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

DE-FOA-0001235

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U.S. Department of Energy
National Energy Technology Laboratory
Office of Fossil Energy
November 16, 2015

Presentation Outline

- **Project Objectives**
- **Process Description**
  - *Background*
  - *Project Technical Approach*
  - *Advantages*
  - *Challenges*
- **Progress to Date on Key Technical Issues**
- **Scope of Work**
- **Tasks to be Performed**

Project Objectives

Overarching Project Objectives:

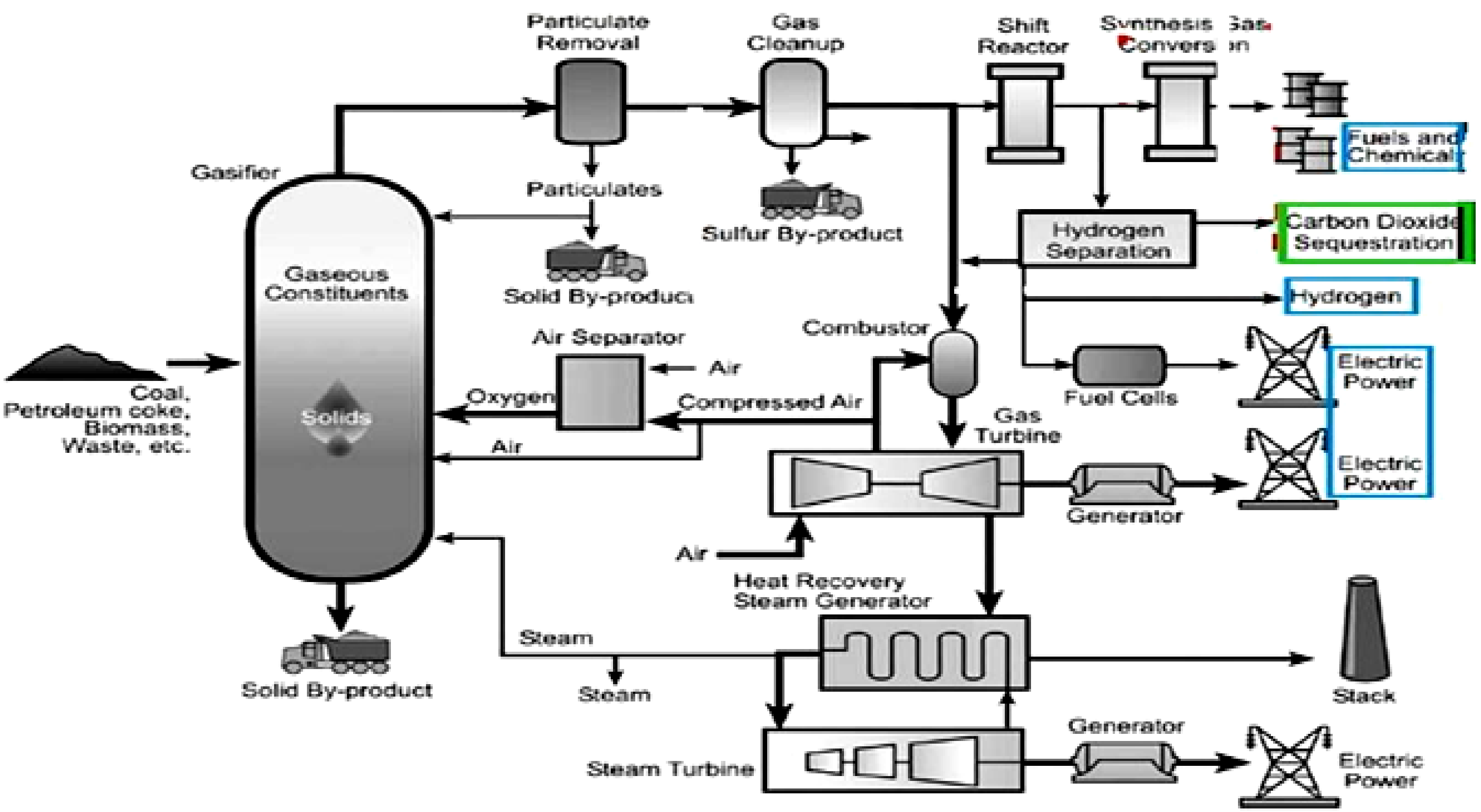
1. *Prove the technical feasibility of the membrane- and adsorption-enhanced water gas shift (WGS) process.*
2. *Achieve the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity of 30% less than baseline capture approaches.*

Key Project Tasks:

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***

Background

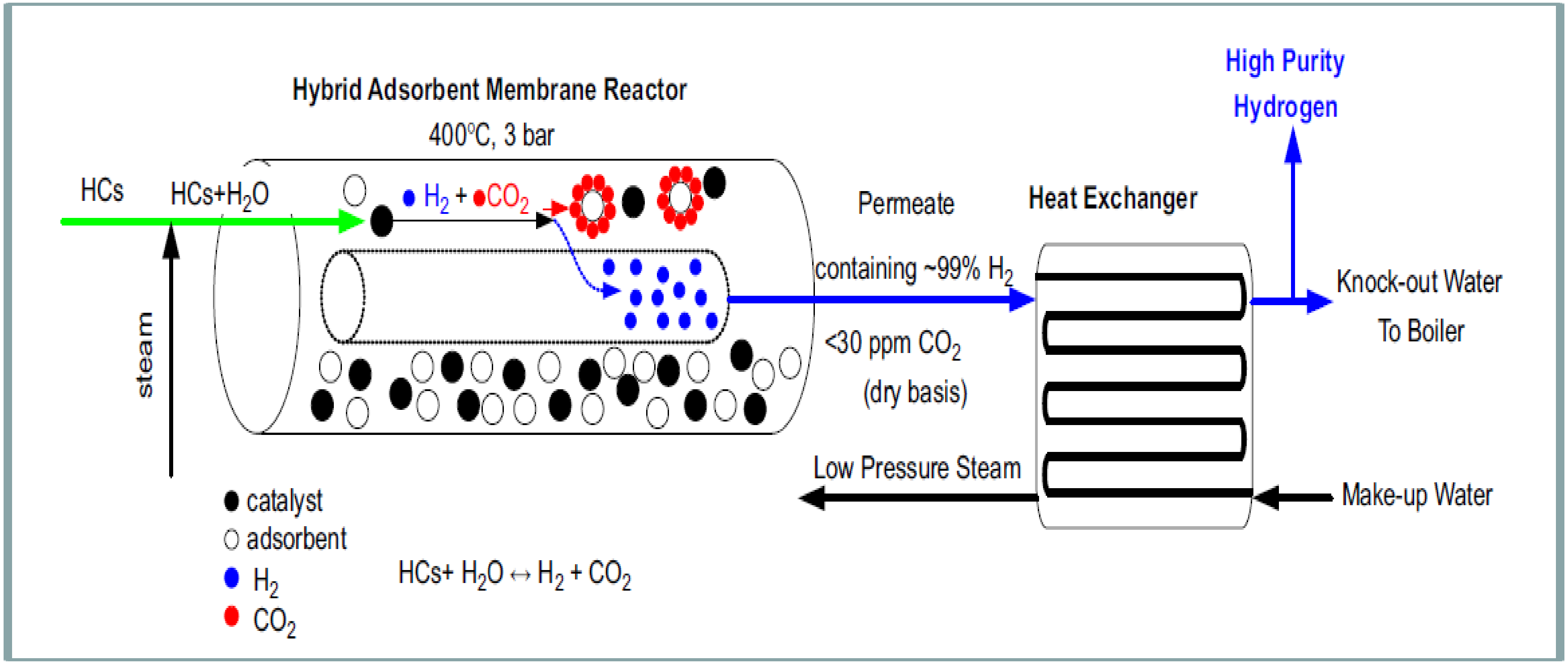
Conventional IGCC Power Plant



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

Background, cont.

Hybrid Adsorbent Membrane Reactor (HAMR)



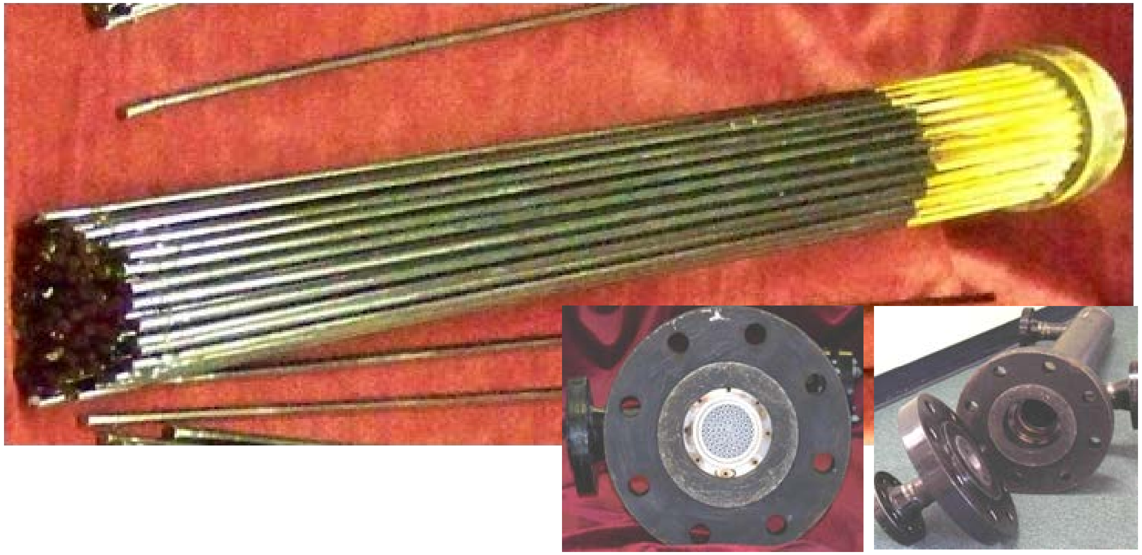
- **The HAMR combines adsorbent, catalyst and membrane functions in the same unit. Previously tested for methane steam reforming (MSR) and the WGS reaction.**
- **The simultaneous in situ removal of H_2 and CO_2 from the reactor significantly enhances reactor yield and H_2 purity. CO_2 stream ready for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

Background, cont.

CMS Membranes for Large Scale Applications

M&PT test-unit at NCCC for hydrogen separation

CMS membranes and modules



Background, cont.

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

Hydrotalcite Adsorbent:

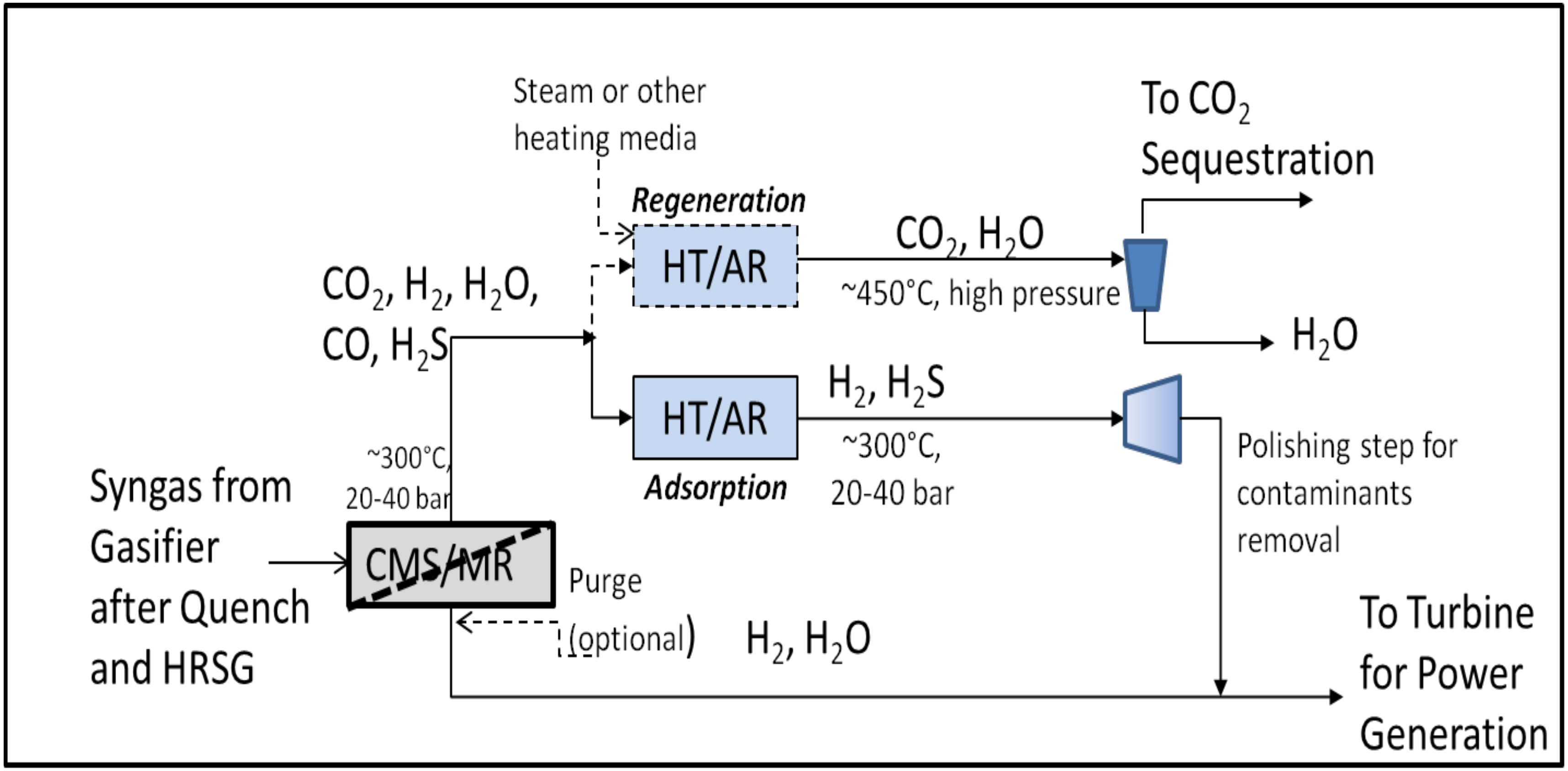
- *The HT adsorbents shown to have a working CO_2 capacity of 3-4 wt.% during the past HAMR studies with the MSR and WGS reactions. Theoretical capacity >16 wt.%.*

Co/Mo-Based Sour Shift Catalyst:

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

Project Technical Approach

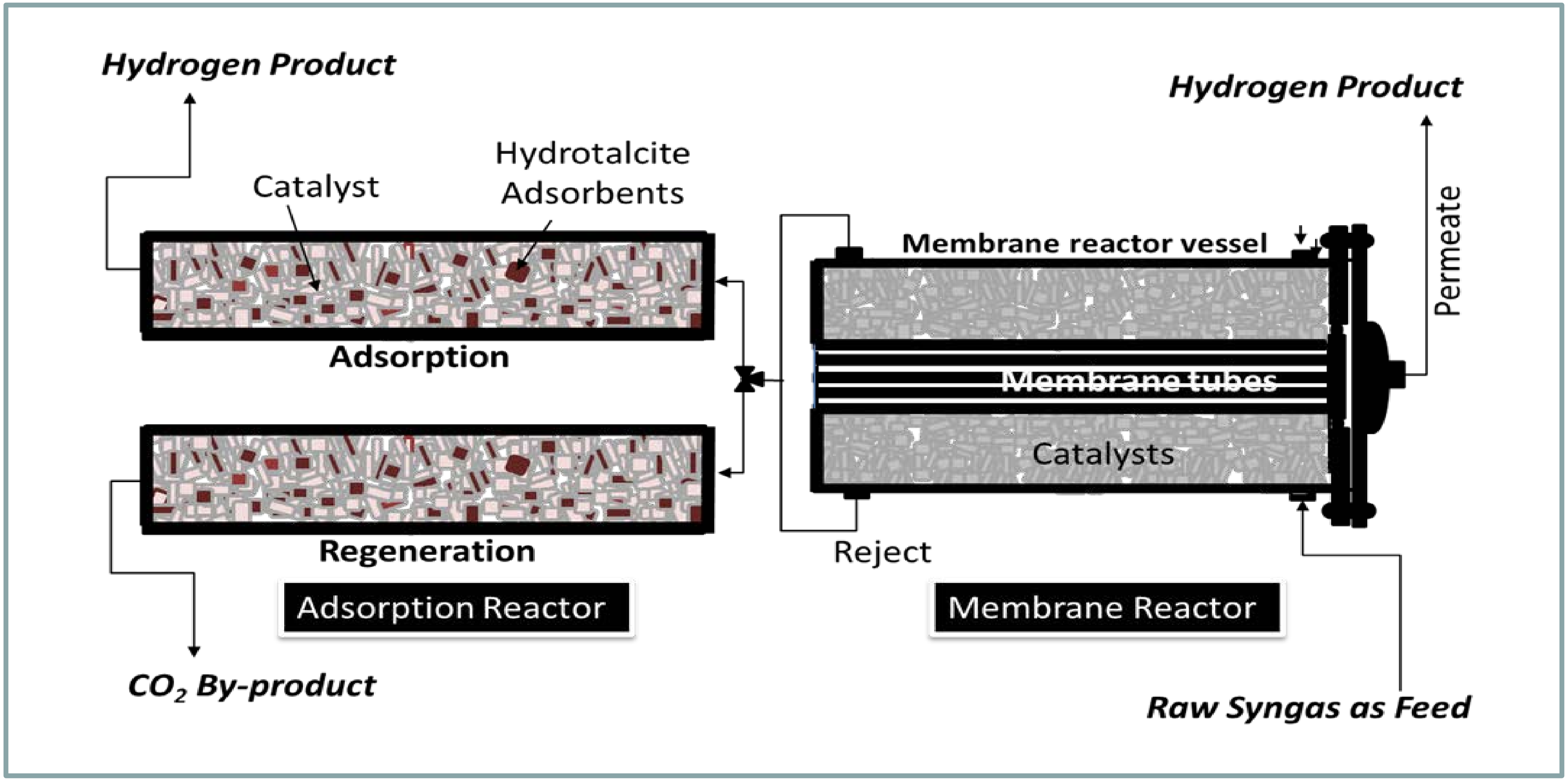
Proposed Process Scheme



- ☐ No CGCU (or WGCU) step is required to clean-up the syngas prior to entering the WGS reactor.
- ☐ No post-treatment absorption step is needed to separate the H_2 from CO_2.
- ☐ No CO_2 recompression step is needed for its further transport and storage.
- ☐ Note that the use of 2 HT/AR is for illustrative purposes only. The full process will require more (typically 4) HT/AR in use.

