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Selection of optimal solid sorbents for CO_2 capture based on gas phase CO_2 composition

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Abstract

One method to reduce anthropogenic CO_2 emissions is carbon capture via the separation of CO_2 from gas streams that would otherwise be released to the atmosphere. In this work, we examine the applicability, performance, and desired material properties of solid sorbent materials to capture CO_2 from gas streams with varying CO_2 compositions. This paper focuses on optimizing material selection and process design for given applications and determines the effect on the calculated imposed load of performing carbon capture on various gas streams. For each gas stream for CO_2 separation, an optimal separation material and operational process can be identified. Previous work on this topic has been focused on sorbent and process selection for CO_2 separation from coal-derived flue gas[1,2]. In the current work, we expand the range of possible gas streams to include a wide range of CO_2 concentrations from 1-99% CO_2 with the balance N_2. The purpose of this is not only to identify the sorbent materials that are energetically optimal for each application, but also to determine the effect of varying CO_2 concentration on overall process performance. By quantifying the effect of increased CO_2 concentration or partial pressure, trade-off curves can be calculated and the effect of combustion, pre-treatment, or recycle processes that can increase CO_2 partial pressure can be analyzed. Further, this can provide a trade-off analysis between using process steps, such as recycling flue gas streams, to increase CO_2 concentrations before carbon capture versus capturing CO_2 directly from a lower concentration gas stream. Results include the range of materials that provide near-optimal energy performance for a given application and act as a guide for material developers.

Keywords: CO_2, Carbon Capture , CO_2 Adsorption, TSA, CCS

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1. Introduction

CO_2 emissions to the atmosphere can be decreased by capturing CO_2 from any CO_2 containing gas stream prior to discharge to the atmosphere. However, performing this CO_2 capture and storage (CCS) requires the separation of CO_2 from the other constituents of the gaseous stream. One of the primary hurdles to implementing widespread CO_2 capture is the cost of the capture and compression of the CO_2 to conditions where the CO_2 can be transported and stored in geological formationas, usually around 150 bar. This cost of capture is dominated by the energy required to separate the CO_2 from the feed gas mixture and subsequent compression CO_2 product. The energy requirement of CCS is in turn related to the composition and conditions of the stream from which the CO_2 is captured, as well as the process used to capture the CO_2 and the separation material used in that process.

One method that has been proposed and tested for capturing CO_2 is using solids sorbent in a temperature swing adsorption separation process [2]. This involves contacting the gas stream with a sorbent material that selectively adsorbs CO_2 until the material is close to saturated, removing the CO_2 from the remaining gas stream. The saturated sorbent material is then heated to desorb the CO_2 from the sorbent and produce the product CO_2 that can be compressed and transported for storage or alternate uses. The main energy requirements for this process come from the regeneration of the material and subsequent compression of the CO_2. The energy consumption is also a function of the initial CO_2 composition and pressure in the gas stream, the separation material used in the process, and the process regeneration conditions.

Gas streams that contain CO_2 can be the products of combustion, industrial process streams, off gases from fermentation, naturally occurring CO_2, or combinations of the above. These vary in CO_2 concentration from roughly 400 ppmv CO_2 for atmospheric concentrations to over 98% CO_2 for fermentation products. The material properties that are optimal for capturing CO_2 will vary as the gas stream composition changes. This is due to competing requirements for the material at different operational states. To have a large working capacity, the material must be able to have a large uptake at the original CO_2 concentration. However, to have a low energy requirement for regenerating the material, the CO_2 must be able to be liberated at moderate temperatures and not have a heat of adsorption that is too high. These requirements shape the materials that will be optimal for separating CO_2 from gas stream of different compositions

