

**Parameterization, Pores, and Processes:
Simulation and Optimization of Materials for Gas Separations
and Storage**

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Abstract

This thesis explores the use of computational chemistry to aid in the design of metal-organic frameworks (MOFs) and other materials. A focus is placed on finding exceptional materials to be used for removing CO₂ from fossil fuel burning power plants, with other avenues like vehicular methane storage and landfill gas separation being explored as well. These applications are under the umbrella of carbon capture and storage (CCS) which aims to reduce carbon emissions through selective sequestration. We utilize high-throughput screenings, as well as machine learning assisted discovery, to identify ideal candidate materials using a holistic approach instead of relying on conventional gas adsorption properties.

The development of ideal materials for CCS requires all aspects of a material to be considered, which can be time-consuming. A large portion of this work has been with high-throughput, or machine learning assisted discovery of ideal candidates for CCS applications. The chapters of this thesis are connected by the goal of finding ideal materials for CCS. They are primarily arranged in increasing complexity of how this research can be done, from using high-throughput screenings with more simple metrics, up to multi-scale machine learning optimization of pressure swing adsorption systems. The work is not presented chronologically, but in a way to tell the best story.

Work was done by first applying high-throughput computational screening on a set of experimentally realized MOFs for vehicular methane storage, post-combustion carbon capture, and landfill gas separation. Whenever possible, physically motivated figures of merits were used to give a better ranking and consideration of the materials. From this work, we were able to determine what the realistic limits might be for current MOFs. The work was continued by looking at carbon-based materials (primarily carbon nanoscrolls) for post-combustion carbon capture and vehicular methane storage. The carbon-based materials were found to outperform MOFs; however, further studies are needed to verify the results.

Next, we looked at ways to improve the high-throughput screening methodology. One problem area was in the charge calculation, which could lead to unrealistic gas adsorption results. Using the split-charge equilibration method, we developed a robust way to calculate the partial atomic charges that were more accurate than its quick calculation counterparts. This led to gas adsorption properties which more closely mimicked the results determined from time-consuming quantum mechanically derived charges.

Simplistic process optimization was then applied to nearly ~3500 experimental structures. To the best of our knowledge, this is the first time that any process optimization has been applied to more than 10s of materials for a study. The process optimization was done by evaluating the desorption at various pressures and choosing the value which gave the lowest energetic cost. It was found that a material synthesized by our collaborators, **IISERP-MOF2**, was the single best experimentally realized material for post-combustion carbon capture. What made this an interesting result is that by conventional metrics **IISERP-MOF2** does not appear to be outstanding. Next, functionalized versions of MOFs were tested in a high-throughput manner, and some of those structures were found to outperform **IISERP-MOF2**.

Although high-throughput computational screenings can be used to determine high-performance materials, it would be impossible to test all functionalized versions of some MOFs, let alone all MOFs. Functionalized MOFs are noteworthy because MOFs are highly tuneable through functionalization and can be made into ideal materials for a given application. We developed a genetic algorithm which, given a base structure and a target parameter, would be able to find the ideal functionalization to optimize the parameter while testing only a small fraction of all structures. In some cases, the CO₂ adsorption was found to more than quadruple when functionalized.

A better understanding of how materials perform in a PSA system was achieved by performing multi-scale optimizations. Experimentally realized MOFs were tested using atomistic simulations to derive gas adsorption properties. After passing through a few sensible filters, they were then screened using macro-scale pressure swing adsorption simulators, which model how gas separation may occur at a power plant. Using another genetic algorithm, the conditions that the pressure swing adsorption system runs at was optimized for over 200 materials. To the best of our knowledge, this is the highest amount of materials that have had been optimized for process conditions. **IISERP-MOF2** was found to perform the best based on many relevant metrics, such as the energetic cost and how much CO₂ was captured. It was also found that conventional metrics were unable to be used to predict a material's pressure swing adsorption performance.

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List of Acronyms

• CBM	Carbon Based Material
• CIM	Competitive Isotherm Model
• CCS	Carbon Capture and Storage
• CSD	Cambridge Structural Database
• DFT	Density Functional Theory
• ESP	Electrostatic Potential
• FGC	Functional Group Code
• fMOF	Functionalized Metal-Organic Framework
• GA	Genetic Algorithm
• GAPI	Genetic Algorithm Performance Index
• GCMC	Grand Canonical Monte Carlo
• GROMACS	Groningen Machine for Chemical Systems
• IAST	Ideal Adsorbed Solution Theory
• LJ	Lennard-Jones (function or potential)
• MAD	Mean Absolute Deviation
• MEA	Monoethanolamine
• MEPO	MOF Electrostatic Potential Optimized
• MOF	Metal-Organic Framework
• MOFF-GA	Metal-Organic Framework Functionalization Genetic Algorithm
• HoA	Heat of Adsorption
• PAW	Projector Augmented Wave
• pGA	Parameter Genetic Algorithm
• PPN	Porous Polymer Network
• PSA	Pressure Swing Adsorption
• QEq	Charge Equilibration
• QM	Quantum Mechanics
• REPEAT	Repeating Electrostatic Potential Extracted Atomic (charge)
• RMSD	Root Mean Squared Deviation
• SBU	Structural (or Secondary) Building Unit
• SQE	Split Charge Equilibration
• SQE-MEPO	Split Charge MOF Electrostatic Potential Optimized
• STP	Standard Temperature and Pressure
• TPSA	Temperature/Pressure Swing Adsorption
• TSA	Temperature Swing Adsorption
• UFF	Universal Force Field
• VASP	Vienna Ab initio Simulation Program (software)
• VdWP	van der Waals Potential

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1 Introduction and Background

With mounting scientific evidence, the relationship between increasing atmospheric CO₂ concentrations and rising global temperatures is hard to ignore. If the current emission rates continue, global temperature is predicted to rise by 2°C, Sea levels could rise anywhere between 60 cm to 7 m, significant aquatic life could be lost, along with global water shortages.^{1,2} These effects make the immediate reduction of CO₂ emissions one of the most pressing concerns in the world. The primary sources of CO₂ emissions are coal and other fossil fuel burning power plants, which produce 15 Gt/year, or roughly 35% of the 49 Gt/year of the world's Greenhouse Gas (GHG) emissions.² Another prominent GHG emission source is from the transportation industry which emitted 14%, 7.0 Gt/year, of total GHG emissions. The total GHG emissions are expected to continue to increase, with an estimated doubling of emissions from 2010 to 2050. Reducing GHG emissions is one of the most pressing scientific concerns that needs to be solved, as it is unlikely that a cheap, sustainable, and environmentally friendly energy source will soon be discovered and widely implemented.

Environment and Climate Change (ECC) Canada wants to reduce the GHG emissions from 2014 levels by 29% by the year 2030.³ In addition to Canada, over 100 countries have agreed to reduce GHG emissions to reach the global warming limit.⁴ One of the primary thoughts for the reduction of GHG emissions is the decarbonizing of electricity generation.² Although this does include using renewable fuel sources, such as wind or solar, it also includes reducing GHGs that are currently emitted from fossil fuel burning plants. This reduction can either be from stopping the CO₂ from being emitted into the atmosphere^{5,6} or from using less carbon-intensive fuels, such as bioenergies or natural gas in place of coal.⁷⁻⁹ For transportation, this requires technological innovation for energy storage of low-carbon fuels which typically have a low-energy density.

1.1 Carbon Capture and Storage

Carbon Capture and Storage (CCS) is an umbrella term used to describe several methods to reduce CO₂ from their emission sources.^{10,11} CCS aims to capture CO₂ selectively and then permanently store it, typically deep underground. Currently, the main cost associated with CCS is the separation of the CO₂ from the other gases which can account for 70% of the total cost.¹² For this reason, there has been significant interest in designing new materials or processes to reduce this cost.¹³⁻¹⁶

There are currently three major strategies to reduce CO₂ emissions from fossil fuel burning power plants: 1) Post-Combustion Carbon Capture (PoCCC),^{17,18} 2) Pre-Combustion Carbon Capture (PreCCC),^{19,20} and 3) Oxy-Fuel Combustion (OFC).²¹ In this section, I will give a brief overview of the advantages and disadvantages of each technology, as others, such as Kanniche *et al.*, have looked at more detailed technological and economical studies between these strategies.^{6,22} In PoCCC, a fossil fuel power plant operates normally, and the CO₂ is removed from the flue gas. PoCCC has the advantage that it can be retrofitted onto an already existing power plant, although it has the disadvantage that the flue gas contains a low concentration of CO₂ (8-15% at 1 bar),^{14,23} making it difficult to remove. The second option, PreCCC, is a method where fossil fuel is gasified to create CO and H₂O, and then the water gas shift reaction is performed.²⁴ The final product is a gas that is 40-60% CO₂ with the remaining gas being H₂, at pressures ranging from 20-40 bar. At this stage, the CO₂ is removed, and the H₂ is used as a fuel source, where the only major product is H₂O. This process has the advantage of having a relatively high concentration and pressure of CO₂ allowing for relatively easy separation. The disadvantage is that PreCCC requires plants that are specifically designed and built with this technology in mind and cannot be as easily retrofitted like PoCCC.⁶ The final method of carbon capture discussed, OFC, works by first separating oxygen from air (mainly N₂), to create a pure O₂ stream. O₂, not air, is used to burn the fossil fuel, which creates a flue gas whose main component is CO₂. The flue gas could then be sent directly to be compressed. This process has the advantage of being able to directly compress and store the flue gas (which may contain other harmful gases such as NO_x or SO_x), but like PreCCC, cannot be retrofitted onto a plant as the O₂ and fossil fuels burn at higher temperatures than air and fossil fuels. From this quick analysis of fossil fuel carbon capture techniques, it is easy to see why PoCCC has received a large portion of the research,^{15,25,26} especially when you consider that power plants need to run for decades before they become profitable. This has allowed PoCCC to become attractive enough to allow a number of pilot-scale CCS plants in the world to use this technology.²² One such plant is the Boundary Dam Carbon Capture Project in Saskatchewan which produces 115 MW of power while capturing up to 90% of its CO₂ emissions.²⁷

Although mitigating CO₂ emissions from power plants is the largest potential application of CCS, it can be applied to other areas, such as reducing emissions from landfills.²⁸⁻³¹ When organic waste is disposed of, the breakdown of the chemicals releases a mixture of gases known as landfill gas (LG). Although there are a large variety of landfills, LG is often 50-65% (by volume) CH₄,

30-40% CO₂,³² with the remainder coming from contaminants such as N₂, O₂, H₂O and a mixture of hydrocarbons and other chemicals. Worldwide, landfills produce 255 Million Metric Tonnes (MMT) of CO₂ and CH₄ annually, with CH₄ accounting for 85 MMT and CO₂ making up the remaining 170 MMT.³³ This number is growing and estimated to rise to a total of 344 MMT (115 MMT of CH₄ and 229 MMT CO₂) by the year 2030. Although it appears that CO₂ is more of a problem, emitting nearly twice the weight, CH₄ is 25 times more potent of a GHG than CO₂. This means that every 1 MMT of CH₄ is equivalent to 25 MMT of CO₂.³⁴ This is known as CO₂-equivalence (CO₂-e); therefore, global landfills currently produce approximately 2380 MMT of CO₂-e every year and are predicted to produce 3219 of CO₂-e by 2030, with 93% of that due to CH₄. For perspective, in 2016 Canada emitted a total of 704 MMT of CO₂-e of GHGs.³⁵

CH₄ is the main component in natural gas (NG), so it is reasonable to assume that if the CH₄ from landfills were captured, it could be sold and used as a fuel. The NG produced from landfills is called Renewable Natural Gas (RNG), as humans will continue to create waste and therefore landfill gas.⁹ In addition to RNG being a renewable form of energy, it can also be viewed as carbon neutral as the carbon that is captured, utilized, and emitted (if it is not captured), would have been released into the air if not captured. There are arguments that this could even be viewed as a carbon negative process as the carbon is converted from the highly GHG potent form of CH₄ into the lower impact CO₂, although the same number of carbon atoms are still emitted into the air. There are other potential sources of GHG emission reductions that could happen; 1) reduction of “dirtier” fossil fuel burning power plants, such as coal, 2) less need for coal mining, and 3) CCS being implemented on power plants that use RNG. In order to be injected into a pipeline, the RNG needs to be a relatively pure stream (>87%) of CH₄.³⁶ To be able to use CH₄ from landfills as a fuel, the CO₂, and ideally other components, need to be first removed. The CH₄ would be compressed to NG transport conditions (approximately 18 bar),³⁷ while the CO₂ and other components would likely be emitted into the atmosphere. Although the CO₂ could be permanently stored like in PoCCC, due to low political and social pressure, it would likely be emitted to keep costs low. There are current facilities, such as the company Bullfrog Power in Dépôt Rive-Nord, Québec, which has a landfill biogas project plant that captures CH₄ and injects it into the national NG pipelines.³⁸

One final application for carbon reduction that will be discussed in this thesis is vehicular methane storage (VMS). According to the U.S. Environmental Protection Agency (EPA), 14% of

all global GHG emissions came from transportation in 2014.³⁹ They also found that the U.S. transportation industry was tied with electricity generation as the largest GHG emission sector, emitting a total of 28% of their GHG emissions. Unlike other GHG emission sources, such as power generation or landfills, transportation is not a single concentrated point emission source. The CO₂ is emitted by millions of vehicles, where employing a carbon capture technology may be unfeasible due to size and weight restrictions. One potential way to mitigate GHG from vehicles is through alternative fuels, such as methane. VMS is a method where instead of using gasoline or diesel as the fuel source for vehicles, methane would be used. The benefit is that methane is a cleaner burning fuel than gasoline, emitting 26% less CO₂ per energy produced. Because of this, and the cheap cost of NG, in 2009 globally ~9.5 million cars, or 1% of all vehicles, were powered through VMS, with the bulk coming from Latin America or Asia.⁴⁰ One reason why VMS is not as widespread is that methane is gaseous at atmospheric conditions, and therefore has a low energy density, roughly 0.036 MJ/L,⁴¹ compared to gasoline (34.2 MJ/L).⁴² Currently, NG vehicles use either liquefied or compressed natural gas (LNG or CNG respectively), which use low temperatures (<111 K) or high pressures (>250 bar),⁴² where the energy density is increased up to 22.2 MJ/L. These methods can be costly or impractical due to their engineering constraints, so the U.S. Department of Energy (DoE) is funding research to find materials that can store NG at the same energy densities as CNG using pressures no higher than 65 bar.⁴² Some research has been done to find suitable candidate materials for this application,⁴³⁻⁴⁵ however no material has been found to reach those targets.

1.2 Gas Separation

Industrial scale gas separations use several different processes,⁴⁶ including cryogenic distillation,⁴⁷ kinetic membrane separation,⁴⁸ or adsorbent separation.^{16,49} Although there are merits to the first two processes, in this thesis I will focus on adsorbent separation. An adsorbent separation process is where a gas mixture is passed through an adsorbent, such as a liquid or material, that selectively holds one type of gas, while allowing another to pass freely. For this thesis, the term “gas scrubber” is a blanket term used to describe any chemical or material that through its chemistry, size, or other property can take an entropically favoured mixture and create relatively pure separate streams. In most cases, the gas scrubber would be used to create two streams, a light stream which is made up of gas that freely passed through the gas scrubber, and a heavy stream, which is gas that remains with the scrubber. For example, in the case of PoCCC,

typically N_2 would be allowed to pass freely and is, therefore, the light stream, while the CO_2 is held by the gas scrubber and would be the heavy stream.⁵⁰ It should be noted that the terminology of “heavy” and “light” is not reflective of the mass of the gas, but is based, respectively, on if the gas is held by the gas scrubber or not.

In the context of CCS for power plants, the current gas scrubbing standard, and the one used by the Boundary Dam among other PoCCC plants,²² are liquid amines, typically MonoEthyl Amine (MEA).^{51,52} Flue gas is bubbled through a liquid amine bath in a container known as an absorber, where the CO_2 chemically reacts with the amine, as shown in Figure 1.1.⁵³ The N_2 does not react with the liquid amine and therefore passes through as the light stream. Once the liquid amines are saturated with CO_2 , the process is reversed. The CO_2 -rich amine is pumped into another container known as a stripper. The stripper raises the temperature of the liquid amine to boiling temperatures ($\sim 120^\circ C$),⁵⁴ which reverses the reaction in Figure 1.1. Once the CO_2 is removed from the liquid amine, the amine is pumped back into the absorber to capture more CO_2 . Although this is an effective method to remove CO_2 , as noted by the 90% capture from the Boundary Dam, this is an energetically expensive process, which is estimated to increase the cost of electricity by 300%. The reason why this process is energetically expensive is primarily due to two reasons: 1) the amines are dissolved in water and raising the temperature of the water is costly and 2) the CO_2 is captured by forming covalent bonds which requires much energy to break.

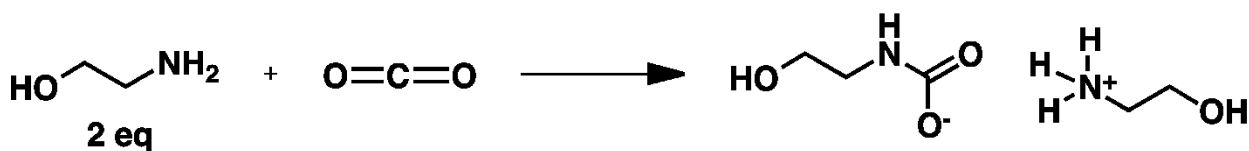


Figure 1.1. The reaction of MonoEthyl Amine with a CO_2 molecule

1.2.1 Solid Sorbent for Gas Separation and Storage

As mentioned, liquid amines are costly due to the need to heat the liquid, as well as the energy needed to break the chemical bonds. Solid sorbents are a class of materials which do not use any liquid and typically have an easy-on, easy-off physical adsorption process. For these reasons, solid sorbents could be cheaper than their liquid sorbent counterparts. In the context of CCS, one prominent class of solid sorbents that are used are known as zeolites. Zeolites are a well-studied class of nano-porous periodic materials made from Si, Al and O. Zeolites are commonly used for the upgrading of mined natural gas.^{55,56} Mined natural gas contains up to 10% by volume of CO_2 ⁵⁷ and needs to be purified to be used as a fuel that contains less than 2% CO_2 .⁵⁸ Zeolites, and Zeolite-

13X in particular, have been used for industrial natural gas upgrading due to their favorable adsorption of CO_2 over CH_4 .⁵⁹ It may seem that zeolites would then be an ideal candidate to use for other CCS purposes, such as PoCCC; however, zeolites have a major problem: their affinity for water. All functional zeolites contain Al atoms which are charge balanced by cations. These cations are what helps give the high CO_2 affinity, but they also have a strong affinity to water. This affinity is even seen in the name zeolite, which translates from Greek to “boiling stone.” This strong water affinity supersedes their CO_2 adsorption capabilities.^{60,61} What this means is that if a gas mixture contained H_2O and CO_2 , the zeolite would preferentially adsorb the H_2O before it adsorbed the CO_2 . For this reason, using zeolites to scrub CO_2 from the combustion of organics, such as fossil fuels, where the other main product is H_2O , is unfeasible. This is because the H_2O will selectively adsorb over CO_2 , or the flue gas would need to be dried before the carbon capture step, increasing the cost of carbon capture. As a result, new solid sorbents need to be found to allow for large scale CCS.

1.2.2 Pressure Swing Adsorption Systems

Pressure swing adsorption (PSA) systems are a gas scrubbing technology that utilizes solid sorbents for gas separation and have been used on an industrial scale since the 1950s to scrub CO_2 from mined NG.⁶² Figure 1.2 shows a picture of a PSA system and a cartoon representation of how PSA systems work. The gas mixture is passed through a packed bed of the solid sorbent. The ideal sorbent then selectively adsorbs only the gas of interest, i.e., CO_2 , while letting the other gas in the mixture pass through. This is represented in Figure 1.2b where the purple gas mixture passes through the packed bed, adsorbing the red gas and allowing the blue gas to pass and exit through the top. Once the packed material in the PSA system is sufficiently saturated, the incoming gas is diverted to another PSA column. The adsorbed gas in the first packed bed is then recovered by applying a vacuum to lower the pressure. This process is shown in Figure 1.2c) where the red gas is pulled by vacuum through the bottom of the PSA system. This process is known as regeneration, as the sorbent material is ideally brought back to the state before any gas adsorption occurred. After the heavy stream is sufficiently removed from the packed bed, the cycle of adsorption and desorption is repeated as needed. A closely related system is a Temperature Swing Adsorption (TSA) system, where instead of decreasing the pressure of the system to remove the gas, the temperature is increased. In this thesis, a focus is placed on PSA systems.

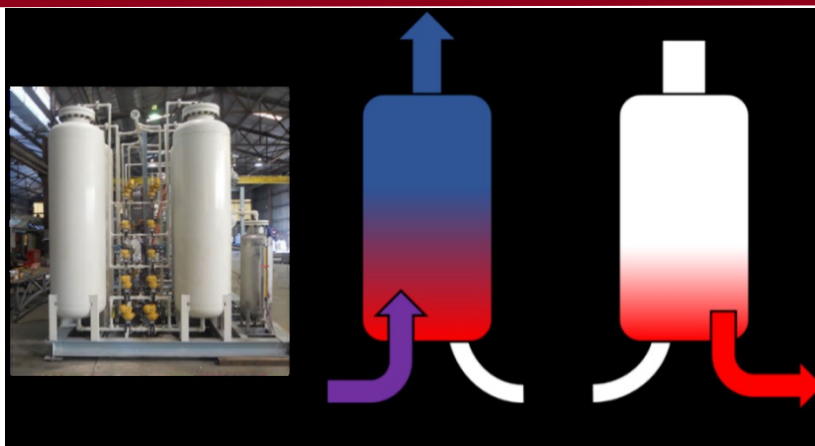


Figure 1.2 Figures showing a) a picture of a PSA system and b) cartoon representation of its adsorption and c) regeneration phase. In b) and c) the purple is a gas mixture, of a blue gas and a red gas.

There are many potential solid sorbents that could be used in a PSA, each with their own advantages and disadvantages. Some potential classes of solid sorbents include zeolites, Metal-Organic Frameworks (MOFs), Porous Polymer Networks (PPNs), or Carbon-Based Materials (CBMs) to name a few. In this thesis, a focus will be placed on MOFs.

