

New Materials and Process Development for Energy-Efficient Carbon Capture in the Presence of Water Vapor

Investigators

All investigators are at Northwestern University. Note that the experimental part of the project is described in a separate document, although experiment and modeling are tightly integrated in the project.

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Abstract

Using quantum chemical methods, we have screened a variety of functional groups for their ability to bind CO₂ and water. Most functional groups bind water more strongly than CO₂, making them ineffective for incorporation into materials for removing CO₂ from humid flue gas. Preliminary calculations suggest that adding perfluorinated functional groups strongly suppresses water binding, while having little effect on CO₂ binding. Preliminary process-level modeling has shown that if materials are not available for capturing CO₂ from humid flue gas, it may be economically feasible to remove much of the water from the flue gas prior to CO₂ removal. This opens up a wider range of material and process combinations for cost-effective CO₂ capture.

Introduction

Adsorption processes based on porous solids are a promising technology for removing CO₂ from power plant flue gas. The premise of this proposal is that game-changing improvement of adsorption separation processes for carbon capture and storage (CCS) will require *simultaneous development of new materials and specially designed processes that take advantage of these new materials*. Competitive adsorption of water is regarded as the single greatest technical hurdle to adsorption-based CCS, but there is very little research on new water-tolerant CCS adsorbents. One goal of this project is to develop new metal-organic framework (MOF) materials with extraordinarily high selectivity for CO₂ over nitrogen and water, together with suitably high absolute capacity for CO₂. Several related strategies are being explored, and molecular modeling is being used to guide the synthetic effort. In addition, we are using state-of-the-art process-level modeling to optimize adsorption processes around the new class of sorbents and explore the real efficiency limits of MOF-based adsorption processes that meet desired CCS technical and economic criteria, while minimizing the life-cycle environmental impact. Adsorption processes are already used in large-scale applications, such as air separation, with high reliability. Discovery of new, water-stable and water-tolerant adsorbents for CO₂ capture and new, optimal process configurations for these sorbents would be a step-out development in CCS.

Background

Research on MOFs continues to explode. Many research groups are investigating MOFs for separation of CO₂/N₂ mixtures, motivated by carbon capture. However, very

few papers report results that take water into account. A small number of papers have appeared recently on the stability of MOFs, including their stability in water or humid gas streams.

Results

Molecular-level Modeling

We are using molecular-level modeling to 1) screen new candidate materials and 2) obtain insights into the structures that provide the best performance. One focus this year was to screen functional groups that could be incorporated into existing MOF materials for selective adsorption of CO₂ over N₂ in the presence of water vapor. ZIF-8 was chosen as a candidate MOF for functionalization due to its stability in the presence of water (even under boiling water conditions). In addition, this material has been shown to be very hydrophobic and to adsorb almost no water. This has been demonstrated experimentally [1-2] and by simulations from our group [3].

A variety of different functional groups were tested for their ability to enhance the target properties of ZIF-8. The binding energies for water and CO₂ were calculated as an initial measure of the ability to adsorb CO₂ in the presence of water. The goal was to find functional groups that would increase the adsorption of CO₂ compared to the unfunctionalized material but that would not adsorb too much water. Quantum mechanical calculations were performed to obtain the binding energies. Calculations were performed on a small and a large cluster extracted from the ZIF-8 structure, as shown in Figures 1. For the small clusters, we used a high level of theory, namely second order Møller–Plesset perturbation theory (MP2) with large basis sets such as 6-311++G(2d,p). For the large clusters, we used less expensive density functional methods using the wB97xD functional and a 6-31G(d,p) basis set.

