Synthesis of Optimal PSA Cycles for Hydrogen/CO_2 Separation

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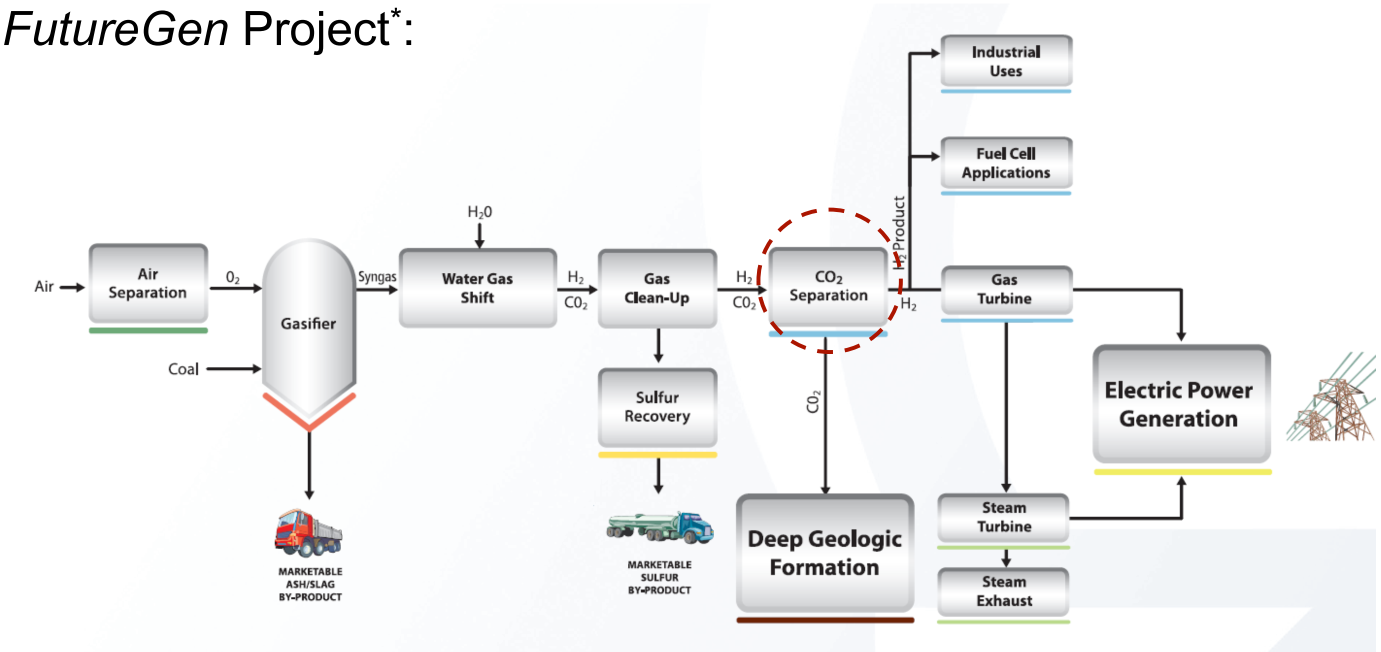
Introduction

DOE's *FutureGen* Project*:



- Shifted syngas composition: H_2 , CO_2 and small amounts of CO, CH_4, N_2 and Ar
- Conditions: ambient temperature (310 K) and high pressure (7 bar)
- Pre-combustion CO_2 capture technologies: absorption, membranes, adsorption etc.

Pressure Swing Adsorption

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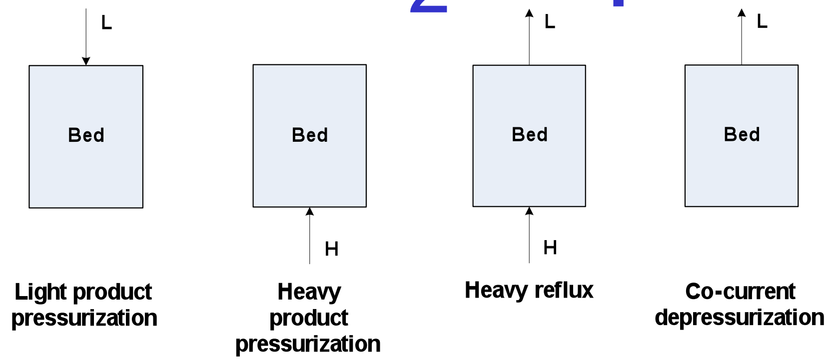
*http://www.futuregenalliance.org/publications.stm

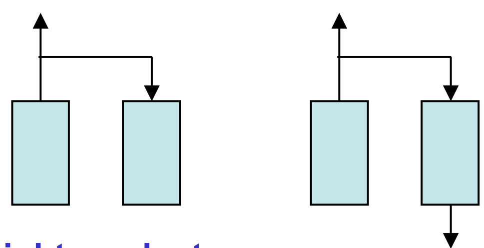
What PSA cycle for CO_2 capture?