2. Minimum Energy of Separation

The energy to completely separate a single component out of a gas mixture is found from the following expression to provide the minimum work to overcome the entropy of mixing:

$$\Delta s_{mix} = -R \sum_i x_i \ln x_i$$

Where Δs_{mix} is the entropy of mixing, R the universal gas constant, and x_i is the gaseous mole fraction of species i. Overcoming this entropy of mixing plus the work, W_{comp}, required to compress the CO_2 to the transport pressure, P_c, of 150 bar, yields the following minimum specific work equation where the minimum work, W_{min} is the work requirement per quantity of CO_2 produced and T is the absolute temperature of the incoming gas stream:

$$W_{min} = RT \ln x_{CO2} + RT \frac{1 - x_{CO2}}{x_{CO2}} \ln(1 - x_{CO2}) + RT \ln \frac{P_c}{P_d}$$

This minimum work can be plotted as a function of x_{CO2} for 1 bar feed gas, compression to 150 bar, at a temperature of 313K, as is seen in Figure 1.
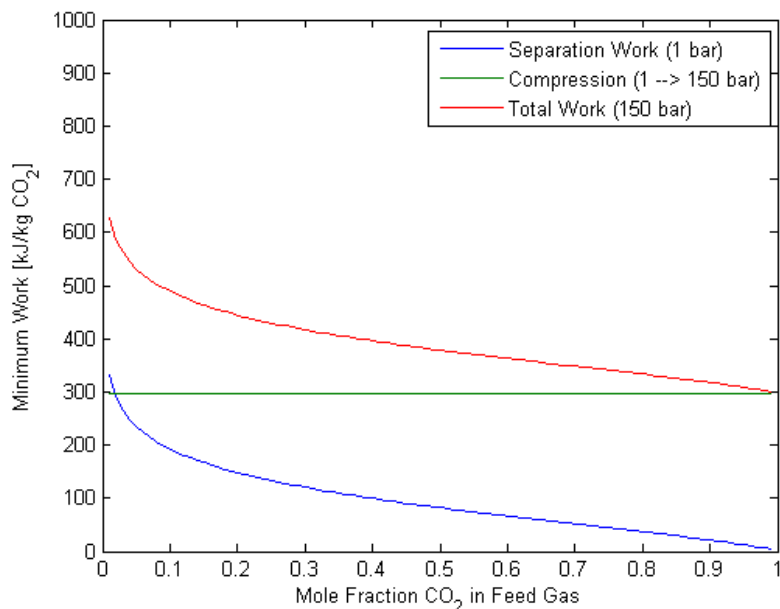
Fig. 1 Minimum theoretical work for overcoming entropy of mixing from 1 bar, 313K feed at
different CO_2 concentrations and compressing CO_2 product gas to 150 bar, 100% CO_2 product

Real processes will not be able to achieve this minimum work value. However, the closer to reversible the entire process is, the closer to this theoretical minimum energy the capture process will be. For compression, this means that the nearer to an isothermal process the compression takes place, the less entropy generation will occur. Normally this is accomplished through interstage cooling between compressor stages to keep the compressed fluid near the original low temperature point. The more stages of cooling and the smaller the compression ratio, the lower the total energy for compression and the closer to the theoretical minimum energy.

Similarly, the thermal energy requirement for TSA systems requires both heating and cooling throughout the full cycle. The smaller the difference in temperature is between the hot and cold temperatures, the smaller the irreversibilities are in capture process. This means that a smaller temperature difference leads to lower imposed load for the full process. For a temperature swing adsorption system, the thermal swing is vital for producing a CO_2 product at high purity.

To decrease the amount of thermal swing required, the heat of adsorption can also be increased. This works to increase the total difference in loading between the adsorption and desorption conditions for a given thermal swing. However, the heat of adsorption must be introduced to the system to desorb the CO_2 from the sorbent, so overly-high heats of adsorption should also be avoided. We simulate the optimal materials and associated processes for performing CO_2 capture from gas streams of varying CO_2 concentration to calculate the minimum imposed load and how that approaches the theoretical minimum work required.

