

Modeling and Optimization of a Two-Stage MOF-Based Pressure/Vacuum Swing Adsorption Process Coupled with Material Selection

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In this paper, we address the optimal design of a pressure/vacuum swing adsorption (PSA/VSA) process for post-combustion CO₂ capture. A mixed-integer partial differential equation constrained optimization model for a two-stage PSA/VSA cycle is developed in order to select the most effective adsorbent material to minimize the process cost of capturing the CO₂ from the flue gas. Consideration is given to the effect of water on the adsorbent material and the design of the upstream dehydration units. Zeolite 13X, zeolite 5A and ZIF-78 are all evaluated for use in the process. The results show that with a two-stage system using ZIF-78 as the adsorbent, a recovery of 90 % of the CO₂ and a purity of 80 % can be achieved at a cost of \$56.7 per ton of CO₂ captured and a 41.2 % energy penalty.

1. Introduction

Every year, large amounts of CO₂ are released into the atmosphere, contributing to the greenhouse effect and climate change (Anderson and Newell, 2004). With growing concern about global warming, technologies are being investigated that are able to reduce CO₂ emissions (Zhao et al., 2013). One method of dealing with emissions from large point sources such as power plants is carbon capture and sequestration (CCS) (Gong et al., 2014). One form of CCS is proposed for use directly after the combustion of the fuel, where the CO₂ would be separated directly from the flue gas, causing the least change to the original infrastructure. For post-combustion CCS, the processes most suitable are absorption (Rao et al., 2002), membranes (Ho et al., 2008), algae (Gebreslassie et al., 2013), and adsorption (Agarwal et al., 2010). Amine-based absorption with monoethanolamine (MEA) is the most commonly studied technology for CO₂ absorption. However, the high energy penalty of amine-based absorption limits its applicability for large scale CCS. Currently, other solvents and sorbents such as Li₄SiO₄ are being investigated as a replacement for amines to lower the regeneration energy (Puccini et al., 2013). Membrane technology has recently received attention as an alternative approach for CCS due to its relatively low operating cost (Barbieri et al., 2011). However, membrane systems require a higher CO₂ concentration to operate than other technologies and also require a large pressure difference across the membrane to operate effectively. Adsorption has also received much attention, as it has been shown to be the most advantageous in terms of economics and energy efficiency (Zhao et al., 2013).

In this work, we consider the optimal design and operations of a pressure/vacuum swing adsorption (PSA/VSA) process for CO₂ capture from flue gas. In a classical Skarstrom cycle for PSA/VSA, four steps are used. First, the column is pressurized by pumping the flue gas into the adsorption column (Yang, 1987). After pressurization, the flue gas continues to be pumped through the bed. During this step, the adsorbent favorably adsorbs the CO₂ over the N₂, enriching the CO₂ in the solid phase. The column is then depressurized, allowing the desorption of both components. Finally, N₂ product is fed back into the system to purge the enriched CO₂ stream out of the column. This process is shown in Figure 1.

Due to its simple configuration, the Skarstrom cycle is preferred for operation and control. However, this traditional configuration is unable to achieve high CO₂ purity and recovery (Agarwal et al., 2010). This is

due to the dilute concentration of CO_2 (10 %~15 %) in flue gas and the use of nitrogen as the purge gas. One method to overcome this limit is to use a multistage separation. Park et al. (2002) numerically analyzed a 2-stage PSA/VSA process to achieve over 99 % purity and recovery. Liu et al. (2011) simulated a 2-stage PSA process using zeolite 5A as the adsorbent and were able to achieve 96 % purity after the second stage.

In this work, we propose an integrated modeling and optimization framework for simultaneous material selection and PSA/VSA process optimization to identify the most effective material for carbon capture and separation from a coal-fired power plant. Although adsorption has many advantages, a possible drawback is that the performance of the sorbent material might be negatively affected by water, which is present in the post-combustion flue gas. The model is formulated as a mixed-integer partial differential equation (PDE)-constrained optimization problem, where integer variables model the decisions for material selection and water removal levels, and the partial differential equations describe the mass balance, energy balance and dynamic behavior of the PSA/VSA processes. A case study is presented to illustrate the application of the proposed modeling and optimization framework on a two-stage PSA/VSA system for CO_2 capture from flue gas.