What operating steps should be included in the cycle



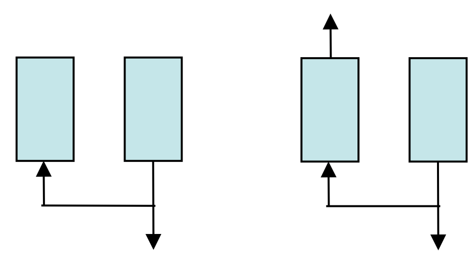
CO_2 is a heavy product
Commercial cycles focus on purifying light product

High purity light product



Light product pressurization **Light reflux**

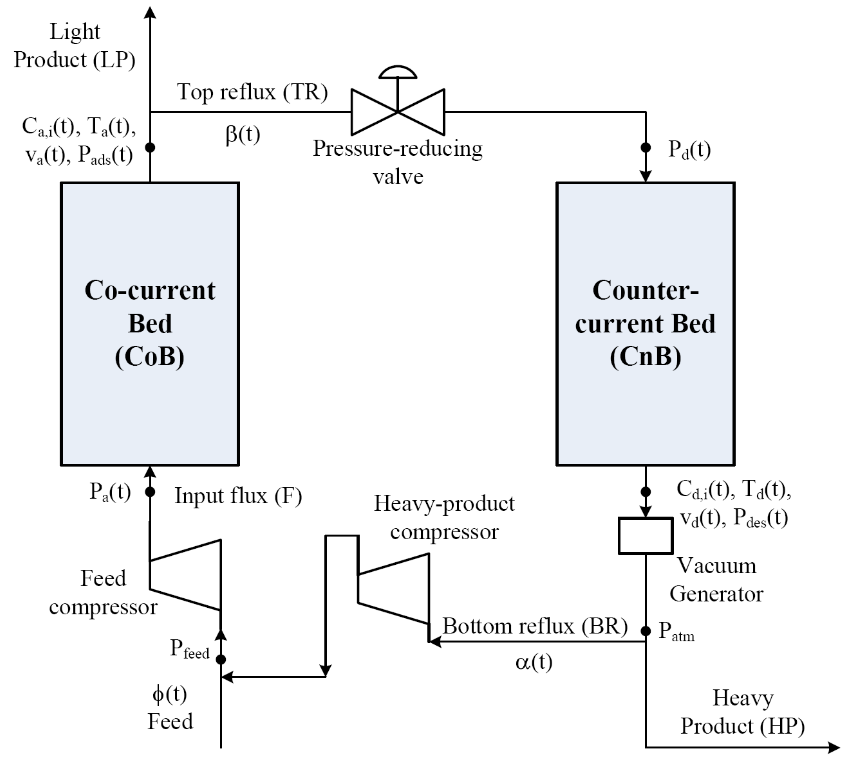
High purity heavy product



Heavy product pressurization **Heavy reflux**

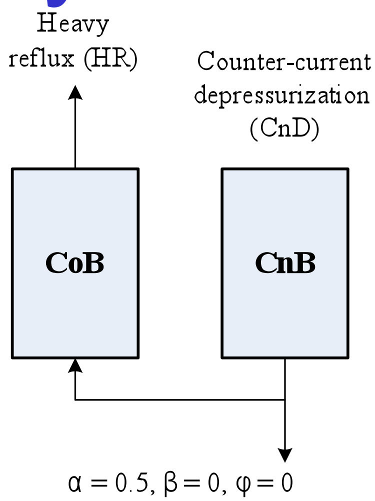
- Numerous PSA configurations suggested in the literature
- No systematic methodology available