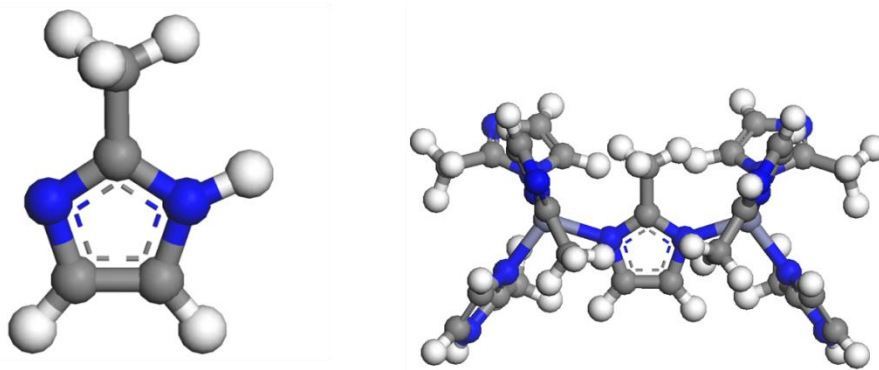


Figure 1. Small and large clusters of ZIF-8 used for the quantum chemical calculations.

For the large cluster, the different functional groups were added not only on the central ring of the cluster but on all of the six peripheral rings as well. This was done to observe any possible synergetic effect between the functional groups of adjacent rings, and indeed we did observe such effects for some functional groups, where the interaction

of guest molecules with the cluster was significantly enhanced when groups were present on every ring of the cluster rather than only on the central ring.

As expected from our choice of functional groups, we observed an increase in the interaction energy between the ZIF cluster and the CO₂ molecules upon functionalization with all of the functional groups tested. In some cases, the enhancement was quite pronounced, for example an increase in the magnitude of the binding energy from -13 kJ/mol to -94 kJ/mol. At the same time, when these groups were tested for their ability to interact with water, the same trend was observed: in every case, the functional group increased the binding of water as well. There was no functional group among the ones tested that could bind CO₂ more strongly than H₂O, supporting our initial idea that simple functionalization was unlikely to be a successful strategy.

Functionalization with perfluoro group was given special attention. In a similar set of calculations, the ZIF-8 methyl groups on the imidazole ring (Figure 1) were replaced by perfluorinated methyl groups. The perfluorination of the methyl groups resulted in a significant decrease in the interaction with water (from -36 kJ/mol to -24 kJ/mol), making the material more hydrophobic. At the same time, this change had almost no effect on the interaction with CO₂, with binding energies of -13 kJ/mol for the original cluster and -12 kJ/mol for the cluster with the perfluorinated methyl groups.¹ Thus, the material with perfluoromethyl groups is predicted to be significantly more hydrophobic than the parent material but to adsorb essentially the same amount of CO₂. While the parent ZIF-8 material is not particularly good for CO₂ capture, this finding may allow us to find other materials that can be made hydrophobic while retaining their ability to adsorb CO₂.

Process-level Modeling

There are two main objectives of the process-level modeling in this project: first, to design a system that utilizes materials discovered in the project and, second, to provide feedback to the materials discovery effort on the desired material properties. While our primary focus is the development of materials that can adsorb CO₂ in the presence of water, we thought it worthwhile to first investigate how much it would cost to remove water vapor from the flue gas prior to the CO₂/N₂ separation. A new graduate student was recruited for this effort, and during the past several months, we designed several different processes for water removal and determined the corresponding cost under different requirements and operating conditions.

The total cost of the water removal system was estimated using a framework proposed by Hasan et al. [4]. The total annualized cost (TAC) was divided into the annualized investment cost (AIC) and the annual operating cost (AOC). The detailed scheme for calculating the AIC is shown in Table 1. The AOC was determined by the usage of utilities including process utilities (cooling water, steam, refrigerant) and electricity. All equipment costs and utility costs were estimated using the Aspen Process Economic Analyzer.

¹It should be noted that with the simple cluster models, these energies are not expected to reflect the adsorption enthalpies measured in the real materials. Rather, we are seeking trends with these calculations.

Table 1. Parameters for the economic analysis

parameter	Value
Equipment (mover) installation cost (EIC)	80% of equipment purchase cost(EPC)
Equipment (column, exchanger, etc.) installation cost (EIC)	4% of EPC
Total installed cost (TIC)	All EPCs and EICs
Indirect cost (IDC)	32% of TIC
Balance of plant cost (BPC)	20% of TIC
Total plant cost (TPC)	TIC+IDC+BPC
Annual maintenance cost (AMC)	5% of TPC
Capital recovery factor	15.4%

There are many different technologies for water removal. We mainly focused on two of them, absorption with triethylene glycol (TEG) and cooling & condensation. Other technologies include compression and condensation, cryogenic separation, membranes, and solid adsorption. Compression and condensation was not considered because of the high installation cost and electricity consumption for compressing the entire flue gas stream. Cryogenic separation requires extensive use of coolant. Membrane technology is also reported to cost more than TEG absorption by Hasan et al. [4] and was not considered here. Solid adsorption needs further evaluation.