Project Technical Approach, cont.

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.

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.*

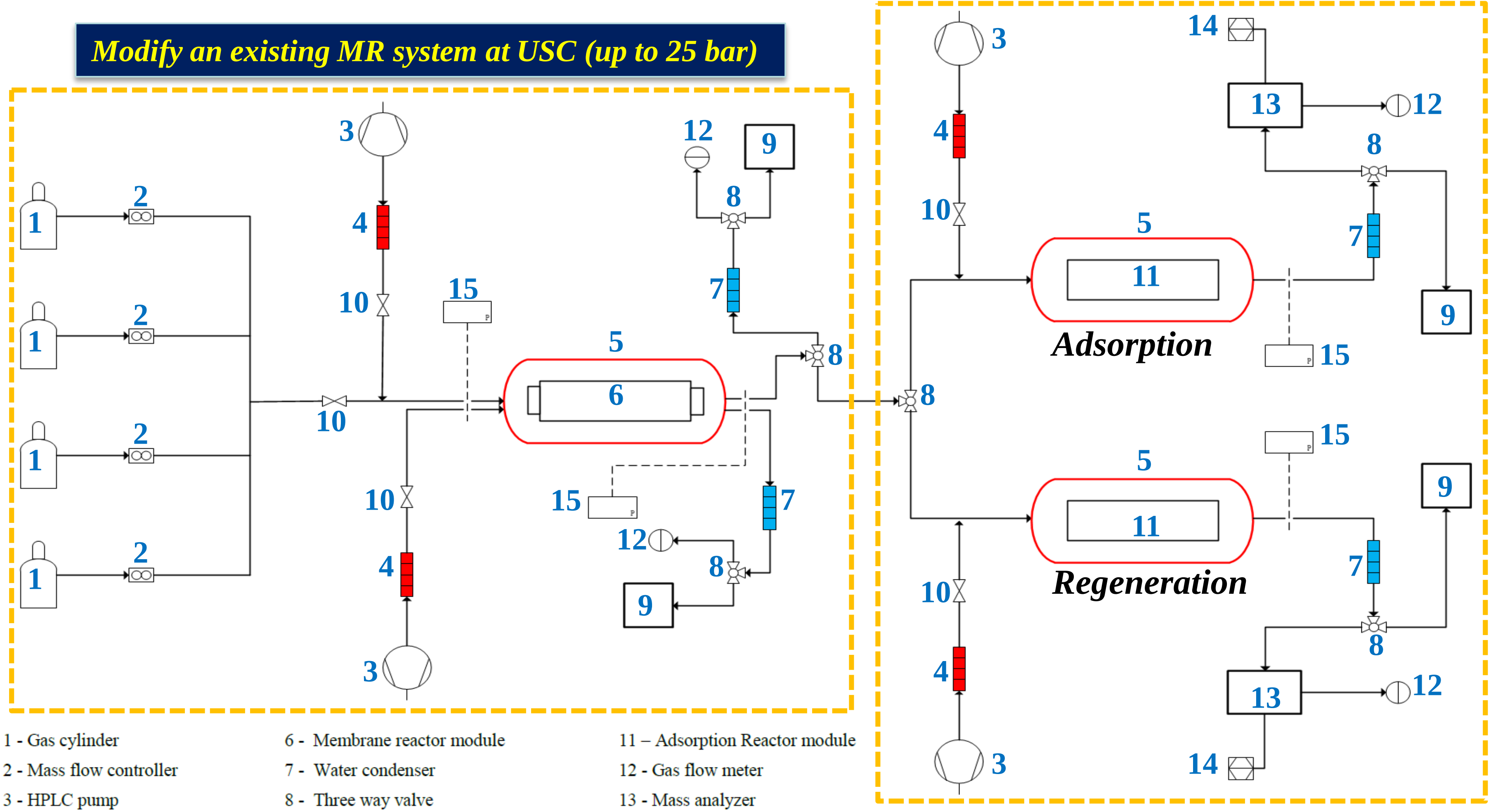
Challenges

Key Technical Challenges Ahead (BP1):

- *Modify an existing lab-scale test unit at USC to permit operation at higher pressure (up to 25 bar).*
- *Design and incorporate a dedicated AR subsystem.*
- *Prepare and characterize membranes and adsorbents and validate their performance at the relevant experimental conditions.*
- *Validate catalyst performance at the relevant pressure conditions. Verify applicability of global reaction kinetics.*
- *Develop and experimentally validate mathematical model.*

Challenges, cont.

Proposed Lab-Scale Experimental System

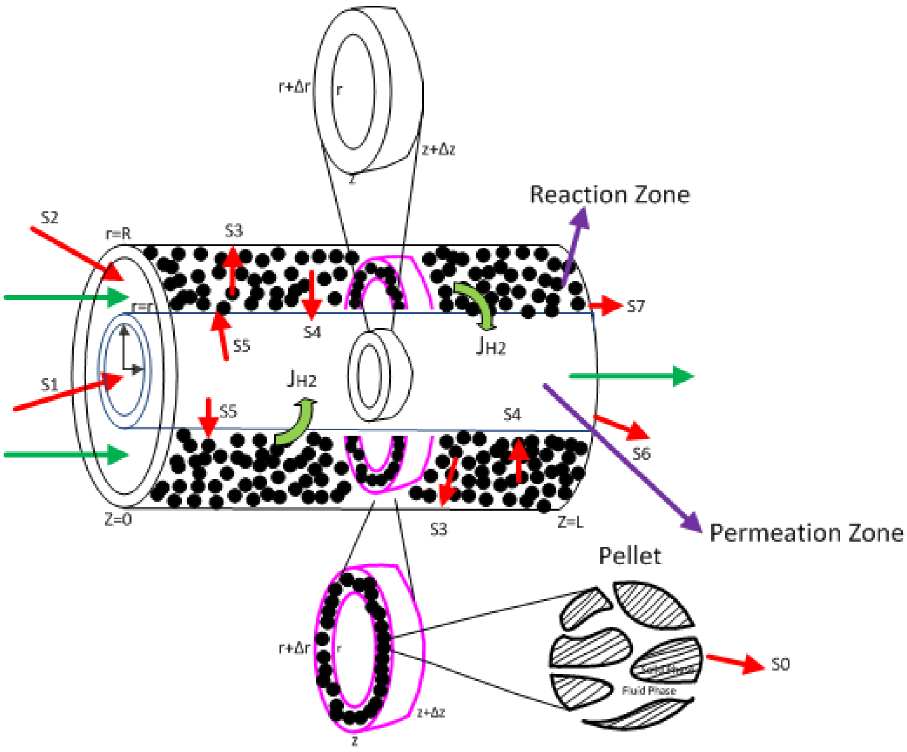


Modify an existing MR system at USC (up to 25 bar)

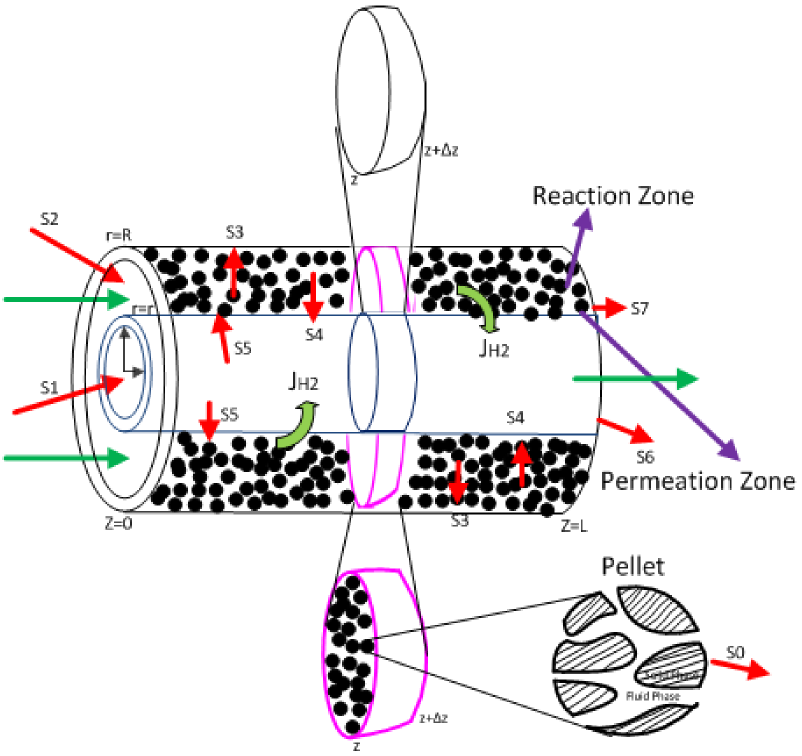
Incorporate a dedicated AR subsystem

1 - Gas cylinder
2 - Mass flow controller
3 - HPLC pump
4 - Water evaporator
5 - Oven
6 - Membrane reactor module
7 - Water condenser
8 - Three way valve
9 - Gas Chromatograph
10 -Valve
11 – Adsorption Reactor module
12 - Gas flow meter
13 - Mass analyzer
14 - Data acquisition system
15 - Pressure indicator

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

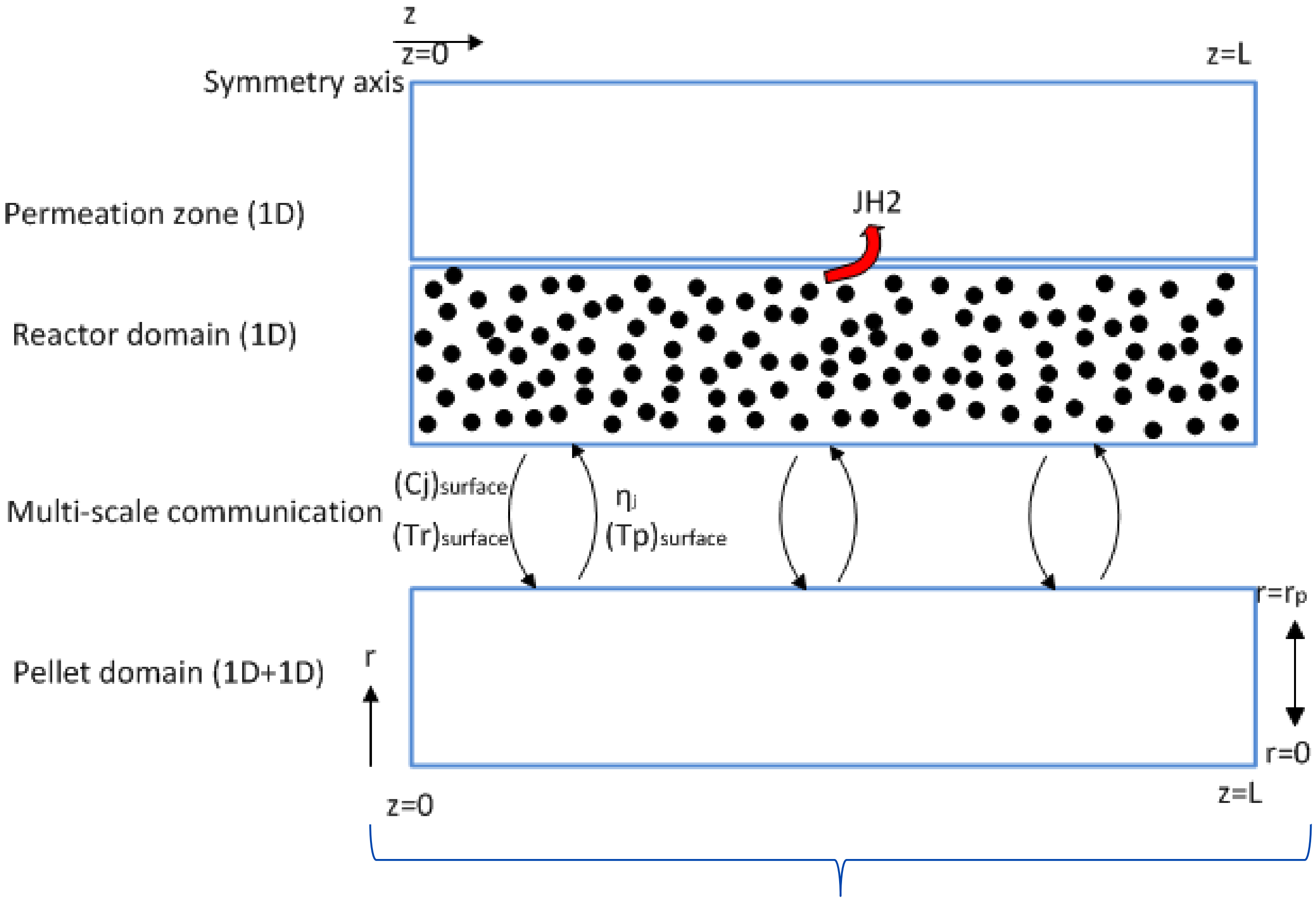


2D Representation of control volumes in Membrane Reactor



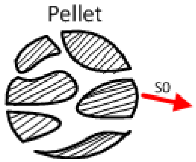
1D Representation of control volumes in Membrane Reactor

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



j-Component Mass Conservation:

$$\boxed{0 = \underbrace{M_j r_j \rho_s \left(1-\varepsilon_V^p\right)}_{\substack{\text{rate of mass generation of } j\\ \text{by reaction per pellet volume}}} - \underbrace{\varepsilon_A^p \vec{\nabla}\cdot\left(\overrightarrow{j_{f,j}^p}\right)}_{\substack{\text{rate of addition of mass of}\\ j\text{ by diffusion per pellet volume}}} \qquad j=1,N_s}$$

B.C.

$$x_{f,j}^r = \left(x_{f,j}^r\right)^{surface} \quad at \;\; S_0$$

Dusty-gas model (DGM) :

$$\boxed{-\vec{\nabla} m_{f,j}^p = \frac{1}{\underbrace{\left(\frac{\varepsilon_V}{\tau}\right)\frac{4d_{pore}}{3}\sqrt{\frac{RT^p}{2\pi M_i}}}_{D_{iK}^{eff}}}\left[\overrightarrow{j_{f,j}^p} + x_{f,j}^p\left(\frac{m_{Tot}\,B_o}{\gamma_f}\right)\vec{\nabla}P_f^p\right] + \sum_1^i \left(\frac{x_i^p}{\underbrace{\left(\frac{\varepsilon_V}{\tau}\right)\frac{3}{16}\frac{\sqrt{2\pi k_B{}^3\left(T^p\right)^3 / m_{ij}}}{p\pi\sigma_{ji}^2\Omega_{ji}^{(1,1)*}}}_{D_{ij}^{eff}}}\frac{1}{M_j}\overrightarrow{j_{f,j}^p} - \frac{x_j^p}{\underbrace{\left(\frac{\varepsilon_V}{\tau}\right)\frac{3}{16}\frac{\sqrt{2\pi k_B{}^3\left(T^p\right)^3 / m_{ij}}}{p\pi\sigma_{ji}^2\Omega_{ji}^{(1,1)*}}}_{D_{ij}^{eff}}}\overrightarrow{j_{f,i}^p}\right)}$$