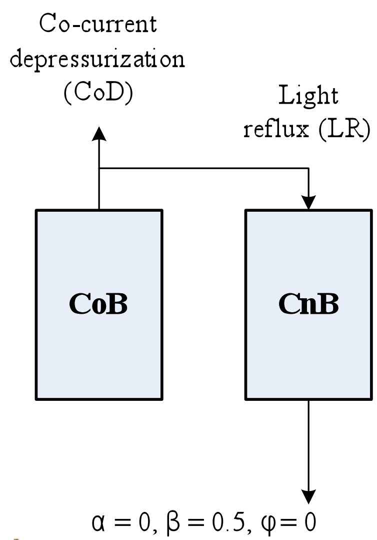
PSA Superstructure

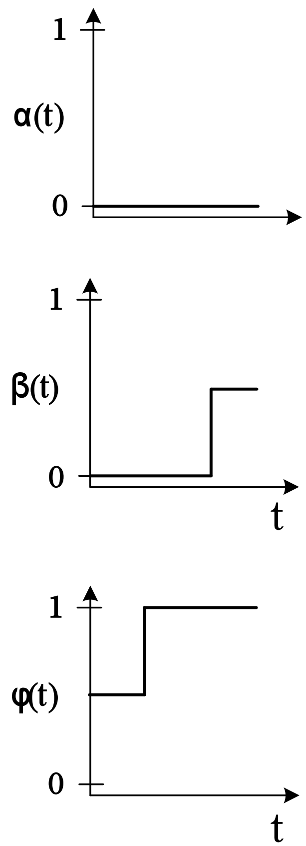


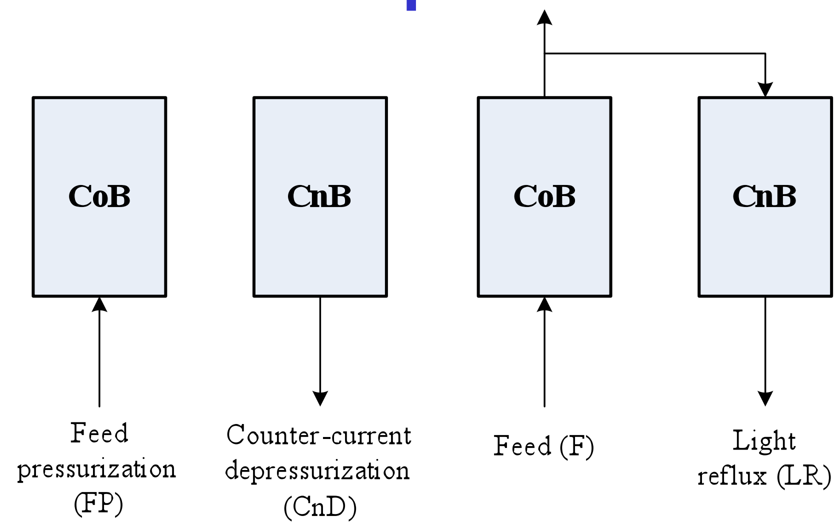
- Most PSA cycles in literature have only two cycles interacting at a given time
- Different operating steps realized by varying the control variables $\alpha(t)$, $\beta(t)$, $\Phi(t)$, $P_{ads}(t)$ and $P_{des}(t)$

Cyclic realization from superstructure









Optimal control problem

$$\min \quad \Omega(t_f)$$

$$s.t.$$

$$f\left(z, \frac{\partial z}{\partial t}, \frac{\partial z}{\partial x}\right) = 0$$

$$0 \le \alpha(t), \beta(t), \varphi(t) \le 1$$

$$g(z, \alpha, \beta, \varphi) \le 0$$

PSA Bed Model

PSA Model

Partial differential and algebraic equations (PDAEs)

Component mass balance

$$\epsilon_B \frac{\partial \rho_i}{\partial t} + \rho_s \frac{\partial n_i}{\partial t} + \frac{\partial(\rho_i \nu)}{\partial z} = 0 \qquad i = 1, 2, ..., N_c$$

Linear driving-force equation

$$\frac{\partial n_i}{\partial t} = \frac{k_i}{R_{PV} T}(P_i - P_i^*) \qquad i = 1, 2, ..., N_c$$

Energy balance

$$\left(\epsilon_B \sum_{i=1}^{N_c} \rho_i (c_p^i - R_E) + \rho_s c_s + \rho_s \sum_{i=1}^{N_c} n_i c_p^i\right) \frac{\partial T}{\partial t} - \rho_s \sum_{i=1}^{N_c} q_i \frac{\partial n_i}{\partial t} + \frac{\partial(\nu h)}{\partial z} = 0$$

Steady-state momentum balance (Ergun equation)

$$-\frac{\partial P}{\partial z} = 150 \frac{\mu \nu}{d_p^2} \frac{(1 - \epsilon_B)^2}{\epsilon_B^3} + 1.75 \frac{\rho M \nu^2}{d_p} \frac{1 - \epsilon_B}{\epsilon_B^3}$$

Dual-site Langmuir adsorption isotherm

$$n_i = m_1 \frac{b_i P_i^*}{1 + \sum_{i=1}^{N_c} b_j P_j^*} + m_2 \frac{b_i P_i^*}{1 + \sum_{i=1}^{N_c} b_j P_j^*} \qquad i = 1, 2, ..., N_c$$

Ideal gas law

$$\rho = \frac{P}{R_{PV} T}$$

Enthalpy

$$h = \sum_{i=1}^{N_c} \rho_i (aT + bT^2 + cT^3 + dT^4)$$

Molecular weight

$$M = \sum_{i=1}^{N_c} y_i M_{0,i} \quad \text{where} \quad y_i = \rho_i / \rho$$

Fluid viscosity

$$\mu = \sum_{i=1}^{N_c} \mu_i y_i \quad \text{where} \quad \mu_i = \mu_{0,i} + \mu_{1,i} T$$

