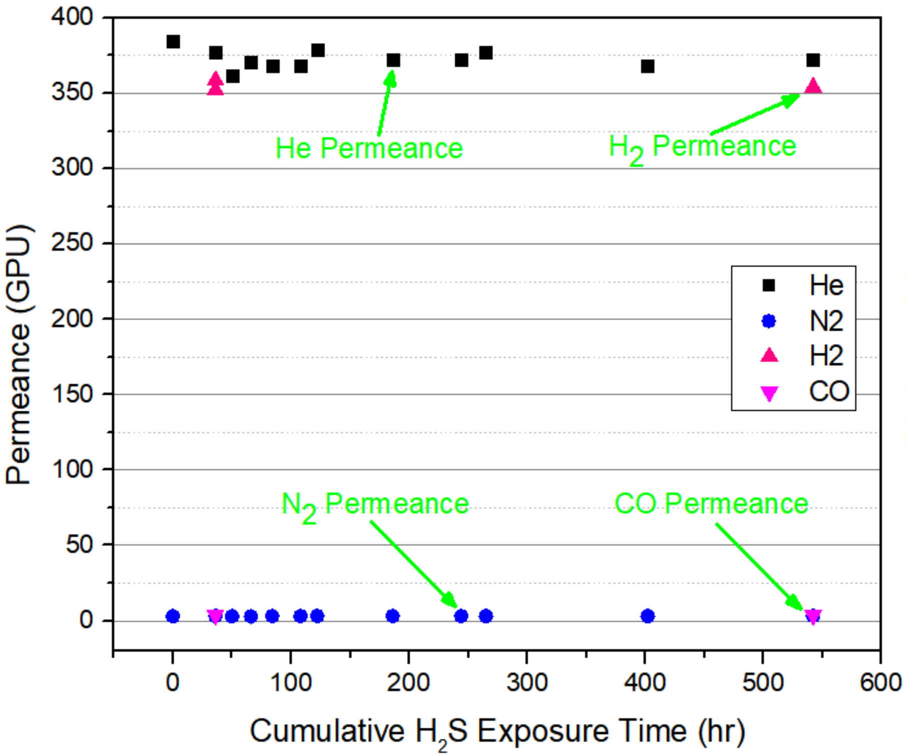
Experimental Results of Catalyst Robustness During Adsorbent Regeneration

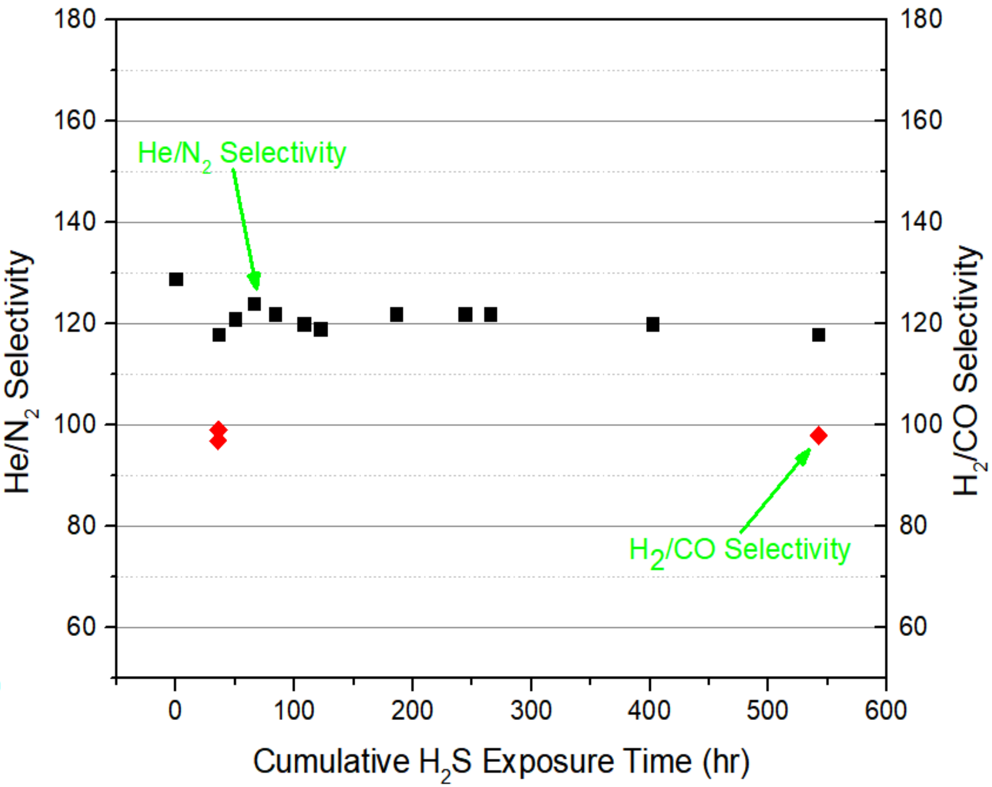


AR pseudo-steady conversion after adsorbent saturation for various regeneration protocols, as shown on the Figure. Temp.=250 °C, pressure=5 bar, W_c/F_{CO}=121 g·h/mol, W_{Ad}/W_c= 6.9:1.