TEG absorption and cooling & condensation processes were simulated using Aspen Plus. We assumed feed flue gas available at 1 bar and 55°C with 15% H₂O, 69.5% N₂, 5.5% O₂ and 10% CO₂ (volumetric fractions). The flue gas then goes through a direct contact cooler where it is saturated with water at 35°C (corresponding to 5.5% H₂O). The flow rate of this stream was taken to be 1kmol/s (which is about the CO₂ emission of a 30 MW power plant) for simplicity.

The process flow diagram for cooling & condensation is shown in Figure 2. Wet flue gas is cooled down, and the liquid phase is separated from the vapor phase in a flash tank operating at 1 atm. The temperature of the cooled mixture exiting the heat exchanger depends on the requirement set for the water content in the dry gas. For example, if we require less than 1% water in the dry gas, the cooling temperature is 75°F. If the requirement is 0.1%, the cooling temperature has to be 41°F.

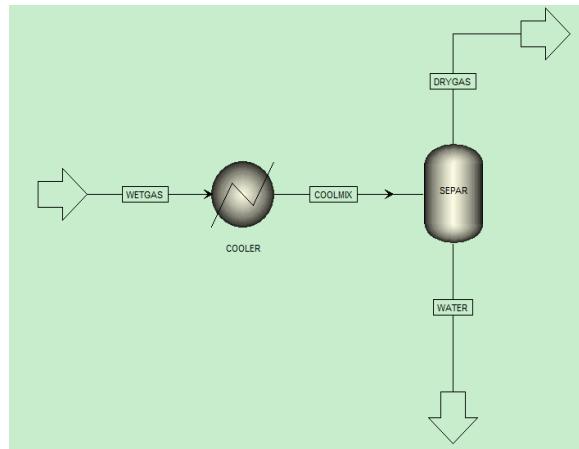


Figure 2. Cooling and condensation process flow diagram.

The cost of this process was estimated for different requirements set on the water content. Refrigerant at 10°F was assumed to be available at \$1.70 per ton-day [5]. With a 1% water requirement, the AIC and AOC are \$39,504 and \$296,154, respectively. The total plant cost (TPC) is then \$335,658, and the water removal costs \$2.4 per ton of CO₂ captured. With a 0.5% water requirement, the cost per ton of CO₂ captured is \$4.2. The cost of cooling and condensation is low, because it is a simple process. The only utility requirement is refrigeration, and the cooling temperature is not very low. However, this simple process leads to significant loss of CO₂, especially when requiring low water content in the dry gas. For example, when a 0.1% water requirement is set, more than 25% of the CO₂ is lost from the bottom of the flash tank. Our goal is to capture at least 90% of the CO₂. If we instead require no more than 10% loss of CO₂, the water content can only go down to as low as 0.5%, which places significant restriction on this technology.

The other technology studied for dehydration was TEG absorption. The process flow diagram is given in Figure 3. Wet flue gas is contacted with 99.5% TEG in the absorption column and dry gas is obtained from the top. TEG absorbed with water is then regenerated using a flash tank operating at high temperature and low pressure.

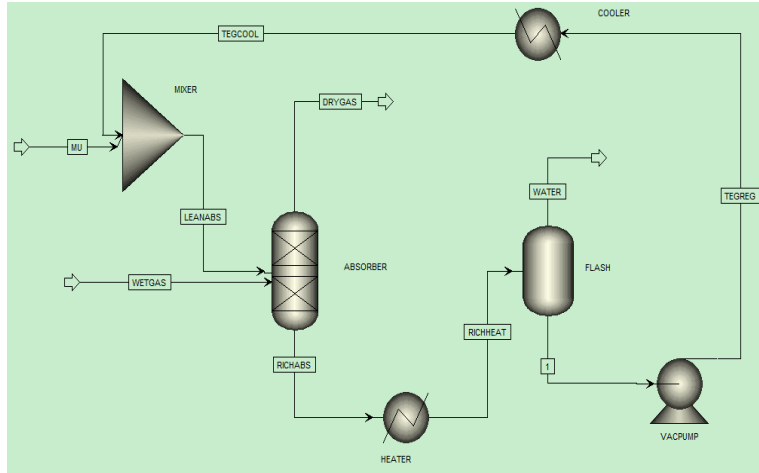


Figure3. TEG absorption process flow diagram.