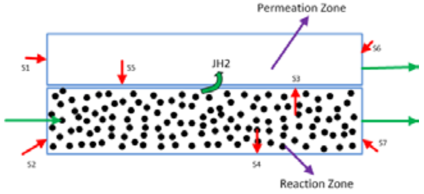
Energy Conservation:

$$\boxed{0 = \underbrace{\vec{\nabla}.\left(\left[\left(1-\varepsilon_A^p\right)k_s^p + \varepsilon_A^p k_f^p\right]\vec{\nabla}T^p\right)}_{\substack{\text{rate of energy addition by heat conduction}\\ \text{per volume}}} - \underbrace{\varepsilon_A^p \vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\frac{1}{M_j}\tilde{h}_{f,j}^p\,\overrightarrow{j_{f,j}^p}\right)}_{\substack{\text{rate of energy addition by species mass}\\ \text{fluxes per volume}}}}$$

B.C.

$$T^p = \left(T^p\right)^{surface} \quad at \;\; S_0$$

1-D Reactor-Scale Steady-State Model



Total mass conservation:

$$\boxed{0=\varepsilon_A^r\vec{\nabla}\cdot\left(\rho_f\overrightarrow{v_f^r}\right)}$$

Momentum conservation:

$$\boxed{\underbrace{\vec{\nabla}P^r}_{\substack{\text{rate of pressure drop}\\ \text{inside reactor}}}=\underbrace{\left(-150\frac{\left(1-\varepsilon_V^r\right)^2}{\left(\varepsilon_V^r\right)^3 d_p^{\,2}}-\mu_f^r 1.75\frac{\left(1-\varepsilon_V^r\right)}{\left(\varepsilon_V^r\right)^3 d_p}\rho_f^r\left|\overrightarrow{v_f^r}\right|\right)\overrightarrow{v_f^r}}_{\text{drag exerted by the fluid on the solid surface per volume}}}$$

B.C.

$$\overrightarrow{v_f^R}=\left(\overrightarrow{v_f^R}\right)_{in},\quad P^r=\left(P^r\right)_{in}\ at\ S_2,$$

$$\vec{\nabla}\overrightarrow{v_f^R}=0\ at\ S_3\ and\ S_4$$

j-Component Mass Conservation:

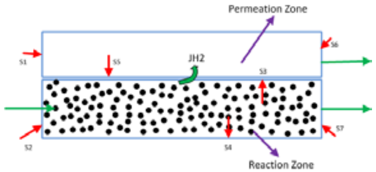
$$\boxed{\underbrace{\varepsilon_A^r\left(\vec{\nabla}x_{f,j}^r\right)\cdot\left(\rho_f\overrightarrow{v_f^r}\right)}_{\substack{\text{net rate of addition of mass of}\\ j\text{ by convection per volume}}}=\left\{\begin{array}{l}\underbrace{M_j\eta_j r_j\rho_s\left(1-\varepsilon_V^r\right)}_{\substack{\text{rate of production of mass of}\\ j\text{ by reaction per volume}}}-\underbrace{\varepsilon_A^r\vec{\nabla}\cdot\left(\overrightarrow{j_{f,j}^r}\right)}_{\substack{\text{net rate of addition of mass of}\\ j\text{ by diffusion per volume}}}-\\[2ex] \underbrace{-\frac{2\lambda_j}{R_{mem}}\frac{B_{Ho}\exp\left(-\dfrac{E_a}{R\cdot T^r}\right)}{\delta}\left(P_{H_2,r}^n-P_{H_2,p}^n\right)}_{\text{rate of addition of mass of }j\text{ by permeation per volume}}\end{array}\right\},\ \lambda_j=\left\{\begin{array}{l}0\ if\ j\neq H_2\\ 1\ if\ j=H_2\end{array}\right\}}$$

B.C.

$$x_{f,j}^r=\left(x_{f,j}^r\right)_{in}\ at\ S_2$$

1-D Reactor-Scale Steady-State Model

Maxwell-Stefan Equation:



$$\vec{\nabla} x_{f,j}^{r} = \sum_{j=1}^{N_s} \frac{x_{f,j}^{r}\, x_{f,i}^{r}}{\left(\frac{\varepsilon_V}{\tau}\right)\frac{3}{16}\frac{\sqrt{2\pi {k_B}^{3}\left(T^{r}\right)^{3}/m_{ij}}}{p\pi\sigma_{ji}^{2}\Omega_{ji}^{(1,1)*}}}\left(\overrightarrow{v_{f,i}^{r}} - \overrightarrow{v_{f,j}^{r}}\right) + \left(w_{f,j}^{r}\, x_{f,j}^{r}\right)\left(\frac{\vec{\nabla} P^{r}}{P^{r}}\right) + \sum_{j=1}^{N_s} \frac{x_{f,j}^{r}\, x_{f,i}^{r}}{\rho_f^{r}\left(\frac{\varepsilon_V}{\tau}\right)\frac{3}{16}\frac{\sqrt{2\pi {k_B}^{3}\left(T^{r}\right)^{3}/m_{ij}}}{p\pi\sigma_{ji}^{2}\Omega_{ji}^{(1,1)*}}}\left(\frac{D_i^{T}}{w_{f,i}^{r}} - \frac{D_j^{T}}{w_{f,j}^{r}}\right)\left(\frac{\vec{\nabla} T^{r}}{T^{r}}\right)$$

Energy Conservation:

$$\underbrace{\varepsilon_A^{r}\vec{\nabla}\cdot\left(\rho_f^{r} h_f^{r}\overrightarrow{v_f^{r}}\right)}_{\substack{\text{rate of energy addition by convective}\\ \text{transport per unit volume}}} = \left\{\begin{array}{l} \underbrace{\varepsilon_I^{r} h\left(T^{r} - \left(T^{p}\right)^{s}\right)}_{\substack{\text{rate of energy addition by heat}\\ \text{convection per volume}}} + \underbrace{\varepsilon_A^{r}\vec{\nabla}\cdot\left(k_f^{r}\vec{\nabla} T^{r}\right)}_{\substack{\text{rate of energy addition by heat}\\ \text{conduction per volume}}} - \underbrace{\varepsilon_A^{r}\vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\frac{1}{M_j}\tilde{h}_{f,j}^{r}\overrightarrow{j_{f,j}^{r}}\right)}_{\substack{\text{rate of energy addition by species}\\ \text{mass fluxes per volume}}} - \\ - \underbrace{4\frac{U}{d_t}\left(T^{r} - T^{W}\right)}_{\substack{\text{rate of energy addition between}\\ \text{reaction zone and external}\\ \text{wall per volume}}} - \underbrace{4\frac{d_{mem}U_1}{d_t^{2}}\left(T^{r} - T^{perm}\right)}_{\substack{\text{rate of energy addition between}\\ \text{reaction zone and internal}\\ \text{wall per volume}}} \end{array}\right\}$$

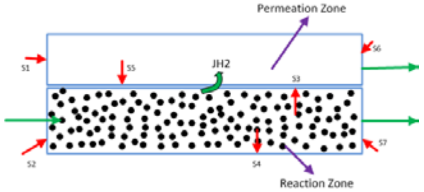
$B.C.$

$$T^{r} = \left(T^{r}\right)_{in} \quad at \ S_2$$

$$\vec{\nabla} T^{r} = 0 \quad at \ S_7$$

2-D Reactor-Scale Steady-State Model

j-Component Mass Conservation:



$$\boxed{\underbrace{\varepsilon^r_A\left(\overrightarrow{\nabla} x^r_{f,j}\right)\cdot\left(\rho_f \overrightarrow{v^r_f}\right)}_{\substack{\text{net rate of addition of mass of} \\ j \text{ by convection per volume}}} = \underbrace{M_j \eta_j r_j \rho^r_s \left(1-\varepsilon^r_V\right)}_{\substack{\text{rate of production of mass of } j \\ \text{by reaction per volume}}} - \underbrace{\varepsilon^r_A \overrightarrow{\nabla}\cdot\left(\overrightarrow{j^r_{f,j}}\right)}_{\substack{\text{net rate of addition of mass of} \\ j \text{ by diffusion per volume}}} \qquad j=1, N_s}$$

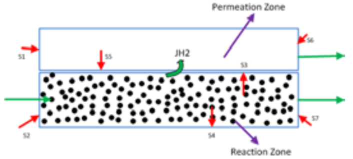
$B.C.$

$$x^r_{f,j} = \left(x^r_{f,j}\right)_{in} \quad at \ S_2$$

$$\left(\overrightarrow{\nabla} x^r_{f,j}\right)\cdot\left(\rho^r_f \overrightarrow{v^r_f}\right) = \frac{P_{e_m}\lambda_j}{d_p}\,\frac{B_{Ho}\exp\left(-\frac{E_a}{R\cdot T^r}\right)}{\delta}\left(P^n_{H_2,r} - P^n_{H_2,p}\right) \ ,\lambda_j = \left\{\begin{array}{l} 0 \ if \ j \neq H_2 \\ 1 \ if \ j = H_2 \end{array}\right\} \quad at \ S_4$$

$$\left(\overrightarrow{\nabla} x^r_{f,j}\right)\cdot\left(\rho^r_f \overrightarrow{v^r_f}\right) = 0 \quad at \ S_3$$

2-D Reactor-Scale Steady-State Model



Momentum Conservation:

$$\underbrace{\varepsilon_A^r \vec{\nabla}\vec{v_f^r}\cdot\left(\rho_f \vec{v_f^r}\right)}_{\text{rate of momentum addition by convection per volume}} = \underbrace{-\varepsilon_V^r \vec{\nabla}P^r - \vec{\nabla}\cdot\left(\varepsilon_V^r \mu_f^r\left(\vec{\nabla}\vec{v_f^r} + \left(\vec{\nabla}\vec{v_f^r}\right)^T\right)\right)}_{\text{rate of momentum addition by molecular transport per volume}} + \underbrace{\left(-150\frac{\left(1-\varepsilon_V^r\right)^2}{\left(\varepsilon_V^r\right)^2 d_p^{\,2}} - \mu_f^r 1.75\frac{\left(1-\varepsilon_V^r\right)}{\left(\varepsilon_V^r\right)^2 d_p}\rho_f^r\left|\vec{v_f^r}\right|\right)\vec{v_f^r}}_{\text{drag exerted by the fluid on the solid surface per volume}}$$

B.C.

$$\vec{v_f^R} = \left(\vec{v_f^R}\right)_{in}, \quad P^r = \left(P^r\right)_{in} \; at \; S_2,$$

B.C.

$$\vec{\nabla}\vec{v_f^R} = 0 \; at \; S_3 \; and \; S_4$$

Energy Conservation:

$$\underbrace{\varepsilon_A^r \vec{\nabla}\cdot\left(\rho_f^r h_f^r \vec{v_f^r}\right)}_{\substack{\text{rate of energy addition by convective}\\ \text{transport per unit volume}}} = \underbrace{\varepsilon_I^r h\left(T^r - \left(T^p\right)^s\right)}_{\substack{\text{rate of energy addition by heat}\\ \text{convection per volume}}} + \underbrace{\varepsilon_A^r \vec{\nabla}\cdot\left(k_f^r \vec{\nabla}T^r\right)}_{\substack{\text{rate of energy addition by heat}\\ \text{conduction per volume}}} \underbrace{-\varepsilon_A^r \vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\frac{1}{M_j}\tilde{h}_{f,j}^r \vec{j_{f,j}^r}\right)}_{\substack{\text{rate of energy addition by species}\\ \text{mass fluxes per volume}}}$$

B.C.

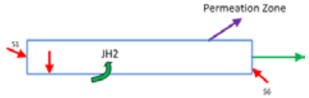
$$T^r = \left(T^r\right)_{in} \quad at \; S_2,$$

B.C

$$\vec{\nabla}\cdot\left(\rho_f^r h_f^r \vec{v_f^r}\right) = 4\frac{d_{mem}U_1}{d_t^2}\left(T^r - T^{perm}\right) \; at \, S_4 \;\; , \;\; \vec{\nabla}\cdot\left(\rho_f^r h_f^r \vec{v_f^r}\right) = 4\frac{U}{d_t}\left(T^r - T^W\right) \; at \, S_3$$

1-D Steady-State Permeation Zone Model

j-Component Mass Conservation :



$$\boxed{\underbrace{\rho^{M}\left(\vec{\nabla}x_i^{M}\right)\cdot\left(\overrightarrow{v^{M}}\right)}_{\substack{\text{rate of addition of mass of } i \text{ by}\\ \text{convection per volum}}} = \underbrace{\frac{2\lambda_i}{R_{mem}}\frac{B_{Ho}\exp\left(-\frac{E_a}{R\cdot T^{r}}\right)}{\delta}\left(P^{n}_{H_2,r}-P^{n}_{H_2,p}\right)}_{\text{rate of addition of mass of } j \text{ by permeation per volume}},\ \lambda_i=\begin{Bmatrix}0 \text{ if } i\neq H_2\\ 1 \text{ if } i=H_2\end{Bmatrix}}$$

B.C.

$$x_i^{M}=\left(x_i^{M}\right)_{in}\ \ at\ \ S_1$$

Momentum Conservation:

$$\boxed{\underbrace{\vec{\nabla}\overrightarrow{v^{M}}\cdot\left(\rho^{M}\overrightarrow{v^{M}}\right)}_{\substack{\text{rate of momentum addition}\\ \text{by convection per volume}}} = \underbrace{-\vec{\nabla}P^{M}-\vec{\nabla}\cdot\left(\mu^{M}\left(\vec{\nabla}\overrightarrow{v^{M}}+\left(\vec{\nabla}\overrightarrow{v^{M}}\right)^{T}\right)\right)}_{\text{rate of momentum addition by molecular transport per volume}}}$$

B.C.

$$\overrightarrow{v^{M}}=\left(\overrightarrow{v^{M}}\right)_{in},\ \ P^{M}=\left(P^{M}\right)_{in}\ at\ \ S_1,$$

Energy Conservation:

$$\boxed{\underbrace{\vec{\nabla}\cdot\left(\rho^{M}h^{M}\overrightarrow{v^{M}}\right)}_{\substack{\text{rate of energy addition by convective}\\ \text{transport per unit volume}}} = \underbrace{\vec{\nabla}\cdot\left(k^{M}\vec{\nabla}T^{M}\right)}_{\substack{\text{rate of energy addition by heat}\\ \text{conduction per volume}}} - \underbrace{\vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\frac{1}{M_j}\tilde{h}^{M}\,\overrightarrow{j_i^{M}}\right)}_{\substack{\text{rate of energy addition by species}\\ \text{mass fluxes per volume}}} \underbrace{-4\frac{d_{mem}U_1}{d_t^{2}}\left(T^{perm}-T^{r}\right)}_{\substack{\text{rate of energy addition between}\\ \text{reaction zone and internal}\\ \text{wall per volume}}}}$$

B.C.

$$T^{M}=\left(T^{M}\right)_{in}\ \ at\ \ S_1$$

$$\vec{\nabla}T^{M}=0\ \ at\ \ S_6$$

2-D Steady-State Permeation Zone Model

j-Component Mass Conservation:

$$\boxed{\underbrace{\rho^M \frac{\partial x_i^M}{\partial t}}_{\substack{rate\ of\ change\ of\ \ mass\ of\\ i\ \ per\ volume}} = \underbrace{\rho^M \left(\vec{\nabla} x_i^M\right)\cdot\left(\overrightarrow{v^M}\right)}_{\substack{rate\ of\ addition\ of\ mass\ of\ i\ by\\ convection\ \ per\ volum}}}$$

$$B.C.$$

$$x_i^M = \left(x_i^M\right)_{in} \ \ at\ \ S_1,$$

$$B.C.$$

$$\left(\vec{\nabla} x_i^M\right)\cdot\left(\rho_f \overrightarrow{v^M}\right) = \frac{P_{e_m}\lambda_j}{d_p}\frac{B_{Ho}\exp\left(-\dfrac{E_a}{R\cdot T^r}\right)}{\delta}\left(P_{H_2,r}^n - P_{H_2,p}^n\right) = J_{H_2} \quad ,\lambda_j = \begin{Bmatrix} 0\ if\ \ j \neq H_2 \\ 1\ if\ \ j = H_2 \end{Bmatrix} \ \ at\ \ S_5$$

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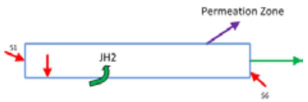
2-D Steady-State Permeation Zone Model