500-hr Integrated MR-AR Run

Evaluation of Membrane Stability

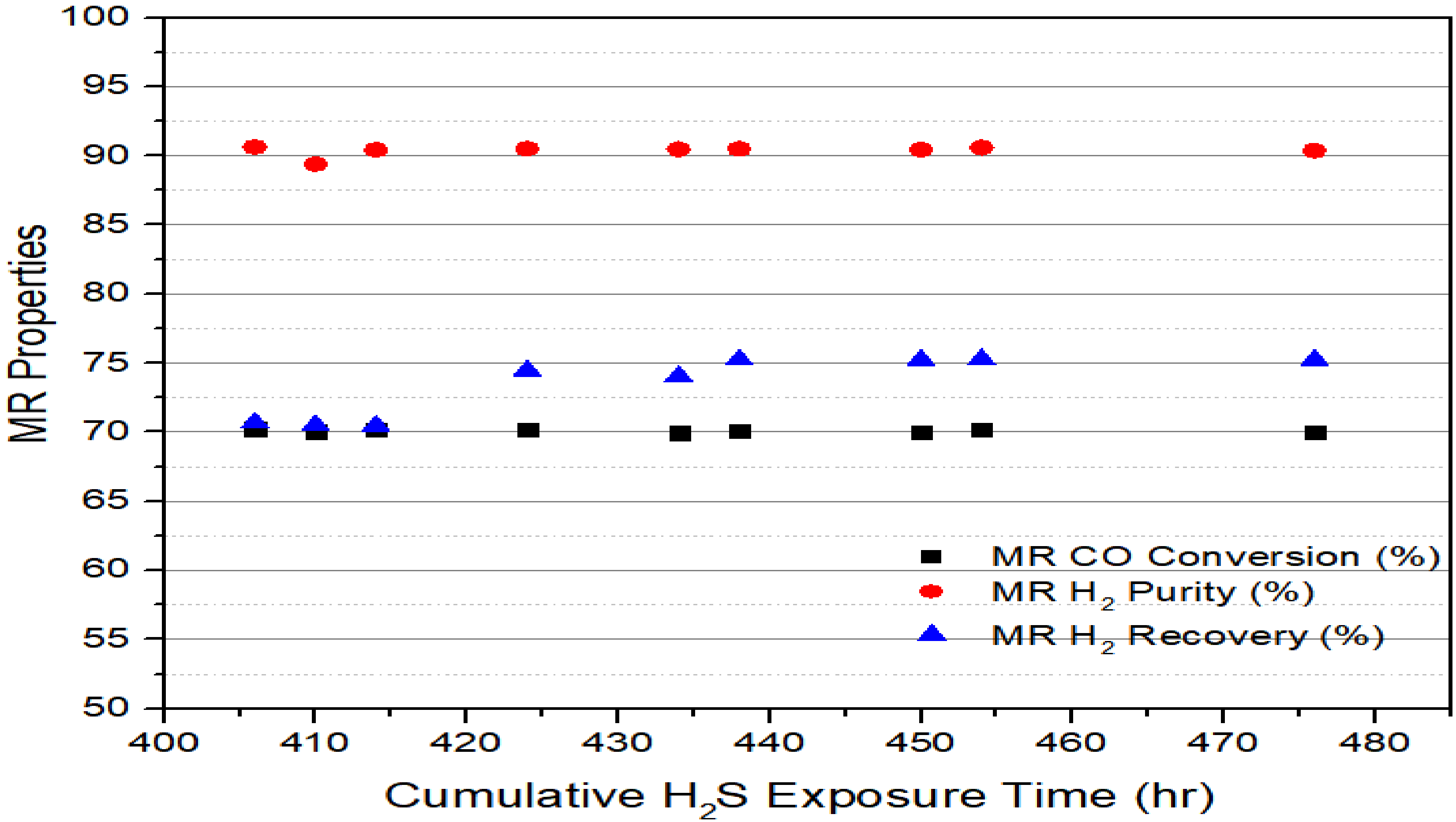




T= 250 ^{0}C, feed pressure of 25 bar with steam sweep (CMS#23).

500-hr Integrated MR-AR Run, Cont.

