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Optimizing Solid Sorbents for CO₂ Capture

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Abstract

One significant hurdle to the deployment of post-combustion carbon capture and storage (CCS) is the energy consumption of separating high purity carbon dioxide from a flue gas stream. In order to minimize this energy consumption, it is necessary to optimize both the process used to separate the CO₂ and the material used in the process. We will present methodology and results for concurrent optimization of both the material and the process for temperature and pressure swing adsorption using solid sorbents. By focusing on the energy penalty we will provide a tool for screening and ranking solid sorbents as well as a means for performing parametric analysis to determine the optimal material properties that would minimize the energy penalty of CCS in an idealized system. These tools are also useful for determining thermodynamically and energetically favourable processes for the materials discovered. We discuss the regimes of favourable operation and necessary advances from both a material and process standpoint to provide goals for process and material developers.

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1. Introduction

To reduce the emissions of carbon dioxide to the atmosphere, it is necessary to limit the CO₂ intensity of power generation. One way to accomplish this is by limiting emissions from fossil-fuel fired power plants through carbon capture and storage (CCS). Currently, CCS is not broadly deployed on a large scale because there are not sufficient economic incentives or regulatory drivers to implement it economically. Available CCS technologies are costly both to build and to operate, and one of the main driving factors in

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this price is the energy required for capture [1]. We will examine ways to minimize the energy penalty of CCS by identifying energetically optimal solid sorbent materials and associated optimal processes.

Currently available capture technologies for post combustion capture tend to be aqueous solvent systems that use an absorber column to capture CO₂ from power plant flue gas. The rich solvent is then transported to a regenerator column that uses steam to strip the CO₂ from the solvent at high purity. The CO₂ is then compressed so that it can be transported for storage or utilization. In this system, much of the energy is consumed in the reboiler of the regenerator to provide the stripping steam. Because the solvent is aqueous, raising the temperature in the regenerator column requires boiling a significant amount of water and the associated energy penalty of providing that heat of vaporization. Solid sorbent capture processes eliminate the requirement to provide this heat of vaporization and provide a very wide range of material properties and structure morphologies that can be fine tuned to create optimal materials.

In a typical adsorption separation process for CO₂ capture from a fossil-fired power plant, the CO₂ rich flue gas is contacted with a lean adsorbent at low temperature and CO₂ is preferentially adsorbed onto the material. Once the sorbent is saturated, it is then regenerated by heating the sorbent (temperature swing adsorption; TSA) or lowering the partial pressure of CO₂ (pressure swing adsorption; PSA), or some combination of the two, which causes CO₂ to desorb from the material at high purity. This high purity CO₂ can then be compressed for storage or utilization. The material properties including the adsorption isotherms and densities will determine the working capacity of the sorbent and how much product CO₂ can be produced for given regeneration conditions. The quality and quantity of separation achieved is dependent on the material properties and the driving force provided by the change in temperature or pressure, both of which have an associated energetic cost or energy penalty on the power plant.

For temperature swing, this energy penalty is the cost of providing the heat to regenerate the sorbent. In a power plant setting, this heat would likely be supplied by extracting steam from the low pressure turbine of the main steam cycle. At the temperatures of regeneration in question, typically 60°C – 200°C, much of the energy has already been extracted from the steam and the loss in electrical output from the power plant due to extracting that steam from the low pressure turbine is significantly lower than the thermal requirement on an equivalent Joule basis. For pressure swing, the energy penalty is the extra energy requirement for compressing the product CO₂ from the regeneration pressure. This compressor work cannot be discounted in the same way as the thermal load because compressor work imposes an electrical load on the power plant.

For any real system, both thermal and compression will be required: thermal energy will be required in PSA processes to overcome the endothermic regeneration of the sorbent and compression will be required in a TSA process to efficiently pressurize CO₂ to pipeline pressures of ~150 bar. As such, we know that the amount of CO₂ produced and the energy penalty of any given process will depend not just on the material properties of the sorbent used for separation, but also on the pressure and temperature of regeneration. Further, the optimal regeneration conditions will vary depending on the material properties of the sorbent.

Current screening and sorbent development efforts do not take this variable process into consideration when evaluating sorbents. Typical sorbent screening processes tend to aim to maximize specific material properties such as total capacity, thermal stability, heat of adsorption, or CO₂ uptake at adsorption conditions [2]. However, by focusing on individual properties, these screening methods do not minimize the energy penalty and may not identify materials that have favorable energetics. On the other end of the

spectrum, technology developers typically create an optimal process around a single sorbent material that has been identified through screening efforts. In this case, we cannot directly compare the results of two materials until they have been fully characterized and integrated into optimal processes.