1.2.3 Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs) are a class of 3D crystalline materials. Although names such as Zeolitic Imidazolate Frameworks (ZIFs), Porous Coordination Polymers (PCPs), Porous Coordination Networks (PCNs), and Microporous Coordination Polymers (MCPs) all describe the same class of materials, for this work only the term MOF will be used, which is also the terminology adopted by the International Union of Pure and Applied Chemistry.⁶³ As their name implies, MOFs are materials made from a combination of inorganic and organic structural building units (SBUs). As MOFs are combinations of organic and inorganic SBUs, they can be combined in a variety of different combinations allowing for a diverse set of materials, as shown in Figure 1.3. In addition to the SBU combinations, there are 1000s of potential topologies⁶⁴ that the SBUs can combine to form; additionally, MOFs can be functionalized.^{65–67} This gives rise to the hallmark property of MOFs—their ability to be tuned for a desired application. MOFs can be permanently porous with some MOFs having internal surface areas larger than any other known material.^{68–70} These properties allow for unique chemical environments within their pores, allowing MOFs to be studied for a variety of applications including catalysis,^{71,72} gas separation and storage,^{13,73,74} and non-linear optics.^{75,76} MOFs have received so much attention in the past two decades that Prof. Omar Yaghi from the University of California and Prof. Makoto Fujita from the University of

Tokyo received the Wolf Prize for Chemistry in 2018 for their work in pioneering reticular chemistry via MOFs.⁷⁷

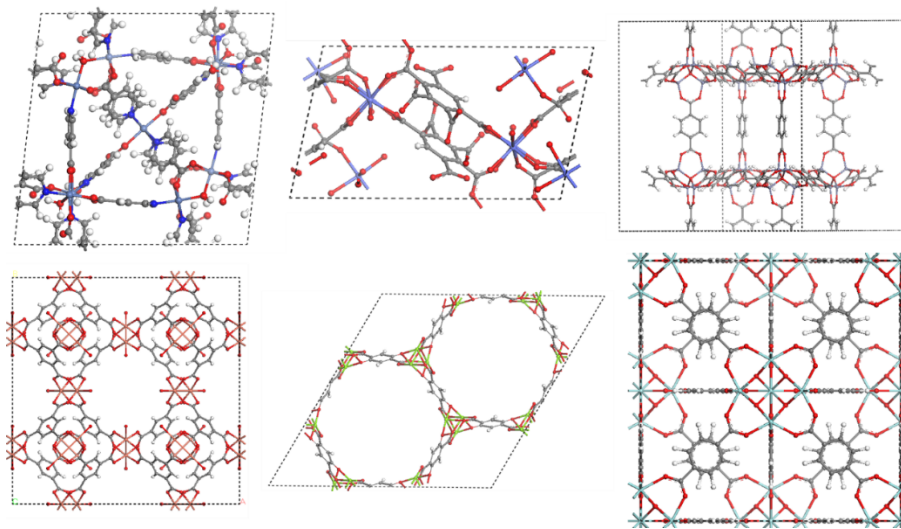


Figure 1.3. Collection of different MOFs showing how they can come in different shapes, sizes, and chemistry.

1.2.4 Carbon-Based Materials

Another potential class of materials that may be useful in gas separation and storage are carbon-based materials (CBMs). CBMs can come in a wide variety of different types such as nanoporous carbons or carbon nanotubes. In this thesis, I will focus on graphene, carbon nanoscrolls (CNSs), and Schwarzites. Graphene is perhaps the simplest CBM, as it is layers of fused aromatic rings. To achieve a functional layering (with enough space to store gas), pillars are needed to hold the layers apart. Some examples of pillars include metal ions or small organic molecules.^{78,79} Graphene is a material which has been studied for a range of applications, including optics,⁸⁰ gas adsorption,⁸¹ and thermal interface.⁸² Carbon nanoscrolls (CNSs) are a class of materials like multi-walled carbon nanotubes. CNSs are formed from a single layer of a carbon-based sheet (e.x. graphene or grapyhne) and rolled into a papyrus shape. Heteroatoms can be introduced into the sheets to create more functional structures.⁸³ The rolled nature of CNSs creates a continuous channel of void space. Like graphene, pillars of different heights can be used to tune the size of the void space which can alter the gas adsorption properties of the CNS. CNSs have shown promise in gas adsorption of H_2 , CO_2 , and CH_4 .^{83–86} The final class of CBMs I will discuss is known as Schwarzites. Schwarzites are a 3D periodic CBM, that can be viewed as the inverse of buckyballs.^{87,88} While buckyballs are made up of 6- and 7-member rings to give them their convex

shapes, Schwarzites are made up of 6- and 5-member rings which gives them their concave nature. It should be noted that although they are believed to exist, to date there has not been any conclusive evidence that they do, even though Density Functional Theory (DFT) predicts that some Schwarzites are more stable than Buckyballs.⁸⁹ They are still of interest to test from a computational standpoint due to the unique environments they provide. As such Schwarzites have already been tested for gas separation and storage processes.^{90–93} A figure of CNSs and Schwarzites is given in Figure 1.4.

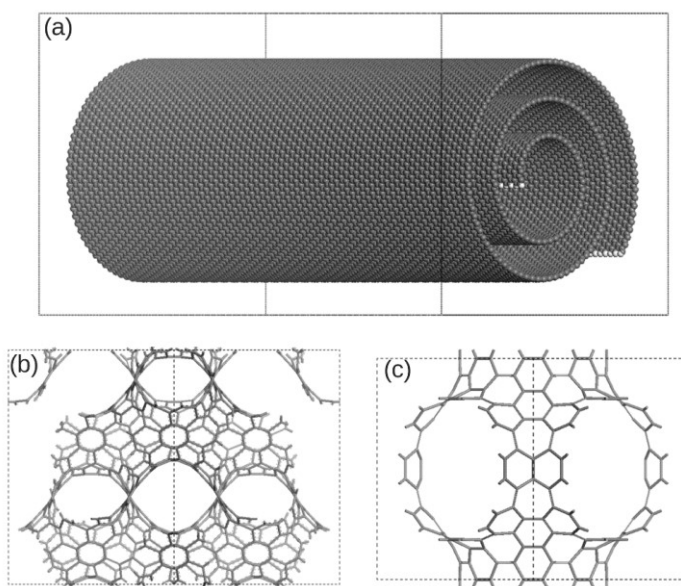


Figure 1.4. a) Image of an idealized graphene-based CNS. The unit cell of the Schwarzite b) C_{168} and c) $P7par$. Copyright 2018, American Chemical Society.⁸⁴

1.3 Gas Adsorbent Criteria

When considering a gas adsorbent, such as a MOF, for use in gas separation and storage, the performance can be described by many different factors. These factors include: 1) the uptake of a guest molecule, 2) the working capacity of a guest molecule, 3) the isosteric heat of adsorption, 4) the selectivity of one guest over another guest, 5) the purity of streams, 6) the parasitic energy, 7) recovery of the heavy stream, and 8) productivity. Each factor is described below in more detail. Other important factors, such as stability or kinetics are also described.

1.3.1 Gas Uptake and Working Capacity

Gas adsorption properties are typically measured from gas adsorption isotherms, an example of which is given in Figure 1.5. To measure a gas adsorption isotherm, or simply an isotherm, a material is exposed to a given partial pressure of a gas at a fixed temperature until the equilibrium

is reached and the amount of gas adsorbed is measured. The adsorption is then measured at various pressures to create what is known as an adsorption isotherm. The amount of gas adsorbed, q , is normalized to the amount of material used and can be given in either gravimetric units (e.g., mmol/g or g/g) or volumetric units (L/L). When reporting the volumetric adsorption, it is customary to report the amount of gas adsorbed in terms of how much volume that gas would take up at standard temperature and pressure (V_{STP}) per unit volume of the material in units of V_{STP}/V . For example, if the volumetric uptake of a gas by material was $35 V_{\text{STP}}/V$, if the adsorbed gas in 1 L of the material were removed and brought to 273.15 K and 1 bar (STP), it would take up 35 L of volume.

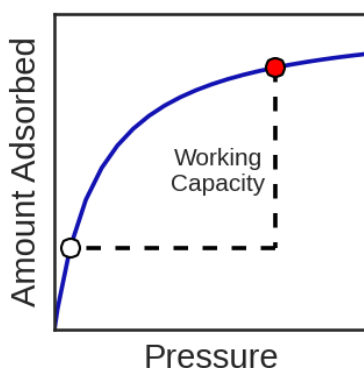


Figure 1.5. Representation of a gas adsorption isotherm. The amount of gas adsorbed at adsorption and desorption conditions are noted by red and white circles respectively. The difference in the amounts adsorbed at those conditions is the working capacity.

A closely related value to the gas adsorption is the working capacity, Δq . The working capacity describes the amount of the guest that can be removed from a material at two different equilibrium conditions. For example, in a PSA unit gas is adsorbed at a high pressure known as “adsorption condition” and the gas is removed by lowering the pressure to the “desorption condition.” The working capacity is the amount of gas that can be removed by the material in one PSA cycle. It is calculated from the isotherm by taking the difference of the amount of gas adsorbed at the adsorption condition and desorption condition as shown in Figure 1.5. In a TSA system, the adsorption and desorption conditions occur at different temperatures, so the working capacity needs two isotherms to be calculated.

It may also be useful in some cases to consider what I term the total working capacity or Δq^T . The total working capacity differs from the working capacity by including the amount of gas removed from the void space due to the packing loss of solid sorbents when placed into a container. This void space would then be filled with the bulk gas phase. In previous MOF-based work, a

value of 25% has been used for the amount of void space and will be the value used for this work.^{44,94,95} To remove the gas molecules the system needs to be placed under vacuum, have its temperature raised, or both. If the pressure of the bulk gas phase decreases, such as in PSA systems, (or temperature increased, like TSA systems), the concentration of the gas molecules in the bulk phase will decrease. This effect would be minimal for most cases except for materials with low volumetric uptakes, or systems with large swings in pressures or temperatures. In a typical PoCCC calculation the adsorption occurs at 313 K of 0.14 bar CO₂ and 0.86 bar N₂ and desorption is at 333 K with 0.0495 bar CO₂ and 0.0005 bar N₂ (explained in Chapter 3). Using those conditions and the ideal gas law, the amount of CO₂ removed from the bulk gas phase is 0.082 V_{STP}/V, while the amount of N₂ is 0.914 V_{STP}/V. To put those numbers in perspective, under the same conditions the typical CO₂ working capacity of a MOF is 20 V_{STP}/V, making the 0.082 V_{STP}/V represent a negligible amount. However, for N₂ the average working capacity is 2.32 V_{STP}/V, making the 0.914 V_{STP}/V from the bulk gas phase important as it is nearly 40% of the adsorbed phase—this shows the impact of accounting for the bulk phase. The adsorbed gas phase results were values from work presented in Chapter 3.

1.3.2 Adsorption Isotherm Models

Gas adsorption isotherms often fit an adsorption isotherm model (AIM) which is a functional representation of the gas adsorption data. This allows the adsorption isotherm data to be reduced to a few parameters, as well as some other benefits discussed later. There are many different AIMs, including Langmuir (equation 1.1),⁹⁶ Freundlich,⁹⁷ Sips (equation 1.2),⁹⁸ and BET,⁹⁹ to name a few. In this thesis, only the Langmuir and Sips AIMs were used and will be discussed in detail. For the Langmuir and Sips AIMs, σ is the amount of gas adsorbed, σ_S is the saturation adsorption capacity, K is the adsorption constant, p is the pressure of the gas. The Sips model contains another parameter, n , the heterogeneity parameter. It should be noted that each model can have multiple adsorption sites, as denoted by the superscript i . Each binding site has its own $\sigma_{S,i}$, K_i , and n_i if applicable, which are summed over to determine the total adsorption. Commonly adsorption models have either 1 or 2 binding sites, although more sites can be considered. Figure 1.6 shows experimental data of CO₂ adsorption from Zeolite-13X by Cavenati *et al.*⁵⁹ that is also fitted to both Dual-Site Langmuir and Dual-Site Sips models.

$$\sigma(p) = \sum_{i=1}^N \frac{\sigma_s^i K^i p}{1 + K^i p} \quad (1.1)$$

$$\sigma(p) = \sum_{i=1}^N \frac{\sigma_s^i K^i p^{n_i}}{1 + K^i p^{n_i}} \quad (1.2)$$

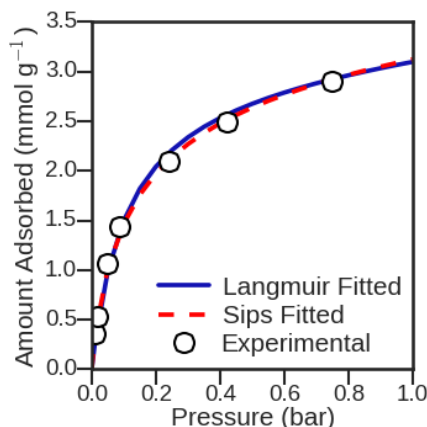


Figure 1.6. Isotherm and the adsorption isotherm models. The white circles are experimental data from Cavenati,⁵⁹ the blue line is the data fitted to a dual-site Langmuir model, and the red dashed line is fit to a dual-site Sips model.

1.3.3 Isosteric Heat of Adsorption

When a guest molecule interacts with a material and adsorbs onto it, a certain amount of energy is released and is quantified as the isosteric heat of adsorption Q_{st} . Q_{st} describes the interaction energy between the guest and the material and is an important quantity for gas separation processes because it gives an estimate of the amount of energy required to reverse the adsorption during regeneration of the material. A material with a large Q_{st} will have a large energetic penalty when trying to remove the guest; however, if the Q_{st} is too low, then it is likely that the guest will not adsorb that well and will suffer from low selectivities (described later). Experimentally the Q_{st} is calculated by measuring isotherms at different temperatures, typically 10 K apart. Each isotherm is then fit to an AIM and calculated using the Clausius-Clapeyron equation, equation 1.3.

$$\ln(p)_N = -\left(\frac{Q_{st}}{R}\right)\frac{1}{T} + C \quad (1.3)$$

Equation 1.3 requires the gas constant (R), temperature (T), and a fitted constant (C). As noted on the left side of equation 1.3 the isosteric heat of adsorption is calculated using a constant guest loading, N . An interesting point for the Q_{st} is the zero-coverage isosteric heat of adsorption, or Q_{st}^0 ,

which is the Q_{st} as the value N tends to 0. This value shows the strength of the interaction between the guest molecules and the material without the interference of other guest molecules.

1.3.4 Selectivity

Up until now, all the adsorption properties discussed can be applied to the adsorption of a single guest. However, gas separation involves mixtures of gases. In an ideal case, an adsorbent would only adsorb a single gas, while the other gases would pass through the adsorbent. However, this is not the case as most guests adsorb to some degree onto an adsorbent. This gives rise to another important gas adsorption property, known as the selectivity. The selectivity describes how readily an adsorbent uptakes one gas compared to another gas. To calculate the selectivity (S_{ij}), the gas adsorption of a gas type i (q_i), is divided by the gas adsorption of the other species. Each adsorption is normalized by the partial pressure of the gas type (p_i), as shown in equation 1.4. Selectivities are typically reported at the adsorption conditions.

$$S_{ij} = q_i/p_i / q_j/p_j \quad (1.4)$$

Current experimental gas adsorption measurement techniques make the direct calculation of the selectivity difficult. This is because gas adsorption measurements typically can only measure the total amount of gas adsorbed. Most instruments cannot determine how much one gas was adsorbed compared to others in the mixture. Therefore, the selectivity is typically calculated using single-component isotherms where a mixing theory is used to estimate the amount of gas adsorbed when in the presence of other gases. With a single guest, all binding sites are free for the same guest to bind, although when there are two or more guests adsorbing simultaneously, one guest might have a stronger affinity for the binding site. This causes lower adsorption for each guest compared to the same partial pressures in single component adsorption. The effect of competition is not the same for each guest type, therefore affecting the selectivity. To determine the amount adsorbed of each guest from a mixture, the most commonly used theory in literature is Ideal Adsorption Solution Theory (IAST), although other methods such as the Competitive Isotherm Model (CIM) are also reported.

1.3.5 Competitive Isotherm Model

The CIM is one of the simplest methods to consider competitive effects. For CIM, first gas adsorption data of all the relevant guests are fit to AImS. For CIM, equation 1.5 is used to calculate

the gas adsorption of guest j at a partial pressure of p_j in the presence of other gases. The competitive binding nature of gases is accounted for by having the relevant binding sites of the other gases added to the denominator of the gases' binding site. When using a dual site model, the choice of which binding sites from one guest interact with the binding site of a different guest is not a definitive process. For example, Huck *et al.* chose to have the weaker binding site (based on the adsorption constant K) of CO_2 interact with the N_2 ,¹⁴ while Faruque *et al.* chose to allow all binding sites from one gas interact with each binding site of the other gas.¹⁰⁰ Another possible scheme is done by Ritter *et al.* was a method where the stronger binding sites (based on experimentally derived heats of adsorption) of each gas interacted with each other, while the weaker sites interacted with each other.¹⁰¹ The choice can have a large impact on the results and should be chosen with care.

$$\sigma_j(p_j) = \sum_{i=1}^N \frac{\sigma_{sat}^i BS^j}{1 + \sum_{k=1}^M BS^k} \quad (1.5)$$

$$BS^k = \begin{cases} K_j^i p_j & \text{if Langmuir AIM} \\ K_j^i p_j^{n_j} & \text{if Sips AIM} \end{cases} \quad (1.6)$$

1.3.6 Ideal Adsorption Solution Theory

The CIM is a simplistic model for calculating the adsorption of gas mixtures, and because of that other models have appeared and are more commonly reported. The current gold standard for calculating the loading of gas mixtures is IAST.¹⁰² IAST is similar to CIM, where first the guest adsorption data is fit to AIMs. After that, IAST works by equating the spreading pressure, Π_j , of all guest types.^{102,103} The spreading pressure is the tendency of the gas to adsorb onto the framework and can be calculated using equation 1.7. To equate the spreading pressures, the gas concentration of a species in the single component, c_j^0 , is modified for each gas, j , until the difference between all guests is minimized. c_j^0 can be expressed in terms of the species concentration of the multi-component mixture, c_j , as shown in equation 1.8 and needs the value z_j . z_j , equation 1.9, is the fraction of adsorbed phase species of j , q_j . Using these equations, IAST is solved in an iterative manner to determine the fractions of adsorbed phase species. To determine the total loading, and therefore the loading of each species, equation 1.10 is used.

$$\Pi_j = \int_0^{c_j^0} \frac{\sigma_j(c_j)}{c_j} \delta p \quad (1.7)$$

$$c_j^0 = \frac{c_j}{z_j} \quad (1.8)$$

$$z_j = \frac{q_j}{\sum q_j} \quad (1.9)$$

$$\frac{1}{\sum q_j} = \sum \frac{z_j}{\sigma_j(c_j^0)} \quad (1.10)$$

Although IAST can be considered an improvement over the CIM, it does have some issues to consider.^{104–106} As noted by its name, it works best for ideal solutions, meaning that if you go outside the range of ideal gases, it becomes less effective. This means that in high pressures and low temperatures it becomes less reliable. In addition, if the guest molecules are significantly heterogeneous (e.g., CO₂ and H₂), then IAST is known to give unreliable results.

1.3.7 Purity

During the PSA process, an ideal material would selectively adsorb one gas type over all others. After the adsorption process is finished, the system is placed under desorption conditions (i.e., under vacuum in PSA unit), where the adsorbed guest molecules are removed. The purity of the resulting gas streams is critical for most applications. For example, in the case of PoCCC, the gas needs to be compressed to 150 bars for transport.^{16,19,100,107} If the stream is not pure, then energy is spent compressing gas that is not the target gas, which will be explained in more detail in the next section. In addition to the cost associated with compression, there is also a requirement for the highly pure stream so the interactions when placed underground will be known. For these reasons, the US DoE has set a target of 95% purity for CO₂.¹⁰⁷ The purity of the stream can be roughly calculated by looking at the amount of each guest type removed during the desorption process, which would be the working capacity of each guest type. In that case, the purity of the product stream is calculated using equation 1.11.

$$P_i = \frac{\Delta q_i}{\sum_j \Delta q_j} \quad (1.11)$$

In equation 1.11, P_i is the purity of guest i , and requires the working capacity Δq_j of each guest j . The purity would be more accurate if it was calculated using the total working capacity Δq^T , discussed in section 1.3.1. More accurate estimates of purity are achieved when performing full process simulations at the macroscopic level.¹⁰⁸

1.3.8 Energetic Cost of Separation

During a gas separation process, energy needs to be spent to place a system under vacuum, raise the temperature, or compress a gas stream. The energetic cost of these processes is one of the key factors in determining if a material is viable for gas separation. In the case of PoCCC, the energetic cost is known as the parasitic energy (PE) and has been estimated to roughly cost 30% of the energy produced from coal-burning power plants.¹⁰⁷ There are two ways to calculate the PE: 1) an easy to calculate equilibrium model and 2) from sophisticated dynamic process simulation models. Although the equilibrium model gives a rough estimate of the PE, it is simple to calculate, requiring only a few gas adsorption properties. Process simulations are computationally expensive as they perform macroscale simulations of a PSA system. For this thesis, I place a focus on the equilibrium PE as it is more commonly used by chemists,^{14,16,49} while chemical and process engineers use the process simulation version.^{107,109}

The equilibrium PE was originally developed by Rochelle and co-workers who gave an estimate of how to calculate the PE for liquid amine systems,⁴⁹ which Smit and co-workers applied to solid sorbents.¹⁶ This PE (equation 1.12) is a physically motivated figure of merit (FoM) that combines three terms: 1) the thermal energy needed to raise the temperature and break guest framework interactions (Q_{therm}), 2) the work needed to place the system under vacuum if needed (W_{vac}), and 3) the work needed to pressurize the heavy stream for transport and storage conditions (W_{Pres}). The work terms are powered fully by electricity to power the vacuums and compressors; however, heating the material and breaking guest-host frameworks can be done using low-grade steam, if available. Low-grade steam is steam that is below a temperature and cannot be used in turbines. If the steam is redirected to the capture system, it can be used to reduce the energetic cost. To account for this, the Q_{therm} is multiplied by 0.75 (typical efficiency of a gas turbine) and η (Carnot efficiency).⁴⁹ This is standard practice for the PE and how it has been calculated in previous work.^{13,14,16,49} In this work, the Carnot efficiency is calculated using equation 1.13 which was used by both Freeman and Huck where T_h is the desorption temperature, and T_c was set to 283 K.^{14,49}

$$PE = 0.75\eta Q_{therm} + W_{vac} + W_{Pres} \quad (1.12)$$

$$\eta = \frac{T_h + 10 - T_c}{T_h + 10} \quad (1.13)$$

Q_{therm} is associated with the energy needed to heat the system to the desorption temperature as well as to break the interactions between the guest molecules and the framework. This is shown in

equation 1.14. Q_{therm} requires the change in temperature between adsorption and desorption conditions (ΔT), the specific heat capacity of the sorbet (C_{sorb}), the heat of adsorption of each guest i (Δh_i), the difference in the adsorbed phase at adsorption and desorption of each guest i (Δq_i^a), and the difference in the total CO₂ at the adsorption and desorption conditions ($\Delta q_{CO_2}^T$). As mentioned in section 1.3.1, $\Delta q_{CO_2}^T$ differs from $\Delta q_{CO_2}^a$ by accounting for the gas in the void space of the container caused by packing losses, which for this work we assume to be 25%, the same as in work by Huck and others.^{14,44,95} To convert the void volume of the system into an amount of gas, the ideal gas law was used due to the mild condition (313-333K and 0.01-1 bar) for PoCCC. The first term in the numerator of equation 1.14 is the heat capacity of the framework and describes the energy necessary to raise the temperature of the adsorbent. If C_{sorb} was not readily available for a sorbent, an average value of 0.985 kJ/kg K was used. This value was chosen to keep in line with the work by Huck,¹⁴ and is based on work done by Mu *et al.* where they studied the heat capacities of 9 MOFs, and 0.985 kJ/kg K was found as the central value.¹¹⁰ In the work done by Huck, they did a sensitivity analysis of PE with respect to the heat capacity and found for low PE structures that a difference in the heat capacity had a minimal impact. The second term in the numerator is a summation over all gas types in the system. This term describes the energy necessary to break the interactions between the gas molecules and the framework.

$$Q_{therm} = \frac{\Delta T C_{sorb} + \sum_i^n \Delta h_i \Delta q_i^a}{\Delta q_{CO_2}^T} \quad (1.14)$$

W_{vac} is the term necessary to place the system under vacuum if needed, and the calculation is shown in equation 1.15. W_{vac} needs the gas constant (R), desorption temperature (T_d), the efficiency of a vacuum (η_{vac}), purity of the heavy stream (P), and the pressure at adsorption and desorption condition (p_a and p_d respectively). In this work, the vacuum efficiency was given to us by engineering collaborators as 74%. The purity of the heavy stream is the amount of CO₂ as a fraction of all the gas in the stream and was calculated by equation 1.11. Whenever possible, the purity used the total working capacities, Δq_i^T , of the gas i .

$$W_{vac} = \frac{RT_d}{\eta_{vac}P} \ln \left(\frac{p_a}{p_d} \right) \quad (1.15)$$

The final term needed for the PE is the W_{Pres} term (equation 1.16), which described the energy needed to compress the heavy stream to transport and storage conditions. S stands for the number of compression cycles that needs to happen (calculated using equation 1.17), γ stands for the adiabatic coefficient (C_p/C_v , typically 1.4) and Y (equation 1.18) is the compression ratio per cycle.