3. Methodology

To determine the impact of capturing CO_2 from gas streams of variable concentrations, we have developed an equilibrium model that simulates the capture and subsequent regeneration and compression of the CO_2 using either a temperature swing or pressure swing adsorption process. This simulation uses the physical properties and adsorption isotherms of a solid sorbent at the adsorption conditions and desorption conditions to determine the total amount of CO_2 that is generated per adsorption/desorption cycle as well as the purity of product. We then calculated the thermal and mechanical energy required to regenerate the material and compress the product CO_2 to the compression

pressure. In order to construct a single metric with which to evaluate the material in that process configuration, we have created a correlation for how thermal energy is converted to work in steam turbines at large power stations, which we are using as a universal conversion efficiency for our thermal load.

The main components of the energy cost for a carbon capture system using solid sorbents are the thermal energy required to heat the sorbent to the required temperature, the thermal energy required to overcome the heat of adsorption between the adsorbed species and the sorbent, and the compressor work required to compress the produced CO_2 to the pressures required for transportation and subsequent storage or re-use. Real processes will also have additional energy requirements, such as fan work for overcoming the pressure drop in the gas/solid contacting system, materials handling in moving bed systems, additional gas pre-treatment, or CO_2 product cleanup. However, the energy requirement for each of these variables will be a function of the type, configuration, and ultimate requirement of the process used for each sorbent material. Because these additional energy requirements are not intrinsic to the material simulated and will change as the configuration is varied, these configuration parameters are ignored in this work to allow a process-configuration agnostic evaluation of the sorbent materials and separation behavior at different gas concentrations. Instead, the optimal process is determined through the study of adsorption and desorption conditions, as well as the material properties, that minimize the energy cost of CO_2 capture at different CO_2 concentrations.

3.1. Model description

To calculate the adsorption of CO_2 onto the material, a competitive single site Langmuir isotherm based on the material properties has been used with loading q calculated as a function of the pressures, temperatures, and compositions:

$$q_i = \frac{q_s P_i b_{0_i} e^{-\Delta H_i / RT}}{1 + \sum_j P_j b_{0_j} e^{-\Delta H_j / RT}}$$

Where q_i is the loading of the species i, q_s is the saturation capacity of the sorbent, P_i the partial pressure of species i. The total number of moles of gas in the gas-sorbent contactor is then $q_i + volume * \varepsilon * {P_i}/{RT}$, where ε is the void fraction of the sorbent packing. The difference between this total gas capacity in the adsorption and regeneration conditions provides the total amount of each species of gas captured per cycle. We call this quantity M_i for each species i.

The total thermal energy requirement per quantity of CO_2 produced can be calculated as the sum of two terms: the sensible energy of heating the sorbent, and the energy required to overcome the heat of adsorption.

$$Q = \frac{C_p \Delta T}{M_{CO_2}} + \sum_j \Delta H_j \frac{M_j}{M_{CO_2}}$$

Where C_p is the heat capacity of the sorbent, ΔT the difference in temperature between the adsorption and regeneration conditions, and Q the total thermal energy requirement per quantity of CO_2 produced. This thermal energy can be converted to a lost electrical work equivalent W_{lost} with efficiency through the correlation below. The assumptions are that the thermal energy is taken as steam with saturation temperature $T_{desorption}+10°K$ in Kelvin from a steam cycle with condenser temperature 313K as modeled by GateCycle steam cycle modelling software, with a range of validity from 333K to 425K. [1]

$$W_{lost} = Q * (-0.69246 + 0.002326 * T_{desorption})$$

The compressor work W_{comp} is calculated as the real-properties binary mixture compression of CO_2 and N_2 from the desorption pressure of 1 bar to 150 bar in equally spaced compression stages with maximum pressure ratio of 2.5 [3]. Each stage is assumed to have isentropic efficiency of 0.85 and stage inlets are intercooled to 313K.

The total imposed load on the power plant of the lost work from the steam extraction and compressor work is then expressed as:

$$IL = W_{lost} + W_{comp}$$

3.2. Sorbent properties

Previous work has calculated the adsorption properties of a dataset of hundreds of thousands of microporous materials for use in carbon capture from coal-fired power plants [3] We use representative values from this dataset to describe hypothetical microporous materials that we will use for exploring the effect of varying CO_2 concentration and material properties on optimal CO_2 capture processes.