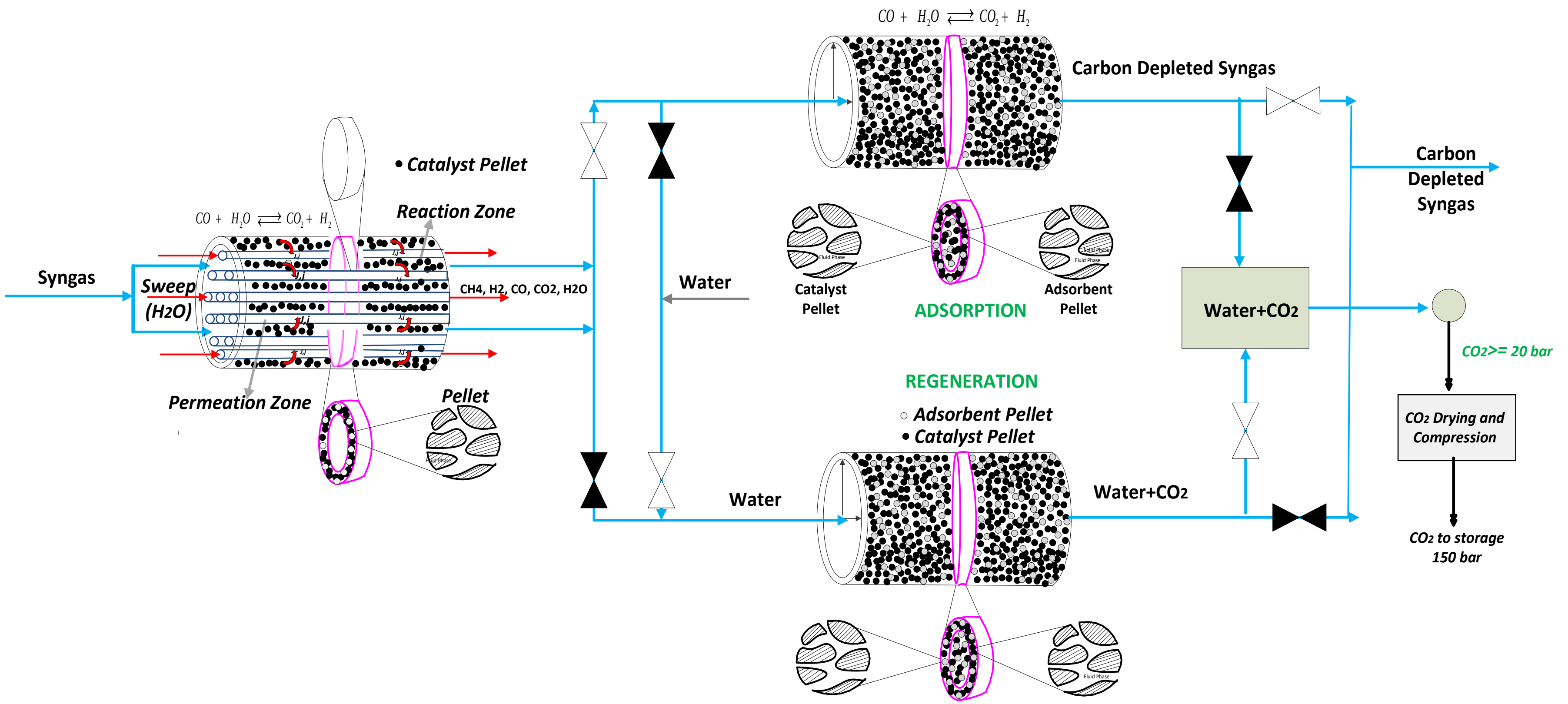
MR Subsystem Conversion – An Indicator of Catalyst and Membrane Stability



T=250 °C, feed pressure=25 bar, permeate pressure 3 bar, with steam sweep, W_c/F_{CO}= 66 g·h/mol, air-blown gasifier model syngas (CMS#23).

Multi-Scale MR-AR Model for Process Scale-Up

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



Multi-Scale MR-AR Model for Process Scale-Up – MR System

Pellet-scale Model Equations & Boundary Conditions

Constitutive laws

Continuity Equation:

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

Component mass conservation:

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

Energy conservation:

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

Initial Conditions:

$$\left.\begin{aligned}&x_j^p=0\\&\overrightarrow{n_j^p}=0\\&T^p=T^r=T_{in}\\&P^p=0\\&Q_r=-\lambda\vec{\nabla}T^p=0\\&\vec{\nabla}P^p=0\end{aligned}\right\}\ \mathit{for}\ t=0,\ \forall r\quad(30)$$

Boundary Conditions:

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

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

Reactor-scale Reaction Zone Model Equations & Boundary Conditions

Bulk Gas Constitutive laws

Continuity Equation:

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

Component mass conservation:

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

Energy conservation:

$$\left\{\begin{aligned}&\left(\varepsilon_A^r\sum_{j=1}^{n_s}x_j^r c_j^r C_j^r\right)\overrightarrow{v_f^r}\cdot\left(\vec{\nabla}T^r\right)-\vec{\nabla}\cdot\left(\lambda^r\vec{\nabla}T^r\right)+\frac{A^{SM}}{V^r}J_j^{perm}\left(H_j^r-H_j^{perm}\right)=\\&a_{cat}h_{cat}\left(T^r-\left(T^{cat}\right)^s\right)+a_{qua}h_{qua}\left(T^r-\left(T^{qua}\right)^s\right)-\frac{A^{SM}U'}{V^r}\left(T^r-T^{perm}\right)+\frac{4U}{d_t}\left(T^{fur}-T^r\right)\end{aligned}\right\}$$

Initial Conditions:

$$\left.\begin{aligned}&x_j^r=0\\&T^r=T_{in}^r\\&P^r=P_{in}^r\end{aligned}\right\}\ \mathit{for}\ t=0,\ \forall z\quad(35)$$

Boundary Conditions:

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

$$\left.\begin{aligned}&\vec{\nabla}T^r=0\\&\overrightarrow{n_j^r}=0\\&\vec{\nabla}P^r=0\end{aligned}\right\}\ \mathit{for}\ z=L$$

Multi-Scale MR-AR Model for Process Scale-Up – MR System

MR Reactor-scale Permeation Zone Model Equations

Bulk Gas Constitutive laws

Continuity Equation:

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

Component mass conservation:

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

Energy conservation:

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

Initial Conditions:

$$\left.\begin{array}{l}x_j^{perm}=0\\ T^{perm}=T_{in}^{perm}\\ p^{perm}=p_{in}^{perm}\end{array}\right\}\ for\ t=0,\ \forall z \quad (47)$$

Boundary Conditions:

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

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

Dusty Gas Model

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

The Stefan-Maxwell Equation

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

Momentum Equation

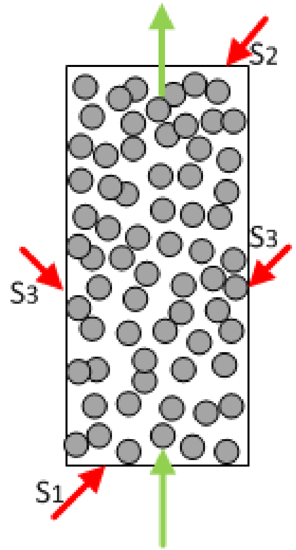
$$\vec{\nabla}P^r=-K_D\overrightarrow{v_f^r}-K_v\overrightarrow{v_f^r}^2=\vec{\nabla}p^r=\left(-150\frac{\left(1-\varepsilon_V^r\right)^2}{\left(\varepsilon_V^r\right)^3 d_p^{\,2}}-\mu_f^r 1.75\frac{\left(1-\varepsilon_V^r\right)}{\left(\varepsilon_V^r\right)^3 d_p}\rho_f^r\left|\overrightarrow{v_f^r}\right|\right)\overrightarrow{v_f^r}$$

Multi-Scale MR-AR Model for Process Scale-Up – AR System

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:

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

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

Momentum balance:

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

Multi-Scale MR-AR Model for Process Scale-Up – AR System

Initial and boundary conditions for the AR model.

Initial Conditions:

$$\left.\begin{aligned} c_j^r &= 0 \\ T^r &= T_{in}^r \\ P^r &= P_{in}^r \end{aligned}\right\} for\ t=0,\ \forall z$$

Boundary Conditions:

$$\left.\begin{aligned} \overrightarrow{v_f^r} &= \left(\overrightarrow{v_f^r}\right)_{in} \\ P^r &= P_{in}^r \\ \overrightarrow{c_j^r} &= \left(\overrightarrow{c_j^r}\right)_{in} \\ T^r &= T_{in}^r \end{aligned}\right\} for\ z=0$$

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

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:

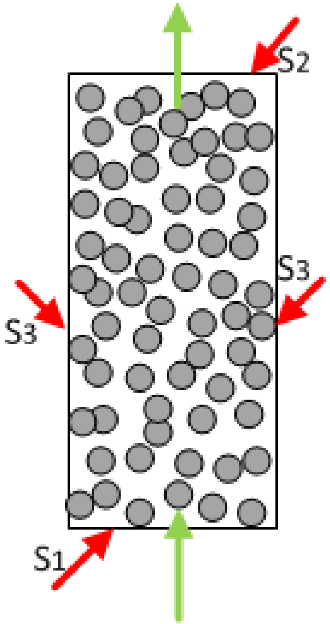
$$\lambda_g = \sum_{i=1}^{N_s} \frac{x_i \lambda_i}{\sum_{j=1}^{N_s} x_i \phi_{ij}}, \qquad \phi_{ij} = \frac{\left[1 + \left(\mu_i/\mu_j\right)^{1/2} \left(M_j/M_i\right)^{1/4}\right]^2}{8\left(1 + \left(M_i/M_j\right)\right)^{1/2}}$$

Specific Heat Capacity of Pure Gases:

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

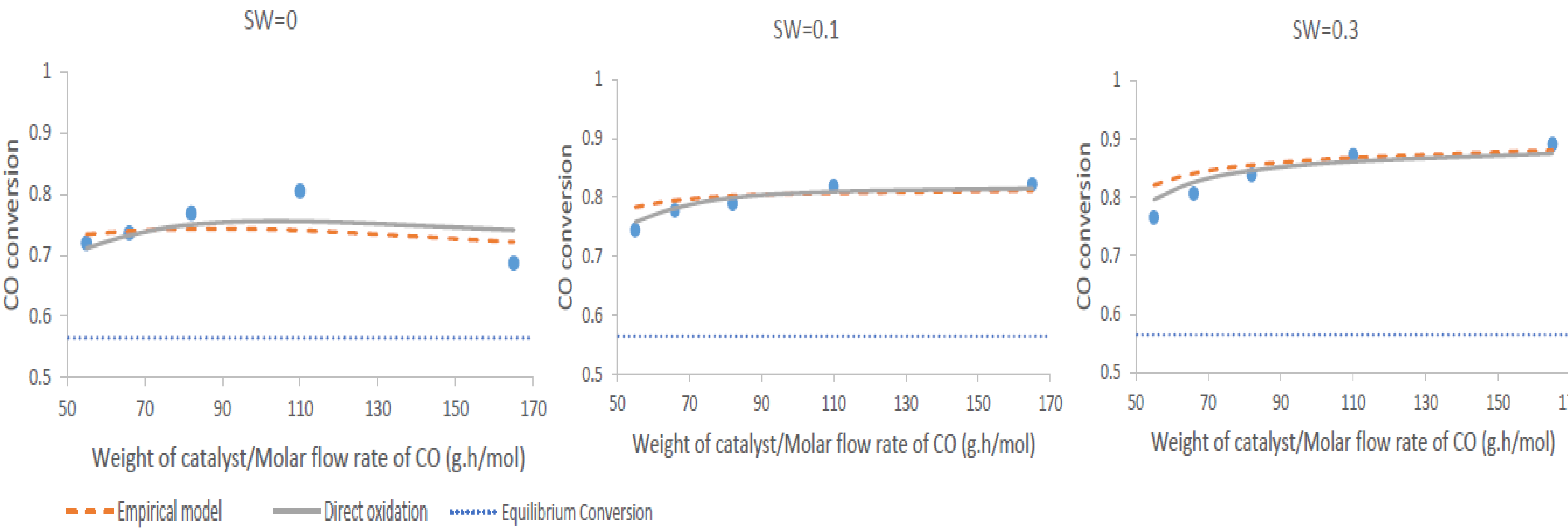
Specific Heat Capacity of Gas Mixture:

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



Lab-Scale Experimental Results and Model Fits - MR

Experimental Conversion for Various Sweep Ratios and Model Predictions

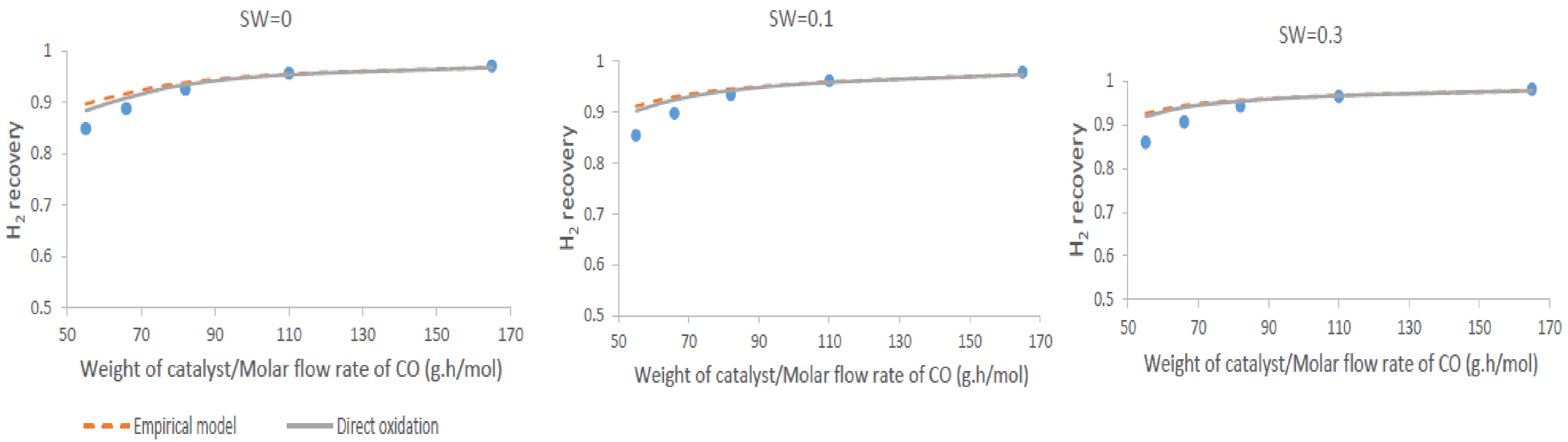


Experimental conversion for the MR with different sweep ratios and the corresponding MR model fits using both the empirical and microkinetic models. (300 ºC, feed pressure of 15 bar, CMS#1)

$$X_{CO} = \frac{n^{F}_{COo} - (n^{F}_{CO,exit} + n^{P}_{CO,exit})}{n^{F}_{COo}}$$

Lab-Scale Experimental Results and Model Fits - MR

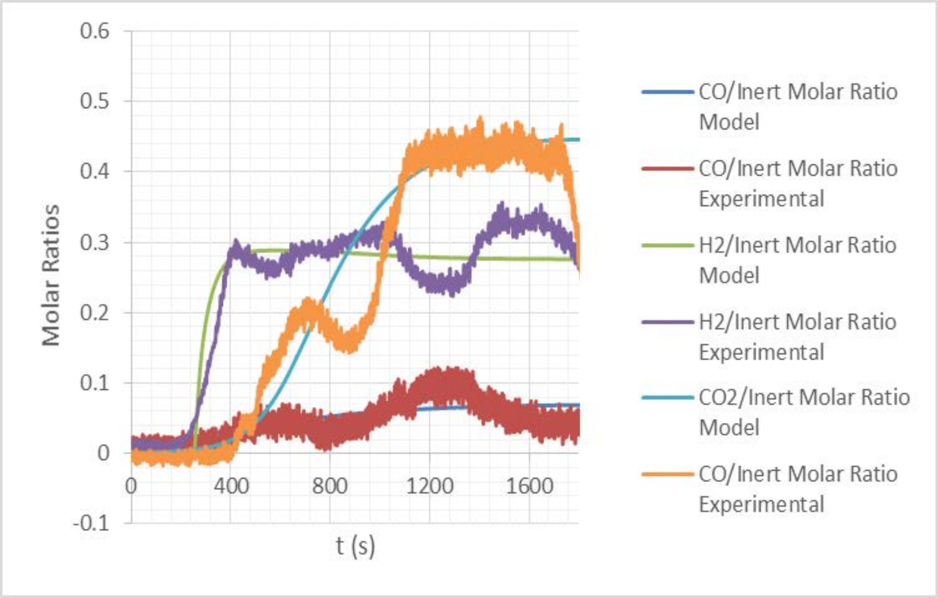
Experimental Hydrogen Recovery for Various Sweep Ratios and Model Predictions