Momentum Conservation:

$$\boxed{\underbrace{\vec{\nabla}\vec{v}^{M}\cdot\left(\rho^{M}\vec{v}^{M}\right)}_{\substack{\text{rate of momentum addition}\\ \text{by convection per volume}}} = \underbrace{-\vec{\nabla}P^{M}-\vec{\nabla}\cdot\left(\mu^{M}\left(\vec{\nabla}\vec{v}^{M}+\left(\vec{\nabla}\vec{v}^{M}\right)^{T}\right)\right)}_{\text{rate of momentum addition by molecular transport per volume}}}$$

$B.C.$

$$\vec{v}^{M}=\left(\vec{v}^{M}\right)_{in},\quad P^{M}=\left(P^{M}\right)_{in}\ at\ S_{1},$$

$B.C.$

$$\vec{\nabla}\vec{v}_{f}^{R}=0\ at\ S_{5}$$

Energy Conservation:

$$\boxed{\underbrace{\vec{\nabla}\cdot\left(\rho^{M}h^{M}\vec{v}^{M}\right)}_{\substack{\text{rate of energy addition by convective}\\ \text{transport per unit volume}}} = \underbrace{\vec{\nabla}\cdot\left(k^{M}\vec{\nabla}T^{M}\right)}_{\substack{\text{rate of energy addition by heat}\\ \text{conduction per volume}}} - \underbrace{\vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\frac{1}{M_j}\tilde{h}^{M}\vec{j}_{i}^{M}\right)}_{\substack{\text{rate of energy addition by species}\\ \text{mass fluxes per volume}}}}$$

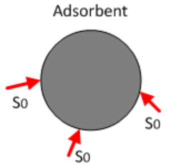
$B.C.$

$$T^{M}=\left(T^{M}\right)_{in}\ at\ S_{1},$$

$B.C$

$$\vec{\nabla}\cdot\left(\rho^{M}h^{M}\vec{v}^{M}\right)=4\frac{d_{mem}U_{1}}{d_{t}^{2}}\left(T^{r}-T^{perm}\right)\ at\ S_{5}\ ,\ \vec{\nabla}T^{M}=0\ at\ S_{6}$$

Adsorbing Reactor (AR)
Multi-Scale (Adsorbent-Reactor Scale) Model
Adsorbent-Scale Dynamic Model



j-Component Mass Conservation:

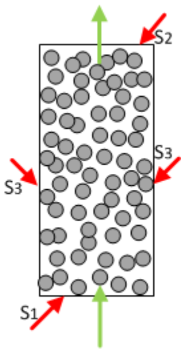
$$\boxed{\underbrace{\varepsilon_V^a \rho_f \frac{\partial x_{f,j}^a}{\partial t}}_{\substack{\text{rate of change of mass of } j\\ \text{per adsorbent volume}}} = \underbrace{M_j \rho_s R_j \left(1-\varepsilon_V^a\right)}_{\substack{\text{rate of addition of mass of } j\\ \text{by adsorption per adsorbent volume}}} \qquad j=1,N_s}$$

$$\frac{dC_j}{dt} = R_j = k_j\left(C_{seq,j}-C_j\right) \quad j=1,N_s,\ C_{seq,j} = \frac{m_j b_j P_j}{1+\sum_{j=1}^{N_s} b_j P_j} \quad j=1,N_s,\ \ b_j = b_j^0 e^{\left(\frac{-\Delta H_i}{R\left(1/T-1/T^0\right)}\right)} \quad j=1,N_s$$

Energy Conservation:

$$\boxed{\underbrace{\left[\left(1-\varepsilon_V^a\right)\rho_s\left(C_V\right)_s^a+\varepsilon_V^a\rho_f\left(C_V\right)_f^a\right]\frac{\partial T^a}{\partial t}}_{\text{rate of change of energy per adsorbent volume}} = \underbrace{\vec{\nabla}.\left(\left[\left(1-\varepsilon_A^a\right)k_s^a+\varepsilon_A^a k_f^a\right]\vec{\nabla}T^a\right)}_{\substack{\text{rate of energy addition by heat conduction}\\ \text{per adsorbent volume}}} - \underbrace{\varepsilon_A^a\vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\tilde{h}_j\rho_s R_j\right)}_{\substack{\text{rate of energy addition by adsorption}\\ \text{per adsorbent volume}}}}$$

1-D AR-Scale Dynamic Model



j-Component Mass Conservation:

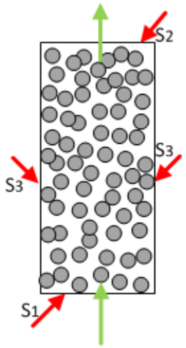
$$\underbrace{\left(\varepsilon_V^{PSA}+\left(\left(1-\varepsilon_V^{PSAR}\right)\varepsilon_V^{a}\right)\right)\rho_f\frac{\partial x_{f,j}^{PSAR}}{\partial t}}_{\text{rate of change of mass of } j \text{ per volume}}+\underbrace{\varepsilon_A^{PSAR}\left(\vec{\nabla}x_{f,j}^{PSAR}\right)\cdot\left(\rho_f\overrightarrow{v_f^{PSAR}}\right)}_{\substack{\text{rate of mass addition of } j \text{ by}\\ \text{convection per volume}}}=$$

$$=\left\{\underbrace{\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(\overrightarrow{j_{f,j}^{PSAR}}\right)}_{\substack{\text{rate of mass addition of } j \text{ by}\\ \text{diffusion per volume}}}+\underbrace{M_j\rho_s R_j\left(1-\varepsilon_V^{PSAR}\right)}_{\substack{\text{rate of mass addition of } j \text{ by}\\ \text{adsorption per volume}}}\right\}\; j=1,N_s$$

Momentum Conservation:

$$\vec{\nabla}P^{PSAR}=\underbrace{\left(-150\frac{\left(1-\varepsilon_V^{PSAR}\right)^2}{\left(\varepsilon_V^{PSAR}\right)^3 d_p^{\,2}}-\mu_f^{PSAR}1.75\frac{\left(1-\varepsilon_V^{PSAR}\right)}{\left(\varepsilon_V^{PSAR}\right)^3 d_p}\frac{\rho_f^{PSAR}}{\rho_s^{PSAR}}\left|\overrightarrow{v_f^{PSAR}}\right|\right)\overrightarrow{v_f^{PSAR}}}_{\text{drag exerted by the fluid on the solid surface per mass of absorbent}}$$

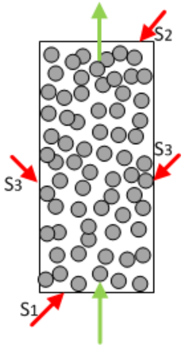
1-D AR-Scale Dynamic Model



Energy Conservation:

$$\boxed{\begin{aligned}&\underbrace{\varepsilon_V^{PSAR}\rho_f\left(C_V\right)_f^{PSAR}\frac{\partial T^{PSAR}}{\partial t}}_{\substack{\text{rate of change of energy}\\ \text{per mass of adsorbent}}}+\underbrace{\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(\rho_f h_f^{PSAR}\overrightarrow{v_f^{PSAR}}\right)}_{\substack{\text{rate of energy addition by convective}\\ \text{transport per mass of adsorbent}}}=\\&=\left\{\underbrace{\varepsilon_I^{PSAR}h\left(T^{PSAR}-\left(T^a\right)^s\right)}_{\substack{\text{rate of energy addition by heat convection}\\ \text{per mass of adsorbent}}}+\underbrace{\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(k_f^{PSAR}\vec{\nabla}T^{PSAR}\right)}_{\substack{\text{rate of energy addition by heat conduction}\\ \text{per mass of adsorbent}}}\underbrace{-\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\tilde{h}_j\rho_s R_j\right)}_{\substack{\text{rate of energy addition by species}\\ \text{per mass of adsorbent}}}\right\}\end{aligned}}$$

2-D AR-Scale Dynamic Model



j-Component Mass Conservation:

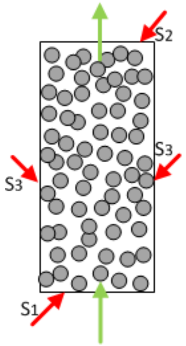
$$\underbrace{\left(\varepsilon_V^{PSAR}+\left(\left(1-\varepsilon_V^{PSAR}\right)\varepsilon_V^{a}\right)\right)\rho_f\frac{\partial x_{f,j}^{PSAR}}{\partial t}}_{\text{rate of change of mass of } j \text{ per volume}}+\underbrace{\varepsilon_A^{PSAR}\left(\vec{\nabla}x_{f,j}^{PSAR}\right)\cdot\left(\rho_f\overrightarrow{v_f^{PSAR}}\right)}_{\substack{\text{rate of mass addition of } j \text{ by}\\ \text{convection per volume}}}=$$

$$=\left\{\underbrace{\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(\overrightarrow{j_{f,j}^{PSAR}}\right)}_{\substack{\text{rate of mass addition of } j \text{ by}\\ \text{diffusion per volume}}}+\underbrace{M_j\rho_s R_j\left(1-\varepsilon_V^{PSAR}\right)}_{\substack{\text{rate of mass addition of } j \text{ by}\\ \text{adsorption per volume}}}\right\}\quad j=1,N_s$$

Momentum Conservation:

$$\vec{\nabla}P_f^{PSAR}=\underbrace{\left(-150\frac{\left(1-\varepsilon_V^{PSAR}\right)^2}{\left(\varepsilon_V^{PSAR}\right)^3 d_p^{\,2}}-\mu_f^{PSAR}1.75\frac{\left(1-\varepsilon_V^{PSAR}\right)}{\left(\varepsilon_V^{PSAR}\right)^3 d_p}\frac{\rho_f^{PSAR}}{\rho_s^{PSAR}}\left|\overrightarrow{v_f^{PSAR}}\right|\right)\overrightarrow{v_f^{PSAR}}}_{\text{drag exerted by the fluid on the solid surface per mass of absorbent}}$$

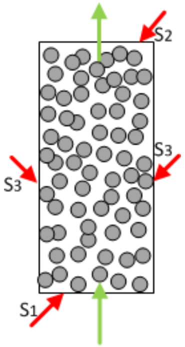
2-D AR-Scale Dynamic Model



Energy Conservation:

$$\boxed{\begin{aligned}
&\underbrace{\varepsilon_V^{PSAR}\rho_f^{PSAR}\left(C_V\right)_f^{PSAR}\frac{\partial T^{PSAR}}{\partial t}}_{\substack{\text{rate of change of energy}\\ \text{per mass of adsorbent}}}+\underbrace{\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(\rho_f^{PSAR}h_f^{PSAR}\overrightarrow{v_f^{PSAR}}\right)}_{\substack{\text{rate of energy addition by convective}\\ \text{transport per mass of adsorbent}}}=\\
&=\left\{\underbrace{\varepsilon_I^{PSAR}h\left(T^{PSAR}-\left(T^a\right)^s\right)}_{\substack{\text{rate of energy addition by heat convection}\\ \text{per mass of adsorbent}}}+\underbrace{\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(k_f^{PSAR}\vec{\nabla}T^{PSAR}\right)}_{\substack{\text{rate of energy addition by heat conduction}\\ \text{per mass of adsorbent}}}\underbrace{-\varepsilon_A^{PSAR}\vec{\nabla}\cdot\left(\sum_{j=1}^{N_s}\tilde{h}_j\rho_s R_j\right)}_{\substack{\text{rate of energy addition by species}\\ \text{per mass of adsorbent}}}\right\}
\end{aligned}}$$

Initial and Boundary Conditions



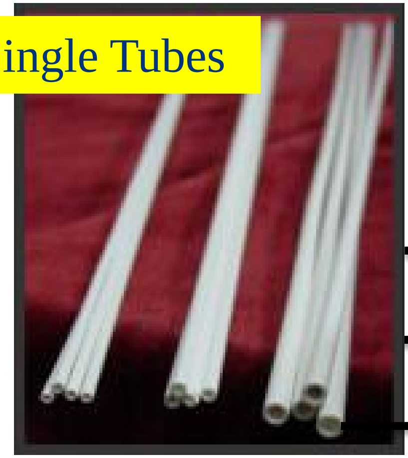
Cycle Step		
I. Adsorption step	t=0	$x_{f,j}^{PSAR}=0,\ C_j=0,\ T^{PSAR}=\left(T^{PSAR}\right)_{ambient},\ P^{PSAR}=\left(P^{PSAR}\right)_{ambient}$
	at S_0	$x_{f,j}^{PSAR}=\left(x_{f,j}^{PSAR}\right)^{surface},\ T^{a}=\left(T^{a}\right)^{surface}$
	at S_1	$x_{f,j}^{PSAR}=\left(x_{f,j}^{PSAR}\right)_{in},\ T^{PSAR}=\left(T^{PSAR}\right)_{in},\ P^{PSAR}=\left(P^{PSAR}\right)_{in},\ \overrightarrow{v_f^{PSAR}}=\left(\overrightarrow{v_f^{PSAR}}\right)_{in}$
	at S_2	$\vec{\nabla} x_{f,j}^{PSAR}=0,\ \vec{\nabla} T^{PSAR}=0$
	at S_3	$\vec{\nabla} x_{f,j}^{PSAR}=0,\ \vec{\nabla} T^{PSAR}=0$
II. Desorption step	t=0	$x_{f,j}^{PSAR}=\left(x_{f,j}^{PSAR}\right)^{I},\ C_j=\left(C_j\right)^{I},\ T^{PSAR}=\left(T^{PSAR}\right)^{I},\ P^{PSAR}=\left(P^{PSAR}\right)^{I}$
	at S_0	$x_{f,j}^{PSAR}=\left(x_{f,j}^{PSAR}\right)^{surface},\ T^{a}=\left(T^{a}\right)^{surface}$
	at S_1	$\vec{\nabla} x_{f,j}^{PSAR}=0,\ \vec{\nabla} T^{PSAR}=0$
	at S_2	$\vec{\nabla} x_{f,j}^{PSAR}=0,\ \vec{\nabla} T^{PSAR}=0$
	at S_3	$\vec{\nabla} x_{f,j}^{PSAR}=0,\ \vec{\nabla} T^{PSAR}=0,\ \overrightarrow{v_f^{PSAR}}=\left(\overrightarrow{v_f^{PSAR}}\right)_{valve}$

MPT Core Technology

Multiple Ceramic Tube Membrane Bundles – versatile, low cost

Ceramic Membrane Features

- Inorganic membranes, tubular format
- Ultra-thin film, nanoporous layers
- Flexible bundle packaging; many size and shape options
- Only US Manufacturer


Single Tubes


1. Close-Packed Bundles

Example: conventional micro- and ultrafiltration


2. Spaced Bundles

Ex: porous heat exchangers & catalytic membrane reactors


3. Candle Filter Bundles

Ex: high pressure intermediate temperature gas separations

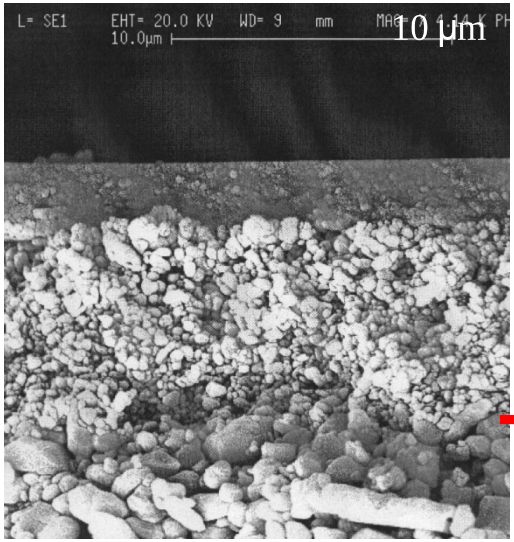
Our Core Expertise/Technology

#1: Packaging individual membrane tubes into commercially viable modules for field use.