The cost of TEG absorption is generally higher than cooling & condensation under the same requirement on water content. Figure 4 shows the cost per ton of CO₂ captured for the TEG absorption process under different requirements when the flash tank is operating at 120°C and 0.04 bar and the cooler outlet temperature is 65°C. The general range is between \$10 and \$20 per ton of CO₂ captured, while the cost goes to \$73/ton CO₂ captured when the water requirement is 0.1%. This is because the operating condition is far from optimal for this case.

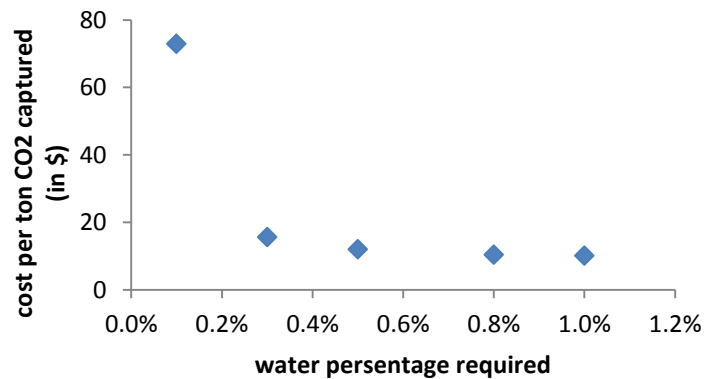


Figure 4. Dependence of cost on water requirement in the outlet stream for TEG absorption.

TEG absorption can achieve good separation of H₂O from flue gas without sacrificing CO₂ recovery. The loss of CO₂ is less than 3% even when the water percentage in the dry gas is set to 0.1%. Unlike cooling & condensation, the operating conditions of TEG absorption are adjustable even when the requirement on water removal is fixed. Changing the temperature and pressure of the flash tank and the temperature of cooler outlet can significantly influence the cost of the process, so the operating conditions need to be optimized in order to achieve lower costs. The three main process variables are the flash temperature (ranging from 100-140°C), the flash pressure (0.04-0.2 bar), and the cooler

outlet temperature (45-65°C). For the 1% water requirement case, 30 sampling points were taken within these ranges using the Latin Hypercube Sampling method in MATLAB. The cost was estimated for each sampling point. Among these sampling points, the cost of CO₂ capture ranges from \$5.8 to \$18.1 per ton of CO₂ captured, with the lowest cost found when the flash temperature is 108°C, flash pressure is 0.09 bar and cooler outlet temperature is 61°C. For the 0.1% water requirement case, the lowest cost is found at \$10.9 per ton of CO₂ captured when the flash temperature, flash pressure and cooler outlet temperature are 140°C, 0.04 bar, and 40°C, respectively.

Progress

Our preliminary process-level modeling indicates that removing water prior to capturing CO₂ from flue gas may be economically and technically feasible. The question of how much of the water to remove requires an integration of the process modeling and the materials development and will be one focus in the coming year.

Development of fluorinated MOFs may provide a solution to the difficult problem of selectively adsorbing CO₂ over N₂ in the presence of water vapor.

Future Plans

Computational screening of MOFs will continue in close association with the experimental effort, as described in the original proposal. One new direction is suggested by the process-level modeling, namely, an assessment of how MOFs perform in the presence of a small amount of water vapor (as opposed to a stream that is essentially saturated with water vapor).

We will finish our assessment of the cost of water removal. We have made good progress in writing a MATLAB code for modeling adsorption units and will soon begin modeling carbon capture processes based on MOF materials.

Publications and Patents

There are no publications or patents yet.

References

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