Systems Analysis of Membrane Reactors for Energy and Environmental Applications

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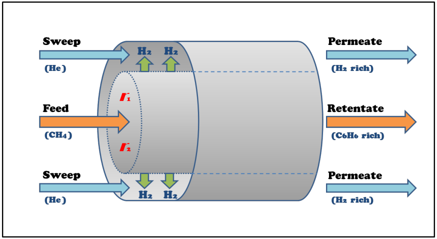
NSF Process Intensification Workshop
Washington, DC
October 1, 2014

Presentation Outline

1. Introduction & Motivation
2. Membrane Reactor Modeling
   - Modeling Approach & Assumptions
   - Simulation Set Up & Case Studies
3. Membrane Reactor Optimization
   - Problem Formulation
   - Solution & Results
4. Conclusions & Future Directions

Membrane Reactors for Process Intensification



- Membrane reactors and their role in process intensification[1]
  - compact and modular
  - environmentally friendly
  - capital cost reduction
  - efficiency improvement
  - higher conversions than conventional reactors
- Process systems engineering approach
  - design and implementation of emerging technologies
  - accelerate process intensification when utilizing major energy sources
  - provide guidelines for experimental research

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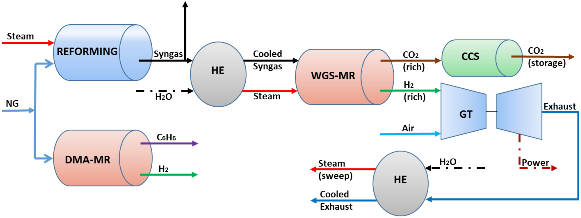
[1] Drioli, Stankiewicz, and Macedonio (2011)

Current Membrane Reactor Applications



- Direct methane aromatization (DMA) to fuels and chemicals
  - ion transport-based membranes
  - focus on production of hydrogen and benzene[2]
- Water gas shift (WGS) for carbon capture and hydrogen production
  - zeolite and polymer-based membranes
  - integration into advanced energy plants (IGCC/NGCC)
    - analysis of membrane placement in the flowsheet[3]
    - optimization of heat integration and generation of products

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[2] Carrasco, Liu, and Lima (2014)

[3] Marano and Ciferno (2009)

Membrane Reactor Systems Approach

- Develop a membrane reactor (MR) model
  - address WGS reaction for CO_2 capture and H_2 production
  - focus on H_2-selective polybenzimidazole hollow fiber (PBI-HF) membranes
- Perform systems studies (simulation, optimization) employing developed model
  - determine membrane characteristics (selectivity, permeance) to achieve specifications reported by the DOE[4]
  - minimize capital cost by optimizing membrane use as function of surface area required

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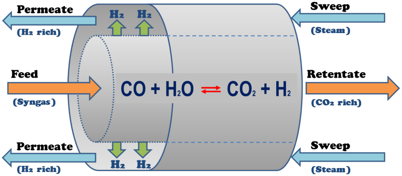
[4] Marano (2010); Marano and Ciferno (2009)

Membrane Reactor Design & Modeling Assumptions



- Reactor design
  - 1-dimensional shell and tube reactor
  - catalyst packed in the tube side
  - thin membrane layer placed on surface of tube wall
  - sweep gas flows in shell side
  - co-current and *counter-current* flow configurations
- Modeling assumptions
  - plug-flow operation
  - constant pressure and controlled temperature[5]
  - steady-state operation

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[5] Georgis, Lima, Almansoori, and Daoutidis (2014)

Membrane Reactor Model

- Mole balance - tube (reaction side)[6]

$$\underbrace{\frac{dF_{i,t}}{dz}}_{\text{convection}} = \underbrace{A_t r_i}_{\text{reaction}} - \underbrace{\pi d_t J_i}_{\text{flux}}$$

in which $r_i = r_{CO}$ for $i = CO, H_2O$;
$r_i = -r_{CO}$ for $i = CO_2, H_2$;

- Mole balance - shell (permeation side)

$$(-)\ \underbrace{\frac{dF_{i,s}}{dz}}_{\text{convection}} = \underbrace{\pi d_t J_i}_{\text{flux}}$$