For the pump portion of equation 1.16 (e.x. the last term), Δp is the difference in pressure between the storage pressure (typically 150 bar)^{16,19,100,107} and when the CO₂ becomes supercritical, and ρ is the density of the supercritical mixture. P_{high} is the pressure when the mixture becomes supercritical, which for this work was set to 80.0 bar, and r_i is the maximum compression ratio achieved per stage, which has a maximum of 3. The value of 80.0 bar was chosen per a 2011 European Commission report which showed the pressurization of CO₂ using a compressor up to 80 bar, and then switching to a pump to further pressurize to 150 bar.¹¹¹ In this work we used a compression ratio of 2.5 as this gave the best energetics. It should also be noted that the density was calculated for a variety of molar CO₂/N₂ compositions at 80 and 150 bar using data from NIST, where the average value of the densities of both pressures then fit a quadratic equation. The η_{comp} to 85% and the η_{pump} to 75%, which once again are values given to us by our experimental collaborators.

$$W_{pres} = \frac{1}{P} \left(S \left(\frac{RT}{\eta_{comp}} \left(\frac{\gamma}{\gamma - 1} \right) \left(Y^{\frac{\gamma-1}{\gamma}} - 1 \right) \right) + \frac{\Delta p}{\eta_{pump} \rho} \right) \quad (1.16)$$

$$S = \frac{\ln \left(\frac{p_{high}}{p_d} \right)}{r_i} \quad (1.17)$$

$$Y = \left(\frac{p_{high}}{p_d} \right)^{\frac{1}{S}} \quad (1.18)$$

The same process for calculating the PE could also be applied to the energy required for LGS; however, the equations need to be modified. A detailed analysis of how to make changes and why they were made are given in Chapter 3..

1.3.9 Recovery and Productivity

The last two gas adsorption-based terms I will discuss are the recovery and productivity. These are terms not often discussed from the chemists' view for gas separation, although they are important values at the process level and for estimating capital costs of PoCCC.^{107,109,112} The reason for this is that advanced process scale simulations are required to obtain accurate estimates for these quantities.¹¹³

The recovery is a term to describe the amount of gas, CO₂ in the case of PoCCC, that is removed from the gas stream. For example, if 100 kg of CO₂ entered a PSA system, and only 90 kgs of the CO₂ was captured, with the other 10 kg being emitted, that would be a recovery of 90%. Although

it appears recovering 100% is the best choice, as all GHG emission would be removed, it needs to be balanced out with other considerations. For example, lowering the recovery rate creates a lower energetic cost. This is simply illustrated with the example where for PoCCC, where if only half the flue gas is scrubbed, it would only cost half the energy as if all the flue gas is scrubbed, while only recovering 50% CO₂ at most. Secondly, it has been shown that there is an antagonistic relationship between purity and recovery in PSA systems.^{109,112,113} This trade-off is a result of how gas scrubbers work in PSA systems. In the case of PoCCC, a gas mixture of CO₂ and N₂ are passed through a gas scrubber, where the N₂ freely passes while CO₂ is adsorbed. This creates a situation where the gas front of the N₂ moves ahead of the CO₂, creating an N₂ rich region and a CO₂ rich region, similar to what is shown in Figure 1.2b), if the CO₂ is the red gas and the N₂ is the blue gas. If the vacuum of the regeneration phase was applied immediately after the adsorption phase, the recovery would be 100%, N₂ gas would also be removed, causing the purity to decrease, and thereby increasing the energetic cost.^{107,109} What is done is practice after the adsorption, but before the desorption, a vacuum is applied from the top of the PSA system, with the intention of removing N₂ from the system, along with some CO₂. For CO₂ scrubbing of flue gas, the US DoE has set a target recovery of 90% of CO₂.¹¹⁴

The productivity is a term which describes the amount of gas that can be removed from a gas mixture as a function of time. A typical unit of productivity is mol / m³s, where the mol is the amount of the mols of heavy stream gas stream captured, m³ is the volume of gas scrubber used, and s is the length of time the entire PSA cycle took. During a PSA cycle, each step (such as adsorption, blowdown, evacuation, etc.) all take an amount of time. Like any process, it would be ideal if they took as little amount of time as possible. A short time span could have negative impacts, though. For instance, if the adsorption phase was short, then the gas scrubber may not become as saturated with the heavy stream as possible. Another example is if the evacuation step was cut short, not as much heavy stream gas would be removed from the system. For power plants, the number of moles of CO₂ per second that are made (mol/s), and can be processed, is relatively constant, so the productivity is a way to describe the amount of material needed for a separation process. Low productivity means that a large amount of volume of material is needed to filter out as much heavy stream as a material with a large productivity value. With all other things being the same, a larger amount of necessary scrubber relates to higher capital costs, in terms of money required to buy the material as well as the necessary infrastructure (PSA systems, pipes, space).

The productivity could be improved by using stronger vacuums and running them for shorter periods of time, although this can have the impact of increasing the energetic cost. Haghighpanah^{109,113} and Rajagopalan¹¹² both found consistent trade-offs between the productivity and PE when trying to optimize both values by use of changing the process parameters.

1.4 Overview and Goals

In this thesis, I look to develop computational tools to aid in the screening of materials for gas separation and storage to provide both further understandings of the systems and to accelerate the discovery process. More specifically, I will explore the development of tools associated with high throughput screening. These tools will include the development of genetic algorithms (GAs)^{115–117} for multiple applications, including materials discovery and parametrization. Another goal of this work is to apply these tools to study specific gas separation and storage applications of current technological interest such as post-combustion carbon capture, vehicular methane storage, and landfill gas separation. In summary, the work in this thesis addresses the need for more rapid screening of MOFs, to determine the ideal candidate for gas separation or storage applications. Finally, I try to find trends or apply machine learning to the results to find any relationships between the results and common metrics. These results could lead to advances in solid sorbent material commercialization, allowing them to be employed to aid in greenhouse gas emissions reduction.

1.5 Summary of Chapters

The contents of the thesis are described briefly herein. In Chapter 2, I present a detailed description of the computational methods used in this thesis. Some of the computational methods discussed include Grand Canonical Monte Carlo (GCMC) simulations, the charge equilibrium (QEq) and split charge equilibrium (SQE) methods, and Genetic Algorithms (GAs).

In Chapter 3, I present my work on screening the Computation-Ready Experimental (CoRE) MOF database for three gas separation and storage applications. Some of the work presented in this chapter has been worked into a manuscript for publication. The CoRE database contained approximately 5000 experimentally realized structures, which I filtered and calculated through DFT derived REPEAT¹¹⁸ partial atomic charges, creating a dataset of 3468 MOFs. I highlight the results when using MOFs from the CoRE database for VMS, PoCCC, and LGS. Although no CoRE MOF was found to meet the DoE deliverable capacity target,⁴² we noted some structures

that had the highest deliverable capacity noted for any MOF. When looking at PoCCC, it was found that using the energetic cost as a metric, 68 CoRE MOFs were found to outperform the benchmark material, Mg-MOF-74. When studying for LGS, over 2100 structures were found to outperform the current standard of Zeolite-13X.

In Chapter 4, I present my work looking at the gas separation and storage properties of carbon nanoscrolls (CNSs) and other carbon-based materials. This work was done in collaboration with the Skaf and Galvão groups from the University of Campinas. The CNSs were optimized by altering geometric properties such as the space between adjacent layers and length of the scroll. We found that when optimized, CNSs had remarkable CO₂ and CH₄ adsorption, making them suitable for either PoCCC or VMS. For PoCCC, CNSs were able to outperform the benchmark materials of Mg-MOF-74 and Zeolite-13X in terms of CO₂ uptake capacity (8.2 mmol/g) and CO₂ selectivity over N₂ (153). For VMS, CNS and LGs were found to give the highest known CH₄ deliverable capacity of any material. With optimized materials, the deliverable capacities reached 252 and 266 V_{STP}/V for CNS and LG respectively. The work in this chapter consists of two papers: the PoCCC work was published in *Carbon*,⁸³ while the VMS work was published in the *Journal of Physical Chemistry C*.⁸⁴

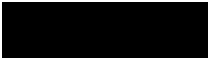
In Chapter 5, I present my work on parameterizing split-charge equilibration (SQE) method for use in porous materials. SQE is a method for rapid determination of partial atomic charges and is an extension of the more commonly used charge equilibration method (QEq). As we wanted as robust of parameters as possible, the SQE parameters (SQ-MEPO) were trained using a GA on a diverse set of MOFs⁶⁴ and porous polymer networks to directly reproduce the *ab initio* electrostatic potential (ESP). Although there has been previous work in developing partial atomic charges in materials,^{119–122} to the best of our knowledge this is the first time SQE has been applied to periodic porous materials. The parameters were shown to give the most accurate electrostatic potential and CO₂ adsorption properties of the tested parameterized methods. This work was published in the *Journal of Physical Chemistry C*.¹²³

In Chapter 6, I present my work on optimizing the PE of MOFs for PoCCC. The PE is a holistic FoM meant to estimate the cost of regenerating a gas scrubber. We alter the desorption conditions of MOFs in order to minimize the PE. Our collaborators in the Ramanathan group from the Indian Institute of Science Education and Research (IISER), Pune, synthesized a MOF, **IISERP-MOF2**,

which had the lowest PE of over 40 experimentally tested MOFs, at 823.4 kJ/kg CO₂. This work was published in the *Journal of the American Chemical Society*.¹³ I expanded the search by optimizing the parasitic energies of the CoRE database by altering the desorption conditions. It was found that no MOF could outperform **IISERP-MOF2**, with the lowest PE coming close with a value of 833.2 kJ/kg CO₂, although 144 structures did outperform the benchmark MOF, Mg-MOF-74. Finally, I functionalized select CoRE MOFs and optimized each of their desorption conditions to find the lowest PE. From these MOFs, the lowest PE was found to be 749 kJ/kg CO₂, and we found a total of 10 that outperform **IISERP-MOF2**. The functional groups were also studied, and high and low-performing functional groups were identified in terms of their impact on the PE.

In Chapter 7, I present my work on developing and using Metal-Organic Framework Functionalization GA (MOFF-GA). MOFF-GA is a machine learning program that can determine the ideal functional groups of a MOF for a given property. MOFF-GA used a small group of 28 functional groups and optimized the hydrogen atoms on the organic SBUs of a MOF. MOFF-GA was optimized to not only determine the best structure for a property but also to find it while testing as few structures as possible and finding many high performers. I used MOFF-GA to optimize 141 experimentally realized MOFs for their CO₂ uptake and PE, as well as their gravimetric surface area. After optimization, on average the CO₂ uptake increased by 340%. This work was published in *Science Advances*.¹²⁴

In Chapter 8, I present my work on optimizing the process conditions of a PSA system for PoCCC. This work was done in collaboration with the Rajendran group of the University of Alberta. Using sophisticated PSA simulations, they developed, the process conditions of the PSA system were studied for 1180 structures. Of those 1180 structures, 211 were further optimized using an in-house developed GA to optimize the four process properties: the purity, recovery, productivity, and PE. 202 of those structures were able to create streams that were at least 95% CO₂ with 90% of the CO₂ from inlet gas. From this work, it was found that **IISERP-MOF2** was the best MOF to use in a PSA system based on these simulations. Machine learning, in the form of Random Forests, was done to see if some steps could be skipped. Even when using a total of 90 descriptors, 11 trees in the forest, and tree depths of up to 10 levels, no suitable model was found. This demonstrates that PSA simulations need to be performed to get an accurate understanding of



a material's performance in a PSA system. Part of this work has been used for a manuscript for publication.

Finally, in Chapter 9, I provide general conclusions for each chapter, as well as discussing future directions.

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2 Computational Tools for Studying Gas Adsorption in MOFs

As computational resources have grown, the use of computational tools to aid chemists has become more commonplace. Computational chemistry could be used for a wide range of applications such as predicting catalytic activity,¹⁻³ ice recrystallization inhibition,⁴ and gas adsorption properties.⁵⁻⁸ The primary tool used in this work, and commonly used in gas adsorption predictions, is Grand Canonical Monte Carlo (GCMC) simulations.⁹⁻¹¹ GCMC is an atomistic simulation method grounded in statistical mechanics that can predict macro-scale properties, such as gas adsorption isotherms. The theory and implementation of GCMC simulations are detailed in 2.1.

One of the primary bottlenecks in terms of computation cost for the study of gas adsorption in MOFs is the calculation of the partial atomic charges.¹² Unlike parameters that account for the dispersion interactions of atoms in simulations which are typically robust and relatively transferable, partial atomic charges, which are used to determine electrostatic interactions, are typically system specific. For example, work by Torrisi *et al.* showed changing functional groups on the organic linkers of MIL-53 could cause the partial atomic charge on an Al atom to change up to 10%.¹³ There are two major ways to calculate charges: 1) directly fitting to Quantum Mechanical (QM) derived Electrostatic Potentials (ESPs), such as with REPEAT¹⁴ or DDEC^{15,16} charges or 2) using parameterized methods, such as Charge Equilibration (QEq)¹⁷ or Split Charge Equilibration (SQE).¹⁸ Details on these charge calculation methods are given in Section 2.2.

Another computational tool used in this thesis is a global search algorithm known as a Genetic Algorithm (GA).^{19,20} As in Darwinian evolution, GAs work under the assumption that there are characteristics of individuals that allow it to perform better (i.e., survival of the fittest). GAs have been used on many types of problems before, such as finding solutions to math problems, parameterizing computational methods,^{21,22} and even materials discovery problems.²³⁻²⁵ To find the optimal solutions, GAs utilize a user-defined fitness function to find the optimal solution to a problem through repetitive cycles of taking a small subset of candidate solutions (CSs) and then testing, ranking, and mating to create an even higher performing subset of individuals. After convergence criteria have been met, the GA is considered converged and stops. All these routines are explained in detail in section 2.3.

2.1 Grand Canonical Monte Carlo Simulations

Grand Canonical Monte Carlo (GCMC) simulations are a widely used method to study the gas adsorption properties of materials.^{24,26–28} GCMC calculations have been found to determine gas adsorption at a given temperature and pressure accurately. As the name implies, GCMC simulation samples a Grand Canonical ensemble (where the chemical potential, temperature, and system volume are fixed, while the number of particles can change) in a Monte Carlo sampling regime. The GC ensemble is then used as it best represents the physical gas adsorption process, where a material adsorbs the gas from a gas reservoir at a given pressure, that reaches equilibrium when the chemical potential of the adsorbed gas is equal to gas in the reservoir. The chemical potential of the gas reservoir is a function of its temperature, T , and pressure p , as shown in equation 2.1.²⁹ In that equation, μ_{gas}^0 is the chemical potential of the gas in a given standard state, R is the gas constant, f^0 is the fugacity of the gas in the standard state, and f is the fugacity of the gas reservoir. The fugacity of the gas can be calculated from the temperature and pressure of a system and any equation of state, such as the Peng-Robinson equation.³⁰

$$\mu_{gas}(T, p) = \mu_{gas}^0 + RT \ln \left(\frac{f}{f^0} \right) \quad (2.1)$$

A Monte Carlo (MC) method is an algorithm that uses random numbers. In molecular simulations, the MC method typically refers to a Metropolis MC, where low-energy configuration states are preferentially sampled, causing them to contribute more frequently to the expectation values, while high-energy configurations have no significant contribution. A Boltzmann distribution of configurations needs to be generated and tested to calculate the expectation values shown in equation 2.2 to give an ensemble average. In this equation, N_{config} is the number of configurations tested, and M is the property associated with each sample i . This sampling method makes for a more efficient method than pure MC methods.

$$\langle M \rangle = \frac{1}{N_{config}} \sum_i^{N_{config}} M \quad (2.2)$$

The steps of how a Metropolis MC method with a single gas molecule A interacts with a framework in a canonical ensemble are given as follows:

1. A guest molecule A is randomly placed inside the framework
2. The potential energy of the system is evaluated, U_{old}

3. Molecule A is perturbed in a randomly chosen way, such as translation or rotation
4. The potential energy of the system is re-evaluated, U_{new}
5. If U_{new} is lower than U_{old} the new configuration is automatically accepted. If U_{new} is higher than U_{old} than the new configuration is accepted based on the acceptance probability (ACC) (equation 2.3) based on the Boltzmann factor. In equation 2.3, ΔU , $U_{new} - U_{old}$, is the change in the potential energies, and kT is thermal energy in the system calculated from the Boltzmann constant, k . A random number between 0-1 is generated, and if the number is lower than ACC , the configuration is accepted.

$$ACC = e^{-\frac{\Delta U}{kT}} \quad (2.3)$$

6. If the new configuration is accepted, it is added to the ensemble average, and this new configuration is used as the starting configuration. ($U_{old} = U_{new}$)
7. If the new configuration is rejected, the old configuration is re-added to the ensemble average, and the old configuration is used as the starting configuration ($U_{old} = U_{old}$)
8. Steps 3 through 7 are repeated until end criteria, such as a set number of steps, are reached.

When a Metropolis MC is used with a GC scheme, two additional moves are included, insertion and deletion, which model the physical process of gas molecules entering or leaving the material. These moves would be able to be selected at step 3 in the above methodology and would be chosen at a user defined probability. The acceptance criteria are different and given in equations 2.4 and 2.5 for insertion and deletion, respectively. In these cases, the energy difference is scaled by a factor which accounts for the total volume of the system, V , pressure, p , Boltzmann constant, k , temperature, T , and the number of guests in the system, N .

$$ACC = \frac{Vp}{kT(N+1)} e^{-\frac{\Delta U}{kT}} \quad (2.4)$$

$$ACC = \frac{N}{kT(Vp)} e^{-\frac{\Delta U}{kT}} \quad (2.5)$$

Following the steps listed above and using equations 2.3-2.5 ensures random sampling of the system, while preferentially sampling more energetically favorable states. Despite these sampling techniques, due to the random nature of MC, to obtain a well-converged averaged thermodynamic property, such as the number of guests in the system, typical GCMC simulations require 10^7 MC moves. This number of steps makes high-level energy calculations, such as *ab initio* methods, unfeasible, which means that empirical methods such as force fields need to be used instead (these

are discussed later). In addition to using force fields, two other approximations are made to speed up the calculations: 1) the MOF framework is frozen, and the guest atoms are considered rigid and 2) simple forms of intermolecular potentials are used. Even when placing these constraints, GCMC simulations have been found to predict gas adsorption properties accurately.^{11,31,32} Additionally, if the parameters are available, the simulation of a gas adsorption isotherm typically takes less than an hour to complete on a high-end PC.

As mentioned, the framework atomic positions are fixed, and all guest molecules are treated as rigid. This has the disadvantage that we cannot treat some materials that are flexible/breathing or that have flexible substituents within the organic SBUs.^{33–35} One also cannot simulate guest molecules that are large and flexible, such as long chain hydrocarbons. The simplicity of our force field also prevents us from simulating gas adsorption involving chemisorption, such as those often observed in MOFs that have open-metal sites. There are programs that are tailored for flexible frameworks or chemisorption, although they typically require more computational resources or highly specialized force fields. In this thesis, an in-house GCMC program based upon the open source molecular dynamics code DL_POLY^{36,37} and written by a previous member of the Woolab, Peter Boyd, was used.³⁸

2.1.1 Periodic Boundary Conditions

When modeling an infinitely periodic system, such as MOFs, a computational technique known as Periodic Boundary Conditions (PBCs) are used. PBCs are a way to reduce the infinitely periodic system into a finite set of transitionally invariant set of atoms, known as the “unit-cell.” Since the unit-cell is a reduction of the material, PBCs are used to simulate the infinitely periodic nature. PBCs create copies of the unit-cell which are known as “image-cells.” These image cells are put in place to surround the unit-cell and are used to calculate all necessary interactions. The information is only stored for the atoms within the unit-cell and not for those in the image-cell. For some calculations, the size of the unit-cell is too small, and therefore a collection of the unit-cell and its neighbouring image-cells are used, which is known as a “super-cell.”

In the GCMC simulations used for this thesis, the difference in energies between two configurations are due to the van der Waals and electrostatic interactions. Both interactions can be estimated using energy potentials. There are many potentials that can be used for the dispersion interactions, such as the Buckingham potential,³⁹ or the Born-Huggins-Meyer potential;⁴⁰

however, in this work the Lennard-Jones (LJ) 12-6 potential (equation 2.6) was used.⁴¹ The LJ potential is one of the most widely used potentials in GCMC simulations and is discussed in detail later in Section 2.1.2. For the electrostatic interactions, the Coulomb potential (equation 2.7) is used. The Coulomb potential is calculated between two charges, q_i and q_j , at a distance r_{ij} . For the Coulomb potential, when looking at materials, the periodic images are accounted for by looking at all periodic image cells, n , which are cell a length, L , away. As mentioned in the previous section the dispersion interactions are short-range interactions, and the Coulomb interactions are long-range. This is seen as the LJ potential decays at a rate of r^{-6} while the Coulomb potential decays at the slower rate of r^{-1} . This means that to account for all relevant Coulomb interactions, more interactions need to be calculated (by using larger values of n), requiring large amounts of computational time. To get around this issue, the Ewald summations (discussed in section 2.1.3) are used. The Ewald summation works by calculating close interactions in real space and then calculating the remaining interactions in reciprocal space.

$$E_{LJ}(i, j) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) \quad (2.6)$$

$$E_{coul}(i, j) = \frac{1}{4\pi\epsilon_0} \sum_n \sum_{i>j}^N \sum_j^N \frac{q_i q_j}{|r_{ij} + nL|} \quad (2.7)$$

The second issue when performing calculations on periodic systems arises from the image cells. As mentioned, the energies can be calculated through the PBCs. This, however, can create some artifacts for the guest molecules in the system. For example, if a guest molecule is placed in a unit-cell and interacts with its own image in an image-cell, that would introduce errors in the simulation. This is primarily an issue with the van der Waals interactions, and therefore the LJ potential is only calculated for atomic pairs within a distance cut-off, typically 12-14 Å. If the unit-cell is too small for the cut-off, a super-cell is created such that an atom and its images are at least the cut-off distance apart.