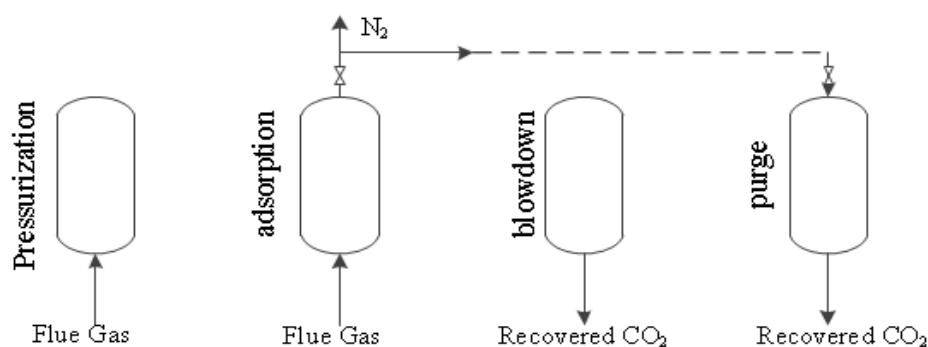


Figure 1: 4-step Skarstrom Cycle

2. Problem Statement

In our work, the objective is to minimize the total capital and operational cost of a two-stage PSA/VSA process and the dehydration unit. The feed flue gas has three components: CO_2 , N_2 , and H_2O . The flow rates are 100 mol/s, 900 mol/s and 55 mol/s, respectively. The flue gas is at 35 °C and a pressure of 1 bar. This corresponds to annual CO_2 emissions of 138,758 ton/year, which is equivalent to a 30 megawatt power plant.

In this work, nine decision variables are used to optimize the PSA/VSA process. Seven of the variables are continuous variables, namely the times for each step (pressurization, adsorption, blowdown and evacuation), the adsorption pressure, the evacuation pressure and the length of the adsorption column. The two binary variables are the decision variables for the adsorbent selection and the water concentration.

3. Model Formulation

The complete model is composed of two parts: the process model for the dehydration unit and the mathematical model for the PSA/VSA cycle. The dehydration unit is first designed and then integrated with the PSA/VSA model to minimize the cost.

3.1 Dehydration Unit

Two dehydration technologies are modeled and simulated: Triethylene glycol (TEG) absorption and cooling & condensation. In TEG absorption, the flue gas is brought into contact with TEG to remove the water. The water-rich solvent is then heated to regenerate the TEG, which is then cooled and recycled. In Cooling & Condensation, the flue gas is cooled and the water condenses. Although Cooling & Condensing is a cheap method of removing the water, it also removes some of the CO_2 . When the desired water level is very low (less than 0.5 %), more than 10 % of the CO_2 is removed, preventing recovery over 90%. In light of this, TEG absorption is selected for desired water levels of 0.1 % and 0.5 % and cooling & condensing is used for 1 % and 3 %.

3.2 PSA/VSA Cycle

The PSA/VSA model consists of five parts: 1) governing equations for the adsorption process, 2) boundary conditions and cyclic steady state criteria, 3) sorbent material selection, 4) bed connection equations, and 5) model equations to analyze the process performance. The flue gas feed is 10 % CO₂ and 90 % N₂. Although water is not treated as an adsorbate, its effect on CO₂ uptake is examined and influences the material selection.