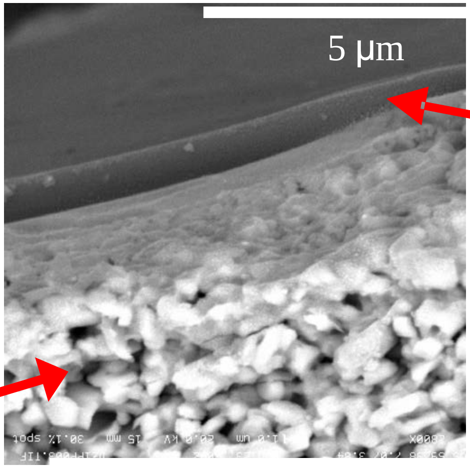
MPT Core Technology

Thin Film Deposition for Pore Size Control

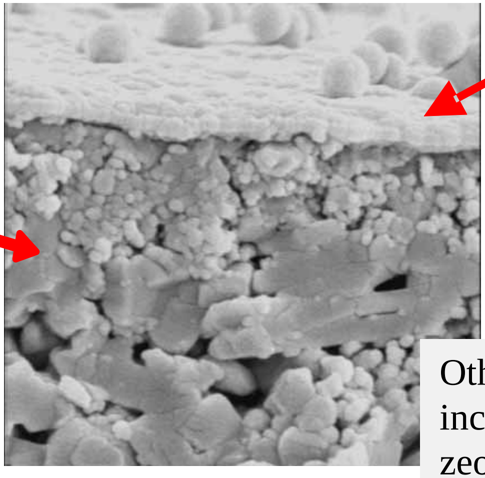
Ceramic Substrate



Ceramic Substrate



Carbon molecular sieve (porous, sulfur resistance)



Palladium (dense, excellent selectivity)

Others, including zeolites, flourinated hydrocarbons, etc.

Important Features of MPT Inorganic Membranes

- Low cost commercial ceramic support
- High packing density, tube bundle
- Module/housing for high temperature and pressure use

Our Core Expertise/Technology

#2: Thin film deposition on less-than desirable but low-cost porous tubular substrates

Progress to Date: CMS Membranes

Some Typical Performance and Operation Capabilities. CMS Membranes

CMS Performance: 86-Tube Bundles

QA/QC Testing Conditions

Temperature: 220 to 250^{o}C

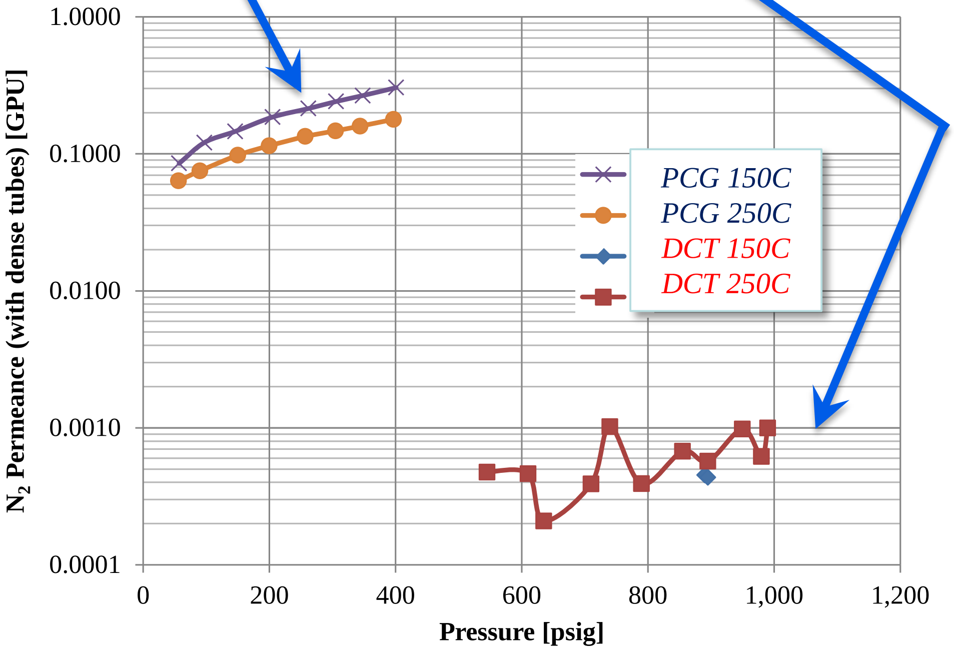
Pressure: 20 to 50 psig

CMS Bundle ID	He Permeance [GPU]	He/N_2 Selectivity [-]
86-6	731	100
86-7	1,020	187
86-8	658	91
86-9	950	102
86-10	365	200
86-11	584	142
86-12	548	77
86-13	840	126
86-14	1,020	117
86-J1	973	120
86-MB1	421	122
86-MB2	665	87
86-MB3	438	85

High-Pressure Leak Rates

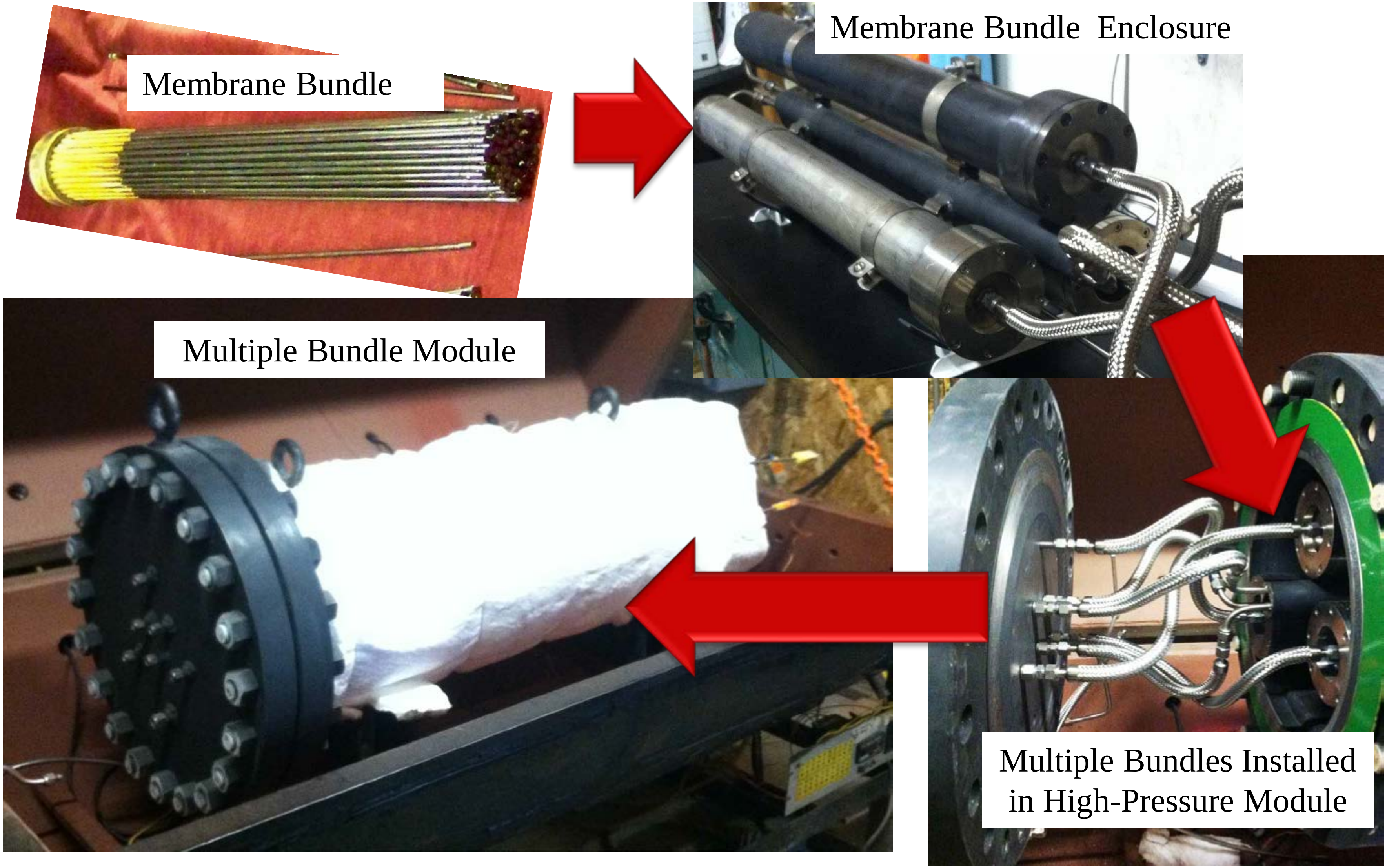
Potted Ceramic/Glass (PCG)

Dense Ceramic Tube Sheet (DCT)



M&P H_2 CMS Selective Membranes

Pilot Module Photographs: 3-CMS Membrane Bundles



Membrane Bundle

Membrane Bundle Enclosure

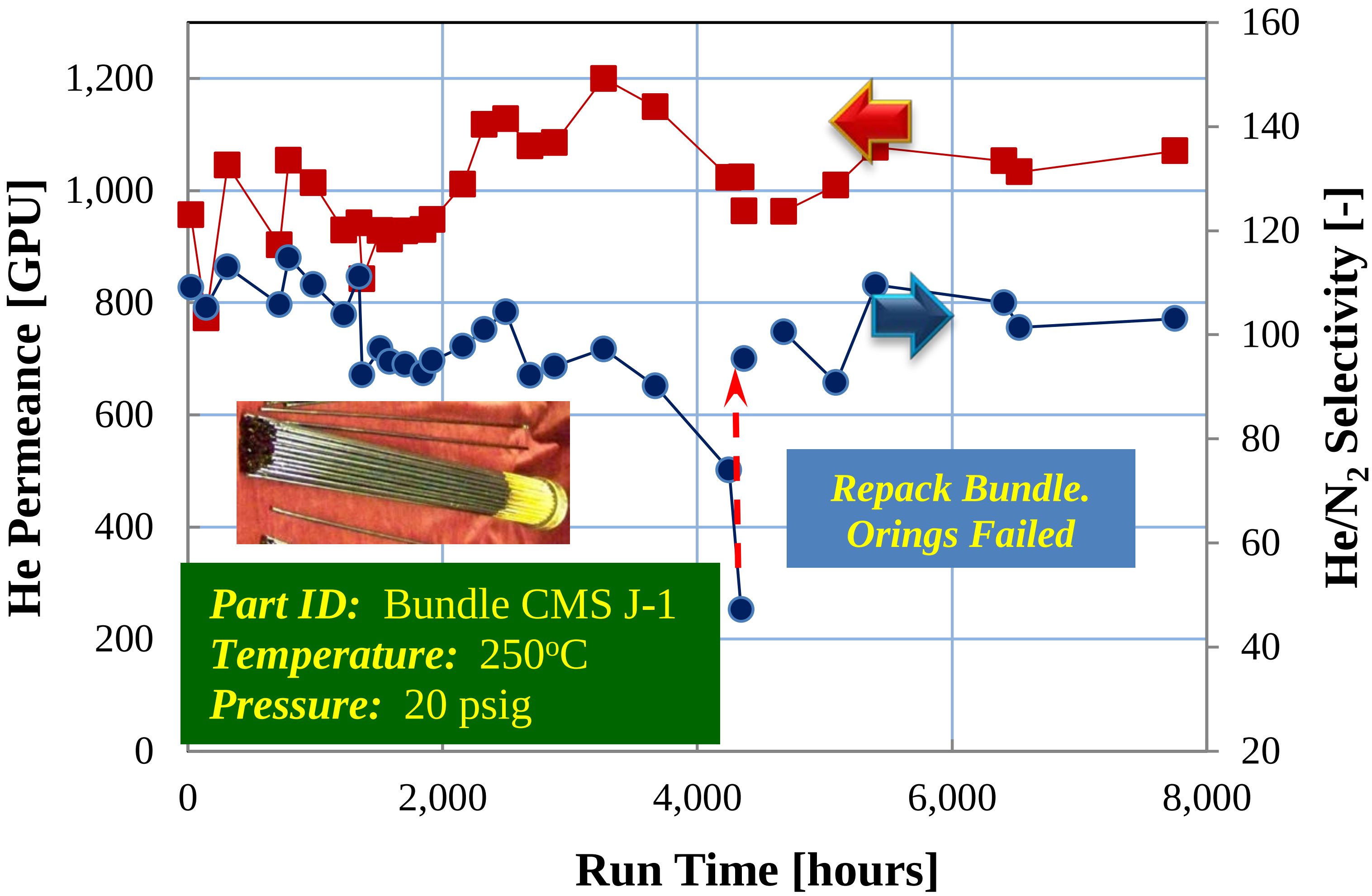
Multiple Bundles Installed in High-Pressure Module

Multiple Bundle Module

Progress to Date: CMS Membranes Stability, cont.

Key Technical Hurdles Focused on Long Term Stability

CMS 86-Tube Bundle Long Term Stability (8,000 hrs)



Part ID: Bundle CMS J-1
Temperature: 250°C
Pressure: 20 psig

Repack Bundle. Orings Failed

Progress to Date: CMS Membranes Stability, cont.

NCCC Testing: CMS Membranes Highly Stable in Coal Gasifier Syngas

Testing Parameters

Membrane
86-tube CMS

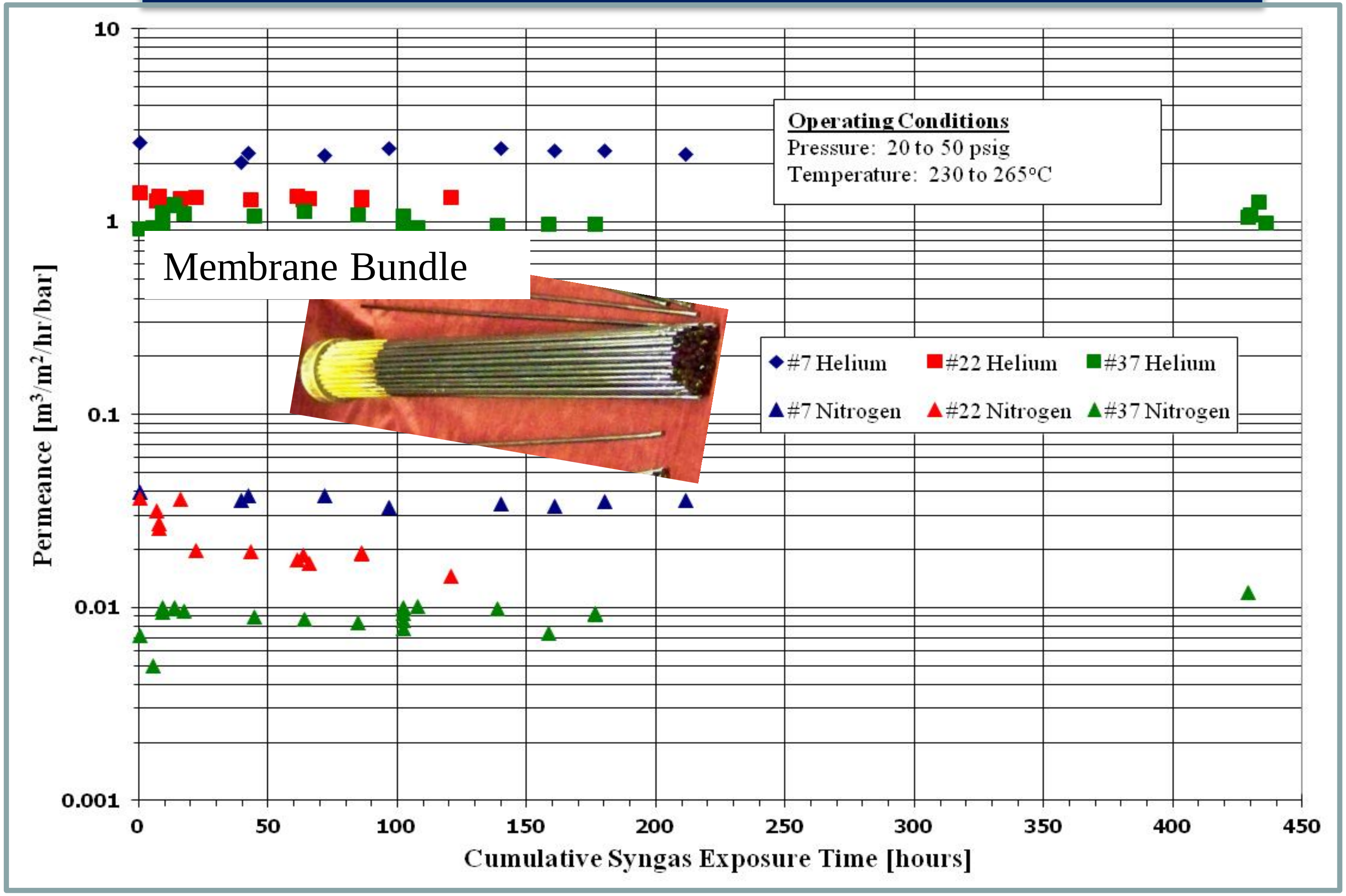
Operating Conditions
T~ 250 to 300°C
P~ 200 to 300 psig

Pretreatment
Particulate trap only,
no other gas cleanup.

Composition
H_2 ~ 10 to 30%
CO ~ 10%
CO_2 ~10%
N_2,H_2O ~Balance

Trace Contaminants
NH_3 ~ 1,000ppm
Sulfur Species ~ 1,000ppm
HCl, HCN,
Naphthalenes/Tars, etc.