- Flux through membrane: Fickian activated diffusion[7]

$$J_i = Q_i \Delta P_i$$

in which $Q_i = Q_{i,0} exp(-E_a/RT)$

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[6] Lima, Marano, Daoutidis, and Tsapatsis (2011)

[7] Berchtold, Singh, Young, and Dudeck (2012)

Membrane Reactor Simulation Set Up

- Simulation conditions from literature or expected lab facilities
    - feed composition[8]: treated syngas
    - catalyst type ($Cu/ZnO/Al_2O_3$) and reaction rate[9]
    - reactor dimensions
        - $d_t = 1.02$ cm
        - $L = 300$ cm
    - operating conditions
        - $P_t = 47.63$ atm, $P_s = 25.86$ atm[10]
        - $T = 300^oC$
- Membrane characteristics and ranges
    - H_2/CO_2 selectivity: $\alpha_{H_2/CO_2} = 15 - 75$
    - H_2 permeance: $Q_{H_2} = 100 - 300$ GPU

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[8] Marano (2010)

[9] Choi and Stenger (2003)

[10] Lima, Marano, Daoutidis, and Tsapatsis (2011)

Parameter Definitions & Target Values

- Membrane reactor parameters: definitions and target values[11]
  - CO_2 capture (C_{CO_2})

$$C_{CO_2} = \frac{\text{Carbon in retentate}}{\text{Carbon in feed}} = \frac{F_{CO,r} + F_{CO_2,r}}{F_{CO,f} + F_{CO_2,f}} \geq 90\%$$

  - CO conversion (X_{CO})

$$X_{CO} = \frac{\text{CO converted}}{\text{CO in feed}} = \frac{F_{CO,f} - (F_{CO,r} + F_{CO,p})}{F_{CO,f}} \geq 98\%$$

  - H_2 recovery/productivity (R_{H_2})

$$R_{H_2} = \frac{\text{H}_2\text{ in permeate}}{(\text{H}_2 + \text{CO})\text{ in feed}} = \frac{F_{H_2,p}}{F_{H_2,f} + F_{CO,f}} \geq 95\%$$

- Other stream constraints[12]
  - CO_2 and H_2O purity in retentate: $\mathrm{P}_{CO_2+H_2O,r} \geq 95\%$
  - H_2 molar fraction in retentate: $\mathrm{y}_{H_2,r} \leq 4\%$
  - H_2 purity in permeate: $\mathrm{P}_{H_2,p} \geq 44\%$

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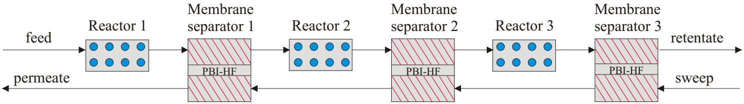
[11] Woods et al. (2007); Koukou et al. (1998); Marano (2010)

[12] Marano (2010)

Benchmark: Multi-stage (3) Configuration



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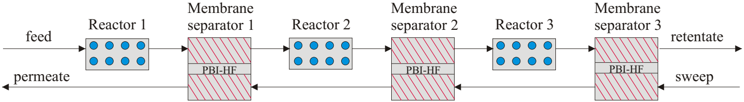
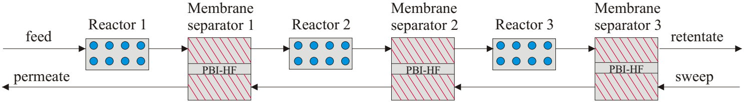


- Simulation conditions
  - total reaction/permeation zone length of 300 cm
  - $Q_{H_2} = 250$ GPU
  - $\alpha_{H_2/CO_2} = 75$
  - $v_t \approx v_s \approx 400\ \mathrm{cm}^3/\mathrm{min}$
  - sweep gas: steam

Benchmark: Multi-stage (3) Configuration



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  - sweep gas: steam

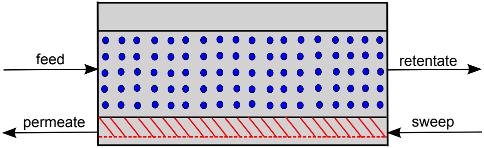
Parameter	Value [%]	Target [%]
X_{CO}	99.19	**98**
R_{H_2}	97.07	**95**
C_{CO_2}	90.28	**90**
$P_{CO_2+H_2O,r}$	95.64	**95**
$P_{H_2,p}$	47.59	**44**