We have developed a model that will allow the direct comparison of different sorbents in idealized, optimal processes to determine energetically optimal materials. To do this, we evaluate the energy penalty of each material in a process that is tailored for that material. Further, we perform parametric tests on the materials to determine what optimal material properties are within a class of sorbents.

2. Model Description

The purpose of the developed solid sorbent screening model is to create a metric with which to calculate and compare the performance of different sorbents. This model is then used to identify optimal materials and material properties as well as the associated processes that minimize the energy penalty of CCS. For a model to be successful as a screening tool, it has to provide a rapid method of determining the performance of a tested material. For the application of screening many diverse materials for CCS, the performance metric we chose is the total energy, which combines the thermal and compression energy on an equivalent basis, required for CCS using the material in a process optimized for that material.

2.1. Equilibrium Model

In order to compare materials in their optimal processes, we need to either design a process configuration in which to optimize or optimize over all process configurations to become process agnostic. The process configuration determines the gas-sorbent interaction in the adsorption and regeneration steps. The mode of contacting during adsorption and regeneration has several different possible configurations including fixed bed, moving bed, fluidized bed, staged fluidized bed, simulated moving bed, and many others. The contacting method helps determine the residence time, flow configuration, extent of the adsorption and regeneration of the sorbent, batch vs. continuous operation, size of system, attrition rate, and possible operating conditions. However, performing an optimization over all such configurations for a large batch of materials is effectively impossible without the kinetic data needed. Even with kinetic data, each material would have to have an optimized process determined for each contacting configuration. Instead, we optimize over all process configurations by performing an equilibrium study of the materials that disregards contacting configuration and kinetics.

Because all configurations rely on cycling the sorbent materials between a loaded state at the adsorption conditions and an unloaded state at the regenerated condition, we evaluate the system at only two conditions: adsorption and regeneration conditions over a wide range of temperatures and pressures. How we move between these two conditions is unimportant, because the thermal and compressor energy required to regenerate the sorbent and compress the product stream from the regeneration pressure to the pipeline pressure is independent of the process path.

The key insight here is that under the equilibrium model case, only the properties of the sorbent along with the adsorption and regeneration conditions are necessary to calculate the energy required and the amount and purity of CO₂ produced. We calculate the amount of CO₂ produced per cycle per mass of sorbent by comparing the CO₂ and N₂ loading, including gas in the interstitial space, at the adsorption and regeneration conditions. The difference in loading is the amount of CO₂ produced and the ratio of CO₂ to

N₂ produced is the purity of product. We can also calculate the thermal and compression loads based on just the material properties and the regeneration conditions. Note that we consider the gas separation process to be a binary mixture of CO₂ and N₂ and do not include H₂O, O₂, or other flue gas components. This is primarily because we do not have good data for water uptake on most materials. We recognize this as a shortcoming of the model and are working to incorporate moisture data when it becomes available.

With this two-point model in place, we can determine the performance of a sorbent through the CO₂ product, purity, and energy usage for a given temperature and pressure of regeneration. In order to optimize the regeneration conditions for a given sorbent, we can simply perform the same calculations over the range of possible temperatures and pressures of regeneration, and find the conditions that minimize the energy penalty of CCS. This provides a fast, inexpensive computational tool for determining the optimal process conditions for a given sorbent and calculating the performance metrics at that optimal condition.

2.1.1. Thermal load

The thermal load of this process is the thermal energy required to bring the sorbent from the adsorption condition to the regeneration condition. This includes two terms, the heat required to heat the bed up to the regeneration temperature and the heat required to overcome the heat of adsorption as the CO₂ and N₂ are desorbed from the sorbent. This can be expressed and normalized per kg of CO₂ produced as:

$$Q = \frac{(C_p \Delta T + \Delta h_{CO_2} \Delta q_{CO_2} + \Delta h_{N_2} \Delta q_{N_2})}{CO_{2\text{Produced}}} \quad (1)$$

Where Q is the specific thermal load normalized to the amount of CO₂ produced, C_p is the specific heat of the sorbent, ΔT the change in temperature between the regeneration and adsorption conditions, Δh the heat of adsorption, Δq the change in adsorbed loading on the sorbent, and CO₂ produced is the total amount of output CO₂ per cycle.