NCCC Slip-Stream Testing: No Gasifier Off-Gas Pretreatment



Performance stability of multiple-tube CMS membrane bundles during H_2 recovery from NCCC slip-stream testing. He and N_2 Permeances measured periodically during >400 hr test.

Progress to Date: CMS Membranes Stability, cont.

CMS Performance Stability: H_2S Removal during NCCC Testing

Testing Parameters

Membrane
86-tube CMS

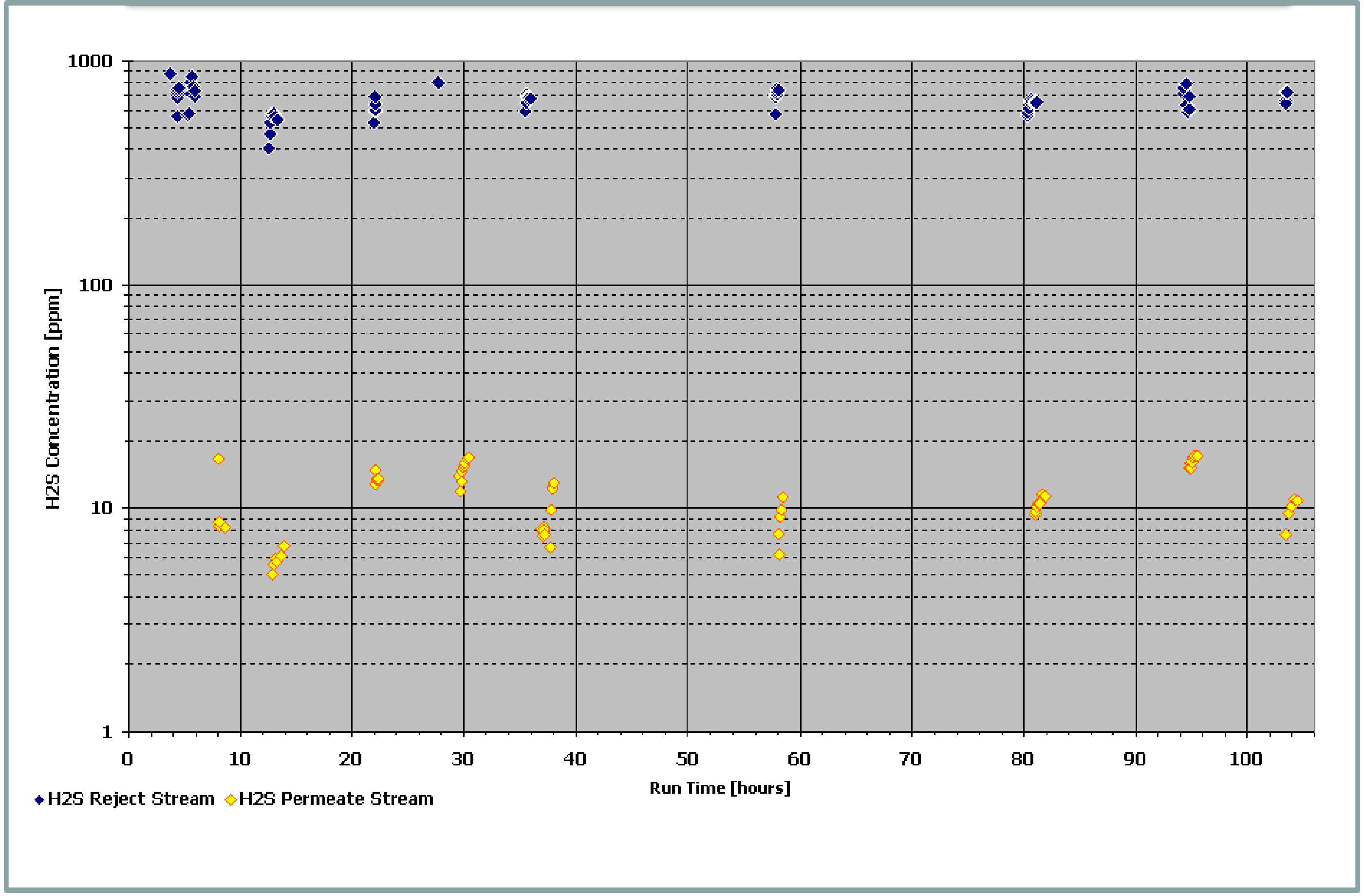
Operating Conditions
T~ 250 to 300°C
P~ 200 to 300 psig

Pretreatment
Particulate trap, no other gas cleanup.

Composition
H_2 ~ 10 to 30%
CO ~ 10%
CO_2 ~10%
N_2,H_2O ~Balance

Trace Contaminants
NH_3 ~ 1,000ppm
Sulfur Species ~ 1,000ppm
HCl, HCN, Naphthalenes/Tars, etc.

NCCC Slip Stream Testing: H_2S Feed and Permeate Composition



Progress: CMS Membranes Stability, cont.

CMS Performance Stability: Tar-like Species in Gasifier Off-gas

Operating Temperatures Above 250^{o}C Required to Prevent Condensation of Tar-like Contaminants

Temperatures ≤230^{o}C

Tar or other residue build-up evident

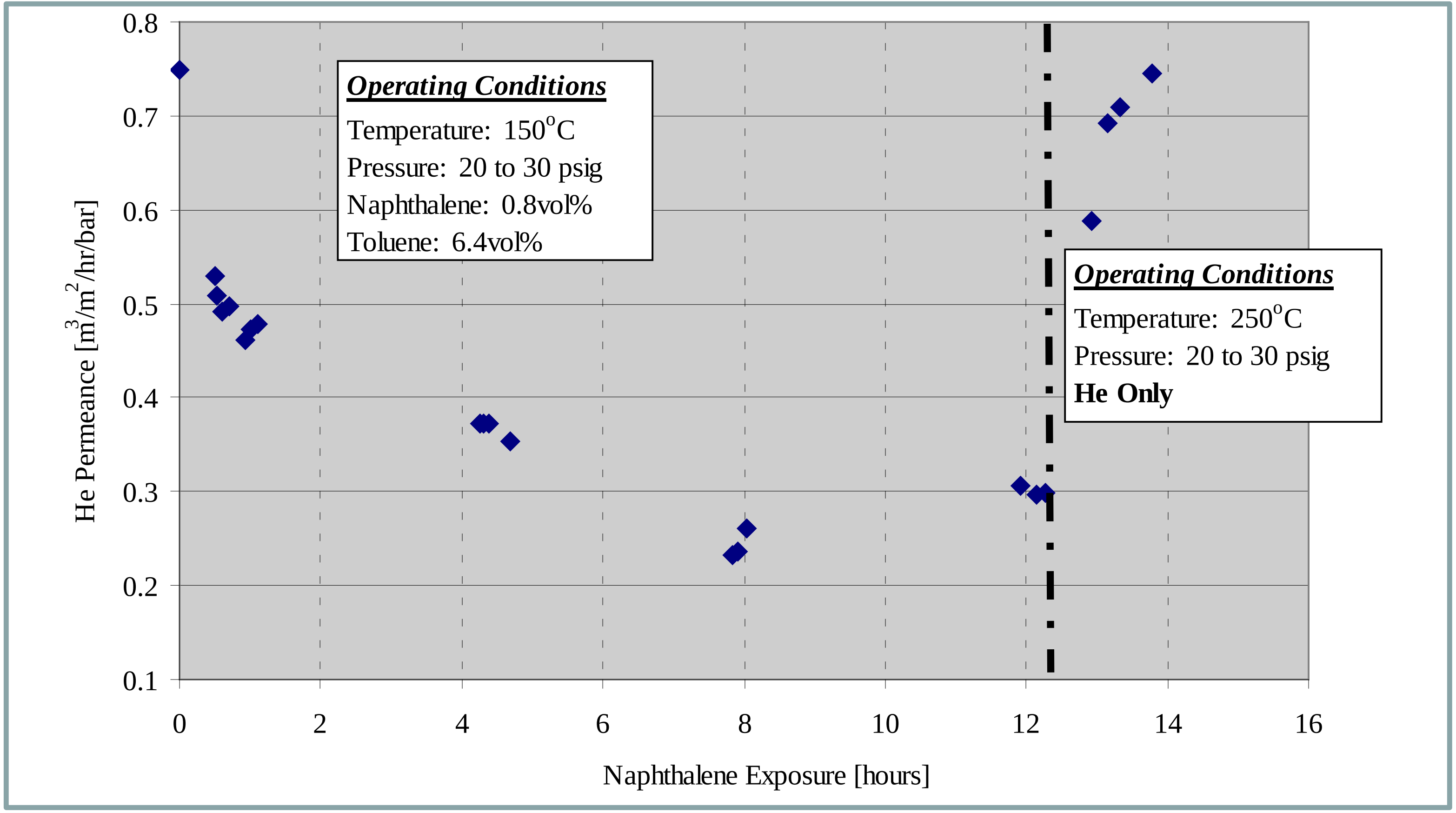
Temperatures >250^{o}C

No evidence of tar or other residue build-up

Progress to Date: CMS Membranes Stability, cont.

Effect of Temperature in the Presence of Model Tar Compounds

Naphthalene/toluene as model tar and organic vapors



Operating Conditions

Temperature: 150°C

Pressure: 20 to 30 psig

Naphthalene: 0.8vol%

Toluene: 6.4vol%

Operating Conditions

Temperature: 250°C

Pressure: 20 to 30 psig

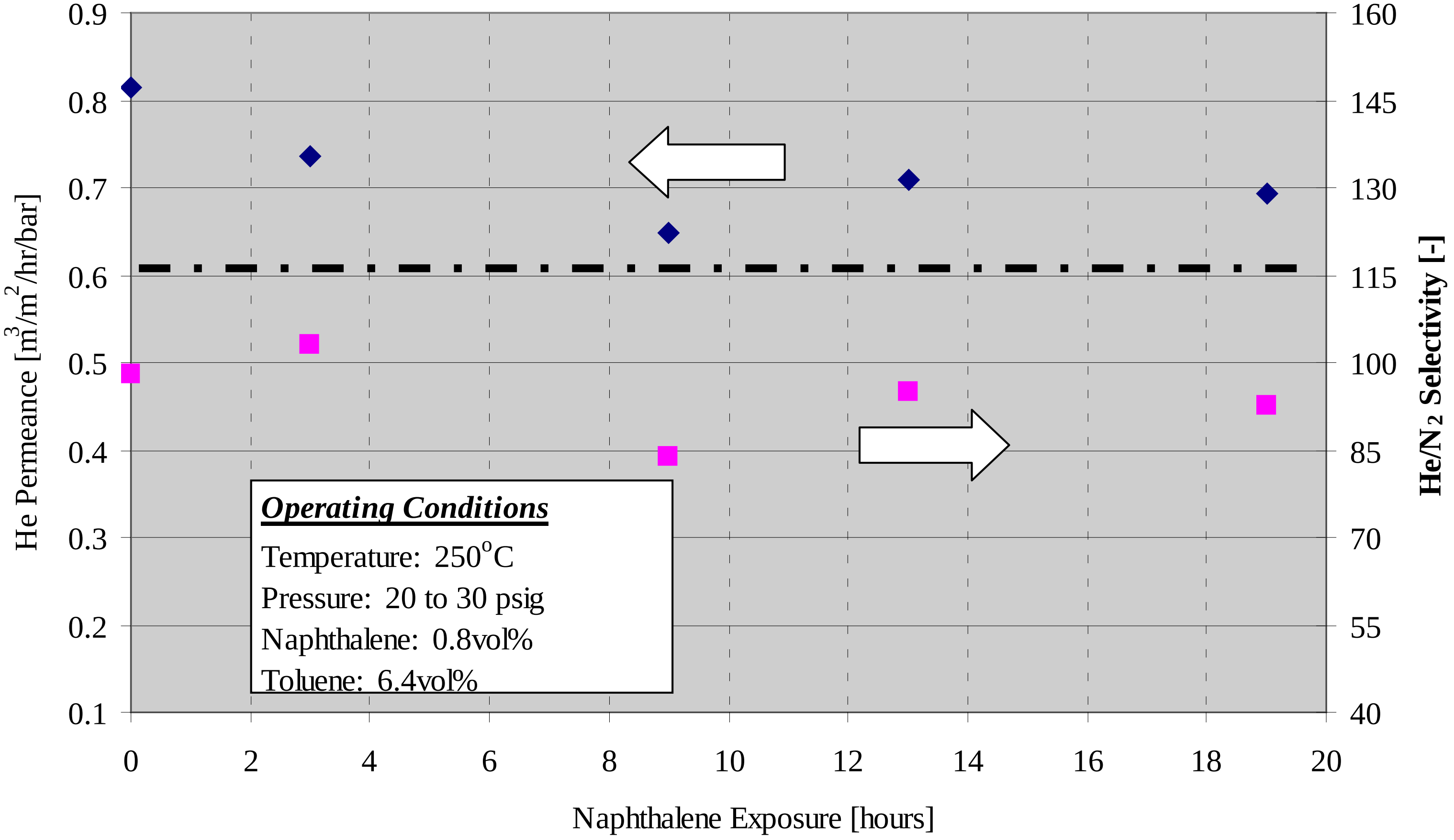
He Only

- ☐ **Membrane fouling occurs at low temperature.**
- ☐ **Membrane regeneration can be achieved rapidly at high temperature.**

Progress to Date: CMS Membranes Stability, cont.

CMS Membrane Stability in the Presence of Model Tar Compound

Membrane performance is stable at high operating temperatures (250°C) in the presence of naphthalene/toluene as model tar and organic vapors compounds.



Operating Conditions

Temperature: 250°C

Pressure: 20 to 30 psig

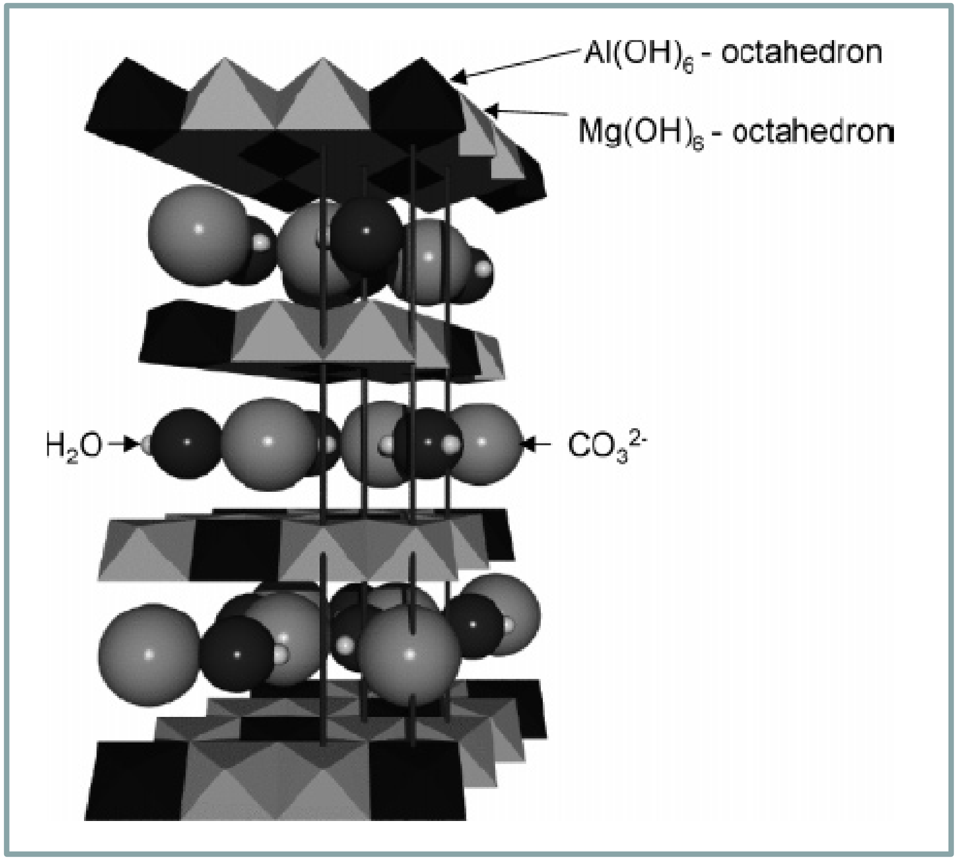
Naphthalene: 0.8vol%

Toluene: 6.4vol%

Progress to Date: Hydrotalcite (HT) Adsorbents

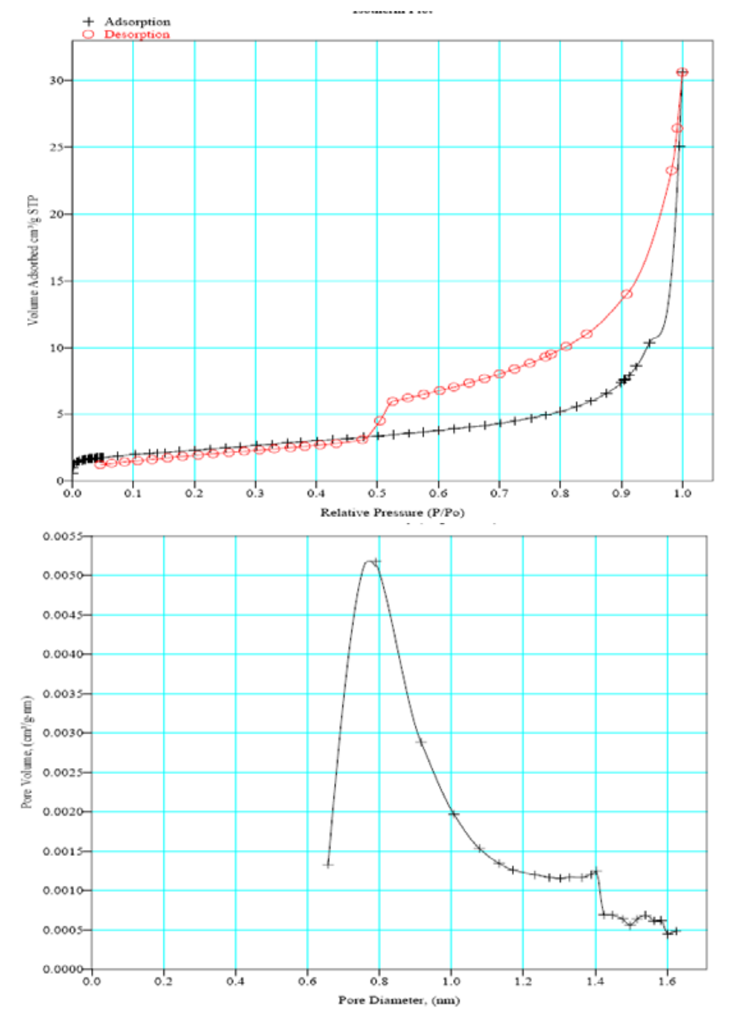
Characterization of the Hydrotalcite (HT) Adsorbents

The structure of the hydrotalcites (HT) adsorbents



Aadesh Harale, PhD Thesis, University of Southern California, Los Angeles, CA, USA, 2012.