2.1.2 Lennard-Jones Potential

In our GCMC code, we calculate the dispersion interactions between atoms using the Lennard-Jones 12-6 potential, or the LJ potential.⁴² The LJ potential (equation 2.6) calculates the dispersion energy of two atoms, i and j , with an interatomic distance r_{ij} , which calculates a repulsive (r^{-12}) and attractive ($-r^{-6}$) term. The potential uses two parameters, the distance scalar, σ_{ij} , and the

potential well, ε_{ij} . When the interatomic distance is the same as the distance scalar, the repulsive and attractive term cancel out, and the potential becomes 0. When the interatomic distance is $2^{1/6}\sigma_{ij}$, the potential reaches its minimum, which is the well depth ε_{ij} . Figure 2.1 shows the LJ potential using various combinations of σ_{ij} and ε_{ij} to show their effects.

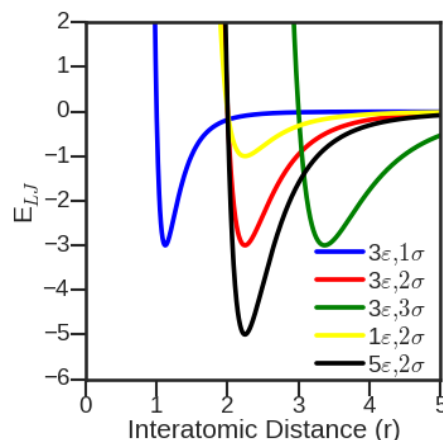


Figure 2.1. LJ potential as a function of interatomic distance (r) using various values for ε and σ .

The parameters σ_{ij} and ε_{ij} are typically trained to reproduce known properties, such as the boiling point of a liquid,⁴³ gas adsorption isotherms,⁴⁴ or DFT energies.⁴⁵ A collection of these parameters is known as a forcefield, of which there are many, including the Universal Force Field (UFF),⁴⁶ DREDING forcefield,⁴⁷ ReaxFF,⁴⁵ and AMBER.⁴⁸ The parameters in forcefields tend to be robust and can be applied to numerous systems. Although it is possible to calculate parameters for each combination of atom pairs, i and j , (e.g., García-Sánchez's forcefield for CO₂ adsorption in zeolites),⁴⁴ some forcefields, such as UFF, only have element specific parameters like σ_i and ε_i . These parameters are then combined in some way, such as using equations 2.8 and 2.9, to create atom pair specific parameters. These equations are known as the Lorentz-Berthelot combining rules,⁴⁹ and are the most widely used combination rules. They are used in the work presented in this thesis.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2.8)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (2.9)$$

2.1.3 Ewald Summation

In addition to dispersion interactions, the other major non-bonding interactions are the electrostatics. Electrostatic interactions are calculated from partial atomic charges that are assigned (discussed in section 2.2) to each atom, and the point charge Coulomb potential is applied. The

Coulomb potential (equation 2.7) is perhaps the most well-known method to calculate electrostatic interactions; however, as mentioned in section 2.1.1, it is not appropriate to use it in that form for MOFs, due to their infinitely periodic nature. The Coulomb potential decays at a rate of r^{-1} which is too slow of a rate to implement a cut-off, like the LJ potential, as potentially meaningful interactions would be lost. This means that a larger number of interactions need to be considered by increasing the value of n , making the electrostatic calculation very slow. In materials simulations, it is better to use an alternative potential for electrostatic interactions, such as the Ewald summation, given in equation 2.10.⁵⁰

$$Ewald(i, j) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \left(\frac{\text{erf}(\alpha r_{ij})}{r_{ij}} + \frac{\text{erfc}(\alpha r_{ij})}{r_{ij}} \right) \quad (2.10)$$

$$\text{erf}(r) = \frac{2}{\sqrt{\pi}} \int_0^r e^{-t^2} dt \quad (2.11)$$

$$\text{erfc}(r) = \frac{2}{\sqrt{\pi}} \int_r^\infty e^{-t^2} dt \quad (2.12)$$

The Ewald summation works by calculating both short- and long-range interactions in real and reciprocal space, respectively. The Ewald summation does this by using an error function, $\text{erf}(\alpha r)$ (equation 2.11), and complementary error function, $\text{erfc}(\alpha r)$ (equation 2.12). The error function represents the long-term interactions, while the complementary error function represents the short-term interactions. The range of these two terms is controlled by the α parameter, which represent the rate of decay in the error function. The equations can be seen in Figure 2.2, where it is noted that the r^{-1} term (like the Coulomb summation) is a combination of the two terms. To calculate the total electrostatic interactions for the system, the Ewald summation is summed over all partial atomic charge combinations of i and j , and over all image cells, n , as shown in equation 2.13.

$$E_{ESP} = \frac{1}{4\pi\epsilon_0} \sum_n \sum_{i>j}^N \sum_j^N q_i q_j \left(\frac{\text{erf}(\alpha |r_{ij} + nL|)}{|r_{ij} + nL|} + \frac{\text{erfc}(\alpha |r_{ij} + nL|)}{|r_{ij} + nL|} \right) \quad (2.13)$$

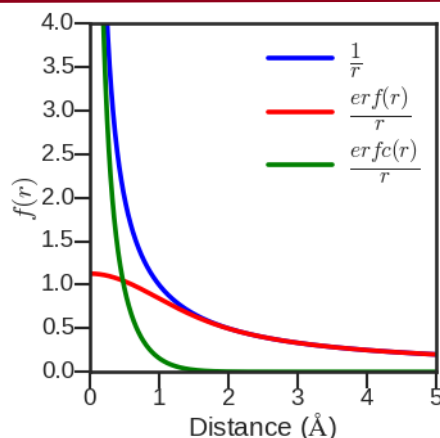


Figure 2.2. A behaviour of functions $\frac{1}{r}$ (blue curve), $\frac{\text{erf}(r)}{r}$ (red curve), and $\frac{\text{erfc}(r)}{r}$ (green curve) against a distance between two atoms, r .

2.1.4 Window Averaging

As GCMC simulations are random by nature, fluctuations in the system occur. For example, the addition and deletion of guest molecules will cause the number of molecules in the system to fluctuate during the simulation. This number relates to the amount of gas adsorbed in an isotherm measurement. However, experimentally, one measures a well-defined value once equilibrium is reached. To get well-defined values from GCMC simulations, they need to be run for a sufficiently long time, allowing for the ensemble to be well sampled. The GCMC is broken into two phases, the equilibration and the production phase. The equilibration phase is a portion of a GCMC simulation where the system can equilibrate to the given conditions (temperature and pressures). In the equilibration phase, the properties are not recorded. After the user-defined amount of equilibration steps have occurred, the production phase begins where information about every step is recorded and used to calculate the results of the simulation. A representation of GCMC output is shown in Figure 2.3, where the number of guest molecules is shown as a function of GCMC steps. The first ~2 million GCMC steps show an increase of the guest molecules, while the remaining 8 million steps have the number of guests fluctuate around 10500 guests.

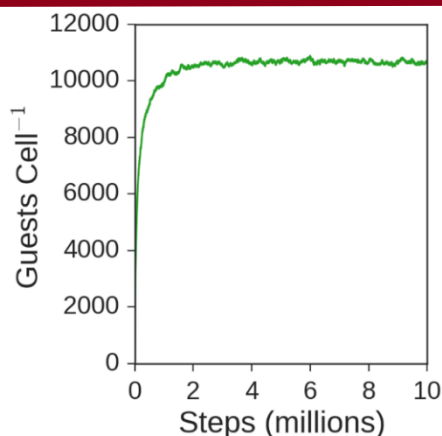


Figure 2.3. Example of the guest molecules in a GCMC unit cell as a function of the total number of GCMC steps performed.

The fluctuations in a GCMC simulation can also give information about the system, such as the statistical uncertainty and error estimate in the measurements, or certain properties such as the heat of adsorption. Expectation values of properties are calculated using window average. The production phase of GCMC simulations is divided into windows of an equal number of MC steps. For each property of interest, the average value is calculated for each window. To calculate the GCMC property, it is simply the average of all the window averages. The uncertainty in the property is calculated by determining the standard deviation of all the window averages. If there are no fluctuations in the data, then all window averages would be equal, resulting in the standard deviation of 0.

Experimentally the isosteric heat of adsorption, Q_{st} , are calculated using multiple isotherms at different temperatures. Data is extracted and fit to equation 2.14.⁵¹ What the equation shows is that the inverse of the temperature, T , is proportional to the natural logarithm of partial pressure of a gas, p , at a fixed adsorption amount, N . When plotted, these values produce a linear graph, where the slope is related to the Q_{st} , and the y-intercept is a fitted value, C . With GCMC, the heat of adsorption can be calculated at every single temperature-pressure point using equation 2.15. In this equation, E is the interaction energies of gases of that type in the system, N is the number of that guest in the system, R is the gas constant, and T is the temperature of the system. In this case, the fluctuations can be used to calculate the heat of adsorption.

$$\ln(p)_N = \frac{Q_{st}}{R} \left(\frac{1}{T} \right) + C \quad (2.14)$$

$$Q_{st} = - \frac{\langle EN \rangle - \langle E \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + RT \quad (2.15)$$

2.2 *Partial Atomic Charge Calculations*

As mentioned in Section 2.1.2, the parameters used for the LJ potential are typically transferable between systems; however, the electrostatic interactions are not as robust, and need to be calculated for each system. In the ideal scenario, the electrostatic interactions would be calculated directly from the electrostatic potentials (ESPs) from quantum mechanical (QM) calculations, typically periodic DFT simulations. One notable disadvantage to this approach is that the ESP would need to be stored in memory during the GCMC simulation, which could be infeasible for MOFs with large unit cells. This problem is overcome by condensing large and complicated ESP due to the MOF frameworks to a set of partial atomic charges located on each atomic centre. A number of methods have been developed to do this for periodic systems, such as ISA⁵² and DDEC,^{15,16} however, REPEAT (Repeating Electrostatic Potential Extracted ATomic)¹⁴ partial atomic charges have been viewed as the most accurate charges for periodic systems.^{15,53} In the work by Manz,¹⁵ it was concluded that over a total of 9 different charge methods, REPEAT was the most accurate method for reproducing the ESP in periodic materials. REPEAT partial atomic charges are ESP-based charges used in this work and is described in Section 2.2.1.

Although REPEAT charges are viewed as the most accurate, performing the QM calculation on each structure to derive the charges can be cumbersome, particularly when screening large numbers of materials. In fact, deriving the REPEAT charges is typically the bottleneck when high-throughput screening materials for gas adsorption calculations.^{53,54} To circumvent the compute-intensive QM calculation, partial atomic charges can be quickly calculated using empirical methods such as the Charge Equilibration (QEq)¹⁷ method or its extension, the Split Charge Equilibration (SQE)¹⁸ method. Both methods use a set of parameters and energy equations to calculate out the partial atomic charges on the MOF. The parameters can be fit to reproduce REPEAT charges. The QEq and SQE methods are described in more detail in Sections 2.2.2 & 2.2.3 respectively. In this thesis, charges were calculated with REPEAT, QEq, and SQE.

2.2.1 *REPEAT Method*

One of the most common methods for generating partial atomic charges in periodic systems for molecular simulation is to fit them to a QM ESP. The REPEAT method, developed by Woo and co-workers, has widely been used in MOFs and is considered the most accurate method for determining charges in porous periodic systems.^{15,55} To calculate the REPEAT charges, first a

periodic DFT calculation is performed to evaluate the ESP. In this thesis, all DFT calculations were performed using the *Vienna Ab Initio Software Package* (VASP).^{56–58} The DFT calculation is done on the unit cell where the wave function is optimized in the presence of its periodic images. This gives a more accurate view of the wave function than other QM charge methods that use cluster models where the individual SBUs have their charges calculated separately.^{53,59,60} The periodic nature of the REPEAT method helps to account for long range effects and periodic boundaries properly. Once the QM ESP is calculated, REPEAT fits the partial atomic charges to give the best representation of the QM ESP as possible. This is done by using a least-squares fitting method to minimize the difference between the gauge-modified QM ESP and the ESP due to the partial atomic charges.

2.2.2 Charge Equilibration Method

QM-based partial atomic charges, such as those from the REPEAT method, give the most accurate results. One notable downside to these charges is the need to evaluate the QM ESP, which usually takes an hour or more on multiple CPUs for a single material, creating a bottleneck for high-throughput screenings. The charge equilibration (QEq) method is an empirical method that can calculate partial atomic charges in seconds or less. This method has been used in previous high-throughput screening of MOFs, such as work done by Sholl and co-workers,⁶¹ Wilmer *et al.*,⁶² and by Woo and co-workers.^{24,63,64} The calculation of QEq charges is done by minimizing equation 2.16, by adjusting each partial atomic charge, Q_i , in the set of all partial atomic charges $\mathbf{Q}$. The QEq method contains two parameters for atomic type, the atomic hardness, κ , and the atomic electronegativity, χ . It should be noted that these are historical naming conventions as when Rappe and Goddard first developed the QEq method, they used the actual atomic hardness and electronegativities.¹⁷ Since that time, there has been work done to fit these parameters in order to give partial atomic charges that are closer to those derived from QM calculations or to reproduce specific observables.^{22,54,65} The final term in the equation, J , is the distance-dependent electrostatic potential, which is a standard r^{-1} Coulomb potential that is modified to be dampened at very short distances. An example of a J term is given in Chapter 5.

$$E_{QEq}(\mathbf{Q}) = \sum_i \left(\chi_i Q_i + \frac{1}{2} \kappa_i Q_i^2 \right) + \sum_{i,j>i} Q_i Q_j J_{ij}(r_{ij}) \quad (2.16)$$

2.2.3 Split Charge Equilibration Method

The split charge equilibration (SQE) model was originally developed by Mueser and co-workers as an extension, or generalization, of the QEq model.¹⁸ SQE has been trained and applied on small organic molecules⁶⁶ and simple periodic systems like silicates.⁶⁷ In the SQE method, each partial atomic charge, Q_i , is a sum of surrounding split-charges, q_{ij} , (equation 2.17) which are associated with the covalent bonds instead of the atoms. A split-charge is a representation of the charge that flows from atom j to atom i .

$$Q_i = \sum_j q_{ij} \quad (2.17)$$

In addition to the atomic hardness and electronegativity in the QEq method, each bond type has an associated bond hardness, κ^b , and electronegativity, χ^b . Once again these are parameters which are fit to give the best result for a given application. SQE charges are determined by minimizing equation 2.18 over the set of all split-charges, $\mathbf{q}$.

$$E_{SQE}(\mathbf{q}) = \sum_{i,j>i} \left(\chi_{ij}^b q_{ij} + \frac{1}{2} \kappa_{ij}^b q_{ij}^2 \right) + E_{QEq}(\mathbf{Q}) \quad (2.18)$$

2.3 Genetic Algorithms

Genetic Algorithms (GAs) are global search space optimizers that are inspired by Darwinian “survival-of-the-fittest” evolution. The aim of GAs is to determine high performing candidate solutions (CSs) or areas, with as few calculations as possible. GAs have been applied to a wide range of problems such as ones in mathematics, physics, and materials science. The core assumption of a GA is that high performing CSs share traits that can be represented and then mixed in such a way to find other high performing CSs. This process is repeated until a satisfactory solution is found.

There are four major steps in a GA: 1) generating an initial population, 2) testing and ranking the population for a user-defined fitness, 3) mating and mutating the population to create a new population, and 4) repeating steps 2) & 3) until a convergence criterion is met. A representation of these steps is shown in Figure 2.4. In this section, I will discuss the general concepts of a GA, while in Chapters 5 & 7 I give specific details of GAs that I used in that work.

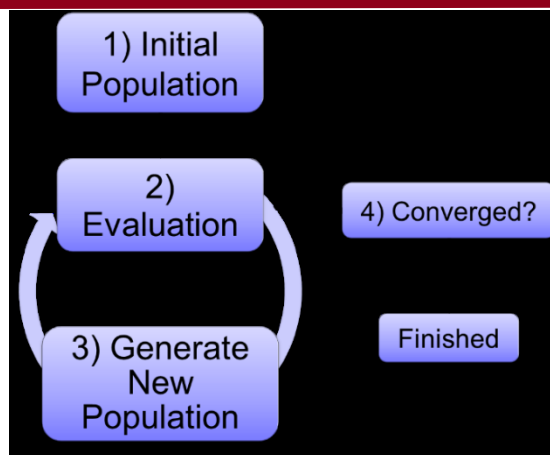


Figure 2.4. Representation of the steps in a Genetic Algorithm.

2.3.1 Chromosome Construction

GAs are based around using information from previously tested CSs to create a new and potentially better-performing set of CSs. To do this for a GA, the properties that you want to modify need to be in a form that the GA can understand and perform modifications on. These computer friendly forms of describing the CS are known as chromosomes. The choice and construction of the chromosomes are important and problem dependent. Some examples of chromosomes used in this thesis are a list of functional groups, where the position in the list encodes to a specific functionalization site in the MOF or a list of numbers where the position in the list encodes to a specific parameter. If the chromosome is a list of values, then each individual value is known as a gene.

2.3.2 Initial Population Creation

To begin a GA, initially, a small amount of CSs are randomly created. The amount of CSs created is known as the *Population Size*, and the collection of CSs is known as a generation. Although the creation of the initial population is random, some techniques can be employed such as Latin Hypercube Sampling⁶⁸ or its extension, Orthogonal Sampling⁶⁹. These are methods which are still random, although they use binning to create an initial population that is widely dispersed in the solution space. Another technique that could be employed during the initial population creation is the use of seeding. Seeding is a method where specifically chosen CSs are placed into the initial population. Seeding can be done either by adding a user-defined CS, or an on-the-fly approach where the top performers from the previously run GA are used to seed the initial population.

2.3.3 Scoring and Ranking

Once the initial generation is created all the CSs are evaluated for their fitness. The actual fitness can be anything, such as energies from DFT, the gas uptake capacity of a MOF, the RMSE between two ESPs, or any other user-defined fitness function. The only restrictions for what can be tested and optimized is that the result needs to be represented as a single value and the chromosome needs to be correlated to the fitness used.

The reason why the fitness needs to be a single number is that the order determines the fittest individuals to pass its chromosomes onto. To do this, the GA needs to be able to create a definitive ranking of what values are good and what values are bad. It is possible to optimize multiple parameters, and this has been an area that has received much interest. This is known as Multi-Objective optimization and is typically done by combining the parameters that you want to optimize into a single figure-of-merit (FoM). The FoM could have some physical meaning, such as the Parasitic Energy of CO₂ capture,^{70,71} or not have a physical meaning and simply be a parameter that is optimized, such as the Adsorbent Performance Indicator.⁷²

Once all CSs of a generation have been tested, the solutions are then ranked. By ranking the values, you determine which CSs are the fittest. Once this is done, each CS is assigned a score. A score is a number between 0 to 1 with the sum of the scores from a generation equal to 1. A function is applied to the fitness value of each CS. These functions can be as simple as $s(x)=x$ if you want to maximize a value or $s(x) = x^{-1}$ if you want to minimize the value. Each value is divided by the sum of all scores to place them all between 0 and 1 with the sum equaling to 1.

2.3.4 New Gene Creation

After the generation has been ranked, a new generation of CSs is created. In this section, I outline steps for creating the subsequent generations. The easiest portion to explain is elitism, which allows the best performers, based on their rank from one generation to pass unchanged to the next generation. The rest of the generation is created by mating. In terms of GAs, mating is the process of combining CSs from one generation to create CSs for the next generation. To determine which CSs act as parents, they are selected by an algorithm known as proportionate fitness selection (FPS). FPS identifies the parents randomly, although with a weighting towards CSs which have higher fitness scores. Common FPS methods include roulette wheel selection, or

stochastic universal sampling.⁷³ FPS is employed to choose how many parents are needed for the mating, with most GAs using two parents to generate a single “off-spring” CS.

Once the parent CSs are chosen, they are then mated, which is another programmable function. In some GAs, it is a simple cut algorithm, where part of one parent’s chromosome is used, and the remainder of the second parent’s chromosome is used. An example of the cut mating process is shown in Figure 2.5. This is a method that would be used when the chromosome is made up of discrete values but could be applied to continuous values. Another mating routine could be to take the two chromosomes and calculate a value between each number in the chromosome. This could be to take an average of the two values, or by selecting any number between the values of the parents.

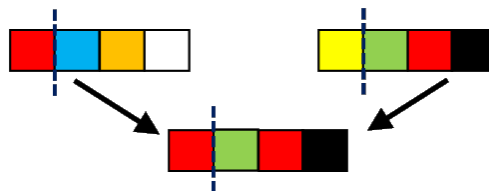


Figure 2.5. Schematic representation of a cut mating process that could be used in a genetic algorithm.

After the mating process, each child CS is potentially mutated. The chance of a mutation occurring is dictated by a mutation rate, which is a value set by the user. A mutation is a random change of chromosome genes to a new value. This can be as simple as increasing or decreasing a number by a randomly chosen percentage, or where the gene is changed to a random allowable value. Mutations are done to add variability into each generation and to prevent premature stagnation in the GA.

2.3.5 Stagnation and Convergence

After the GA has run for multiple generations, it will enter a stagnation phase. This is a period where there is little to no improvement in the performance from one generation to the next. When a GA stagnates, it could be because it is stuck in a locally optimal value, or that it has found the globally optimal value. The former case is not ideal as the GA might end prematurely. There are methods to overcome this stagnation, such as mutation of genes previously mentioned. Other methods include creating completely random CS in a generation that is not related to any parents from the previous generation. This adds a large amount of chromosomal variety into the new generation, with the idea that the new solution could perform better, or that if it were to mate with one of the top performers, allow the GA to search a different part of the surface. Like all



optimization procedures, the GA needs to have convergence criteria. When the GA considers all criteria met, the program considers the GA finished. One potential convergence criterion, and the one used the most often in the GAs in this thesis, is the top performing CS remaining the same for several generations.

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3 Computation-Ready Experimental Database Screening

In this chapter, I discuss the work that I have done in screening the Computation-Ready Experimental (CoRE) database of MOFs for multiple projects. At the time of writing this thesis, parts of this chapter have been used in a manuscript getting prepared for submission for publication. All the work presented in this chapter is my own work.