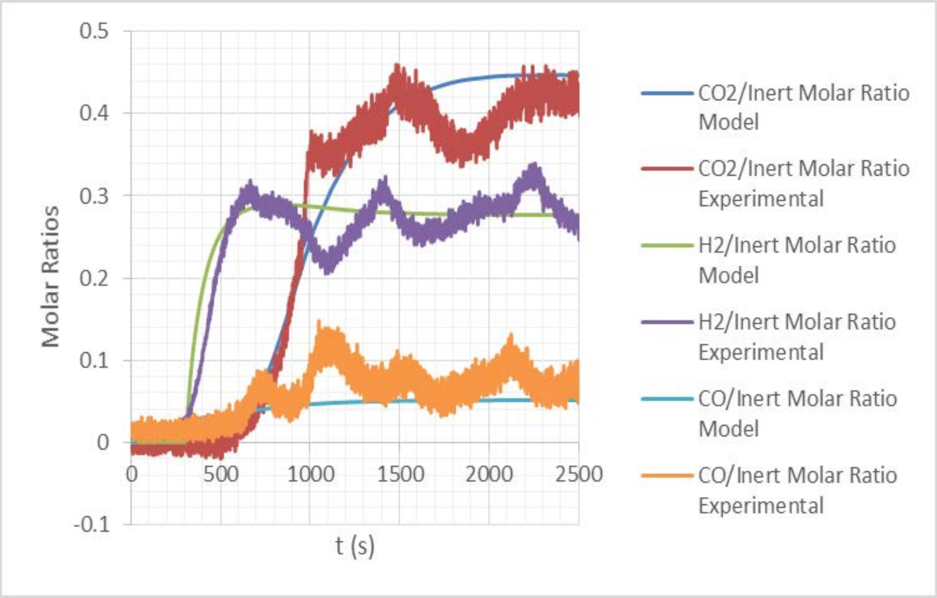


Experimental hydrogen recovery and the corresponding MR model fits using both the empirical and microkinetic models. (300 ⁰C, feed pressure of 15 bar, CMS#1)

$$Re_{H_2} = \frac{n^P_{H_2,exit}}{(n^F_{H_2,exit} + n^P_{H_2,exit})}$$

Lab-Scale Experimental Results and Model Fits - AR



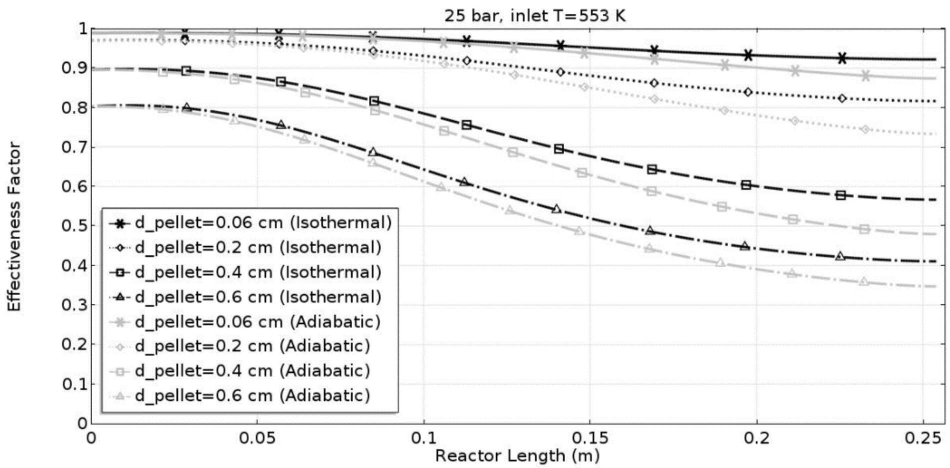


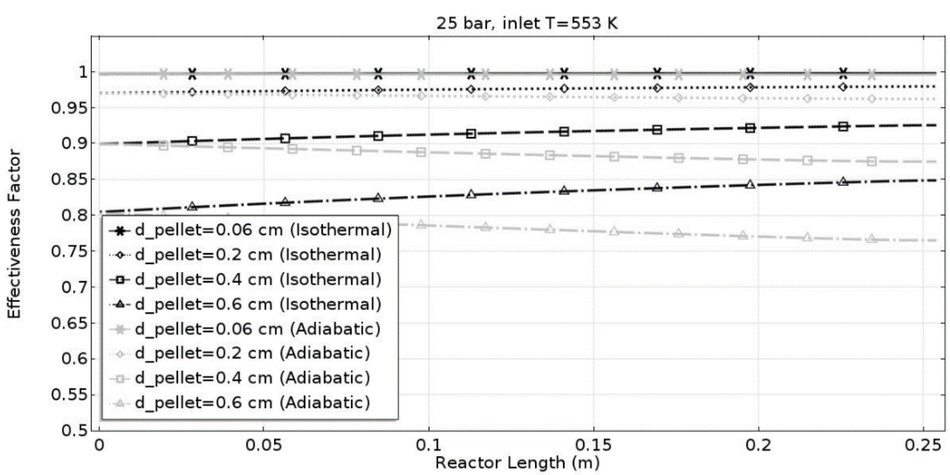
Temperature = 250 °C, Pressure = 15 bar.
(W_{cat}/F_{CO}=55 on MR)

Temperature = 250 °C, Pressure = 15 bar.
(W_{cat}/F_{CO}=66 on MR)

Model Predictions for Industrial-Scale Systems

Axial Profiles of Catalyst Effectiveness Factors in MR (Top) and PBR (Bottom)