- Simulation results

Stream	**Pressure [atm]**	**Compositions [%]**				
		CO	**H_2O**	**CO_2**	**H_2**	**N_2**
feed	47.63	24.43	48.86	5.68	19.33	1.70
retentate	47.63	0.23	54.07	41.57	1.67	2.46
sweep	25.86	0	100	0	0	0
permeate	25.86	0.06	49.02	3.22	47.59	0.11

MR Simulation Results: Counter-current Flows

- Simulation conditions
  - MR length of 300 cm
  - $Q_{H_2} = 250$ GPU
  - $\alpha_{H_2/CO_2} = 75$
  - $v_t \approx v_s \approx 400\ \text{cm}^3/\text{min}$
  - sweep gas: steam



- Simulation results

Stream	Pressure [atm]	Compositions [%]				
		CO	H_2O	CO_2	H_2	N_2
feed	47.63	24.43	48.86	5.68	19.33	1.70
retentate	47.63	0.05	54.10	41.51	1.89	2.44
sweep	25.86	0	100	0	0	0
permeate	25.86	0.15	51.19	2.93	45.62	0.11

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  - $Q_{H_2} = 250$ GPU
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  - sweep gas: steam

Parameter	**Value [%]**	**Target [%]**
X_{CO}	99.27	**98**
R_{H_2}	96.75	**95**
C_{CO_2}	90.49	**90**
$P_{CO_2+H_2O,r}$	95.61	**95**
$P_{H_2,p}$	45.62	**44**

- Simulation results

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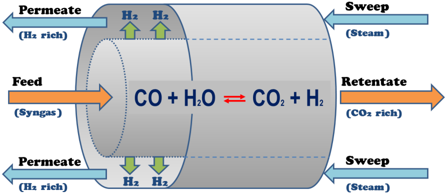
Counter-current Results: Changing Membrane Selectivity



Parameter	**Value** [%] ($\alpha_{H_2/CO_2} = 75$)	**Value** [%] ($\alpha_{H_2/CO_2} = 45$)	**Value** [%] ($\alpha_{H_2/CO_2} = 15$)	**Target [%]**
X_{CO}	99.27	99.32	99.44	**98**
R_{H_2}	96.75	97.60	99.41	**95**
C_{CO_2}	90.49	**84.58**	**56.13**	**90**
$P_{CO_2+H_2O,r}$	95.61	95.89	95.86	**95**
$P_{H_2,p}$	45.62	**43.88**	**37.07**	**44**
$y_{H_2,r}$	1.89	1.45	0.30	**($\leq$)4**

Membrane Reactor Optimization

- Constrained optimization problem
  - systematic determination of optimal membrane reactor design
  - cost parameters assigned
    - maximize performance (hydrogen recovery)
    - minimize cost (membrane area)

Parameter	**Price [$]**
PBI-HF membrane	500/m^2
H_2 fuel	1.78/kg

Nonlinear Programming: Mathematical Formulation

- Objective function

$$\Phi = \min_{x} \left[\text{cost}_m - \text{credit}_{H_2}\right]$$

$$\text{s.t.: target specifications and constraints}$$

in which

$$\text{cost}_m = A_m \times \$_m$$

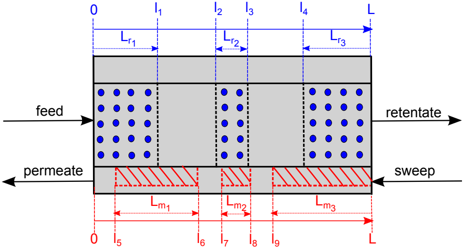
$$\text{credit}_{H_2} = F_{H_2,p} \times \text{HHV}_{H_2} \times \$_{H_2} \times Op$$

$$A_m = \pi d_t (\underbrace{l_6 - l_5}_{L_{m_1}} + \underbrace{l_8 - l_7}_{L_{m_2}} + \underbrace{L - l_9}_{L_{m_3}})$$