3.1 Abstract

The Computation-Ready Experimental (CoRE) database of MOFs is a collection of experimentally realized MOFs from the Cambridge Structural Database (CSD) that have been cleaned for use in simulations. In this work, the CoRE database was further checked and pruned, after which DFT derived REPEAT partial atomic charges were calculated for every structure. The CoRE database was computationally screened for three different gas adsorption processes; vehicular methane storage (VMS), post-combustion carbon capture (PoCCC), and landfill gas separation (LGS). Each process has unique targets, a large deliverable capacity for VMS, low parasitic energy for PoCCC, and a low energetic cost while also producing a highly pure CH₄ stream for LGS. In terms of VMS, no CoRE MOF was found to reach the U.S. Department of Energy (DoE) targets for deliverable capacity (330 V_{STP}/V), with the top performer having a value of 239 V_{STP}/V. For PoCCC, the best-performing CoRE MOF had a parasitic energy of 992 kJ/kg CO₂, and 73 CoRE MOFs outperformed state-of-the-art liquid amine carbon capture plants. Finally, using MOFs for LGS provided an array of potential targets with 5 structures forming a Pareto front of CH₄ and purification energy. 1229 of CoRE MOFs were found to outperform an industrial standard for CO₂/CH₄ separation, Zeolite-13X, in both CH₄ purity and purification energy.

3.2 Introduction

Metal-Organic Frameworks (MOFs) can be combined in a variety of ways by using different organic Structural Building Units (SBUs), inorganic SBUs, topologies, and functionalizations.^{1,2} This has allowed MOFs to be tuned for a variety of applications, especially when searching for ideal performance in gas storage and separation.³⁻⁵ This tunability has allowed MOFs to reach record-breaking values. For example, Mg-MOF-74 is often held as the standard when it comes to CO₂ capture, due to its high CO₂ adsorption capacity of 5.28 mmol/g at 0.15 bar and 313 K, which

are conditions relevant for post-combustion carbon capture (PoCCC).⁶ This is a large amount of CO₂ adsorbed, especially if it is compared to an industrially used CO₂ scrubber, Zeolite-13X, which has a CO₂ adsorption of roughly 2.41 mmol/g at 0.15 bar CO₂ and 308 K.⁷ The CO₂ adsorption capacity is not the only reason why Zeolite-13X is used as a CO₂ scrubber, but it does give a sense of scale. MOFs have also been looked at for other gas adsorption properties such as removing toxic gas,⁸ hydrogen storage,⁹ or noble gas separation.¹⁰ When trying to find a high-performing material for a process, or looking at how MOFs perform in general, there are two major problems. One issue is the lack of consistency in the results as they are tested at different conditions, or some MOFs not being tested at all. The other problem is that testing all MOFs experimentally would be time-consuming and financially expensive.

One way to overcome these problems is by using high-throughput computational screening. This has typically been done on hypothetical MOF structures that are created by using algorithms that combine different SBUs, topologies, and functional groups to create millions of unique structures.^{11–13} These structures are then evaluated using computational algorithms, such as Grand Canonical Monte Carlo (GCMC), where the gas adsorption properties are evaluated.^{14,15} Previous work has been done to determine the theoretical limits of gas adsorption properties. For example, Bao *et al.* looked at determining the limits of methane deliverable capacity by using a genetic algorithm to create hypothetical MOFs to optimize the CH₄ deliverable capacity between 65 and 5.8 bar at 298 K.^{16,17} The highest deliverable capacity they noted was 190 V_{STP}/V. Zein Aghaji *et al.* performed a screening on 324,500 hypothetical MOF structures and found that over 60% of structures have higher CO₂ working capacities than Zeolite-13X and some MOFs had higher selectivities.¹⁸ These studies have the notable advantages of being a more systemic method to determine high-performing materials as well as having the materials tested using consistent methods. The disadvantage is that because the materials are hypothetical, there is the possibility that they may not be able to be synthesized, or they could be structurally different from those made in a lab.^{11,19} This led Chung *et al.* to create the Computation-Ready Experimental (CoRE) database of MOFs which contains nearly 5100 experimentally realized structures.²⁰

The CoRE database was created by initially taking MOF structures from the Cambridge Structural Database (CSD)²¹ and passing them through various filters, such as removing solvent molecules and frameworks with pore limiting diameters less than 2.4 Å. These filters were used to ensure that the MOFs would be ready for computations, such as gas adsorption simulations, and

would be reasonable materials. The CoRE database is seen as an improvement over a similar database published by Goldsmith *et al.*,²² as the CoRE database was able to remove more solvent molecules, contains charged frameworks, and allows MOFs to remain interpenetrated. The CoRE database allows systematic computational evaluation of MOFs with known synthetic pathways, unlike hypothetical databases. It has previously been evaluated for some gas adsorption properties such as Vehicular Methane Storage (VMS),^{20,23} PoCCC, and Natural Gas Purification.²⁴ The previous screenings of the CoRE database have their own issues, which are discussed later, but the largest issue are the charge calculations. Wilmer noted that one of the largest bottlenecks in high-throughput screenings for MOFs is the calculation of highly accurate quantum mechanical partial atomic charges for the frameworks.²⁵ The previous screenings have either not required charges or have rapid, but likely inaccurate, charges calculated using the charge equilibration (QEq) method.²⁶

In this Chapter, I present the work I have done on screening the CoRE database for three different gas separation and storages, VMS, PoCCC, and landfill gas separation (LGS). Unlike previous work done on the CoRE database for gas storage and separation processes, each CoRE MOF had DFT derived REPEAT charges calculated,²⁷ to give the most accurate electrostatic potentials, and therefore, gas adsorption predictions available.^{28,29} A more holistic approach is taken when evaluating the MOFs for a given process than what was previously done, using physically motivated figures of merit (FoMs) when possible. The results from this work give a greater understanding of the capabilities of MOFs for a variety of gas storage and separation processes and help to define the theoretical limits.

3.3 Methodology

Before any calculations were performed, each CoRE MOF was inspected by hand. It was noted that the CoRE database, although being advertised as computation-ready, contained problems in their structures. Some of the issues were minor (i.e., missing bonding information), while some were major issues such as missing hydrogen atoms or the structure still having disorder. Using Materials Studio,³⁰ all of the issues identified were fixed. It should be noted that approximately 200 MOFs needed to be fixed, while another approximately 30 structures were deemed too difficult to fix. The CoRE MOF database also contained charged frameworks, and although there are methods to deal with the charged frameworks,³¹ the influence of the counter-ion is difficult to

simulate accurately. As a result, we decided not to screen charged frameworks in this work. The CoRE database also contained duplicate structures which were filtered out for this chapter and for any work done for this thesis. This was done so the results would not contain duplicate information, which could skew any statistical analysis performed. It is likely that the same structure could contain minor differences, such as slightly different bond lengths and angles. The best way to determine similarity was therefore to compare the bonding structure. This was done by first finding structures that contained the same atomic ratios, and then comparing the structural bonding information by using molecular fingerprints from OpenBabel.³² Of the original 5083 structures obtained from work by Chung *et al.*, 3468 passed all filters.

After fixing and pruning the CoRE Database, each MOF had an ESP calculated using the *Vienna Ab-initio Simulation Package* (VASP).^{33,34} VASP calculations were performed with no atomic position relaxation using the PBE functional^{35,36} and a plane wave cutoff of 400 eV. REPEAT partial atomic charges²⁷ were calculated on the gauge-modified QM ESP. Gas adsorption properties were calculated using an in-house developed Grand Canonical Monte Carlo (GCMC) program based on the DL_POLY-2 package.^{37,38} Atomic positions of the frameworks were frozen during the GCMC simulations, while guest molecules were held rigid. The intermolecular interactions were calculated using Lennard-Jones (LJ) potentials for van der Waals interactions and Ewald summation for the electrostatic interactions. For the framework atoms, the LJ parameters from the Universal Force Field (UFF)³⁹ were used, and the partial atomic charges were assigned fit to the DFT electrostatic potential using the REPEAT method. The parameters for the CO₂ guest molecules were developed by Garcia-Sanchez,⁴⁰ the CH₄ parameters came from a transferable potential for alkanes,⁴¹ and the N₂ parameters were developed in-house to reproduce N₂ gas adsorption isotherms in MOFs,⁴² and are given in Table 3.1. For the GCMC calculations, 30,000 cycles were used for the equilibration phase, and an additional 30,000 cycles were used for the production phase. A GCMC cycle is equal to N MC steps, where N is equal to the total number of guest molecules in the system at any given step. The gas adsorption, selectivities, and heats of adsorptions (HoAs), along with the associated errors, were calculated from windowed averages, with windows set to 100,000 GCMC steps. The errors for the gas adsorption properties were determined from the standard deviations of the window averages.

For VMS, the adsorption and desorption conditions were those set by the U.S. Department of Energy (DoE).⁴³ The adsorption was set to 298 K and 65 bar, and the desorption was set to 338 K

and 5.8 bar. Although the desorption condition differs slightly from the conditions in other work,^{20,44} they were the conditions defined by the DoE.⁴³ For PoCCC, adsorption conditions were set to 313 K, 0.14 bar CO₂, and 0.86 bar,^{23,45} and desorption at 313 K, with a total pressure of 0.05 bar. The desorption pressure for this work was chosen with some *a priori* knowledge of MOF performance when working on a paper⁴⁵ discussed in Chapter 6. For LGS, the adsorption and desorption conditions were given by industrial collaborators:⁴⁶ adsorption at 338 K with 3.24 bar CO₂ 4.48 bar of CH₄, 0.2 bar N₂, 0.08 bar O₂ and 80 ppm of H₂S, and desorption was 338 K and a total pressure of 0.27 bar. For both PoCCC and LGS, the desorption conditions were set to 99% of the heavy stream guest (CO₂) and 1% of the light stream guest (N₂ and CH₄ for PoCCC and LGS respectively). This was done to give conservative estimates of the performance, as this assumed that not as much of the desired gas could be removed in a single cycle. For all calculations, the Peng-Robinson equation of state was used to calculate the fugacity of the bulk gas phase including binary interactions.⁴⁷

3.4 Results and Discussion

3.4.1 Vehicular Methane Storage

The first screening that I will discuss is using the CoRE database for VMS. As explained in Chapter 1, in VMS, the material is used to adsorb methane at low pressures such that a form-fitting fuel tank can be used, rather than a bulky cylindrical fuel tank required for high-pressure storage. As a note, when discussing VMS, the term deliverable capacity is used in place of working capacity, although they are the same. The DoE has set guidelines for VMS, such as a material should be able to store the same amount of energy as liquid natural gas (LNG) but at a lower pressure than what LNG requires at ambient temperature.⁴³ In terms of numbers, a material should have a deliverable capacity of CH₄ equal to 263 V_{STP}/V from 65 bar to 5.8 bar. Although this is the value given in the DoE guidelines for VMS, a single perfect crystal of the material cannot be used in the fuel tank. This is because the sorbent material is typically structured into beads and packed into the fuel tank resulting in empty space and a so-called “packing loss.” Using a typical packing loss value of 25% means that in order to achieve an overall deliverable capacity of 263 V_{STP}/V, the crystalline material should have a deliverable capacity of 330 V_{STP}/V.⁴⁸ The DoE also mentions that the gravimetric deliverable capacity should be 50% by weight, although this

requirement is not discussed nearly as much. All values given are for the perfect materials should be compared against the value of $330 \text{ V}_{\text{STP}}/\text{V}$.

VMS has already been studied experimentally with some of the high-performing materials being MOF-5,⁴⁹ HKUST-1,⁴⁸ USTA-76,⁵⁰ and MOF-519,⁴⁴ which had deliverable capacities of 185, 185, 194, and $208 \text{ V}_{\text{STP}}/\text{V}$, respectively. Smit and co-workers computationally studied the CoRE database as well as 650,000 other materials for VMS and found the highest predicted deliverable capacity of $196 \text{ V}_{\text{STP}}/\text{V}$ which was for a hypothetical porous polymer network.²⁰ In that work, the value for the highest deliverable capacity for a CoRE MOF was not explicitly stated, although, from one of their figures, the highest deliverable capacity of a CoRE MOF was estimated to be $188 \text{ V}_{\text{STP}}/\text{V}$. The values were found assuming a fully PSA system, meaning the adsorption and desorption temperatures were set to 298 K. Smit and co-workers did a search at higher desorption temperatures, with the highest deliverable capacities of $240 \text{ V}_{\text{STP}}/\text{V}$ at 400 K and $255 \text{ V}_{\text{STP}}/\text{V}$ assuming an infinite temperature. One notable difference between most of the previous works and the work in this thesis is that the previous works were performed using a desorption temperature of 298 K. The DoE regulations state that during VMS the desorption temperature can go up to 358 K (85°C), as there is potential to redirect heat from the engine to the VMS storage, which is the desorption temperature used in this work.⁴³ Using the conditions set by the DoE, I screened the CoRE database with results shown in Figure 3.1.

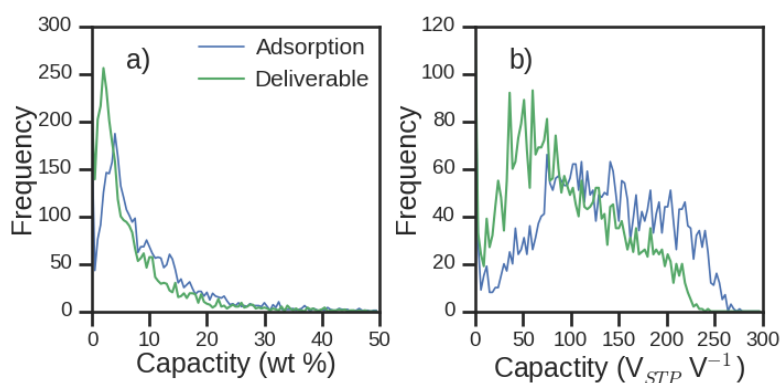


Figure 3.1. Histograms of the a) gravimetric and b) volumetric CH₄ adsorption (blue) and deliverable capacities (green) of the CoRE database.

In terms of the gravimetric deliverable capacities, no MOF was able to meet the DoE targets of 50% by weight, with the maximum value reaching 42.7% while the median deliverable capacity was only 4.0%, as shown in Figure 3.1a). For the volumetric capacities, the screening results showed a more normal distribution (Figure 3.1b) compared to the gravimetric results, as noted by

the median value of 83 V_{STP}/V and a maximum of 239 V_{STP}/V . The maximum volumetric deliverable capacity is a copper-based MOF, with a CSD RefCode SUKYON,⁵¹ with a picture of the structure shown in Figure 3.2. From the original work, SUKYON was found to have permanent porosity and showed hydrogen gas adsorption at 77 K, giving validation on its structural stability and capability to adsorb gas. No work was done to determine the exact reason as to why SUKYON was the highest performing structure, however based on other work done in this thesis, I believe it is due to its relatively large open pores, among other factors. While SUKYON does have the highest deliverable capacity predicted for a MOF within the DoE operational conditions, it does not reach the DoE target of 263 V_{STP}/V , let alone the packing loss accounted value of 330 V_{STP}/V .

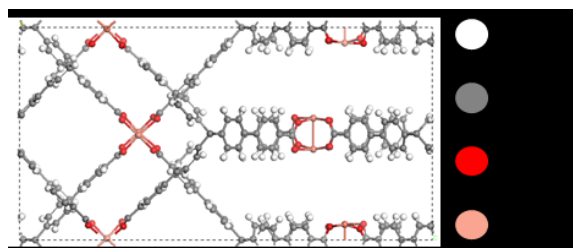


Figure 3.2. Image of the MOF with CSD RefCode SUKYON.

SUKYON's deliverable capacity was found to be 239 V_{STP}/V when using a desorption temperature of 358 K. For comparison, Smit and co-workers calculated the maximum working capacities to be 188 and 240 V_{STP}/V when using desorption temperatures of 298 and 400 K, respectively. To put the comparison on level footing, the CoRE database was re-evaluated using a desorption temperature of 298 K, and the maximum deliverable capacity was found to be 181 V_{STP}/V , which is in line with Smit's work, which makes sense as the force fields used were the same. When looking into why the deliverable capacity of SUKYON was nearly equal to the maximum deliverable capacity of Smit at a desorption temperature of 42 K lower, the reason seemed to be due to how the change in temperatures was handled. In our methodology, all gas adsorptions are calculated using GCMC. In work by Smit and co-workers, they used GCMC to simulate isotherms at 298 K for each structure. Isotherms were fit to adsorption isotherm models (AIMs), and then using equations 3.1 and 3.2, the Henry's coefficients and saturation loading σ_s , were calculated at elevated temperatures.⁵² The way the change in temperatures were handled could account for the differences in the results.

$$K_H \sim e^{-\frac{\Delta H}{RT}} \quad (3.1)$$

$$\sigma_s \sim \frac{1}{T} \quad (3.2)$$

The results from this screening give an idea of how experimental MOFs can perform for VMS. Although some MOFs near the target of 263 V_{STP}/V with deliverable capacities of 239 V_{STP}/V, no CoRE MOF was found to reach it. The results are further away from the target if the packing loss is accounted for, and the target is 330 V_{STP}/V. This was the case when the desorption temperature was set to operational limit of 358 K, unlike what has been conventionally done.

3.4.2 Post-Combustion Carbon Capture

Next, we looked at screening the CoRE database for PoCCC. In this area, Mg-MOF-74 is often promoted as a high performing MOF due to its exceptional CO₂ adsorption capacity, determined experimentally to be 4.91 mmol/g at flue gas conditions, along with its good CO₂/N₂ selectivity of 175.^{6,53} Another commonly discussed material for the process is SIFSIX-3-Zn which has a CO₂ adsorption capacity of 2.39 mmol/g and a CO₂/N₂ selectivity of 1800.^{54,55} Although these are high performing materials, there is interest in trying to find the limits of MOFs for use in PoCCC. Because of this, screenings have been performed with thousands of MOFs to find high-performing MOFs for PoCCC.^{23,56–58} The CoRE database was screened for PoCCC by Qiao and co-workers;²⁴ however, a primary issue in that work is the use of QEq²⁶ charges with MEPO parameters.⁵⁹ In addition to REPEAT charges being more accurate than QEq charges, the CoRE database contains 77 elements, while MEPO was parameterized for 10. The CoRE database also contains elements in configurations not included in the training of MEPO, which could lead to inaccurate charges. These are problems for gas adsorption studies, particularly when CO₂ is involved because in the parameterization of MEPO, Kadantsev *et al.* showed how using an ill-fitting set could give drastically different CO₂ adsorption results than using the more accurate REPEAT charges.⁵⁹ Using the CoRE database with REPEAT partial atomic charges, the results for screening for PoCCC are shown in Figure 3.3.

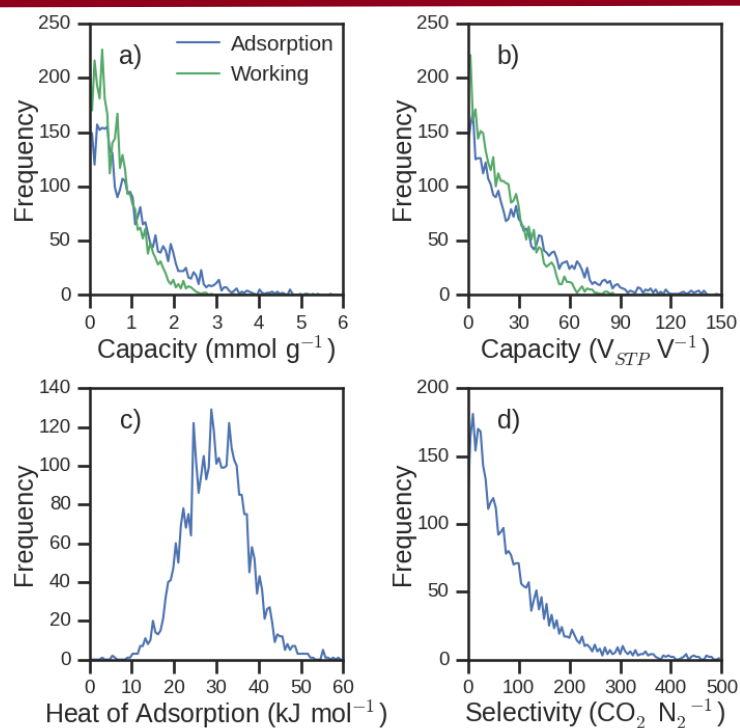


Figure 3.3. Results of computational screening of the CoRE database using PoCCC relevant conditions shown as histograms for a) gravimetric capacities, b) volumetric capacities, c) heats of adsorption, and d) selectivities. For a) and b) blue lines are adsorption values while green lines are working capacities.

What can be seen from Figure 3.3a) and b) is that for CO_2 , both gravimetrically and volumetrically, the CoRE MOFs are weighted to lower values, unlike volumetric capacities for VMS. Even though there was a weighting towards lower gravimetric uptakes (noted by the 0.82 mmol/g median and a maximum of 6.69 mmol/g), a total of 107 of the 3468 tested CoRE MOFs were able to reach a high-performance target of 3 mmol/g . The highest performing CoRE MOF for CO_2 adsorption was 6.69 mol/g which is substantially higher than the experimentally derived uptake of Mg-MOF-74 of 4.91 mmol/g . Although these values are not directly comparable due to the different methods used (computational vs. experimental, among other differences), it does give a sense of scale. In addition to the uptake, another commonly discussed metric is the CO_2/N_2 selectivity, with the results from the CoRE screening shown in Figure 3.3c. Overall, the CoRE MOFs are selective to CO_2 over N_2 , noted by a median selectivity of 67 CO_2/N_2 . Although no MOF was able to outperform SIFSIX-3-Zn, which has an experimentally derived CO_2/N_2 selectivity of 1800 (the highest CoRE MOF value was 1259 CO_2/N_2), 435 CoRE MOFs were able to exceed the benchmark material Mg-MOF-74, with selectivities greater than 175.