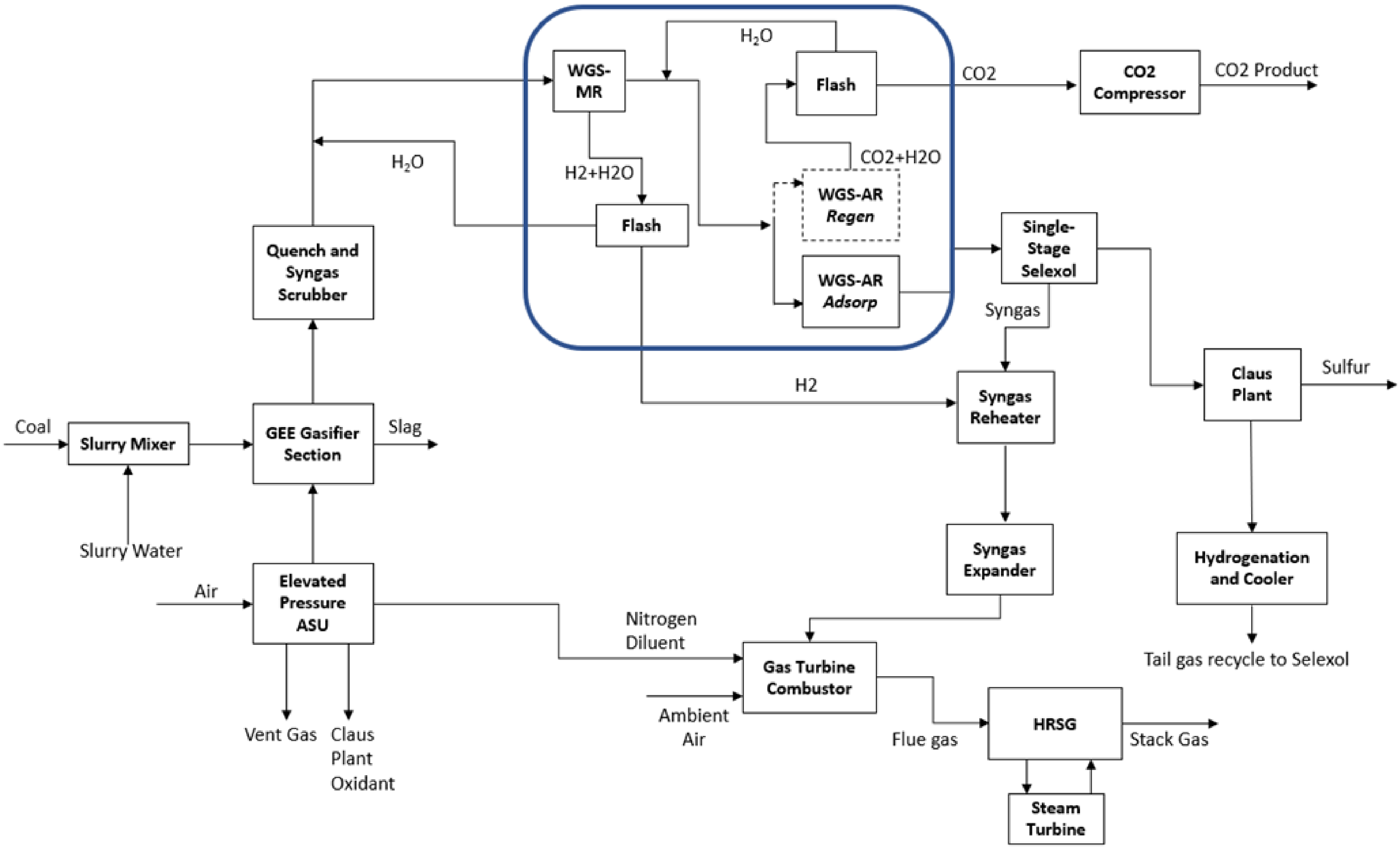




Key Results

- Catalyst effectiveness factors in PBR and MR vary significantly along reactor length
- Catalyst pellets of same diameter exhibit different effectiveness factors
- Sweep gas pressure/temperature and membrane area have a significant impact on MR behavior
- The adiabatic MR gives higher conversion values as compared to the wall-isothermal MR for the same operating conditions

Preliminary TEA - MR-AR IGCC Process Scheme



Preliminary TEA - MR-AR IGCC Process

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	593	92

Preliminary TEA - MR-AR IGCC Process

	Conversion	Catalyst Amount (ft^3)	Adsorbent (kg)
MR-AR Combined System	99%	4,064* (2,553**)	606,912
IGCC WGS Reactor	97%	6,246	0

	% CO Conversion	% H_2 Recovery	% CO_2 Purity	% CO_2 Recovery
Target	>95	>90	>95	>90
MR-AR Realization	99%	99	99	92

***Initial Purchase Catalyst:** Amount of catalyst needed to initially load all MR-AR reactors (which contributes to the catalyst capital cost) is 4,064 ft^3

****Operating Purchase Catalyst:** AR is operated periodically and catalyst is not exposed continuously to reaction, and thus catalyst's lifetime is longer than baseline design. Amount of catalyst for replacement (which contributes to the catalyst operating cost) is 2,553 ft^3

Preliminary TEA - MR-AR IGCC Process

	Capital Cost ($/1000)	Variable Operating Cost ($)	Net Power (MWe)	N_2 Product (ton/h)	COE (No N_2 sale/ N_2 Sale) ($/MWh)	% COE reduction vs Baseline (No N_2 sale/ N_2 Sale)
IGCC CCS	$1,840,115	$46,580,032	543	0	135.4	0
MR-AR Realization	$1,539,820	$47,672,487	593	619	113.1 / 86.3	16.4% / 36%

	Net Power (MWe)	COE (No N_2 sale/ N_2 Sale) ($/MWh)	CO_2 Captured Cost (No N_2 sale/ N_2 Sale) ($/tonne)
IGCC CCS	543	135.4	63.2
MR-AR Realization	593	113.1 / 86.3	39.3 / 5.1