2.1.2. Compression work

The work required to compress the CO₂ rich product stream to pipeline pressure of 150 bar is modeled as a multi-stage compressor intercooled to 40°C with a maximum pressure ratio of 2.5 between each stage. In order to accurately account for the fluid property changes due to the purity of product and to capture the behavior of compression around the critical point, we use the real fluid properties from NIST REFPROP [3] which implements the GERG 2004 equation of state [4] for fluid mixtures of many species including CO₂, N₂, H₂O, and O₂. For this model, we assume an isentropic efficiency of 85% up to the critical pressure and 90% above that point once the CO₂ mixture has become a dense-phase supercritical fluid.

Because we developed this as a tool for screening hundreds of thousands of materials, the queries to REFPROP to calculate the compressor work for each material for each combination of temperature and pressure of regeneration were determining the speed of the calculation. In order to expedite the calculations and make the compression model a standalone unit that did not require additional software, we created a closed analytic function that captures the compressor work required for a range of CO₂ purities and desorption pressures (Figure 1).

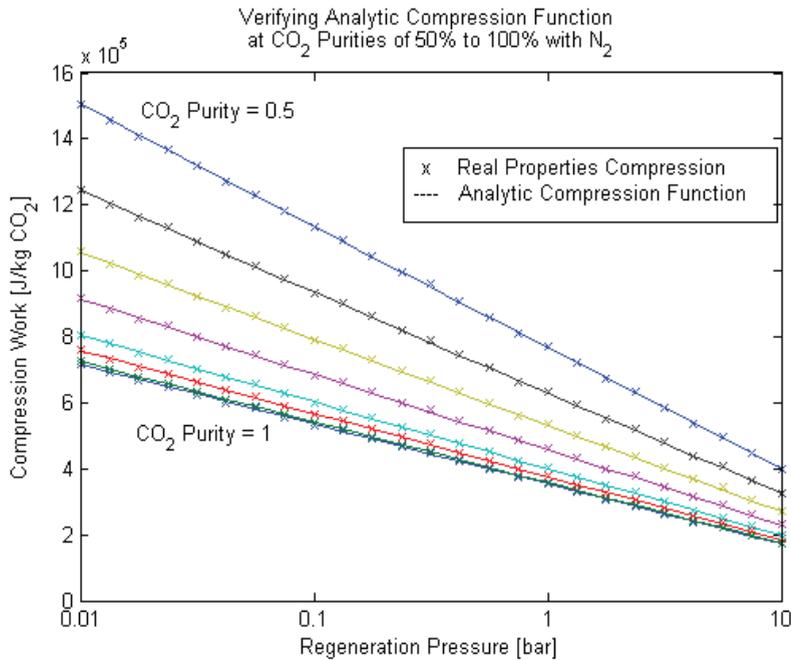


Figure 1: Calculated compressor work required (x's) and analytic fit (solid lines). Agreement is within 2.5% for the entirety of the range 50%-100% CO₂, 0.01-10 bar, and below 1% error for 90+% CO₂.

2.2. Equivalent Energy

In order to determine the total imposed parasitic load on the power plant, we combine the thermal and compression energy requirements. The thermal load is supplied by extracting steam from the steam cycle at the needed temperature and pressure, while the compressor load is the electrical requirement, and these impose a parasitic load on the power plant in different ways. To account for the different effects of thermal and compression energy on the plant output, we calculate a parasitic energy, or separation energy requirement as [5,6]:

$$E_p = (0.75Q \cdot \eta_{carnot} + W_{comp}) \quad (2)$$

Where E_p is the parasitic energy, Q is the thermal load, η_{carnot} is the Carnot efficiency at the steam extraction temperature and W_{comp} is the compressor work required. Applying this parasitic energy calculation to a material over the range of possible regeneration temperatures and pressures yields the results in Figure 2. From these results, we can determine the optimal temperature and pressure of regeneration as well as quantify the electrical energy penalty seen by the plant to implement CCS with this material. Using the parasitic energy calculation, a baseline value for MEA from the U.S. Department of Energy bituminous baseline report [7] is calculated to be 1060 kJ/kg CO₂. Materials and processes well below this number indicate the potential for significant energy savings.