While direct comparisons of the adsorption capacity can be easily made to previous results, comparisons of the working capacity are more difficult. This is because the working capacity requires both the adsorption and desorption conditions to be specified, and while the adsorption conditions are well defined, the desorption conditions are not. In fact, there has been work on changing the desorption conditions of a PoCCC process in order to optimize the performance,^{23,45,60,61} which is discussed later in this thesis (Chapter 6). In this screening, the desorption condition was kept constant at 0.05 bar for each structure, as this was found to be where many MOFs had the best performance using *a priori* knowledge.⁴⁵ Using this constraint, the CoRE MOFs had a median working capacity of 0.60 mmol/g, compared to a high performing MOF, such as Mg-MOF-74, which using experimental results and similar conditions as the CoRE MOFs, had a working capacity of 1.53 mmol/g. The screening was able to find 257 CoRE MOFs with larger working capacities than Mg-MOF-74, with the highest value found is 3.95 mmol/g. Having a MOF which is both selective for CO₂ over N₂, as well as having a large CO₂ working capacity, is desirable. This would be a MOF that selectively removes CO₂ from the flue gas, allowing N₂ to pass freely, while simultaneously removing a lot of CO₂ per adsorption-desorption cycle. Figure 3.4 shows the relationship between the working capacity and the selectivity. Although at low values there is a linear correlation between the increase of CO₂ working capacity and selectivity, at high values there appears to be a trade-off, with some exceptions. The bulk of the CoRE MOFs had low working capacities of less than 1 mmol/g and selectivities less than 50, as noted by the high intensity in the lower left corner of Figure 3.4. Many CoRE MOFs were found to out-perform current benchmark standards of Mg-MOF-74,⁶ or Zeolite-13X.⁷ The data for calculating the results of all experimental structures was taken from the work of Huck.²³ This data was used in IAST⁶² calculations to determine the composition of the adsorbed phase, as implemented by Simon *et al.*⁶³

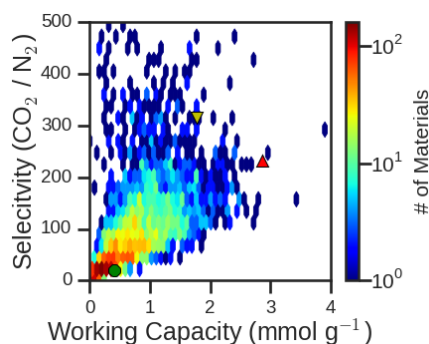


Figure 3.4. Heatmap of GCMC calculated CO₂/N₂ selectivity vs. CO₂ working capacity. Experimentally derived results for Mg-MOF-74 (green circle), Zeolite-13X (yellow triangle), and HKUST-1 (red triangle) are shown.

Determining the ideal candidate for PoCCC is difficult as determining the trade-off between the working capacity and selectivity is not intuitive. For this reason, figures-of-merit (FoMs) are important, as they combine multiple metrics into a single value to easily rank the results. Although some FoMs do simple combinations of values,^{64–66} in this work the Parasitic Energy (PE) was used.^{23,45,56,67} The PE gives an estimate of the amount of energy necessary to separate the gas mixture and subsequently pressurize it to 150 bar for storage and transportation. This makes the PE a more physically meaningful FoM than some others, with the trade-offs between values implicit from the equations, as shown in Section 1.3.8. Using those equations and the results from the simulations, the PE of each CoRE database structure was calculated and shown in Figure 3.7. The median PE was calculated to be 1196 kJ/kg CO₂ captured and compressed to storage conditions, with the lowest PE reaching 991 kJ/kg CO₂. For comparison, a perfect material using similar conditions would have a PE of 625 kJ/kg CO₂ (section 3.7.4). 563 MOFs were found to outperform state-of-the-art liquid amine PoCCC plants, which has a PE of 1060 kJ/kg CO₂.⁶⁸ This PE is derived from detailed engineering analysis and is significantly more thorough than the PEs calculated in this chapter. Thus, a more reasonable benchmark would be to compare to Mg-MOF-74, using the same analysis, which was found to have a PE of 1028 kJ/kg CO₂ and of which 68 of the 3468 CoRE MOFs outperformed (with lower being better). As mentioned, the PE for Mg-MOF-74 was calculated using the experimentally derived gas adsorption results.

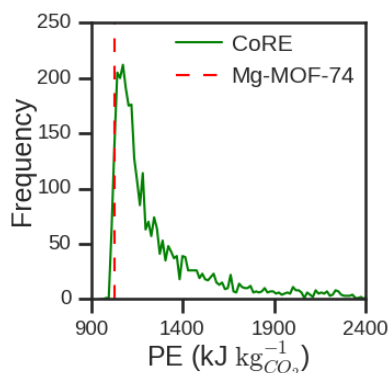


Figure 3.5. A histogram of the PE calculated using GCMC results for the CoRE database. The dashed line is the PE associated with Mg-MOF-74. Lower PEs are better.

To better understand the PE, it is worthwhile to try and find a relationship between it and easily calculated properties. These properties included the gas adsorption properties, gravimetric and volumetric uptake, gravimetric and volumetric working capacity, and the heat of adsorption. Each property value for both CO₂ and N₂ were considered, as well as the CO₂/N₂ selectivity, and the CO₂ purity of the heavy stream. Geometric values were also considered and included the unit cell

size, the density, three different pore sizes (largest pore in the structure, largest continuous channel, and largest accessible pore), the total, gravimetric, and volumetric surface areas (at probe sizes of 0.0, 1.0, 1.42, 1.72, and 1.82 Å), and the unit cell, gravimetric, and volumetric void space using the same probe sizes. The probe sizes were chosen to mimic the accessible surface area for nothing, helium, water, carbon dioxide, and nitrogen, respectively. The geometric properties were calculated using the Zeo++ software package.⁶⁹ In total, 47 properties were used in order to determine relationships with the PE. The best relationships with the PE, according to Spearman correlations, were the volumetric and gravimetric working capacities, with R^2 of 0.939 and 0.937, respectively. Two of the main reasons why the working capacities are strongly correlated with PE are: 1) the thermal term, Q , is divided by the working capacity, where high working capacities minimize PE and 2) the working capacity is correlated to the purity (spearman R^2 of 0.892 for volumetric and 0.743 for gravimetric). The vacuum and compression terms are divided by the purity terms, and having a high purity, which is correlated to the working capacities, will lower the PE. The purity did also show a high correlation with the PE (R^2 of 0.895), although the purity does not affect the thermal term directly, which could be why the correlation was lower. The geometric properties showed very little correlation, with the strongest correlation being from the gravimetric surface area of the 0.0 Å probe, with a Spearman rank of 0.031. Heatmaps of the PE as a function of the volumetric working capacity and the 0.0 Å probe are given in Figure 3.6. Although a singular geometric term was unable to give a meaningful relationship with the PE, a combination of geometric terms might. In work by Fernandez *et al.*, machine learning was applied, where combinations of geometric properties, as well as chemical properties in the form of atomic property weighted radial distribution functions, were used to determine if a material would be high performing, specifically in terms of the CO₂ adsorption.^{13,57} The PE is a more complicated property than the CO₂ uptake, so it follows that advanced descriptors are needed to predict it.

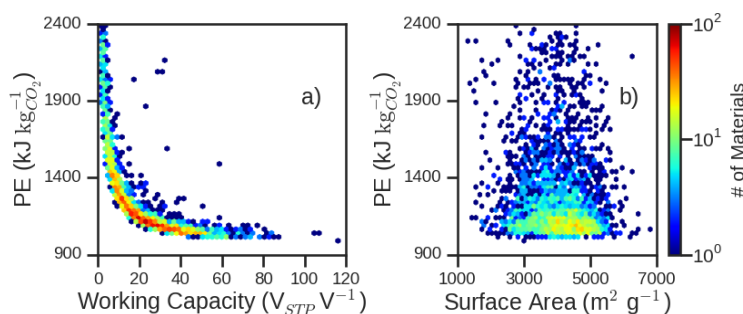


Figure 3.6. Heatmaps showing the relationships between the PE and the a) CO₂ purity and b) the van der Waals surface area of the framework.

Overall the CoRE MOFs were found to have some high-performers in terms of uptake, working capacities, and selectivities. Perhaps most notable is that 68 CoRE MOFs have PEs lower than the benchmark material Mg-MOF-74. When looking at relationships, it was found that the volumetric working capacity had the strongest correlation, with the PE having a Spearman rank of 0.939, while the best geometric property correlation was the van der Waals gravimetric surface area, with a Spearman rank of 0.031.

3.4.3 Landfill Gas Separation

LGS is a process that has interested researchers since the 1980s;^{70,71} however, it has not been as rigorously studied as PoCCC. Some recent examples of LGS studies include work by Qiao *et al.*²⁴ and Altintas *et al.*⁷² where the CoRE database was screened and subsequently analyzed. In these works, the CoRE database was screened to find high-performing materials, based primarily on working capacities and selectivities. One of the main problems of these works is the fact that the charges were calculated using QEq methods, which can give inaccurate results, even for the CoRE database.⁷³ Additionally, in those works the conditions were set to 50/50 CO₂ and CH₄ at 1 or 5 bar. In this work, we used industrially motivated conditions,⁴⁶ using ~40% CO₂, ~55% CH₄ as well as trace amounts of O₂, N₂, and H₂S. Simple gas adsorption metrics relevant for LGS from the screening are shown in Figure 3.7. Unlike PoCCC, where the frequency was inversely related to the adsorption capacity, for LGS the frequency appears to be a more normal distribution. The largest difference between the values for PoCCC and LGS are the selectivities (Figure 3.7d), where CO₂/CH₄ selectivities are lower with a maximum value of 50 and the most probable value of ~5. However, the lower selectivities are in line with other studies of MOFs for LGS: ~10 for Mg-MOF-74,⁷⁴ 6 to 12 for UiO-66 and its derivatives,⁷⁵ and ~4 for HKUST-1.⁷⁶ Although those works used different conditions (i.e., 50:50 CO₂/CH₄ at 5 bar and 298 K), in this work MOFs had CO₂/CH₄ selectivities above 50, which is likely due to structure and not the conditions.

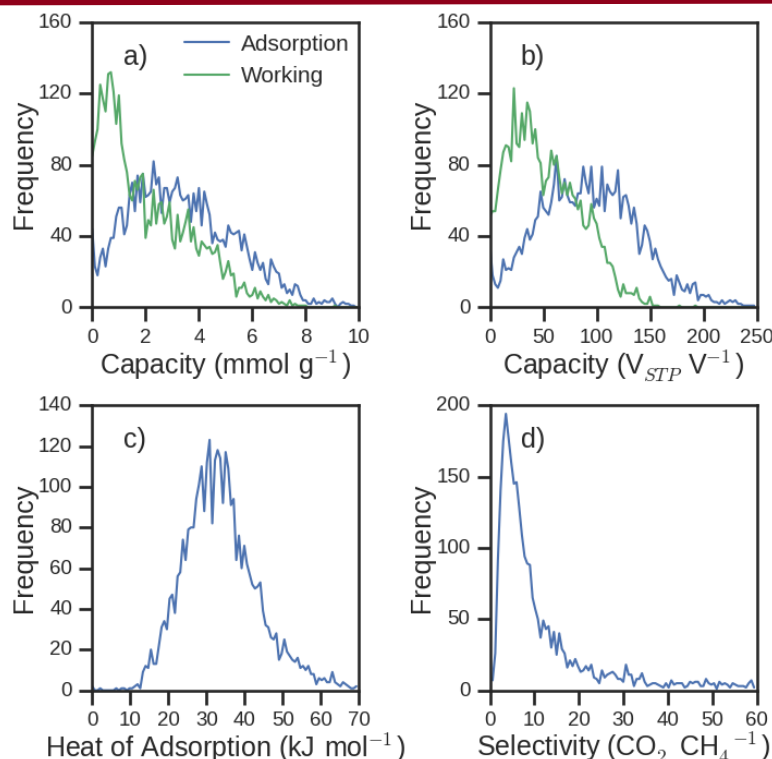


Figure 3.7. Results of computational screening of the CoRE database using LGS relevant conditions shown as histograms for a) gravimetric capacities, b) volumetric capacities, c) heats of adsorption, and d) selectivities. For a) and b) blue lines are adsorption values while green lines are working capacities.

For LGS, an ideal material would allow the CH_4 to pass and go into the light stream while capturing CO_2 to be removed as the heavy stream. An ideal material should, therefore, have a high selectivity for CO_2 over CH_4 and a large CO_2 working capacity. As with the previous section, although the gas adsorption properties presented in Figure 3.7 can be predictors for performance, they do not directly describe the values of interest. One important value is the purity of CH_4 in the light stream. It is desirable to have pure CH_4 for the RNG, so it can be transported at low cost. Calculating the purity of the light stream is not as simple as the heavy stream, since knowing how much CH_4 passes through is difficult without knowing about the kinetics of the system. As our simulations give equilibrium data, kinetic based properties are not easily determined, so the amount of inlet CO_2 captured was assumed to be 98%. This is a reasonable assumption as the concentration of CO_2 in the light stream can be monitored using breakthrough curves, and when CO_2 leaves the system, it can be switched into the desorption phase. As this is a gas separation process, having a low energetic cost is desirable. To calculate this value, a different version of the PE, which I term the Purification Energy (P_{fE}) is used. The P_{fE} is derived from the PE and shown in the appendix (Section 3.7.3). The CH_4 purity and P_{fE} were calculated for all CoRE MOFs, with

the results of the screening shown in Figure 3.8. The CH_4 purity and PfE have a Spearman R^2 of 0.20, showing a weaker correlation than CO_2 purity and PE for PoCCC. This is because in LGS the gas stream is only pressurized 2-fold for transport (8 to 18 bar),⁷⁷ whereas in PoCCC the stream is pressurized 3000-fold (0.05 to 150 bar). Thus, the energy penalty of pressuring impurities in the gas stream is much less in LGS than in PoCCC. As seen in Figure 3.8, high CH_4 purity does not guarantee a low PfE, so they need to be simultaneously considered when determining the best material for LGS.

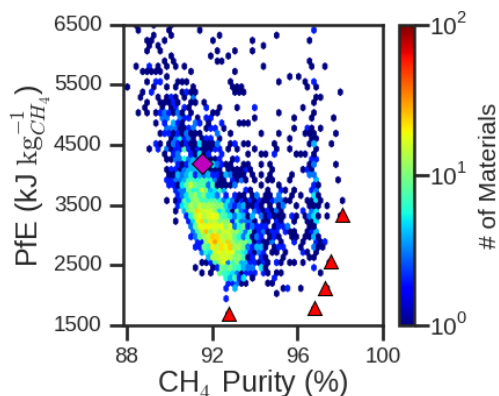


Figure 3.8. Heatmap of the purification energy vs. the CH_4 purity in the light stream of the CoRE database calculated from GCMC simulations. The red triangles are the Pareto front while the purple diamond denotes Zeolite-13X.

Determining which material is the best for this process can be difficult as two competing terms need to be balanced. Instead of a single point, a Pareto front of 5 of the CoRE MOFs was created, as shown by the red triangles in Figure 3.8. A Pareto front is a collection of points from a dataset which are not dominated (i.e., perform better) by any other point in the dataset for all considered values. In other words, all structures not on the Pareto front have higher PfEs and lower CH_4 purity than at least one point on the Pareto front, and every point on the Pareto front has an increasing purity at an increased cost of the PfE. For example, the structure with the lowest PfE on the Pareto front was 1689 kJ/kg CH_4 and has a CH_4 purity of 92.8%, while the second lowest PfE on the Pareto front has a value of 1789 kJ/kg CH_4 and the CH_4 is 96.8%. Although the PfE values seem high in comparison to PoCCC, a perfect material for LGS would have a PfE of 1184.4 kJ/kg CH_4 (Section 3.7.3). Finding the single best performer for this process is difficult, as both values should be optimized; however, no single point optimized both values. Deciding the degree of trade-off is something that would need to be done using relevant information about the process. For LGS, one potential guideline is to use pipeline specifications for commercial sale, which requires a minimum

CH₄ purity of 94% (<3% CO₂ and <3% N₂).⁷⁸ Without having filters or thresholds that remove some points, all points on the Pareto front should be considered as a potential candidate for LGS.

In addition to the CoRE MOFs, Zeolite-13X was evaluated because it is a commercial sorbent currently in use for LGS. Using experimental adsorption data from Cavenati *et al.*⁷ Zeolite-13X was able to produce an RNG stream that was 91.5% CH₄ at a PfE of 4192 kJ/kg CH₄. When comparing the CoRE database results against Zeolite-13X, it was found 2107 of the 3468 MOFs were able to outperform Zeolite-13X both in terms of PfE and CH₄ purity. The reason Zeolite-13X has such a high PfE seems to be due to its high CO₂ HoA, 50.1 kJ/mol, which is larger than 92.0 % of the CoRE MOFs (Figure 3.7c). Although Zeolite-13X is inexpensive to manufacture, these results suggest that there may be commercial opportunities for MOFs in the LGS arena. Of course, other properties of the materials need to be considered in addition to the ones studied here, such as stability and kinetics to name a few.

3.5 Conclusions

In this chapter, I looked at screening the CoRE database for three different gas storage and separation processes: vehicular methane storage (VMS), post-combustion carbon capture (PoCCC), and landfill gas separation (LGS). It was found that all the CoRE MOFs fall short of the packing loss accounted deliverable capacity (330 V_{STP}/V) with the highest deliverable capacity being 239 V_{STP}/V. Although this is far off from the DoE guidelines, it is the highest of any MOF that falls within the operational guidelines. When looking at CoRE MOFs for PoCCC and examining the energy necessary to run the gas separation, it was found that the lowest energetic cost was 991 kJ/kg CO₂. 68 CoRE MOFs were found to outperform the benchmark MOF, Mg-MOF-74, with PEs lower than 1028 kJ/kg CO₂. It was found that the PE correlated to the volumetric working capacity, although no geometric properties showed a strong correlation with the PE. Finally, when looking at LGS, CoRE MOFs were found to perform quite well, with 5 CoRE MOFs forming a Pareto front optimizing the CH₄ purity and PfE. One of the 5 structures created a natural gas stream that was 96.7% pure CH₄ and required 1789 kJ/kg CH₄ compressed for transport in natural gas pipelines. This far outperforms an industrial CO₂/CH₄ sorbent, Zeolite-13X, which was calculated to produce a 91.5% pure stream for 4192 kJ/kg CH₄. Although specific examples of high-performing MOFs were given over the course of this chapter, the results should be treated as a primary filter for finding candidate materials for a given process. Individual



structures may have complications not tested by our simulation methods, such as low hydrolytic or thermal stability. Such properties are very challenging to predict by simulation, so any high performing materials identified here would need to be synthesized and experimentally studied to evaluate their potential for a given process further.

3.6 References

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3.7 Appendix

3.7.1 Nitrogen GCMC Parameters

Given in Table 3.1 are the parameters used in this work for the N₂ guest molecules. These parameters were developed in house by a previous student, Bianca Provost.⁴² Parameters were fit to replicate experimental gas adsorption data over multiple temperatures, pressures, and MOFs.

Table 3.1. LJ potential parameters for N₂.

Species	Atom	bl (Å)	q (e)	(ϵ/k_b) (K)	σ (Å)
N ₂	N	0.5500	−0.4820	39.966	2.4549
	CoM ^a	0.0	0.9640	0	0

^aCentre of Mass

3.7.2 Light Stream Composition

The GCMC calculations used in this work only give information on the heavy stream (through working capacities), so to determine the light stream composition, other techniques need to be applied. A mass balance analysis states that at a steady state, the mols of each gas entering the PSA system must equal the mols of each gas exiting the PSA system. The gas comes into the PSA system through the inlet and then exits as part of the heavy stream or the light stream. Equation 3.3 shows this principle, where it is rewritten that the number of moles in the light stream of gas i , n_i^{light} , equal the number of moles in the inlet, n_i^{in} , less the number of moles that goes into the heavy stream, n_i^{heavy} .

$$n_i^{light} = n_i^{in} - n_i^{heavy} \quad (3.3)$$

The moles of gas in the heavy outlet is the total working capacity found using equation 3.4. The total working capacity is a combination of the amount removed from the framework during desorption, Δq_i , and the amount in the bulk gas phase. To get those values in the same units, the packing fraction of the material (pf with a typical value of 0.75), crystal density, ρ , and change in the partial pressure of gas i , Δp_i , are needed as well as the gas constant, R , and temperature, T .

$$n_i^{heavy} = \Delta q_i^T = \Delta q_i + \left(\frac{1 - pf}{\rho * pf} \right) \frac{\Delta p_i}{RT} \quad (3.4)$$

The amount of gas in the inlet gas can be calculated by assuming the amount of CO₂ that is recovered, Rec_{CO_2} . The recovered CO₂ is the fraction of CO₂ that is in the heavy phase with respect to the inlet phase. A value of 98% was used in this work, which although arbitrarily chosen, does have some physical backing. The CO₂ concentration in the light gas could be monitored, and once

the concentration reaches the appropriate level, would be switched into the desorption phase. This calculates the amount of CO₂ in the inlet stream, which would then be scaled to calculate the amount in the inlet stream, n_i^{in} , for the other gas components, i , using the inlet pressure of the gas, p_i^{in} , as shown in equation 3.5.

$$\Delta n_i^{in} = \frac{n_{CO_2}^{heavy}}{Rec_{CO_2}} \frac{p_i^{in}}{p_{CO_2}^{in}} \quad (3.5)$$

Having the n_i^{in} and n_i^{heavy} for a gas, the light stream value, n_i^{light} , could be calculated for each gas. Afterward, the light stream CH₄ purity, $Pur_{CH_4}^{light}$, can be calculated using 3.6.

$$Pur_{CH_4}^{light} = \frac{n_{CH_4}^{light}}{\sum_i n_{CH_4}^i} \quad (3.6)$$

3.7.3 Purification Energy for Landfill Gas Separation

The PfE of LGS can be calculated in a similar way to the PE of PoCCC, presented in Section 1.3.8; however, it needs to be modified. This is primarily due to two reasons: 1) this process does not occur in a power plant, so no low-quality steam is available to reduce the thermal cost, and 2) the light stream is important, not the heavy stream. In this section, I describe how these changes affect the PfE calculations, by each of the three terms in the PE (equation 1.12).

For the thermal contribution, Q_{therm} , the first thing to mention is that it would no longer be multiplied by the 0.75 and η terms. This is because there is no longer any low-quality steam readily available to offset the thermal cost of the regeneration. For the actual calculation of Q_{therm} , the only difference is that now instead of dividing by $\Delta q_{CO_2}^T$ term, the equation would be divided by $n_{CH_4}^{light}$. This is because the energy cost is still the same, but it should be in the term the CH₄ sent off to be used for fuel. This means instead of equation 1.14; equation 3.7 would be used. Similarly, for the W_{vac} term, the purity term is replaced with n^{heavy} divided by $n_{CH_4}^{light}$ (equation 3.8). The reason why is because the heavy stream is the only one to feel the effect of the vacuum, as the light stream freely passes. It is divided by the CH₄ in the light stream as that is the normalizing value.

$$Q_{therm} = \frac{\Delta T C_{sorb} + \sum_i^n \Delta h_i \Delta q_i^a}{n_{CH_4}^{light}} \quad (3.7)$$

$$W_{vac} = \frac{RT_d}{\eta_{vac}} \ln\left(\frac{p_a}{p_d}\right) \frac{n^{heavy}}{n_{CH_4}^{light}} \quad (3.8)$$

The final term is the W_{Pres} , (equation 1.16) which is replaced with equation 3.9. There are a few differences in this equation, first being that the purity of CO₂, Pur_{CO_2} , is replaced with the purity of CH₄ in the light stream, $Pur_{CH_4}^{light}$. Another notable difference is that the pump term is removed. This is because a compressor is used to pressurize the gas until it becomes supercritical fluid, after which a pump is used. For LGS, the CH₄ is only pressurized to a total pressure of 18 bar.⁷⁷ This value comes from a study from the DoE where although some sites had an injection pressure of up to 120 bars, the average across 1000 sites was found to be 18 bar.⁷⁷ This pressure is well below when CH₄ becomes a supercritical fluid or even a liquid, so only a compressor is used. As it is only going to a total of 18 bar, that means the calculations for S (equation 1.17) and Y (equation 1.18), also use 18 bar for the high pressure, p_{high} . Additionally, for those equations it is no longer the desorption pressure, p_d , that would be used, but it would be the pressure that adsorption occurred at, p_a , which is 8 bar for this process. The reason for this is because it is the light stream that is getting pressurized, which freely passes through the gas scrubber at relatively the same pressure.

$$W_{Pres} = \frac{1}{P_{CH_4}^{light}} \left(S \left(\frac{RT}{\eta_{comp}} \left(\frac{\gamma}{\gamma - 1} \right) \left(Y^{\frac{(\gamma-1)}{\gamma}} - 1 \right) \right) \right) \quad (3.9)$$

3.7.4 Limits of Parasitic Energy

Although it may seem reasonable that the PE will range from an ideal case of 0 kJ/kg CO₂ to infinite energy, this is not so. This is because even in an ideal case, there is an entropic cost to be paid for separating a gas mixture into pure streams, and mechanical costs to compress the gas stream for transport. On the other hand, having infinite energy for the upper limit is also not reasonable. It is much more reasonable to consider the cost of directly compressing the gas mixture without any separation involved. To calculate the extremes, equations 1.12-1.18 were used, and values were substituted on the extreme ends while still following the same physical and mechanical processes that will be used.