The hypothetical material we will be using has the following properties:

Table 1. Simulated Sorbent Properties

Property	Symbol	Value	Units
Bulk Density	ρ	640	Kg/m^3
Porosity	ε	0.35	--
Heat Capacity	C_p	1000	J/kg K
Saturation Adsorption Loading	q_s	4	mol/kg
CO_2 heat of adsorption	ΔH_{CO2}	variable	J/mol
CO_2 henry's constant	kH_{CO2}	variable	mol/kg Pa
N_2 heat of adsorption	ΔH_{N2}	-13,000	J/mol
N_2 henry's constant	kH_{N2}	3e-7	mol/kg Pa

The heat of adsorption and Henry's constant for CO_2 are both measures of the strength of adsorption of CO_2 to the sorbent. Instead of allowing these variables to vary freely, we constrain them through the correlation below [4]

$$\Delta H_{CO_2} = 10944 \log_{10}(kH_{CO_2}) + 80873$$

We can thus calculate the properties for each hypothetical material based on the strength of adsorption of CO_2 to the sorbent. To calaculated a wide range of materials, we use the limits of kH_{CO2} ranging between 10^{-6} and 1 mol CO_2/kg Pa, which equates to a range of ΔH_{CO_2} values between -15,209 J/mol and -80,872 J/mol CO_2 adsorbed.

3.3. Simulations

The minimum energy for each gas-phase CO_2 concentration is calculated by fixing the adsorption conditions and varying both the material properties and the desorption conditions to find the minimum imposed load condition. This provides a means of calculating the material that is best suited for each application as well as providing a guideline for the temperatures and pressures of operation. By searching over the entire parameter space in the regions where our correlations are valid, we discover the minimum energy materials and processes for each process or gas stream, and can provide an estimate of the relative energy savings involved with increasing the CO_2 concentration at each point along the gas inlet distribution.

4. Results

CO_2 capture from nitrogen containing gas streams are used for every concentration from CO_2 capture from air (400 ppm), natural gas combustion products (3-5%), coal-fired combustion products (10-14%), Steel production (10-30%), cement kilns (15-30%), and ethanol production (98+%). [5-6]

These results look at the effect of varying CO_2 concentration within an N_2 environment, using the CO_2 and N_2 adsorption isotherms described in the methodology section. By varying the mole fraction of CO_2 from 0.01 to 0.99 with the balance N_2, we can compare the theoretical minimum results for a shown in figure 1 with the minimum energy numbers for a TSA process with desorption at 1 bar based on the class of materials described in table 1.
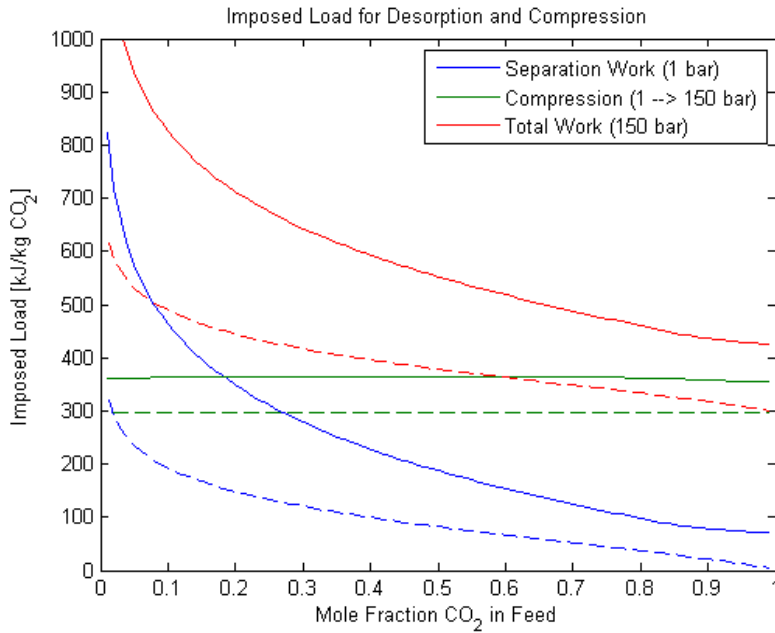