Optimization Problem

Decision variables (p)
- step times
- flow rate, valve constants
- bed geometry

Objective function (ϕ)
- minimize power
- maximize product yield
- maximize overall profit

$$
\begin{aligned}
\min \quad & \Phi(z(x,t_f), y(x,t_f), \alpha(t_f), \beta(t_f), \phi(t_f), P_{ads}(t_f), P_{des}(t_f), z_0, p) \\
s.t. \quad & \boxed{f\left(\frac{\partial z}{\partial t}, \frac{\partial z}{\partial x}, z(x,t), y(x,t), \alpha(t), \beta(t), \phi(t), P_{ads}(t), P_{des}(t), z_0, p\right) = 0} \quad \textbf{PDAE model} \\
& \boxed{\begin{aligned} z_{CoB}(x,0) &= z_{CnB}(x,t_f) \\ z_{CnB}(x,0) &= z_{CoB}(x,t_f) \end{aligned}} \quad \textbf{CSS conditions} \\
& \boxed{\begin{aligned} & s(z(x,t), y(x,t), \alpha(t), \beta(t), \phi(t), P_{ads}(t), P_{des}(t), p) = 0 \\ & g(z(x,t), y(x,t), \alpha(t), \beta(t), \phi(t), P_{ads}(t), P_{des}(t), p) \le 0 \end{aligned}} \quad \textbf{Design specs} \\
& 0 \le (\alpha(t), \beta(t), \phi(t)) \le 1 \\
& b_L \le (P_{ads}(t), P_{des}(t), p) \le b_U
\end{aligned}
$$

Handling PDAEs: Simultaneous method

Sequential method

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Case Study: Simultaneous Approach

$$
\begin{array}{lll}
\min & \text{power} & \\
\text{s.t.} & c(z) = 0 & \\
& \text{CO}_2 \text{ purity} \geq 0.9 & \\
& \text{CO}_2 \text{ recovery} \geq 0.92 & \\
& Q_{feed,L} + Q_{feed,H} \geq 35 \text{ kgmol}\,\text{m}^{-2}\text{hr}^{-1} & \\
& P_{ads} \geq P_d & \\
& P_{des} \leq P_{feed} & \\
& P_a \geq P_{feed} & \\
& 0 \leq \alpha(\text{t}_i), \beta(\text{t}_i), \phi(\text{t}_i) \leq 1 & \forall \text{t}_i \\
& 10 \text{ sec} \leq T_c \leq 500 \text{ sec} & \\
& 101.32 \text{ kPa} \leq P_{ads}(\text{t}_i) \leq 1000 \text{ kPa} & \forall \text{t}_i \\
& P_{des}(\text{t}_i) \geq 50 \text{ kPa} & \forall \text{t}_i
\end{array}
$$

- Feed composition: 55% H_2 and 45% CO_2
- Activated carbon is used as the adsorbent
- No. of temporal finite elements: 10
- No. of spatial finite volumes: 10
- Large-scale nonlinear program: solved using AMPL/IPOPT