The first extreme I will look at is the theoretical maximum energy as this is the easiest one to explain. The maximum is calculated by assuming no separation occurs, and the gas mixture is directly compressed to storage conditions. In terms of equation 1.12, this means that the Q_{therm} and W_{vac} term are both 0; however, the purity in equation 1.16 is set to the inlet purity of CO₂, which for this analysis will be 0.14. This value was chosen to compare to previous minimum energy work

done by Huck *et al.*²³ Using these conditions, the maximum PE for PoCCC would be 2574.7 kJ/kg CO₂.

Determining the minimum theoretical PE is more complex than determining the theoretical maximum, which will be shown in the following analysis. As mentioned, even if a binary gas mixture were to separate into two pure streams, there is an associated entropic cost associated with this process. This is the entropy of mixing and follows the 2nd law of thermodynamics, which would rather have ‘disordered’ mixed systems. To create pure streams from a binary gas mixture, the minimum energy of separation, W_{min}^{sep} , can be calculated using equation 3.10, which is the same equation used by Huck *et al.*²³ This works by multiplying the entropy, s , of the heavy, light, and flue gas stream (subscripts h , l , and f respectively), by the number of moles in each stream, n . The entropy of each stream is calculated using equation 3.11, which works by using the fractional amount of each stream (x) and the gas constant (R).

$$W_{min}^{sep} = T \left(n_l s(x_l) + n_h s(x_h) - n_f s(x_f) \right) \quad (3.10)$$

$$s(x) = -R(x \ln(x) + (1 - x) \ln(1 - x)) \quad (3.11)$$

The theoretical minimum is achieved when the heavy stream is be 100% pure CO₂, as no energy is spent compressing other gases. Also, for the minimum theoretical PE, the recovery of CO₂ would need to be near 0%. This is because having as little recovery as possible would mean paying as little entropic cost as possible as the inlet stream remains relatively unchanged. Finally, we would assume the process of compressing the gas to be 100% efficient, and therefore the η_{comp} and η_{pump} were set to 100%. Using all these values and the previous inlet conditions the minimum theoretical PE for PoCCC is 307.9 kJ/kg.

Although these are the bare minimum values, other “minimum” values may be more useful to compare to. First, it would be preferable to recover more than a near 0 amount of CO₂. The DoE guidelines for PoCCC set the target recovery of at least 90% of the CO₂ from the flue gas.⁶⁸ Secondly, the vacuums, compressors, and pumps are mature technologies, with well-known efficiencies, so it makes sense to use their associated efficiencies rather than 100% efficiency. Finally, to put the minimum theoretical PE on a reasonable footing, we will assume that the 0.75η term in equation 1.12 is replaced with 0.4. This is because we could assume nearby low-quality heat as a source to offset the entropic cost of separation comes from the powerplant. 0.4 is on the assumption that the heat will have a maximum thermal efficiency of 40%.⁷⁹ The value of 0.75η

was not used to keep in line with Huck, as well as the fact that this process is a thermodynamic limit, and the idea that steam could be used to help regenerate the material is not possible. Updating the analysis, a reasonable minimum PE cost of PoCCC is 624.6 kJ/kg CO₂. This is notably different from the minimum energy of 424.8 kJ/kg CO₂ reported by Huck *et al.*²³. However, in that work, they ignored the energy required to lower the pressure for desorption of the gas. If we also ignore the energy to run the vacuum, we obtain a minimum PE of 426.8 kJ/kg CO₂ which compares well to the value of Huck *et al.* Considering that we use a different model for the compression energy and different efficiencies, the agreement is good. In summary, although the absolute theoretical minimum PE for PoCCC is 307.9 kJ/kg CO₂, a more practical minimum is 624.6 kJ/kg CO₂.

3.7.5 Limits of Purification Energy for Landfill Gas Separation

A similar analysis that was applied to PoCCC in Section 3.7.4 could be applied to LGS. There are notable differences in the LGS analysis; 1) the heavy stream is emitted into the atmosphere, while the light stream is compressed, 2) as the light stream is compressed, the low pressure in the compression term is the adsorption pressure, and not the desorption pressure, 3) there is no heat available to offset the entropic cost, and 4) the energy would be placed in terms of CH₄ delivered as fuel and not CO₂ captured. The LGS inlet stream is 338 K with 55% CH₄, 40% CO₂, and 5% other gases. If the same assumptions were applied as in PoCCC, (Maxwell's daemon, next to no recovery, etc.) than the theoretical minimum P_{fE} for LGS is 241.1 kJ/kg CH₄, assuming the CH₄ is compressed to a total of 18 bar, and the CO₂ is directly emitted into the atmosphere.⁷⁷ Using reasonable values (90% recovery of CH₄, machine efficiencies, and placing a vacuum onto the system to 0.27 bar) the minimum P_{fE} is 1184.4 kJ/kg CH₄.

Calculating the upper limit is also different as we are not looking at compressing the heavy stream, but instead, we are interested in selling or utilizing the light stream for NG. This means that using a similar analysis as presented in section 3.7.4 is not useful. Instead, a good way to determine a good maximum value is to consider the amount of energy required to make the separation process viable. If the RNG would be sold for fuel, we could look at how much the fuel could be sold for and consider what the electrical cost would be to make the fuel. The NIST webbook states the CH₄ has a heat of combustion of 55.5 GJ/kg,⁸⁰ and according to the Independent Electricity System Operator, in 2016 NG sold for \$2.73 / GJ in Ontario,⁸¹ meaning that the price for NG (assuming it is pure CH₄) is \$151.51/kg. If all the energy for separation comes from

electricity, a 24-hour averaged value for the electricity from Hydro Ontario is \$24.72/GJ.⁸² Dividing the amount of the CH₄ that can be sold by the cost of electricity gives a value of 6128.7 kJ/kg. This number represents the maximum PrE for LGS that would make the process economically viable. It should be noted that on weekdays the cost of electricity drops to \$18.0 /GJ, making the maximum PfE increase to 8391 kJ/kg. These are roughly calculated maximum economic PfEs and should be taken as such. In summary, a reasonable minimum PfE is 1184.4 kJ/kg CH₄, while the economic maximum is 6128.7 kJ/kg CH₄.

4 Carbon Nanoscrolls for Gas Separation and Storage

In the first part of this chapter, I present results about studying carbon nanoscrolls for use in post-combustion carbon capture. For this work, our collaborator from the University of Campina, Eric Perim, was responsible for creating the Cartesian coordinates of the carbon nanoscrolls. A colleague from my lab, Dr. Thomas Daff, was responsible for running many of the GCMC calculations. I performed some GCMC simulations, and all the MD simulations reported here. Additionally, I performed most of the analysis of the data including calculating working capacities, selectivities, and determining the ideal properties of the carbon nanoscrolls. Dr. Daff and I were co-primary authors of this manuscript. This work was originally published in *Carbon*, Volume 101, Pages 218-225 in 2017.¹ Copyright 2016, Elsevier Ltd.

In the second part of the chapter, I present results about studying carbon-based materials, namely Schwarzites, graphene, and carbon nanoscrolls for use in vehicular methane storage. In this work once again our collaborator, Eric Perim, created molecular structures of the carbon nanoscrolls used. Using these structures, I created the relevant unit cells for periodic simulations of each material. I also performed all GCMC calculations and analysis of the results and was the primary author of the manuscript. This work was originally published in the *Journal of Physical Chemistry C*.² Copyright 2019, American Chemical Society.

Formatting of the manuscripts has been changed to maintain a similar style to the rest of the thesis, although all content is the same from the original publications. Changes made include the layout of the manuscript, font, numbering of sections, re-numbering of the figures, and combining the works cited list of the main text and appendix.

4.1 Evaluation of Carbon Nanoscroll Materials for Post-Combustion CO₂ Capture

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4.1.1 Abstract

Carbon nanoscrolls are like multi-walled carbon nanotubes but constructed from rolled graphene sheets into papyrus-like structures. In this work, molecular simulations are used to evaluate the post-combustion CO₂ capture properties of nanoscrolls made of graphene, α -, β -, and γ -graphyne, boron nitride, and three types of carbon nitride. The CO₂ uptake capacity, CO₂/N₂ selectivity and CO₂ working capacity were computed with grand canonical Monte Carlo simulations at conditions relevant to post-combustion CO₂ capture. The interlayer spacing of the nanoscrolls was optimized for each property and sheet material. For graphene nanoscrolls, the optimal interlayer spacing of 7.3 Å was identified for both the CO₂ uptake and selectivity, while for working capacity the optimal interlayer spacing was determined to be 8.6 Å. It was found that the CO₂ uptake capacity of the materials correlated to the density of the sheets from which they were formed. Nanoscrolls made from graphene and boron nitride, which have the highest number of atoms per unit area, also showed the highest CO₂ uptakes. At 0.15 bar CO₂, 313 K, graphene and boron nitride nanoscrolls exhibited exceptional CO₂ uptake capacities of 7.7 and 8.2 mmol/g, respectively, while also exhibiting high CO₂/N₂ selectivities of 135 and 153, respectively. Molecular dynamics simulations were used to examine the adsorption kinetics. The simulations showed that an empty graphene nanoscroll with a roll length of 200 Å could adsorb CO₂ into the center of the roll within 10 ns. Materials with pores that can allow CO₂ to pass through, such as graphynes, showed much faster adsorption times.

4.1.2 Introduction

Anthropogenic CO₂ emissions are the primary cause of global climate change.³ Since power generation from burning fossil fuels is one of the largest sources of such emissions, technologies that can capture CO₂ from the combustion flue gas of existing power plants are garnering significant attention. Here the challenge is to separate CO₂ from a humid gas stream that is composed of 10-15% CO₂ and 75-85% N₂, to obtain a high purity CO₂ stream that can be transported for permanent storage underground.⁴ The current technology for large-scale CO₂ scrubbing involves the use of aqueous amines which selectively traps CO₂ via chemical absorption.⁵ Although this method is being widely used for methane purification from acidic natural gas reservoirs,⁶ the regeneration of aqueous amines requires high temperatures and is too costly for large-scale post-combustion carbon capture. It was shown that the use of aqueous amine

CO₂ scrubbers in coal burning power plants would consume almost a third of the energy output of the plant⁷ and make electricity 60-80% more expensive.⁸ Due to these prohibitive energetic and monetary costs, new CO₂ capture technologies are needed in order for large-scale carbon capture and storage (CCS) to become a reality.

Solid sorbents have been investigated for use in CCS and have been found to possess several key advantages over aqueous amines. First, solid sorbents interact less strongly with CO₂ (20 - 40 kJ/mol vs. 90 kJ/mol for aqueous amines), which means less energy is required to remove CO₂ from the sorbent in the regeneration process. Second, solid sorbents have lower heat capacity in comparison to aqueous amines (< 1 vs. $\sim 4 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$),⁹ thus less energy goes into heating the material during regeneration. Lastly, there are mature gas separation systems that use solid sorbents that can be retrofitted to current power plants. In these systems, the flue gas flows through a stationary bed of the solid sorbent that selectively adsorbs the CO₂ while allowing the other gasses to pass through. When the bed has reached maximum capacity, the CO₂ captured in the sorbent is desorbed either with the application of a vacuum (PSA⁹) or high temperature (TSA¹⁰) or a combination of the two (TPSA¹¹). The resulting desorbed gas stream is near pure CO₂, which can then be compressed and transported for permanent storage. The ideal sorbent for use in PSA/TSA systems will have a high CO₂ uptake capacity or more formally a large CO₂ working capacity (the difference in uptake at the adsorption and desorption conditions), and high CO₂/N₂ adsorption selectivity. Since water is a primary combustion product, the favorable adsorption characteristics must be maintained in a humid gas stream. The material also needs to possess high thermal and hydrolytic stability as they are expected to go through hundreds of thousands of adsorption and desorption cycles.⁸

Nanoporous materials, such as zeolites¹² and metal-organic frameworks (MOFs)¹³ that have ultra-high internal surface areas for gas adsorption have been intensely studied as potential solid sorbents in T/PSA systems for post-combustion CO₂ capture. Amongst the highest performing MOFs is Mg-MOF-74 which possess a very high CO₂ uptake capacity (6.16 mmol/g at 298 K and 0.15 atm)¹⁴ and high selectivity (94 CO₂/N₂ at 298 K and 0.15 atm CO₂ and 0.75 atm N₂) with moderate regeneration conditions.¹⁵ However, the material possesses open metal sites that make it susceptible to degradation in the presence of relatively small amounts of water, losing approximately 90% of its CO₂ capacity upon exposure to 70% RH at 298 K.¹⁶ Zeolite-13X is one of the highest performing zeolites for CO₂ adsorption using the PSA process and is currently used

on an industrial scale for scrubbing CO₂ from natural gas. Although it has high CO₂ uptake capacity (2.8 mmol g⁻¹) at 298 K and 0.15 atm of CO₂,¹⁷ its selectivity for CO₂ over N₂ is rather small, and its adsorption capacity declines rapidly with humid gas streams and at temperatures relevant to industrial post-combustion CO₂ capture.¹⁸

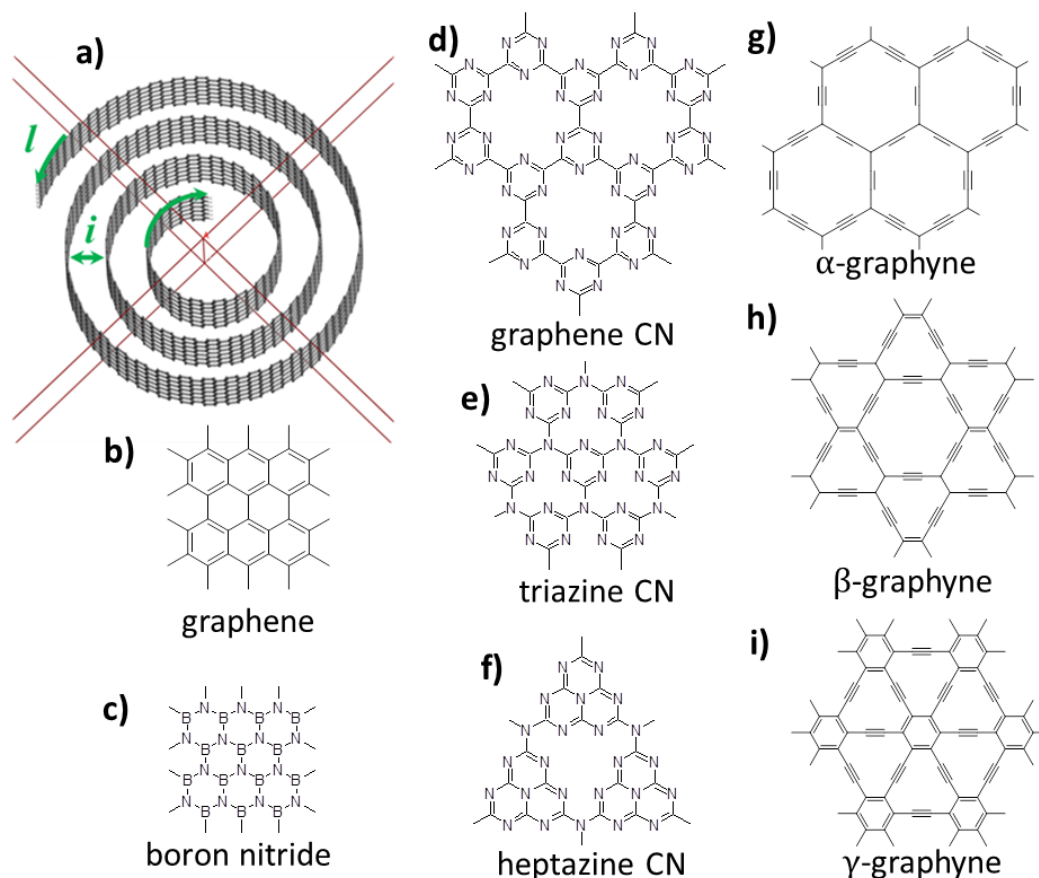


Figure 4.1. a) An idealized graphene nanoscroll showing the interlayer spacing, *i*, and length of rolled up scroll, *l*. b-i) Various nanoscroll materials examined in this work. (CN = carbon nitride)

One potential solid sorbent that has not been well studied is carbon nanoscrolls (CNS). CNS are similar to multi-walled carbon nanotubes but constructed from a graphene sheets rolled up into papyrus-like structures,¹⁹ as depicted in Figure 4.1a. Due to not having caps and being able to easily change their radius, CNSs have higher solvent accessible surface area than nanotubes. They are durable under heat and humidity, and their raw materials make them potentially cheap for large scale production.²⁰ Under normal conditions, the concentric sheets lie against each other with no space between them, however intercalating nanoparticles of alkali metals from Li to Rb can give layered carbon structures a highly tuned interlayer spacing.^{21,22} In addition to graphene, nanoscrolls constructed from other sheet-like materials can be envisioned. Computational studies

have predicted hexagonal boron nitrides (Figure 4.1c) and carbon nitrides (Figure 4.1d-f) to form stable nanoscrolls,²³ the former of which have since been successfully synthesized.^{24,25} Three graphene-like carbon nitride sheets with varying pore sizes²⁶ and monolayers of graphyne (Figure 4.1g-i) have all been synthesized,²⁷ although none has been successfully formed into nanoscrolls to date.

The CO₂ adsorption capacity of graphene CNSs under high-pressure conditions (1 to 90 bar) has been previously studied with grand canonical Monte Carlo simulations.^{22,28} Most notably, scrolls with an interlayer spacing of 15 Å were predicted to have an exceptionally high gravimetric CO₂ uptake capacity of 34.6 mmol/g at 273.15 K and 30 bar. However, these conditions are very different from that in the post-combustion flue gas where the partial pressure of CO₂ is only 0.15 bar, and the temperature is approximately 313 K or higher. To date, the CO₂ capture performance of nanoscrolls made from other materials such as boron nitride or carbon nitride has not been examined.

In this work, we use molecular simulations to investigate the performance of CNS materials as solid sorbents in TPSA gas separation systems under typical post-combustion flue gas conditions. We examine not only the CO₂ uptake but also the CO₂/N₂ selectivity and the working capacity for CO₂ capture. In addition to nanoscrolls constructed from graphene, we also consider those made from boron nitride (Figure 4.1c), three types of carbon nitride sheets (Figure 4.1d-f), and three types of graphyne (Figure 4.1g-i). Finally, we look at the kinetics of CO₂ adsorption into the nanoscrolls.

4.1.3 Methods

For all models, 3-dimensional periodic boundary conditions were utilized where the width of the nanoscroll repeating unit was not less than 25 Å and that the vacuum distance between nanoscrolls was at least 25 Å. Thus, isolated nanoscrolls of infinite length were simulated, serving as a model for scrolls of long length. A total of 8 chemically unique nanoscrolls, including graphenes, graphynes, carbon nitrides, and boron nitrides were examined, all of which are shown in Figure 4.1. For each type of scroll the interlayer spacing, (*i* from Figure 4.1a), was tested from 4.7 Å to 9.9 Å, in size increments of 1.3 Å. The length of the scrolls varied from ~200 Å to 400 Å. For every nanoscroll, we used an internal diameter, *d*, of at least 20 Å, which has been shown to be the optimum diameter in nanoscrolls.¹⁹

We determined the gas adsorption on the nanoscrolls using grand canonical Monte Carlo (GCMC) simulations using an in-house code based on DL_POLY 2 molecular dynamics package²⁹ that has been previously applied to study gas adsorption in metal-organic frameworks.^{30–33} The atomic positions of the nanoscrolls were fixed in the simulations. Non-bonding interactions were calculated using Lennard-Jones (LJ) potentials and electrostatic interactions calculated with partial atomic charges. The LJ parameters for the nanoscrolls were assigned from the universal force field (UFF)³⁴ and partial atomic charges were assigned by a charge equilibration method that was fitted to reproduce the quantum mechanical electrostatic potentials in nano-porous materials.³⁵ Parameters for the CO₂ guest molecules were developed by Garcia-Sánchez *et al.* to reproduce adsorption in zeolites,³⁶ and parameters for the N₂ guest were taken from a model fitted to reproduce experimental adsorption in metal-organic frameworks, with all parameters used given in the Appendix. Single component (CO₂) and binary component (CO₂ and N₂) GCMC calculations were performed up to a total pressure of 1 bar and 6 bar, respectively. GCMC simulations were run for 10,000 cycles, for both the equilibration and the production phases. A cycle consists of N Monte Carlo steps where N is the number of guest molecules present at any given point. For example, one nanoscroll tested in this work adsorbed a total of 425 guests per simulation cell, and thus 4.25 million Monte Carlo steps were performed to equilibrate the system and a further 4.25 million Monte Carlo steps were used during the production phase. For this run the number of guest molecules as a function of Monte Carlo steps is plotted in Figure 4.22 showing that equilibrium is reached at approximately 2 million steps. Errors in the uptake were calculated by taking the standard deviation over window averages of the uptake during the production phase of the GCMC simulation. Windows were set to have 500,00 steps per window.

Molecular dynamics (MD) simulations were performed using the DL_POLY Classic 1.9 molecular dynamics package³⁷ using the same parameters and conditions used for the GCMC simulations. The amount of molecules placed into the cell was equaled to the quantity of the gas and adsorbed phases at a specific temperature and pressure. The MD simulations were using rigid guests and nanoscrolls at 10 fs time steps for a total of 11 ns and attached to a Nosé-Hoover thermostat.³⁸ As the CO₂ guests were held rigid CO₂ and the framework was frozen, a 10 fs time step would be able to catch all significant movements.