Characterization of the hydrotalcites

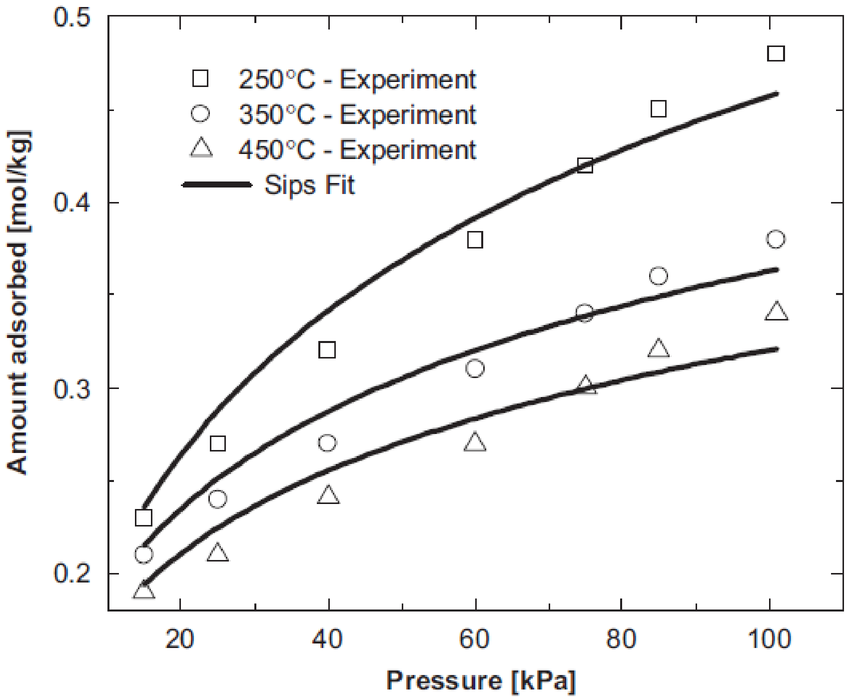


Progress to Date: Hydrotalcite (HT) Adsorbents, cont.

Equilibrium Adsorption (Isotherm) Data & Adsorption Kinetics Data

Experimental results with model fits

CO_2 isotherm data

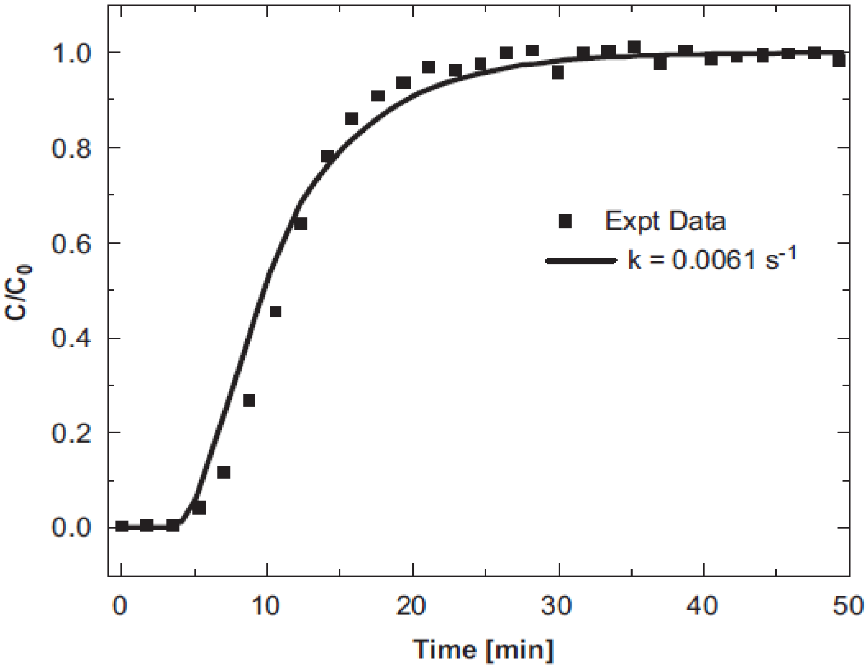


Sips isotherm parameters

Temperature (°C)	m_{CO_2} (mmol/g sample)	b_{CO_2} (kPa^{-1})	n
250	0.9801(±0.0021)	0.0078(±0.0012)	1.8628(±0.0011)
350	0.7796(±0.0013)	0.0073(±0.0026)	2.2867(±0.0016)
450	0.7443(±0.0015)	0.0050(±0.0018)	2.4779(±0.0014)

Experimental results with model fits

CO_2 breakthrough data

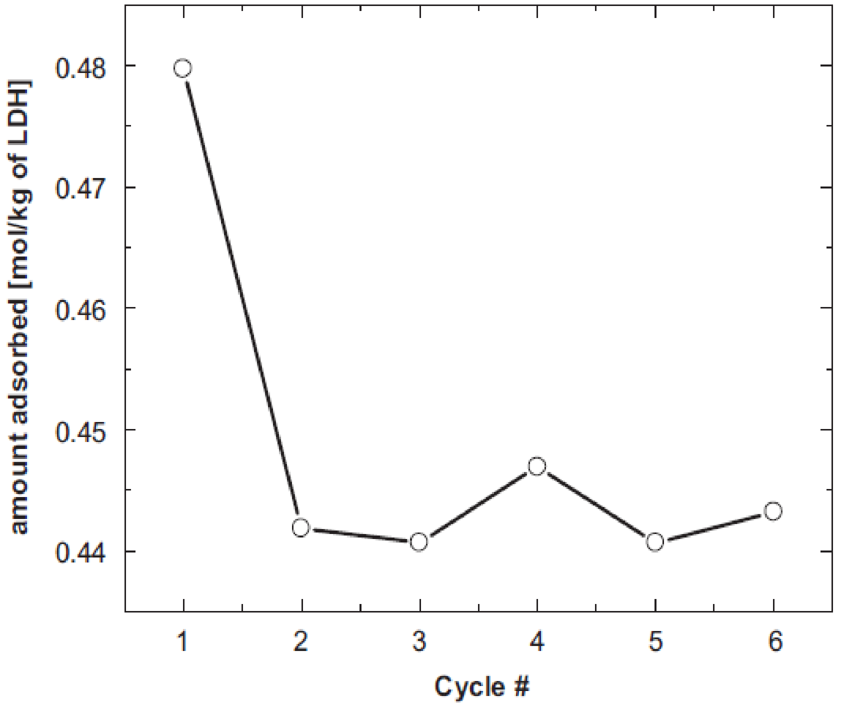


Chem. Eng. Sci.,4126, 62 (2007).

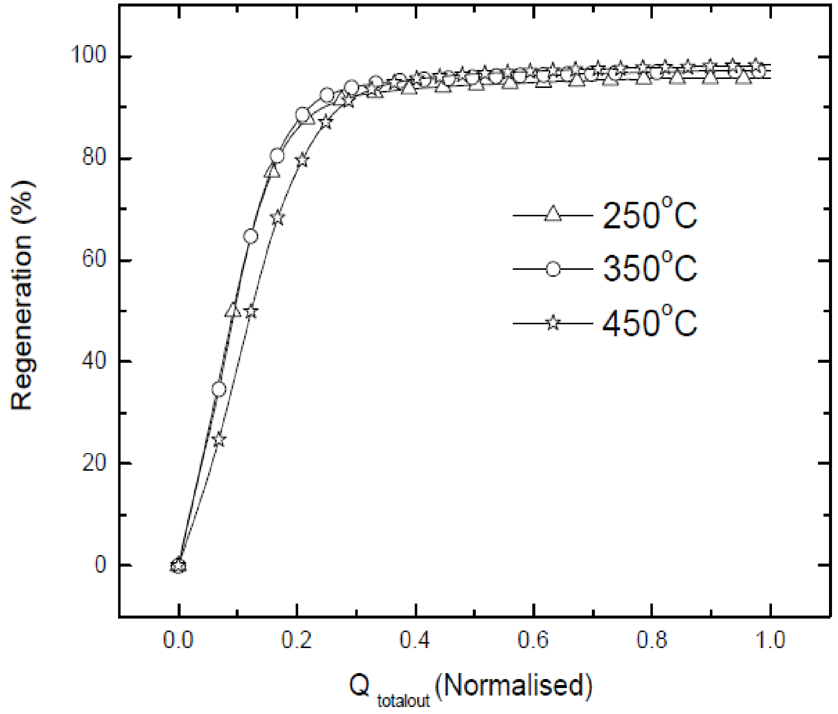
Progress to Date: Hydrotalcite (HT) Adsorbents, cont.

Cyclic Adsorption Behavior & Regeneration

Effect of cycle number on adsorption capacity of hydrotalcite at 250°C, Pressure = 1 atm



CO_2 desorption profiles using Argon as a purge gas



Chem. Eng. Sci., 4126, 62 (2007).
Aadesh Harale, PhD Thesis, University of Southern California, Los Angeles, CA, USA, 2012.

Progress to Date: CMS Membrane for WGS-MR

CO Conversion and Hydrogen Recovery

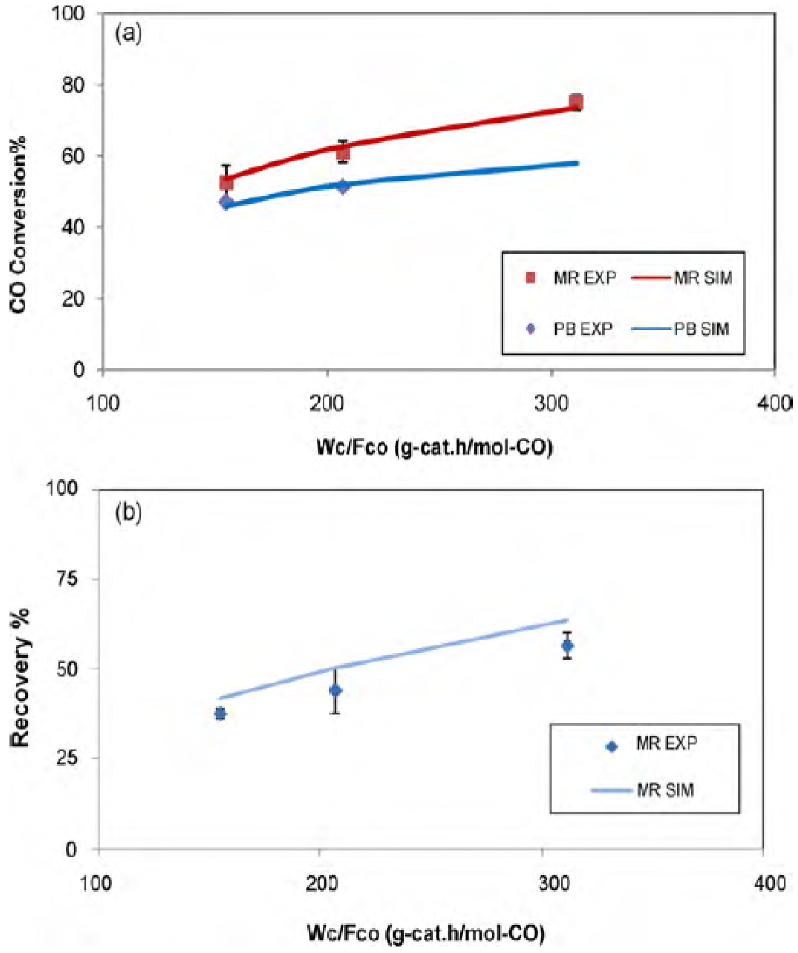


Fig. 10. Comparison of the experimental (a) conversion and (b) recovery with the model predictions at *T* = 300 °C, *P* = 5 atm and sweep ratio = 0.3 using CMS#2.

Comparison of
Experimental Results
vs.
Model Predictions
for WGS/MR using
CMS Membranes
(Co/Mo Sulfided Catalyst)

Temperature (°C): 300
Pressure (atm): 5
Weight of catalyst (g): 12
W/F_{CO} (g-cat.h/mol-CO): 150 -311
Feed Composition
H_2:CO:CO_2:CH_4:H_2O:H_2S 2.6:1:2.14:0.8:1.2:0.05

J. Membr. Sci., *363*, 160 (2010);
Ind. Eng. Chem. Res., 819, 53 (2014).

Progress to Date: CMS Membrane for WGS-MR, cont.