Fig. 2 The minimum separation (blue), compression (green), and total work (red) for theoretical (dashed) and simulated (solid) processes on the class of microporous materials
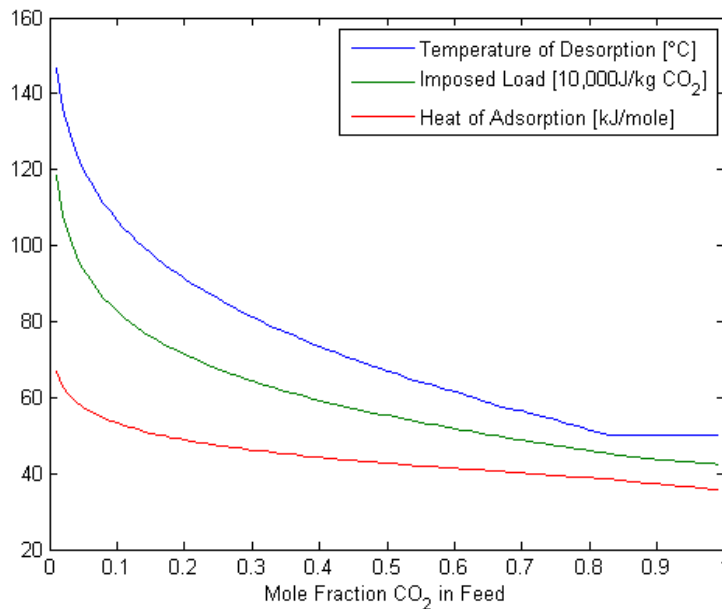

Fig. 3 The effect of increasing CO_2 mole fraction in the feed is seen in the solid sorbent's optimal heat of adsorption in kJ/mol (red), temperature of regeneration in K (blue) and total imposed load in 10,000J/kg CO_2 (green) all decreasing. Note different units for each parameter.

From figure 2, we can see that the compression energy remains almost constant because of the constant pressure of regeneration. The electrical impact of the thermal energy requirement, however, decreases significantly as the mole fraction of CO_2 in the feed increases as we would expect from the minimum energy calculations. This is due to the fact that the processes at high feed concentrations can use both a lower temperature of desorption and a sorbent with a lower heat of adsorption than at lower feed concentrations. This is because at high CO_2 concentrations, even a material with relatively low Henry's constant will have a high CO_2 uptake, but materials that must work with low CO_2 concentrations have to have a very high Henry's constant for CO_2 to maintain the same loading. This means that the materials that perform best at low concentration are the materials with high heats of adsorption, and those are the materials that must be heated to the highest temperatures to desorb the CO_2. This is visible in figure 3 where the trend for heats of adsorption, regeneration temperature, and total imposed load all follow the same downward trajectory as CO_2 mole fraction in the feed increases.

Each of these impacts have ramifications not just for the energy use, but for the implementation. The impact of the lowered imposed load is that there is less of a requirement for steam or other heating transfer material to heat the sorbent. The lower heat of regeneration means that less heat has to be rejected during the adsorption phase of the cycle, and lower temperature of desorption changes the types of materials and sorbents that can be used to ones that may be more heat sensitive.