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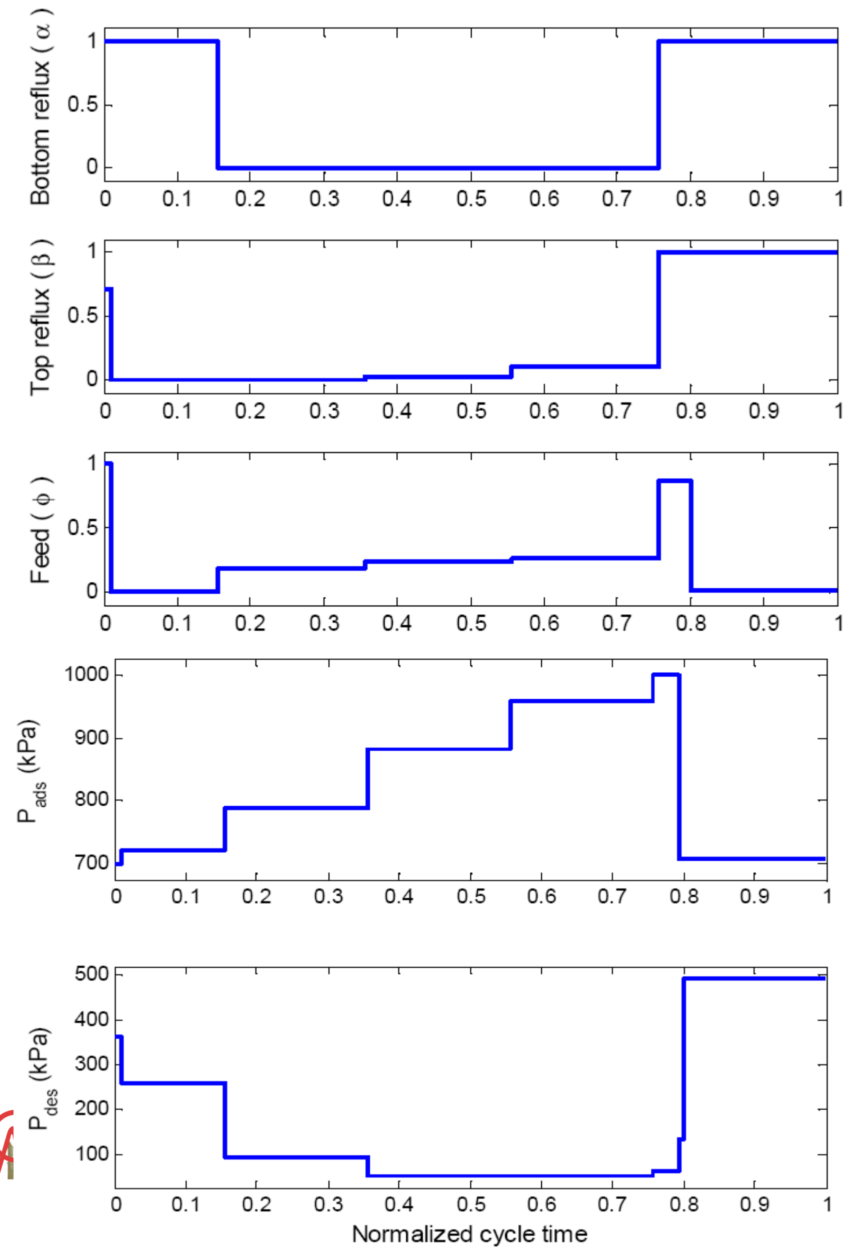
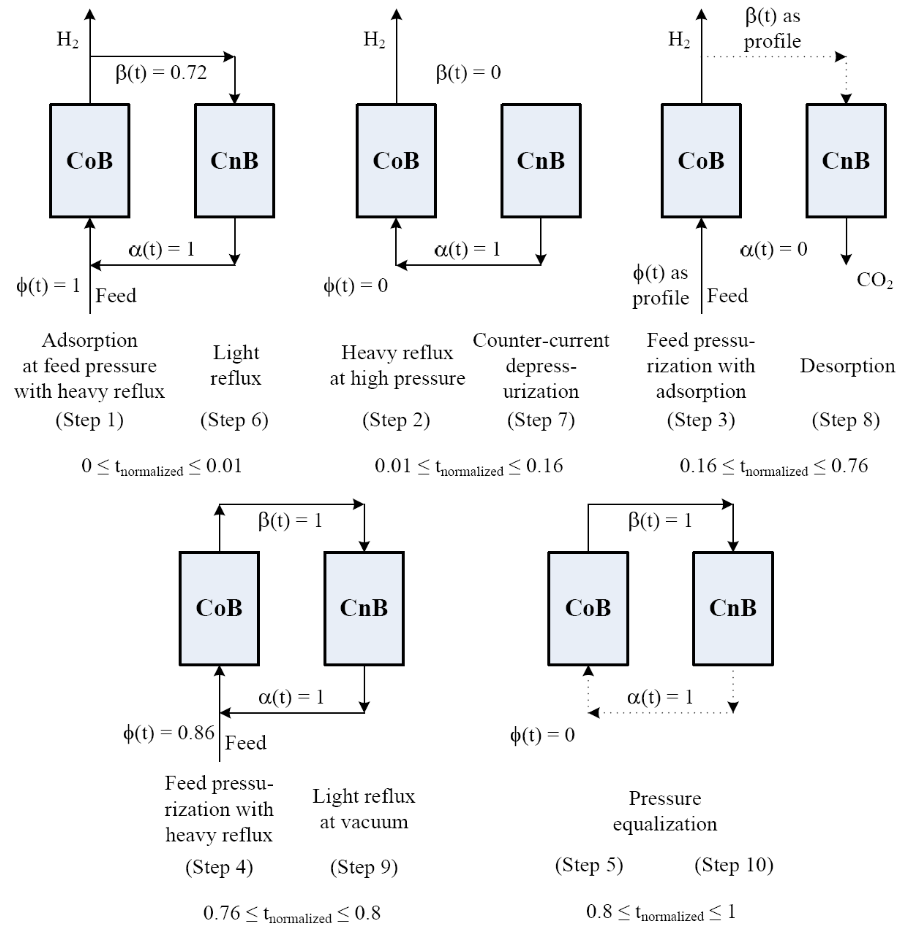
Case Study: Simultaneous Approach (contd..)



2-bed 10-step cycle



Case Study 2: Simultaneous Approach (contd..)

No. of variables: 10512

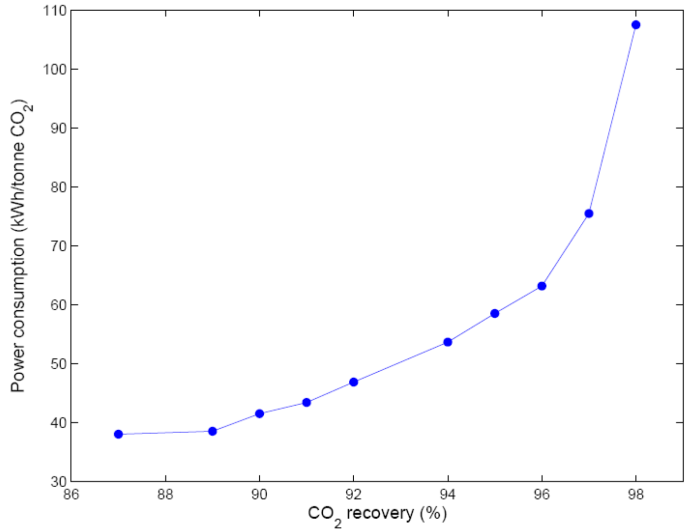
No. of constraints: 10434

Optimal cycle time: 424.74s

Feed flux: 96.61 kgmol/(m^2 h)