Sensitivity Analysis for Critical Technology Parameters

Sensitivity Analysis – Membrane Reactor Lifespan					
	Consumption				Cost ($)
	Initial Fill	Per Day	Per Unit	Initial Fill	Annual Cost
10-Year MR Lifespan					
Membrane Packs (m^2)	w/equip	n/a	$650	$0	$535,780
Total Variable Cost:				$16,547,652	$47,672,487
Total COE:					86.3
5-Year MR Lifespan					
Membrane Packs (m^2)	w/equip	n/a	$650	$0	$1,071,560
Total Variable Cost:				$10,074,435	$48,208,277
Total COE:					86.5
2-Year MR Lifespan					
Membrane Packs (m^2)	w/equip	n/a	$650	$0	$2,678,900
Total Variable Cost:				$10,074,435	$49,815,607
Total COE:					86.8

- ***MR Lifespan utilized in TEA is 10-year lifespan***
  - ***A 5-year lifespan increases total COE by 0.2%***
  - ***A 2-year lifespan increases total COE by 0.6%***

Sensitivity Analysis for Critical Technology Parameters

Sensitivity Analysis – Nitrogen Sale Price					
	Consumption				Cost ($)
	Initial Fill	Per Day	Per Unit	Initial Fill	Annual Profit
$30/ton Nitrogen Price					
Nitrogen (tons)	0	14,591	$30	$0	$111,228,000
Total COE ($/MWh)					86.3
$1/ton Nitrogen Price					
Nitrogen (tons)	w/equip	n/a	$1	$0	$3,707,600
Total COE ($/MWh)					112.2
$414/ton Nitrogen Price					
Nitrogen (tons)	w/equip	n/a	$414	$0	$1,,534, 946, 400
Total COE ($/MWh)					-255.8

- ***Baseline COE 135.4 $/MWh***
- ***A N_2 sale price of $30/ton reduces COE from the baseline by 36.3%***
- ***A N_2 sale price of $1/ton reduces COE from the baseline by 17.1%***
- ***A N_2 sale price of $414/ton yields a negative COE***

Compact 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 Product***
- ***Low-Grade Quality Nitrogen Product***
- ***CO_2 capture cost ($/ton)***
  - IGCC w/CCS Baseline: 63.2
  - MR-AR with no N_2 Sales: 39.3
  - MR-AR with N_2 Sales (30$/ton) : 5.1
- ***COE Reduction target approached/met***
  - Target: Proposed Technology COE 30% lower than IGCC w/CCS COE
  - No N_2 Sales: MR-AR COE 16.5% lower than IGCC w/CCS COE
  - N_2 Sales (30$/ton) : MR-AR COE 36% lower than IGCC w/CCS COE

Publications in Peer-Reviewed Journals

1. Karagöz, S., Da Cruz, F.E., Tsotsis, T.T., and Manousiouthakis, V.I., "Multi-Scale Membrane Reactor (MR) Modeling and Simulation for the Water Gas Shift Reaction," *Chemical Engineering & Processing: Process Intensification*, 133, 245, 2018.
2. Chen, H., Cao, M., Manousiouthakis, V.I., and Tsotsis, T.T., "An Experimental Study of an Intensified Water-Gas Shift Reaction Process Using a Membrane Reactor/Adsorptive Reactor Sequence," *Ind. Eng. Chem. Res.*, 57, 13650, 2018.
3. Karagöz, S., Tsotsis, T.T., and Manousiouthakis, V.I., "Multi-scale Modeling and Simulation of a Novel Membrane Reactor (MR)/Adsorptive Reactor (AR) Process," In Press, *Chemical Engineering & Processing: Process Intensification*, 137, 146, 2019.
4. Karagöz, S., Tsotsis, T.T., and Manousiouthakis, V.I., "Energy Intensification of H_2 Generation and CO_2 Capture/Utilization by Carrying-out the Water Gas Shift Reaction in an Adsorptive Reactor: Multiscale Dynamic Modeling and Simulation," *AIChE J.*, 2019.doi: 10.1002/aic.16608.
5. Pichardo, P., Karagöz, S., Ciora, R., Tsotsis, T.T., and Manousiouthakis, V.I., "Technical Economic Analysis of an Intensified Integrated Gasification Combined Cycle (IGCC) Power Plant Featuring a Sequence of Membrane Reactors," *J. Membrane Sci.*, 579, 266, 2019.
6. Garshasbi, A., Chen, H., Cao, M., Karagöz, S., Ciora, R.J., Liu, P.K.T, Manousiouthakis, V.I., and Tsotsis, T.T., "Membrane-based Reactive Separations for Process Intensification during Power Generation", Catalysis Today, 331, 18, 2019.
7. Pichardo, P., Karagöz, S., Ciora, R., Tsotsis, T.T., and Manousiouthakis, V.I., "Techno-Economic Analysis of an Intensified Integrated Gasification Combined Cycle (IGCC) Power Plant Featuring a Combined Membrane Reactor - Adsorptive Reactor (MR-AR) System," DOI: 10.1021/acs.iecr.9b02027, *Ind. Eng. Chem. Res.*, 2019.
8. Karagöz, S., Tsotsis, T.T., and Manousiouthakis, V.I., "Multi-scale Model based Design of Membrane Reactor/Separator Processes for Intensified Hydrogen Production through the Water Gas Shift Reaction," In Press, *Int. J. Hydrogen Energy.*

Acknowledgements

The financial support of the US Department of Energy, the technical guidance and assistance of our Project Manager Andrew Jones, and helpful discussions with Mr. Walter W. Shelton, Mr. Travis R. Shultz, and Ms. Lynn Brickett are gratefully acknowledged.