The adsorption process is governed by a set of mixed integer nonlinear algebraic and partial differential equations. All state variables are scaled in order to aid numerical convergence. For the process, the mass balance constraint for CO₂ and total mass balance is:

$$\frac{\partial y_i}{\partial \tau} = \frac{1}{Pe} \left(\frac{\partial^2 y_i}{\partial z^2} + \frac{1}{P} \frac{\partial y_i}{\partial z} \frac{\partial \bar{P}}{\partial z} - \frac{1}{T} \frac{\partial y_i}{\partial z} \frac{\partial \bar{T}}{\partial z} \right) - u_z \frac{\partial y_i}{\partial z} + \frac{\psi \bar{T}}{P} \left((y_i - 1) \frac{\partial x_i}{\partial \tau} + y_i \frac{\partial x_{N_2}}{\partial \tau} \right); i = CO_2 \quad (1)$$

$$\frac{\partial \bar{P}}{\partial \tau} = \left(-\bar{P} \frac{\partial \bar{u}_z}{\partial z} - u_z \frac{\partial \bar{P}}{\partial z} + u_z \frac{\bar{P}}{T} \frac{\partial \bar{T}}{\partial z} \right) - \psi \bar{T} \sum_i \frac{\partial^2 \Omega}{\partial \tau} + \frac{\bar{P}}{T} \frac{\partial \bar{T}}{\partial \tau} \quad (2)$$

The energy balance is divided into two parts: the wall energy balance and the energy balance inside the column. The wall energy balance is calculated by:

$$\frac{\partial \bar{T}_w}{\partial \tau} = \pi_1 \frac{\partial^2 \bar{T}_w}{\partial z^2} + \pi_2 (\bar{T} - \bar{T}_w) - \pi_3 (\bar{T}_w - \bar{T}_a) \quad (3)$$

The column temperature is calculated by the following equation:

$$\frac{\partial \bar{T}}{\partial \tau} = \pi_4 \frac{\partial^2 \bar{T}}{\partial z} - \pi_5 u_z \frac{\partial \bar{T}}{\partial z} + \sum_{i=1}^N (\pi_{6i} + \pi_7 \bar{T}) \frac{\partial x_i}{\partial \tau} - \pi_8 (\bar{T} - \bar{T}_w) \quad (4)$$

The velocity in the column is calculated using the Ergun equation and information on the pressure gradient in the bed:

$$-\frac{\partial \bar{P}}{\partial z} = \frac{150 \mu (1 - \varepsilon_b)^2}{4 r_p^2 \varepsilon_b} u_z + \frac{1.75}{2 r_p} \left(\frac{1 - \varepsilon_b}{\varepsilon_b^3} \right) \rho \bar{u}_z |\bar{u}_z| \quad (5)$$

The adsorption rate is estimated using the linear driving force approximation:

$$\frac{\partial x_i}{\partial \tau} = \left(\frac{c_i}{q_i^*} \frac{15 \varepsilon_p D_p}{r_p^2} \right) \frac{L}{v_0} (x_i^* - x_i) \quad (6)$$

For the PSA/VSA cycle, the different steps are characterized by their different boundary conditions at the ends of the column. In the boundary condition, exponential equations are used to represent the pressure at the entrance of the bed. This is done in order to avoid sharp pressure gradients at the beginning of the steps.

Finally, the PSA/VSA cycle has to operate at a cyclic steady state. This occurs when the spatial profile of the bed at the end of the Purge step is the same as the profile of the bed at the beginning of the Pressurization step.

3.3 Material Selection

The material selection equations are:

$$\frac{\partial x_i}{\partial \tau} = \sum_{j=\text{materials}} sel_j \times \left(\frac{\partial x_i}{\partial \tau} \right); i \in \{CO_2, N_2\} \quad (7)$$

$$\sum_{j=\text{materials}} sel_j = 1;$$

In these equations, sel_j are the binary decision variables that decide whether or not to choose material j for the process. In order to ensure that only one material is chosen for the process, the summation over all the binary variables is equal to 1.