Quantifying the effect of increasing the CO_2 concentration is also useful, especially in cases where decisions on the operation of a power plant or other industrial process could be implemented with a known tradeoff between efficiency and CO_2 content in the resulting gas stream. Examples of this could be changing fuel composition, partial-oxy fired boilers, or selective flue gas recycle. In order to analyze the tradeoff between increasing CO_2 concentration and maximizing performance, we have produced results showing the effect on the imposed load of increasing the CO_2 concentration by 1%. These results are shown in figure 4 and show that the sharpest benefit occurs at the lowest concentration of CO_2 in the feed stream. The cumulative benefit of rising from 5% CO_2 to 20% CO_2, for example, which could be achieved through selective flue gas recycle on a natural gas fired power plant, would have a simulated reduction in imposed load on that plant of roughly 225 kJ/kg CO_2.
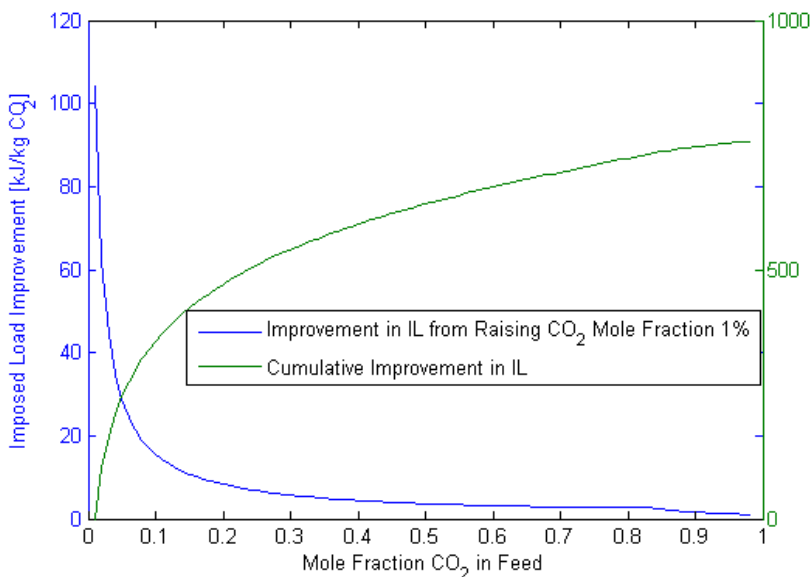

Fig. 4 The benefit to the total imposed load of increasing the CO_2 concentration by 1% is shown for each CO_2 mole fraction in blue. The cumulative improvement above 1% CO_2 is shown in the green line.in kJ/kg CO_2. Thus, an optimal process using 30% CO_2 as opposed to 1% CO_2 as the feed gas would expect a savings of roughly 540 kJ/kg CO_2.

5. Conclusion

The composition of the CO_2 feed to a solid sorbent capture process is vital for determining the optimal process, separation material, and operation for capturing the CO_2. Very low concentrations of CO_2 in a gas stream require a material with a high heat of adsorption and Henry's constant, as well as a process with a high temperature of regeneration. Together, these create a process with a much high imposed load than materials that can be used at lower heats of adsorption and lower temperatures of regeneration. In those cases, the main imposed load is caused by the requirement to compress the CO_2 to the pipeline pressure of 150 bar, and the thermal load to separate the CO_2 at 1 bar is only a minor addition to the total imposed load.

Further, in analyzing the difference between the theoretical minimum work and simulated minimum work for TSA processes, several trends are noticeable. First, the higher the CO_2 concentration in the feed is, the lower the difference between the theoretical minimum and simulated results (figure 2). At low CO_2 concentrations, the theoretical minimum thermal energy increases significantly, but the simulated thermal energy impact rises much more quickly. This is in part because the larger the difference in temperature between the adsorption and desorption conditions, the more exergy is lost in the heating and cooling of the system, making the process less reversible and further from the theoretical minimum energy. As solid-solid heat exchange is not a currently available technology, the heating and cooling of the sorbent has to be accomplished with a hot heat transfer medium and a cold heat transfer medium instead of a cross exchanger, such as in a solvent system, that would be able to recover the intermediate temperature heat.

We have quantified the effect of using higher CO_2 feed gas streams and of enriching the CO_2 concentration of the gas streams for separation using our hypothetical microporous material. This should provide insight into the tradeoff between increasing system performance and elevating CO_2 concentrations in the stream to be captured. We have also described the behavior and some of the properties of our ideal sorbent for each capture process. However, while the exact material or class of materials described in this paper does not exist, materials with similar physical properties, and ranges of heats of adsorption, can be used for carbon capture using the processes best suited for the gas stream.

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