Power consumption: 46.82 kW h/tonne CO_2

CPU time ~ 1h



Spatial finite volumes	Full discretization	MATLAB simulation
H_2 purity	93.33%	94.92%
H_2 recovery	91.64%	91.05%
CO_2 purity	90%	89.42%
CO_2 recovery	92%	93.67%

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Summary

- PSA superstructure to determine optimal cycle configurations and design parameters for pre-combustion CO_2 capture is presented
- Formulated as an optimal control problem with binary feed mixture which is solved using a complete discretization approach
- Optimal PSA cycles obtained for pre-combustion CO_2 capture
- Framework can be used to evaluate different feedstocks and adsorbents

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Ongoing Work

Ongoing Work

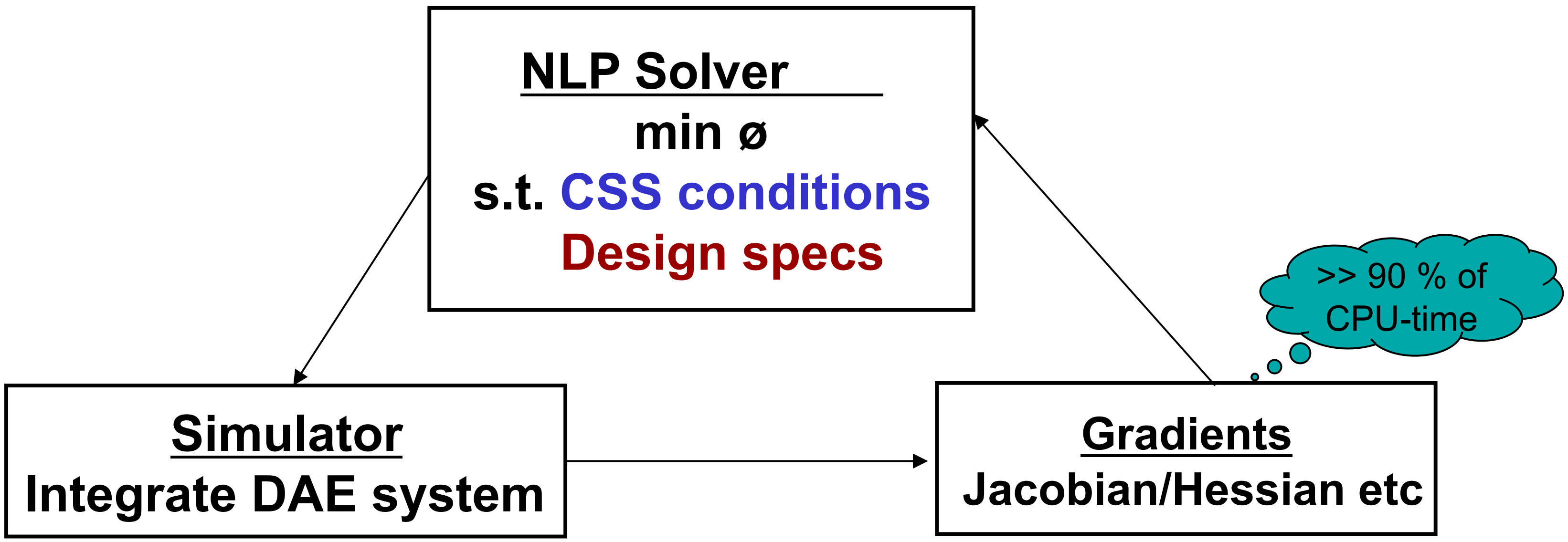
Limitations of Simultaneous Method:

- Discretization error caused due to fewer temporal and spatial nodes
- Problem size grows cubically with increase in number of spatial and temporal nodes
- Multi-component feed mixtures and multi-adsorbent layers becomes very hard to solve
- Higher CPU times

Sequential Method

Sequential Method

Discretize only in the spatial domain



- NLP problem is decoupled from the embedded dynamic system
- Use of error-controlled integrators like CVODES, DASPK etc.
- Smaller NLP sub-problem

Sequential Method

- Periodic Operation results in dense constraint Jacobian
- Dominant computational cost: forming and factorization of Jacobian
- Instead work with exact Jacobian-vector and Hessian-vector products
- Developed and implemented a novel NLP algorithm to work with exact matrix-vector products and inexact Jacobian
- Tested on small scale Simulated Moving Bed and PSA applications
- Obtained an order of magnitude reduction in CPU time compared to current methods
- Next step: Solve the PSA superstructure optimization problem using the sequential method