To complete the material selection model, the isotherms of each material are needed. The three candidates for the adsorbent material are zeolite 13X, zeolite 5A, and ZIF-78. For zeolites 13X and 5A, a competitive Langmuir isotherm is used to describe the adsorption equilibrium:

$$x_{i,j}^* = A_{i,j} \frac{B_{i,j} y_i}{1 + \sum_i B_{i,j} y_i} \quad (8)$$

where

$$B_{i,j} = b_{i,j}^0 P \exp \left[-\frac{\Delta H_{i,j}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (9)$$

For ZIF-78, a Langmuir isotherm is used to describe the CO₂ adsorption, and Henry's law is used to describe N₂ adsorption:

$$x_{CO_2,3}^* = A_{CO_2,3} \frac{B_{CO_2,3} y_{CO_2}}{1 + B_{CO_2,3} y_{CO_2}} \quad (10)$$

$$x_{N_2,3}^* = A_{N_2,3} y_{N_2} \quad (11)$$

$$B_{CO_2,3} = b_{CO_2,3}^0 P \exp \left[-\frac{\Delta U_{CO_2,3}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (12)$$

The presence of water in the flue gas generally has a negative impact on the sorbent performance. In order to account for this, a relationship is assumed between the water mole fraction and the decrease of equilibrium CO₂ uptake on the adsorbent. We assume a 10 % decrease in CO₂ uptake for every 1 % mole fraction of water in the flue gas.

3.4 Bed Connection Equations

The feed for the second stage is the enriched CO₂ product stream from the first stage, which is modeled by:

$$\text{Feed}_{stage2} = \frac{\text{Feed}_{stage1} \cdot y_{feed,stage1} \cdot \text{Recovery}_{stage1}}{\text{Purity}_{stage1}} \quad (13)$$

$$y_{feed,stage2} = \text{Purity}_{stage1}$$

All other model equations for the second stage are the same as the first stage.

3.5 Process Performance Analysis

The recovery and purity of CO₂ are calculated using the following equations:

$$\text{Recovery} = \frac{\text{moles}_{CO_2,out}}{\text{moles}_{CO_2,in}} \quad (14)$$

$$\text{Purity} = \frac{\text{moles}_{CO_2,out}}{\text{moles}_{CO_2,out} + \text{moles}_{N_2,out(bldwn/evac)}} \quad (15)$$

where

$$\text{moles}_{CO_2,out} = \frac{P_h u_0}{RT_0} \varepsilon_b A \left[\int_0^{t_{bldwn}} \left(-u_z \frac{y_{CO_2} \bar{P}}{T} \right) d\tau + \int_0^{t_{evac}} \left(-u_z \frac{y_{CO_2} \bar{P}}{T} \right) d\tau \right] \quad (16)$$

$$\text{moles}_{CO_2,in} = \frac{P_h u_0}{RT_0} \varepsilon_b A \left[\int_0^{t_{pres}} \left(-u_z \frac{y_{CO_2} \bar{P}}{T} \right) d\tau + \int_0^{t_{adsorp}} \left(-u_z \frac{y_{CO_2} \bar{P}}{T} \right) d\tau \right] \quad (17)$$

$$\text{moles}_{N_2,out(bldwn/evac)} = \frac{P_h u_0}{RT_0} \varepsilon_b A \left[\int_0^{t_{bldwn}} \left(-u_z \frac{y_{N_2} \bar{P}}{T} \right) d\tau + \int_0^{t_{evac}} \left(-u_z \frac{y_{N_2} \bar{P}}{T} \right) d\tau \right] \quad (18)$$

The objective is to minimize the total cost of the process, which is the sum of the annualized investment cost (AIC) and the annual operating costs (AOC). The AIC is estimated from the equipment purchase cost, and the AOC is calculated from the utilities required for the operation of the process.

3.6 Solution Strategy

In order to optimize the dynamic system, the partial differential equations are fully discretized. A finite volume method is used for the spatial discretization where the column is divided into 10 separate volumes (Agarwal et al., 2010). A Radau collocation method is used for the temporal discretization (Biegler et al., 2002). In this method, the time domain is divided into equal finite elements. Three collocation points in the element are selected and sampled. A continuous function is then approximated using the sample points. The MINLP problem is solved using GAMS with CONOPT as the nonlinear programming solver and SBB as the MINLP solver on a PC with Intel® Core™ i5-2400 CPU @3.10 GHz and 8.00 GB Ram.