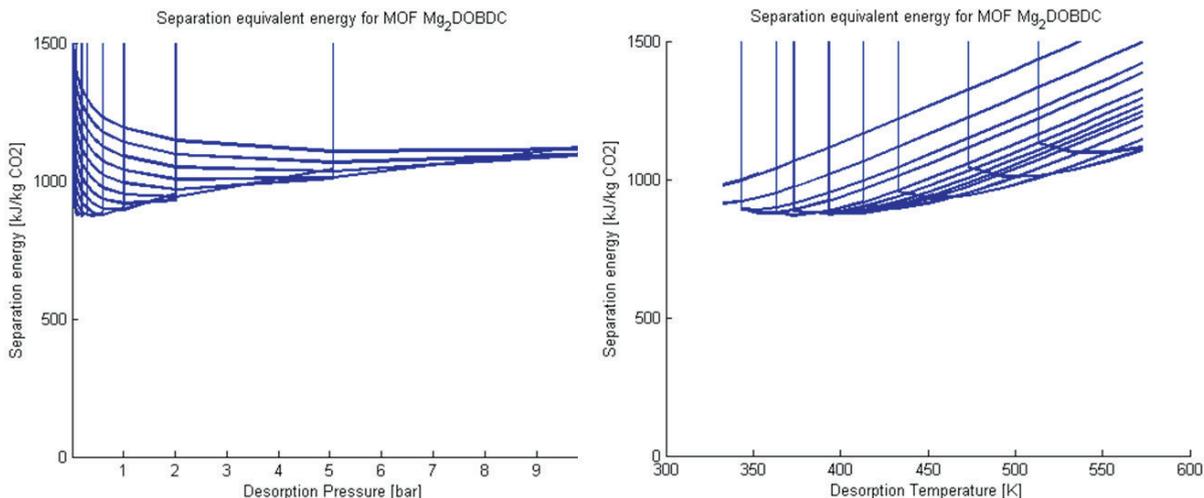


Figure 2: a) Separation energy as a function of regeneration pressure. Each line is at a constant temperature of regeneration. b) Separation energy as a function of regeneration temperature. Each line is at a constant pressure of regeneration.

As we can see for this material, the process conditions influence the total performance of the material significantly. If this material were evaluated at only atmospheric desorption, the total energy penalty would be judged to be significantly higher than at its actual minimum value.

3. Results and Discussion

We have applied the model and screening methodology to a database of over 4 million zeolites and zeolitic imidazolate frameworks [6]. A few hundred promising new materials have already been identified that exhibit ~30% lower energy consumption relative to aqueous monoethanolamine. For the more promising materials, we further correlated the heat of adsorption to the Henry’s coefficient as shown in Figure 3.

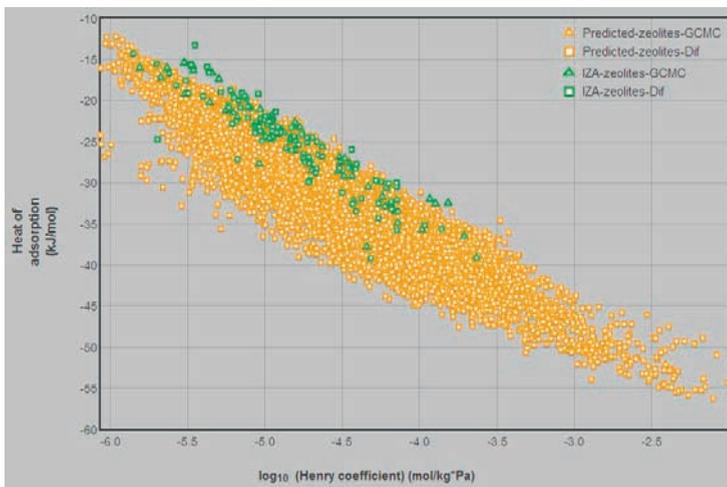


Figure 3. k_H vs. Δh for a large number of promising adsorbents

By starting with the material properties of a single sorbent, we can perform a parametric study on sorbent parameters. We can parameterize a sorbent by varying the CO₂ heat of adsorption and Henry's constant in tandem along the line of best fit for the dataset in Figure 3 given by Equation 3.

$$\Delta h = -80.873 - 10.944 * \log_{10}(k_H) \quad (3)$$

For each value of the heat of adsorption and Henry's constant along that line, we can create a theoretical sorbent. We then optimize the regeneration conditions and minimize the parasitic energy for each theoretical sorbent to determine the optimal heat of adsorption for this class of sorbents. Further, we can use these results to determine the optimal material properties for a process with a set pressure of regeneration by varying the material properties of the sorbent and temperature of regeneration. This gives insight into what materials and conditions are most advantageous for CO₂ capture (Figure 4).