Thank you

Summary

- PSA superstructure to determine optimal cycle configurations and design parameters for pre-combustion CO_2 capture is presented
- Formulated as an optimal control problem with binary feed mixture which is solved using a complete discretization approach
- Min. power case study resulted in a 2-bed 10-step cycle
- Resulted in high purity and recoveries of H_2 and CO_2 with a significantly low power consumption of 46.82 kWh/tonne of CO_2

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Case Study: Simultaneous Approach

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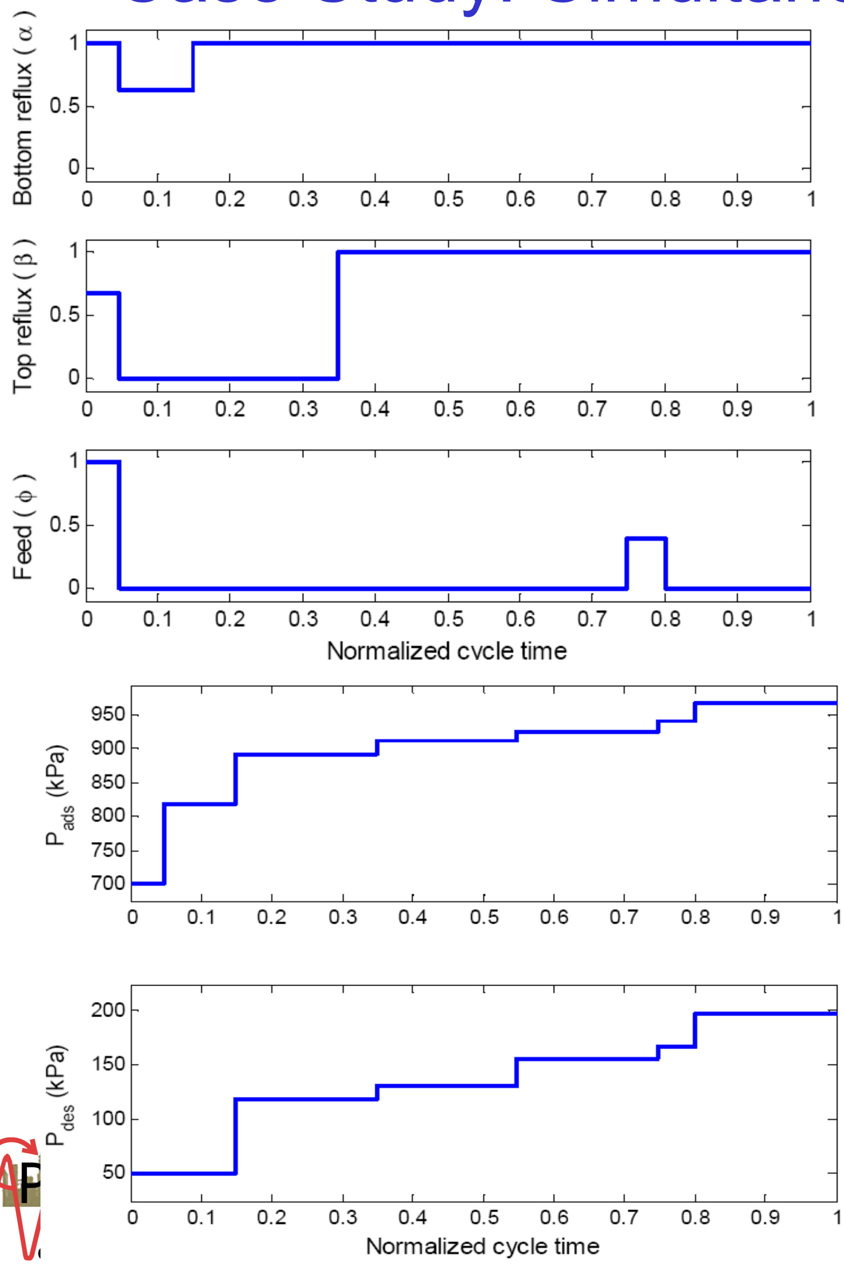
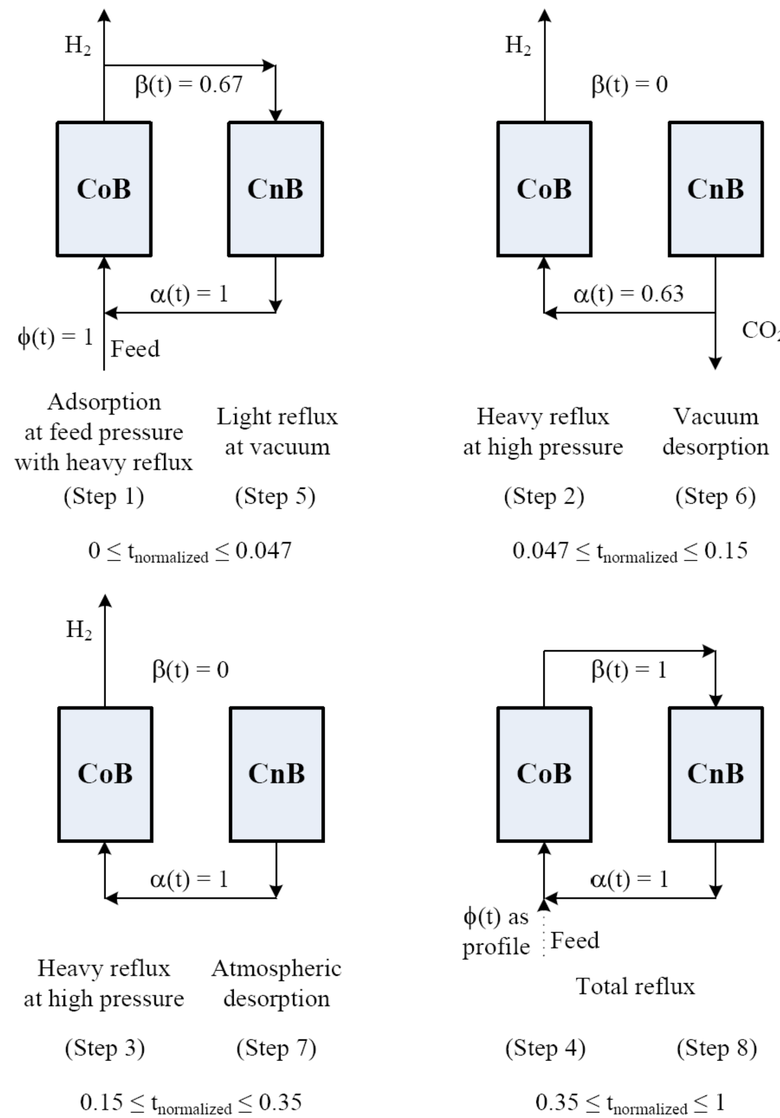
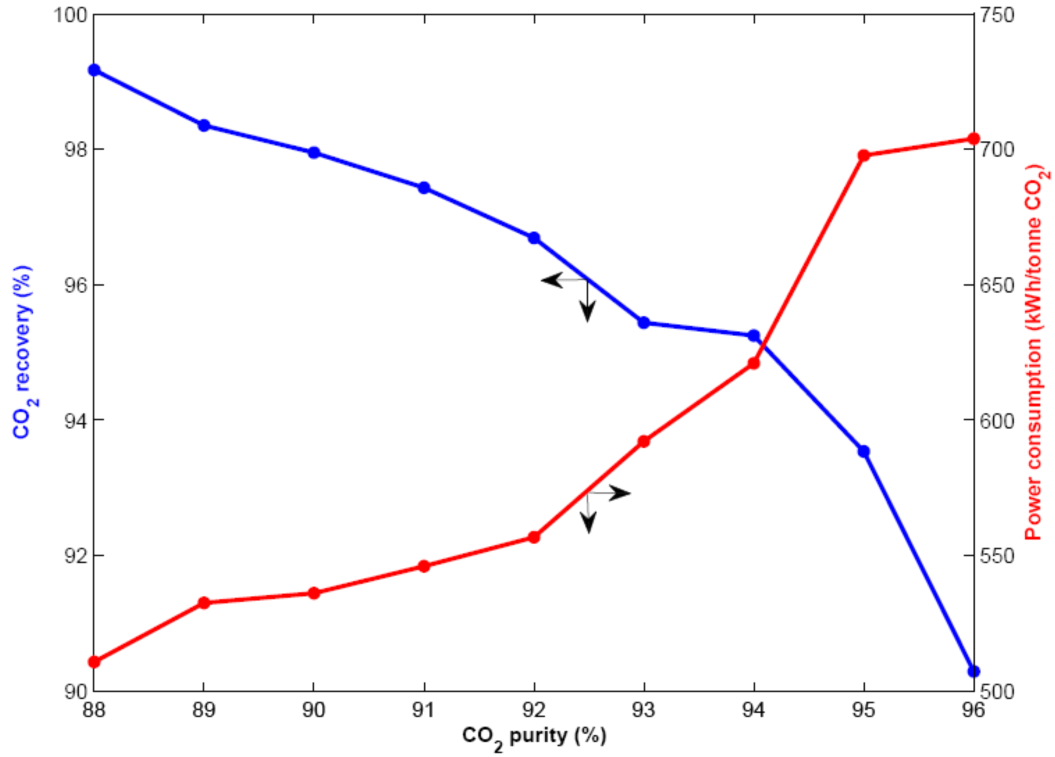


2-bed 8-step cycle



Case Study: Simultaneous Approach (contd..)



Case Study: Simultaneous Approach (contd..)

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No. of constraints: 10434

CPU time ~ 1h

Spatial finite volumes	Full discretization	MATLAB simulation
H_2 purity	98.20%	95.92%
H_2 recovery	91.09%	91.73%
CO_2 purity	90%	90.99%
CO_2 recovery	97.95%	96.03%