4. Results

In order to determine the optimal conditions and material for the lowest cost for CCS, cost analysis is performed. The overall cost of the process was minimized with the purity constrained to be greater than 80 % and recovery greater than 90 %. In addition, the adsorbent materials were also considered. The problem had 160,605 variables and 161,266 equations.

With ZIF-78 determined to be the optimal adsorbent material, the optimal adsorption pressure is 213.8 kPa for the first stage and 145.0 kPa for the second stage. The optimal desorption pressure was determined to be 40.4 kPa for the first stage and 18.5 kPa for the second stage. When comparing the operating parameters of the two stages, it is seen that the required compression for the first stage is higher than the second stage. However, required vacuum for the second stage is higher than the first stage.

Table 1: Optimal conditions of the first stage for minimum cost

	ZIF-78	Zeolite 13X	Zeolite 5A
t_{pres} (s)	112.7	100	100
t_{ads} (s)	2,000	1,389.4	1,582.6
t_{bldwn} (s)	200	200	200
t_{pur} (s)	200	200	200
L (m)	9.01	10	10
P_H (Pa)	2.14×10^5	2.14×10^5	1.45×10^5
P_L (Pa)	40,400	27,400	11,700

Table 2: Optimal conditions of the second stage for minimum cost

	ZIF-78	Zeolite 13X	Zeolite 5A
t_{pres} (s)	451.2	384.6	428.2
t_{ads} (s)	1,925.1	1,315.1	1,896.9
t_{bldwn} (s)	200	343.9	200
t_{pur} (s)	546.9	566	1,121
L (m)	5.94	6.36	6.95
P_H (Pa)	1.45×10^5	1.57×10^5	1.45×10^5
P_L (Pa)	18,500	13,000	11,700

Table 3: Cost decomposition for ZIF-78

	Cost (\$ millions)	Percentage of Total
AIC compressor	1.12	17.4
AOC compressor	2.30	5.0
AIC vacuum	0.32	36
AOC vacuum	1.47	22.9
AIC everything else	1.20	18.7
Total	6.42	100

Table 4: Comparison of cost with and without water

	Without Water	With Water
PSA/VSA Cost (\$ million/ year)	6.42	6.75
Dehydration Cost (\$ million/year)	-	0.33
Total (\$ million/year)	6.42	7.08

The optimal operating conditions for this material are shown in Tables 1 and 2. At the optimal solution, the first stage cost \$4.81 million and the second stage cost \$1.61 million. The difference in cost can be explained by the difference in the quantity of flue gas the stages must handle. Since the first stage removes much of the nitrogen from the flue gas, the second stage can be much smaller, resulting in a lower cost. A decomposition of the costs for ZIF-78 is shown in Table 3. After calculating the cost of the other two materials, it can be seen that choosing ZIF-78 results in savings of almost \$1 million. The optimal values and the costs with zeolite 5A and zeolite 13X are also shown in Table 1.

After the optimal adsorbent material was determined, dehydration costs were taken account. The material was fixed to ZIF-78, and the model was run accounting for the effect of water on the process performance. When considering water, the optimal water level was determined to be 3.0 % for ZIF-78 with Cooling & Condensing technology. The change in cost between the two cases considering and not considering water can be seen in Table 4. Since the total annual cost of the ZIF-78 process with water was still lower than the other materials optimal cases, no further material selection was performed.

5. Conclusion

In this paper, we proposed a mixed-integer PDE-constrained optimization model for a two-stage PSA/VSA system with adsorbent material selection and a dehydration unit for post-combustion CO₂ capture from flue gas. After full discretization of the PDEs, the model is reformulated as an MINLP.

Optimization results revealed that when the purity and recovery were constrained to 80 % and 90 %, respectively, the minimal cost of the system resulted in a cost of \$56.7/ton of CO₂ separated. This corresponded to an energy consumption of 454 kWh/ton or a 41.2 % energy penalty. The optimal water level for the flue gas entering the adsorption system was 3 %, with cooling & condensation as the dehydration technology.

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