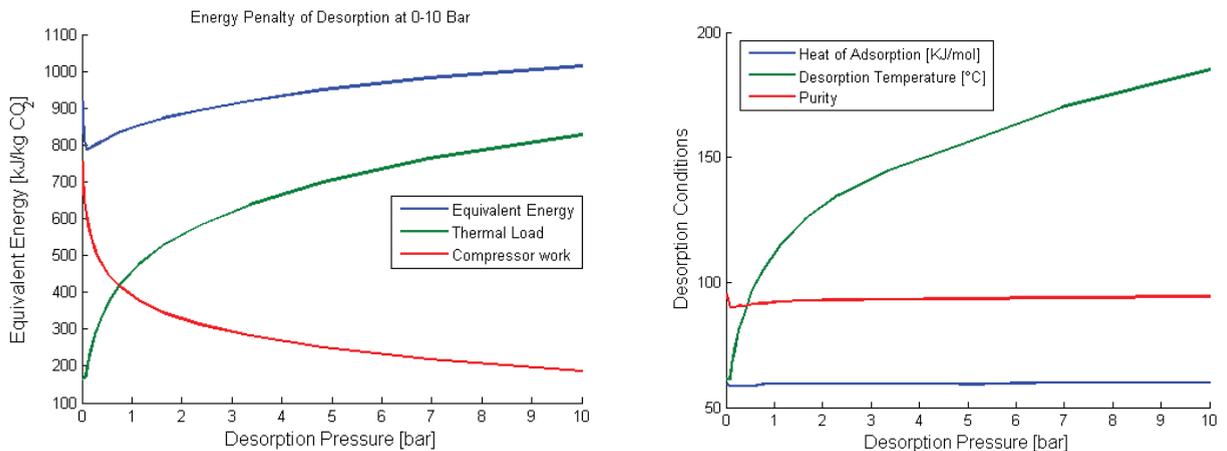


Figure 4. a) Minimum energy penalty for the class of parameterized sorbent for regeneration pressures from 0.01 to 10 bar. The equivalent energy calculation (blue) is the sum of the compressor work (red) and the discounted thermal load (green). b) Sorbent and process conditions that minimize the energy penalty at specific regeneration pressures. Purity of product is molar purity in % CO₂, with the balance N₂ for the sorbent and regeneration conditions described.

We note that at low regeneration pressures, compressor work dominates the equivalent energy, and as the pressure increases, the thermal load dominates the equivalent energy. The two terms contribute evenly at a pressure of about 0.9 bar. We further note that the equivalent energy is minimized at very low pressures of between 0.1 and 0.15 bar. However, such low pressures may be difficult to achieve economically in a practical system at large scales. That is, the capital cost of such low pressure vacuum systems at the scale needed for power plants may be prohibitive without additional advances in low-cost vacuum systems. We notice that the optimal heat of adsorption is approximately -60 kJ/mol for the range of all regeneration pressures for the class of adsorbents used in this study. This implies that a single material may be the optimal sorbent for a wide operating range for temperature and pressure conditions.

4. Conclusion

We have developed and implemented a simple equilibrium model to calculate the parasitic energy that would be imposed by a CCS process on a power plant. Using this technique, we have previously screened a large number of adsorbents, all computationally. In this effort, we extend the previous study to explore the class of single site zeolitic and similar adsorbents parametrically to determine optimal material properties including the CO₂ heat of adsorption. We focus on this adsorption parameter because most other physical properties are either very closely correlated with the heat of adsorption, such as the Henry's constant, or cannot be optimized without being maximized, such as total capacity. We find that the optimal heat of adsorption is close to -60kJ/kg for a wide range of regeneration pressures. Further, we find that the most efficient operating range uses regeneration pressures of 0.1 to 0.15 bar to operate primarily as a vacuum-swing process. One reason for this is that at low pressures, we can utilize very low quality heat (60-80 °C), which has only a small impact on the steam cycle total power.

While we have calculated thermodynamically optimal material properties and process configurations, we have not discussed how such materials and process can be created. This paper is intended to act as a guide for material and process developers and help push new technologies in the direction of the most energetically favourable materials and processes.

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