Reject and Permeate Stream Compositions

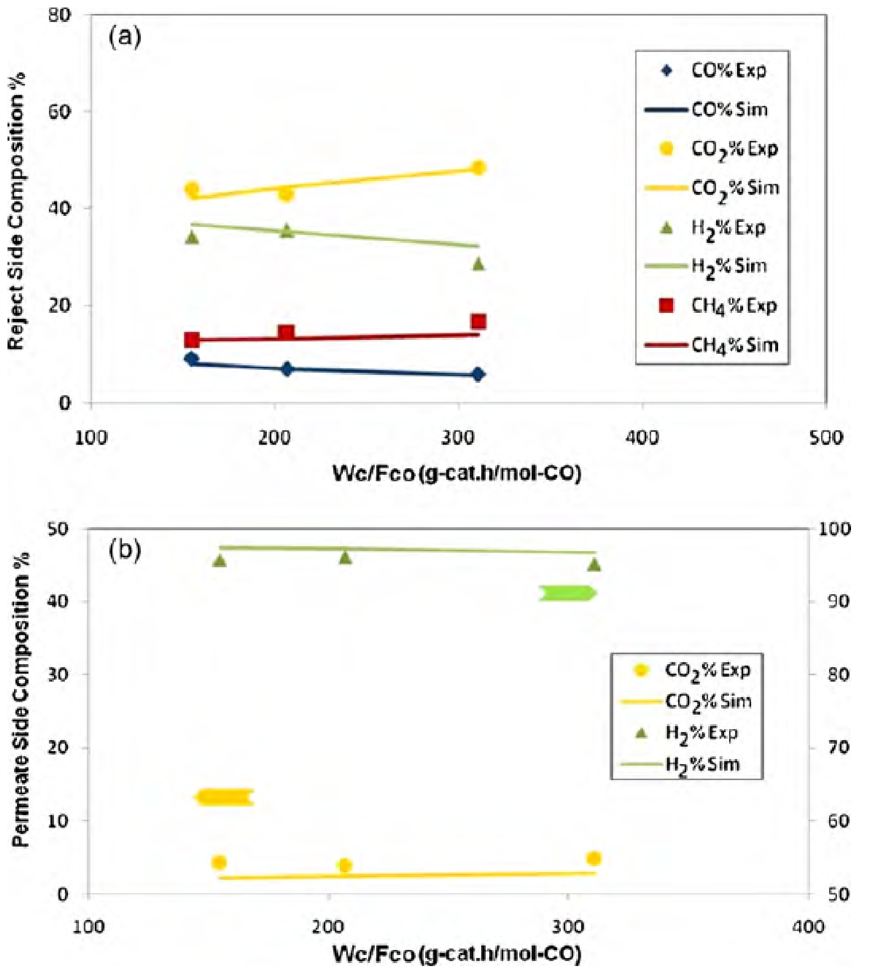


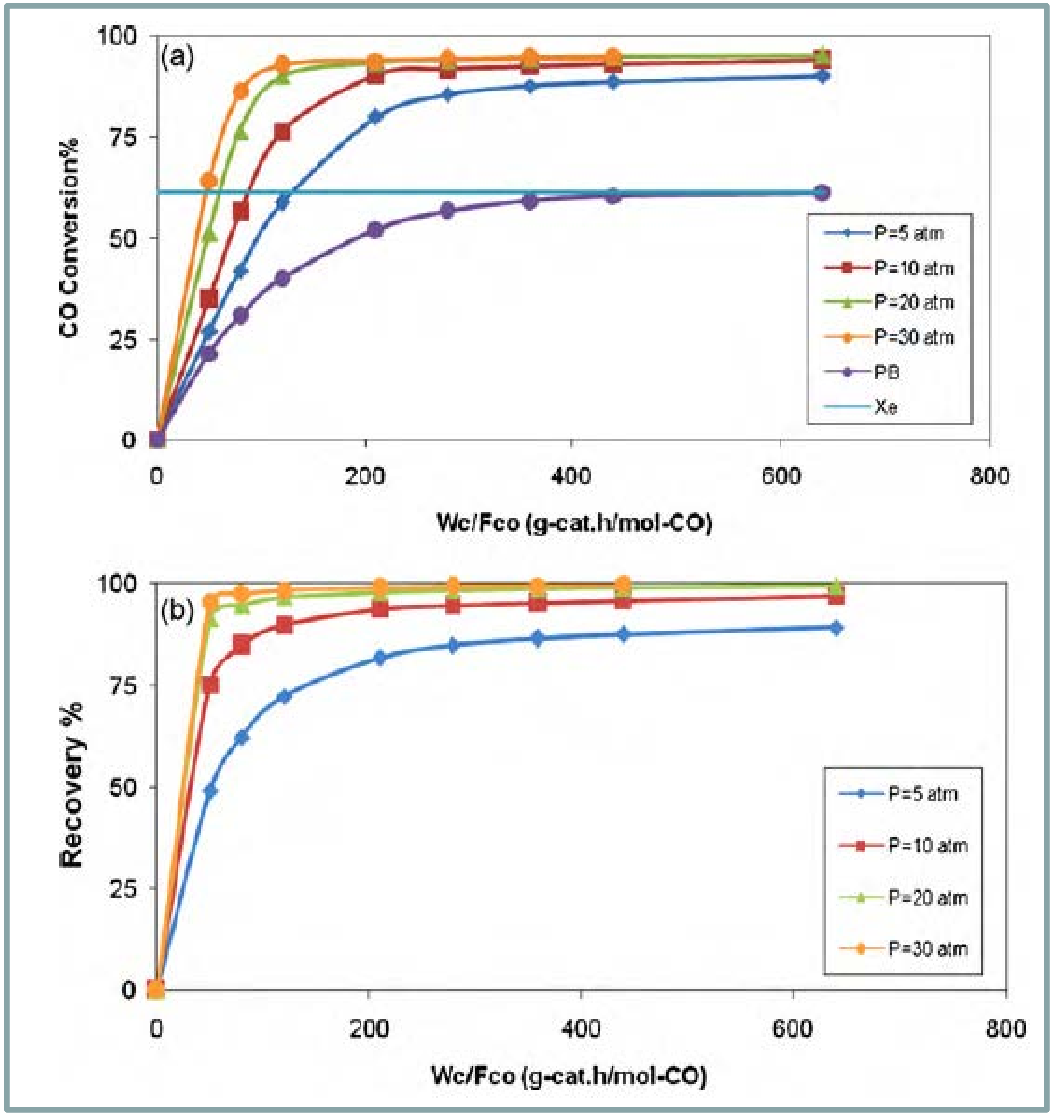
Fig. 6. Compositions of (a) reject and (b) permeate side at $P = 3$ atm and sweep ratio = 0.3.

Comparison of Experimental Results vs. Model Predictions for WGS/MR using CMS Membranes (Co/Mo Sulfided Catalyst)

J. Membr. Sci., *363*, 160 (2010);
Ind. Eng. Chem. Res., 819, 53 (2014).

Progress to Date: CMS Membrane for WGS-MR, cont.

Effect of Pressure on the CO Conversion and Hydrogen Recovery



Simulations for
WGS/MR using
a CMS Membrane
under a
Coal Gasificatioin
Environment
(Co/Mo sulfided Catalyst)

J. Membr. Sci., *363*, 160 (2010);
Ind. Eng. Chem. Res., 819, 53 (2014).

Scope of Work: Key Objectives

Budget Period 1 (BP1):

1. *Design, construct, and test the lab-scale MR-AR system.*
2. *Select baseline membranes, adsorbents and catalysts from those already available in-house, and characterize their performance for the proposed application.*
3. *Upgrade and experimentally validate the in-house mathematical model.*

Budget Period 2 (BP2):

1. *Experimentally test the proposed novel process in the lab-scale apparatus using simulated fuel gas.*
2. *Complete the initial technical and economic feasibility study.*

Tasks to be Performed

Budget Period 1(BP1):

Task 2.0 - Materials Preparation and Characterization.

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

Subtask 2.2- Preparation and Characterization of Adsorbents and Catalysts.

Task 3.0 - Design and Construction of the Lab-Scale MR-AR Experimental System.

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

Subtask 4.1 - Unit Operation Testing.

Subtask 4.2 - Mathematical Model Development and Simulations.

Budget Period 2 (BP2):

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

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.

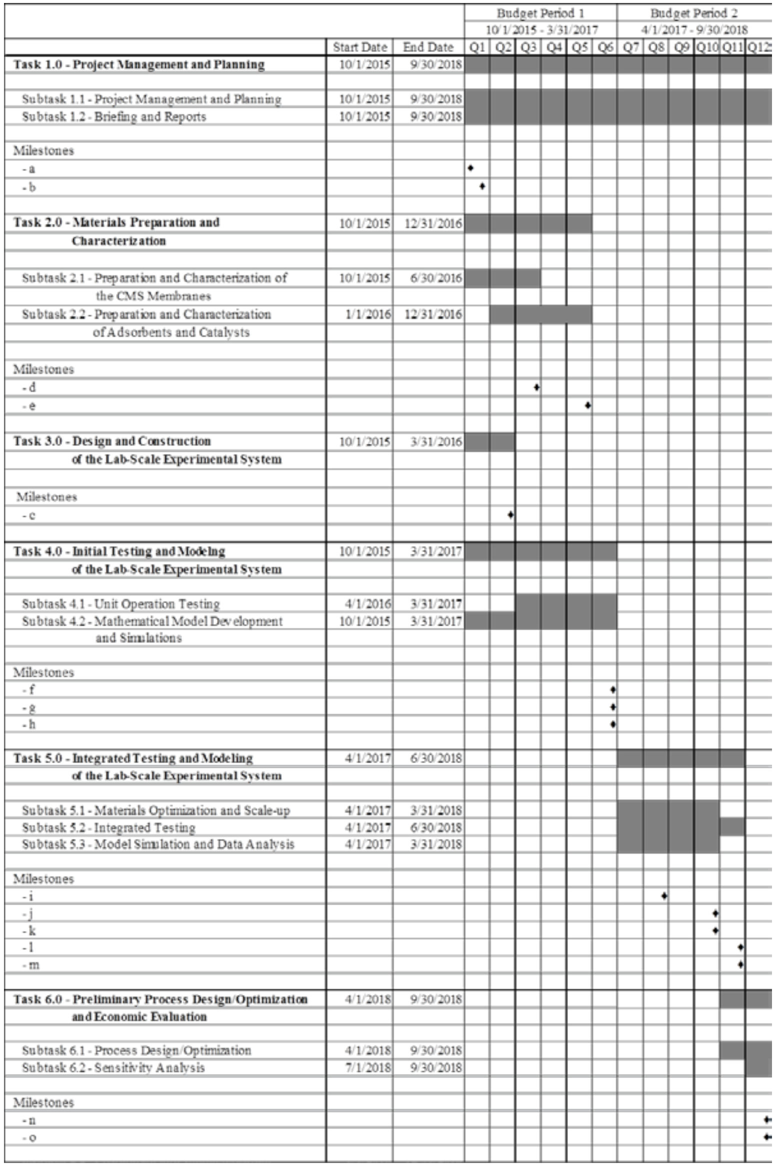
Subtask 6.1 - Process Design/Optimization.

Subtask 6.2 - Sensitivity Analysis.

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

Resource-Loaded Schedule



			Budget Period 1						Budget Period 2					
			10/1/2015 - 3/31/2017						4/1/2017 - 9/30/2018					
	Start Date	End Date	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1.0 - Project Management and Planning	10/1/2015	9/30/2018	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Subtask 1.1 - Project Management and Planning	10/1/2015	9/30/2018	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Subtask 1.2 - Briefing and Reports	10/1/2015	9/30/2018	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
Milestones														
- a			◆											
- b			◆											
Task 2.0 - Materials Preparation and Characterization	10/1/2015	12/31/2016	▨	▨	▨	▨	▨							
Subtask 2.1 - Preparation and Characterization of the CMS Membranes	10/1/2015	6/30/2016	▨	▨	▨									
Subtask 2.2 - Preparation and Characterization of Adsorbents and Catalysts	1/1/2016	12/31/2016		▨	▨	▨	▨							
Milestones														
- d					◆									
- e							◆							
Task 3.0 - Design and Construction of the Lab-Scale Experimental System	10/1/2015	3/31/2016	▨	▨										
Milestones														
- c				◆										
Task 4.0 - Initial Testing and 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														◆

Milestone Log

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

Milestone Log, cont.

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

Success Criteria

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

Notation

$p = pellet\,,\ r = reactor,\ M = permeation\ zone$

$\varepsilon_V^p\left(\frac{m^3\ fluid}{m^3\ pellet}\right)$: pellet volume void fraction

$\varepsilon_A^p\left(\frac{m^2\ permeable\,surface}{m^2\,total\ surface}\right)$:pellet area void fraction

$\varepsilon_I\left(\frac{m^2\ fluid - solid\ interfacial\,area}{m^3\,reactor}\right)$ is the area to volume interfacial factor

$r_j\left(\frac{mol\ \ j}{(kg\ \ solid \cdot s)}\right);\ j = 1, N_s$: mass generation rate of jth species per mass of solid

$M_j\left(\frac{kg\ j}{kmol\ \ j}\right);\ j = 1, N_s$: molar mass of the jth species

$\overrightarrow{j_{f,j}^p}\left(\frac{kg\ \ j}{m^2 \cdot s}\right);\ j = 1, \mathrm{N}_s$: diffusive mass flux of the jth species in pellet

$k_s^p\left(\frac{J}{m.s.K}\right)$: thermal conductivity of solid phase

$k_s^p\left(\frac{J}{m.s.K}\right)$: thermal conductivity of fluid phase

$T^p\left(K^\circ\right)$:temperature of pellet

$\rho_f\left(\frac{kg\ \ fluid}{m^3\ \ fluid}\right)$: density of fluid phase

$\overrightarrow{v_f}\left(\frac{m}{s}\right)$: velocity of fluid phase

$\varepsilon_V^p\left(\frac{m^3\ fluid}{m^3\,reactor}\right)$: reactor volume void fraction

$\varepsilon_A^r\left(\frac{m^2\ permeable\,surface}{m^2\,total\ \,surface}\right)$: reactor area void fraction

$P^r\left(Pa\right)$: pressure inside reactor

$x_{f,j}^r\left(\frac{kg\ \ j}{kg\ fluid}\right);\ j = 1, \mathrm{N}_s$: mass fraction of the jth species

$\eta_j;\ \ j = 1, N_s$: effectiveness factor of jth species

$\overrightarrow{j_{f,j}^p}\left(\frac{kg\ \ j}{m^2 \cdot s}\right);\ j = 1, \mathrm{N}_s$: diffusive mass flux of the jth species in reactor

$J_{H_2}\left(\frac{kg}{m^2.s}\right)$:hydrogen flux through the membrane

$E_a\left(\frac{J}{mol}\right)$:is the membrane permeability activation energy

$B_{H_o}\left(\frac{mol\ \ H_2}{m^2.s.Pa^n}\right)$: is the membrane permeability pre-exponential factor

P_{e_m} : mass effective radial Peclet number

R_{mem} : selective membrane radius

$P_{H_2,r}$: Hydrogen partial pressure in Reaction zone

$P_{H_2,p}$: Hydrogen partial pressure in permeation zone

$d_t\left(m\right)$: diameter of the reactor tube

$d_p\left(m\right)$: diameter of the pellet

$\tilde{h}_j\left(\frac{J}{mol\ j}\right) j = 1, N_s$: molar enthalpy of jth species

$h\left(\frac{J}{m^2 \cdot s \cdot K}\right)$: heat transfer coefficient between fluid and pellet

$U\left(\frac{J}{m^2 \cdot s \cdot K}\right)$: heat transfer coefficient between fluid and reactor external wall

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Notation

$a = adsorbent\,,\; PSAR = pressure\;\; swelling\;\; adsorping\;\; reactor$

$U_1\left(\frac{J}{m^2\cdot s\cdot K}\right)$: heat transfer coefficient between fluid and membrane wall

$d_t\,(m)$: diameter of permeation zone

$T^W\,(K^\circ)$: temperature at reactor external wall

$T^{perm}\,(K^\circ)$: temperature at membrane wall

$T^r\,(K^\circ)$: temperature of reactor

$(T^p)^s\,(K^\circ)$:temperature at pellet surface

$x_i^M\left(\frac{kg\;\; i}{kg\;\; fluid}\right);\; j=1,\mathrm{N}_s$:mass fraction of the ith species in permeation zone

$\rho^M\left(\frac{kg\;\; fluid}{m^3\;\; fluid}\right)$: density of fluid phase in permeation zone

$\overrightarrow{v^M}\left(\frac{m}{s}\right)$: velocity of fluid phase in permeation zone

$P^M\,(Pa)$: pressure in permeation zone

$\tilde{h}_i^M\left(\frac{J}{mol\, i}\right) i=1,N_s$: molar enthalpy of ith species in permeation zone

$h^M\left(\frac{J}{kg\;\; fluid}\right)$: enthalpy of fluid in permeation zone

$k^M\left(\frac{J}{m.s.K}\right)$: thermal conductivity of fluid phase in permeation zone

$T^p\,(K^\circ)$: temperature of permeation zone

$\varepsilon_V^p\left(\frac{m^3\;\; fluid}{m^3\;\; pellet}\right)$:adsorbent volume void fraction

$\varepsilon_A^p\left(\frac{m^2\;\; permeable\, surface}{m^2\; total\;\; surface}\right)$: adsorbent area void fraction

$(C_{\mathrm{v}})_s\left(\frac{J}{kg\cdot K}\right)$: constant volume heat capacity of the solid phase

$x_{f,j}^a\left(\frac{kg\;\; j}{kg\;\; fluid}\right);\; j=1,\mathrm{N}_s$ mass fraction of the jth species

$R_j\left(\frac{mol}{kg-adsorbent.s}\right)$: adsorption rate of jth species per kg adsorbent per second

$C_{seq,j}\left(\frac{mol}{kg-adsorbent}\right)$: molar equilibrium concentration of jth species

$C_j\left(\frac{mol}{kg-adsorbent.}\right)$: molar concentration of jth species

$b_j\left(Pa^{-1}\right);\; j=1,N_s$: adsorption equilibrium constant of jth species

$b_j^0\left(Pa^{-1}\right);\; j=1,N_s$: adsorption equilibrium constant of jth species at standard state

$T^a\,(K^\circ)$: temperature of adsorbent

$\varepsilon_V^{PSA}\left(\frac{m^3\;\; fluid}{m^3\;\; PSA}\right)$: PSAR volume void fraction

$\varepsilon_A^{PSA}\left(\frac{m^2\;\; permeable\, surface}{m^2\; total\;\; surface}\right)$: PSAR area void fraction

$m_j\left(\frac{mol}{kg-adsorbent.}\right)$: Total adsorbent capacity