- Decision variables

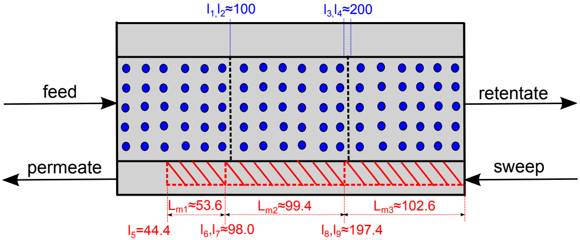
$$x = \left[l_1,\ l_2,\ l_3,\ l_4,\ l_5,\ l_6,\ l_7,\ l_8,\ l_9\right]'$$

- MR constraints
  - parameters $(X_{CO},\ R_{H_2},\ C_{CO_2})$
  - purities $(P_{CO_2+H_2O,r},\ y_{H_2,r},\ P_{H_2,p})$



Membrane Reactor Optimization: Results

- Benchmark for study: improve successful counter-current case
- Problem initial guess: stand-alone MR configuration
- Solution for 1 year operating cycle



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[13] Lima, Daoutidis, and Tsapatsis (2014)

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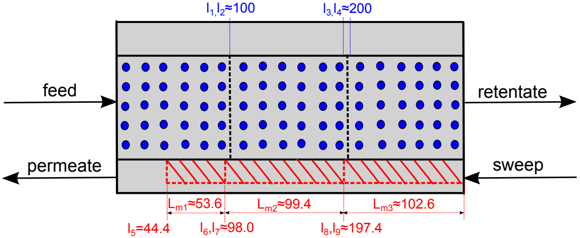

- Length of membrane layer: $L_{m_1} + L_{m_2} + L_{m_3} = 255.60$ cm
- Solution indicates
  - optimal design: short pre-shift reactor followed by long MR
  - potential savings in membrane material ($\approx 15\%$)
    - large-scale[13] ($A_m \approx 6800\ m^2$) $\Longrightarrow$ savings as high as \$ half million

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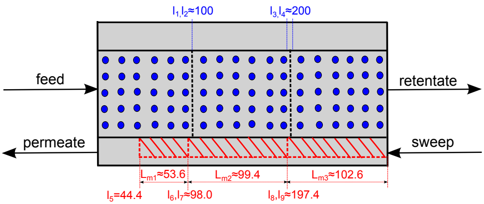
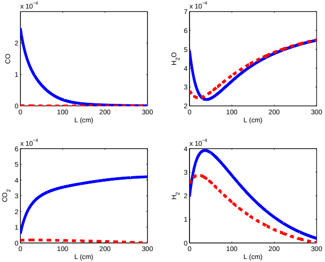
[13] Lima, Daoutidis, and Tsapatsis (2014)

Analysis of Optimization Results

Counter-current





Concentration profiles [mol/cm^3] vs. reactor length

- Optimal design not obvious from counter-current profiles in permeate
- Flexible optimization problem
  - could be adapted for other applications
    - autothermal coupling of methane steam reforming and methane catalytic combustion[14]
    - methane conversion processes
  - could be used for minimization of catalyst layer

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[14] Zanfir, Baldea, and Daoutidis (2011)

Conclusions and Future Directions

- Membrane reactor model developed for systems analysis
- Membrane reactor simulation studies performed
  - screen for successful cases that satisfy constraints (e.g., CO_2 capture)
  - help guiding membrane experimental research by determining $(\alpha_{H_2/\mathrm{all}}, Q_{H_2})$ pairs
- Constrained optimization problem formulated
  - systematic selection of optimal reactor design
  - more efficient membrane use by optimal placement
  - flexible for different applications
- Future/ongoing membrane reactor systems studies
  - detailed modeling of reaction and transport phenomena
  - process design optimization and operability
  - model predictive control and estimation
- Systems studies facilitate MR integration into emerging energy processes

Acknowledgments

- Collaborators:
  - Drs. Kathryn Berchtold and Rajinder Singh (LANL) - WGS-MR
  - Dr. Dongxia Liu (UMD) - DMA-MR
- WVU Students: Andrew Radcliffe and Juan Carlos Carrasco
- West Virginia University

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