4.1.4 Results and Discussion

First, we will examine the gas adsorption properties of graphene nanoscrolls. The CO₂ uptake capacity, CO₂/N₂ selectivity, and CO₂ working capacity are computed using the adsorption conditions of 0.15 bar CO₂ and 313 K, and desorption conditions of 0.75 bar CO₂ and 413 K. For CO₂/N₂ selectivity, conditions are binary mixtures of CO₂ and N₂ at a ratio of 1:5 respectively.

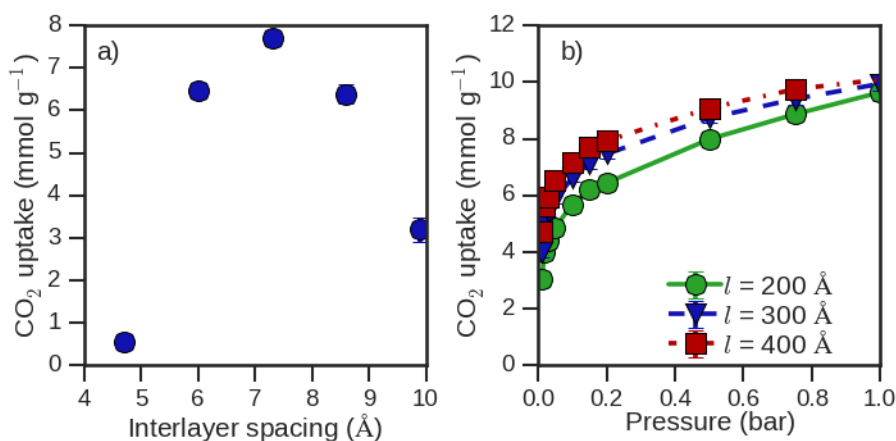


Figure 4.2. a) Computed CO₂ uptake at 313 K and 0.15 bar for 400 Å long graphene nanoscrolls as a function of the interlayer spacing, i (defined in Figure 4.1a). b) Computed CO₂ isotherms at 313 K with changing scroll length at constant interlayer spacing at 7.3 Å. Error bars for some data points may be smaller than the data symbols.

Figure 4.2a shows the computed CO₂ uptake capacity of a 400 Å long graphene nanoscrolls as a function of the interlayer spacing, i . There is a strong dependence of the CO₂ uptake on the interlayer distances with a clear maximum at 7.3 Å. Since the graphene atoms in these simulations have no net charge, this interlayer distance maximizes the dispersion interactions between the CO₂ and two graphene sheets. The optimal interlayer distance of 7.3 Å roughly corresponds to the sum of the van der Waals radii of two carbons (of the graphene sheets), and the van der Waals diameter of C (of the CO₂). Figure 3 shows a cross-section of the CO₂ center of mass probability distribution from a GCMC simulation with an interlayer distance of 7.3 Å. The probability distribution reveals that there is relatively little adsorption of the CO₂ on the outer surface of the nanoscrolls where the guest can only interact optimally with one graphene sheet. Finally, we note that, the optimal nanoscrolls interlayer distance of 7.3 Å determined for CO₂ uptake at low pressure (0.15 bar), is significantly different from the 15 Å optimal interlayer distance previously determined for CO₂ uptake at high pressure (30 bar).

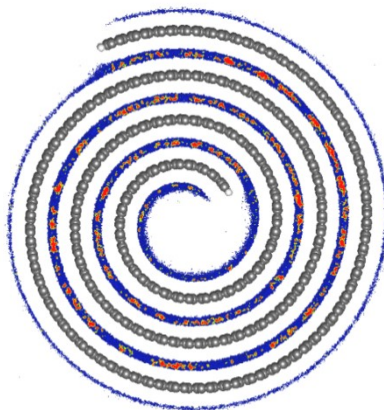


Figure 4.3. Probability of CO₂ center of mass in graphene nanoscroll at 313 K and a pressure of 0.15 bar CO₂. Blue are areas of lower probability, and red are areas of higher probability.

We next examine how the length of the roll affects the CO₂ uptake. Plotted in Figure 4.2b, is the CO₂ adsorption isotherm at 313 K of graphene nanoscrolls of length 200, 300 and 400 Å at optimal interlayer separation of 7.3 Å. Figure 4.2b reveals that as the length of the roll increases, so does the CO₂ uptake. However, an infinite length roll will not give an infinite uptake capacity because the uptakes reported are gravimetric uptakes (uptake capacities are per unit mass of the graphene). The reason that there is a dependence on the nanoscrolls length is that with longer lengths, a smaller fraction of the graphene sheet is part of the outermost roll where there is relatively little CO₂ adsorption as shown by Figure 4.3. This is consistent with the diminished increase in CO₂ uptake observed in going from a scroll-length 300 to 400 Å as compared to the increase in going from 200 to 300 Å. Since these trends persist in all uptake properties as the length of the roll increases, from here on forward we will report the adsorption properties calculated with scroll lengths of 400 Å.

Although CO₂ uptake capacity is an important property for evaluating a material's performance for post-combustion CO₂ capture, the material's selectivity for CO₂ over N₂ is equally important as the energetic cost of CO₂ capture is strongly dependent on the selectivity.³⁹ The post-combustion flue gas is roughly 80% N₂, and a sorbent material that has poor selectivity will result in significant energy being used to desorb N₂. A poor selectivity will also lead to an outgoing stream of captured CO₂ gas that is contaminated with N₂, resulting in energy being wasted to compress, transport and store N₂.

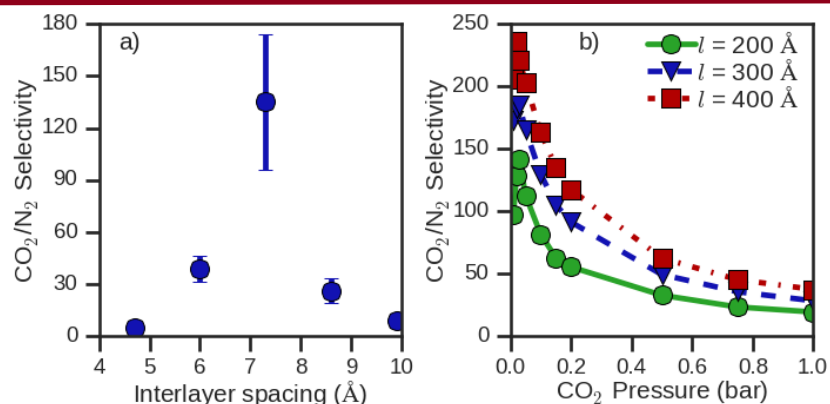


Figure 4.4. a) CO₂/N₂ selectivity at 313 K for a) 400 Å long graphene at 0.15 bar nanoscrolls at differing interlayer spacing (Error bars for some data points may be smaller than the data symbols.) b) for 7.3 Å interlayer spacing at multiple pressures and differing lengths of scrolls.

Figure 4.4a plots the CO₂/N₂ selectivity at the adsorption conditions for graphene as a function of the interlayer spacing. Again, there is a strong dependence of this property on the interlayer spacing, and there is a maximum at 7.3 Å. The trend observed in selectivity is essentially identical to that of the CO₂ uptake capacity plotted in Figure 4.2. The primary reason for this is that the N₂ uptake is very low for all interlayer spacings meaning the selectivity is dominated by the CO₂ uptake. Figure 4.4a shows that the computed selectivity at 7.3 Å has a large absolute error compared to other interlayer distances. This is since the N₂ uptake is very low compared to the CO₂ uptake, and small fluctuations in the N₂ uptake result in large changes in selectivity. We note that the relative error of the selectivity at 7.3 Å is 28%, which is like the relative error at other distances (e.g. 29% for 8.6 Å and 35% for 9.9 Å). Figure 4.4b shows that as the length of scroll increases from 200 to 400 Å the selectivity for CO₂ over N₂ increases (A similar trend shown in Figure 4.2b was observed with the uptake as the scroll length is increased.). As the scroll length increases, the ratio of the length between sheets of the nanoscroll to the length of the outer layer increases as well. This suggests that the ‘inside’ of the nanoscrolls have better separation capability than the outer layer of the nanoscroll. This is corroborated by the diminished probability density on the outside of the scroll as shown in Figure 4.3.

The final adsorption property we considered is what is known as the working capacity. The working capacity is the amount of CO₂ adsorbed at adsorption conditions less the amount of CO₂ adsorbed at desorption conditions. In other words, it provides an estimate for how much CO₂ can be adsorbed by a material per adsorption/desorption cycle. A material may have an exceptional CO₂ uptake capacity, but if it does not easily release the gas at the given desorption conditions,

then more adsorption/desorption cycles must be used to extract the same amount of CO₂ compared to a material with a larger working capacity. We note that there is wide variation in choice of desorption conditions since it is highly dependent on the T/PSA system being used. This is one reason why CO₂ uptake capacities are generally reported for sorbent materials, even though the working capacities is formally more relevant to calculating the CO₂ capture efficiency of a sorbent. Furthermore, desorption conditions can be optimized for a given material as to minimize the energy consumption of the gas separation. For our work, we have set a static desorption condition for each material at 0.75 bar CO₂ and 413 K. The conditions we use fall within typical ranges of pressure and temperature used in the optimization process of TPSA for porous materials.⁴⁰

Depicted in Figure 4.5 is the computed CO₂ working capacity of the graphene nanoscrolls plotted as a function of the interlayer spacing, i . Compared to the CO₂ uptake capacity, the working capacity has a more complicated dependence on the interlayer distance, with a maximum at 8.6 Å and a slight dip at 7.3 Å. Although the 7.3 Å interlayer spacing is able to adsorb more CO₂ at the adsorption condition, it also holds onto more CO₂ at the desorption condition than the 8.6 Å interlayer spacing. This can be seen in Figure 4.5b, where the CO₂ uptake capacity at the adsorption conditions and the desorption conditions are both plotted - the working capacity is the difference in these uptakes. It is important to note that the optimal interlayer distance that maximizes the CO₂ working capacity is likely to change with different desorption conditions.

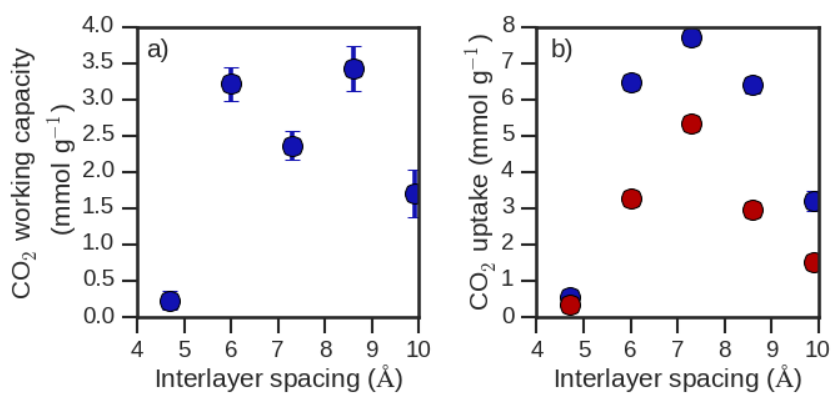


Figure 4.5. a) CO₂ working capacity of 400 Å long graphene nanoscrolls with adsorption at 0.15 bar CO₂ and 313 K to desorption at 0.75 bar CO₂ and 413 K, at different interlayer spacing. b) CO₂ uptake at the adsorption (blue) and desorption (red) conditions. Error bars for some data points may be smaller than the data symbols.

We now turn our attention to other nanoscrolls materials shown in Figure 4.1c-i, including graphynes, carbon nitrides, and boron nitrides. For each material, the optimal interlayer spacing was determined in an identical way as was done with graphene by varying the interlayer distance

from 4.7 Å to 9.9 Å, in increments of 1.3 Å. For all materials, a scroll length as close as possible to 400 Å was used. In comparing the properties of the different materials, the optimal interlayer distance is utilized for each material. Figure 4.6 compares the CO₂ uptake capacity and CO₂/N₂ selectivity of each material as a function of the pressure at a 313 K. At 0.15 bar, there is a large variation in the uptake ranging from a high of 8.2 mmol/g for boron nitride to a low of 1.3 mmol/g for α -graphyne. The trends observed in the uptake capacity are mirrored in the selectivities, with boron nitride giving the highest CO₂/N₂ selectivities as shown in Figure 4.6b.

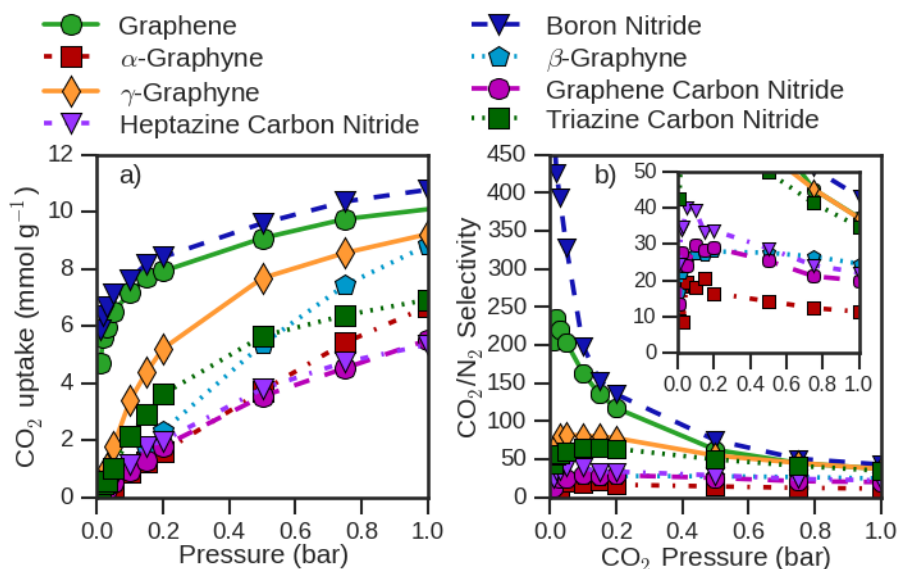


Figure 4.6. a) CO₂ uptake and b) CO₂/N₂ selectivity isotherms at 313 K for nanoscrolls tested using the optimal interlayer spacing for every sheet.

With the large variation in the computed uptakes and selectivities for the 8 materials examined, the natural question that arises is how much of the variation is due to the chemistry of the sheets. Although graphene has no net charges on its atoms, the other materials do have local polarization of charges, which may enhance their interaction with CO₂. On the other hand, we notice that there is a large difference in the uptake capacity of α -graphyne and γ -graphyne. α -graphyne is significantly less dense than γ -graphyne as can be seen visually in Figure 4.1. To explore whether the performance of the materials is dominated by the chemistry or density we have plotted the CO₂ uptake capacity for each material as a function of the number of atoms per unit area of the sheet material in Figure 4.7. The data shows that there is a roughly linear dependence of the CO₂ uptake on the atom density of the unrolled material. However, there is a clearly a different linear dependence for the carbon nitride (CN) nanoscrolls as there is with the other mostly pure carbon based nanoscrolls. This could be because the dispersion interactions between CO₂ and nitrogen are

smaller than with carbon, seen in the Lennard-Jones parameters. The boron nitride nanoscroll still maintains high CO₂ adsorption, even with the nitrogen atoms, as the dispersion interaction between CO₂ and boron are stronger than even the CO₂-C interaction.

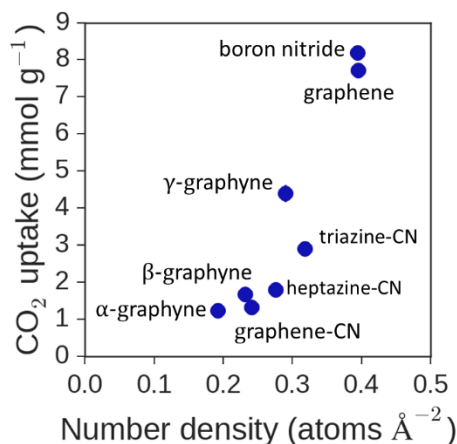


Figure 4.7. CO₂ uptake at 313 K and partial pressure of 0.15 bar as a function of the atomic density for the various types of nanoscrolls at optimal interlayer spacing and length. Error bars for the data points are smaller than the data symbols.

Both graphene and boron nitride nanoscrolls exhibit exceptional CO₂ adsorption properties for post-combustion CO₂ capture. With optimized interlayer spacings, the CO₂ uptake capacity is computed to be 7.7 mmol/g and 8.2 mmol/ for graphene and BN nanoscrolls, respectively, while the CO₂/N₂ selectivity is 135 and 153, respectively. Mg-MOF-74¹⁴ and Zeolite-13X¹⁷ are often used as benchmark materials for post-combustion CO₂ capture. While Mg-MOF-74 has one of the lowest reported parasitic energies⁴⁰ for CO₂ capture using a T/PSA system, Zeolite-13X is currently used for large-scale CO₂ scrubbing of natural gas. The CO₂ uptake isotherms at 313 K for graphene and BN are compared to that of Mg-MOF-74 and Zeolite-13X in Figure 4.8a, while the CO₂/N₂ selectivities are given in Figure 4.8b. At pressures relevant for post-combustion CO₂ capture (0.15 bar CO₂) the graphene and BN nanoscrolls outperform Mg-MOF-74 and Zeolite-13X, in terms of both CO₂ uptake, and selectivity. Whereas, the selectivities of all materials are comparable, the nanoscrolls materials significantly outperform Mg-MOF-74 and Zeolite-13X in terms of CO₂ uptake capacity. In the case of the CO₂ uptake capacity, if metal ions are used to maintain a given interlayer spacing, this would diminish the gravimetric uptake of the materials.

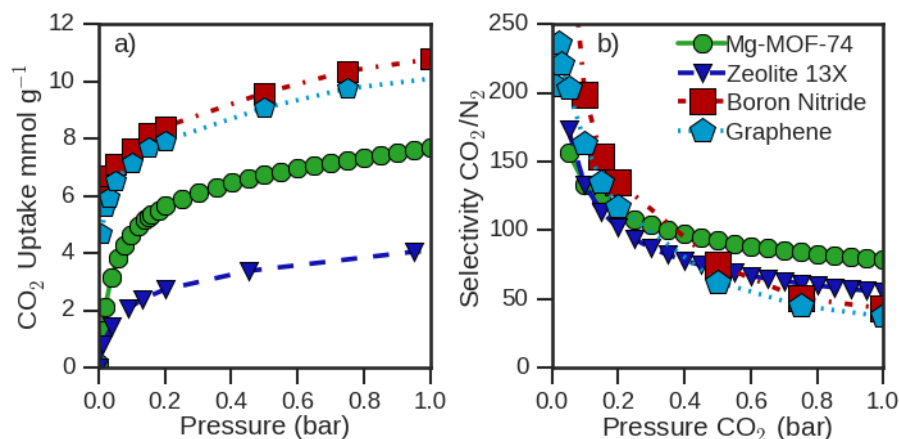


Figure 4.8. a) CO₂ uptake and b) CO₂/N₂ selectivity isotherms for Mg-MOF-74 and zeolite (experimental data), and graphene and boron nitride nanoscrolls (simulated data). Data for Mg-MOF-74, boron nitride, and graphene are at 313 K, and the Zeolite-13X data is at 308 K. Experimental selectivities were calculated from single component measurements using the Sips isotherm model ⁴¹.

One potential downside of using nanoscrolls as sorbent materials for T/PSA based CO₂ capture is poor adsorption/desorption kinetics. With both graphene and boron nitride sheets, CO₂ cannot pass through the sheets and, therefore, for full CO₂ adsorption to be achieved, some guest molecules must traverse the whole length of the sheet to reach the center of the nanoscroll. With some of the materials examined, such as γ -graphyne, there are pores large enough for CO₂ to pass through, as seen in the CO₂ probability distribution maps from the GCMC simulations (Appendix, Figure 4.39). These show that there are CO₂ binding regions within the pores of the sheets. The pores would presumably enhance the adsorption and desorption kinetics as the guest molecules could more directly travel through the layers into the center of the nanoscrolls, like diffusion in a crystallite of a porous solid. To evaluate this, we performed molecular dynamics simulations of graphene (200 Å in length) and graphyne (190 Å in length) nanoscrolls wherein the empty nanoscrolls were placed in a large simulation cell filled with CO₂ molecules amounting to the adsorption capacity of the material at 0.15 bar, 313 K. In all cases, the simulation cell was large enough that the initial pressure of the gas was approximately 1.15 bar (based on the number of molecules in the free volume of the cell).

Given in Figure 4.9 is the average distance of the centre of mass of the CO₂ molecules to the center of the nanoscrolls during the molecular dynamics simulation for graphene, α -, β - and γ -graphyne. For all materials, visual inspection of the configuration after 10 ns of simulation time revealed that all the CO₂ molecules had been adsorbed into the nanoscrolls. Although 400 Å length

nanoscrolls rolls are not long, the simulations suggest that CO₂ can adsorb relatively quickly into the materials even if they do not have pores large enough for CO₂ to pass through. It can be seen from Figure 4.9 that the large pores in the graphyne sheets do enhance the rate at which the CO₂ can diffuse into the nanoscrolls. Furthermore, the larger the pores, the faster the adsorption rate - the pore sizes for α -, β - and γ -graphyne are 7.95, 5.82, 4.13 Å, respectively. The adsorption rates can be quantified by fitting an exponential decay function to the distance plotted in Figure 4.9. This gives full adsorption half-lives of 0.17, 0.68, 1.23, and 3.66 ns for the α -graphyne, β -graphyne, γ -graphyne, and graphene, respectively. Although introducing pores into the nanoscrolls improves the adsorption kinetics, there is a trade-off because the pores reduce the number density of the material, which in turn reduces the CO₂ adsorption capacity of the materials.

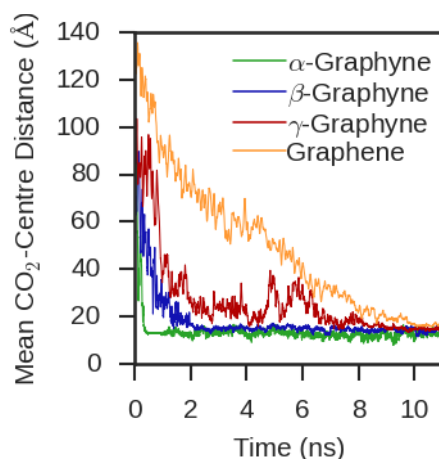


Figure 4.9. Average distance of the CO₂ center of mass to the center of the nanoscroll as a function of time during a molecular dynamics simulation at 313 K of initially empty nanoscrolls.

4.1.5 Conclusions

The gas adsorption properties of nanoscrolls made from various materials (graphene, graphyne, boron nitride and carbon nitride) have been examined at conditions relevant to post-combustion CO₂ capture using molecular simulations. It was found that the CO₂ uptake capacity of the nanoscroll was strongly dependent on the atom number density of the sheet that made up the scroll. The more atoms per unit area of the nanoscrolls material, the higher the CO₂ uptake. The densest materials, graphene and boron nitride, were found to have the best adsorption properties of the materials evaluated with both possessing exceptional CO₂ uptake capacities, above 7 mmol/g at 0.15 bar and 313 K, while also having exceptional CO₂/N₂ selectivities (greater than 150). For comparison, Mg-MOF-74, which is considered a benchmark material for post-combustion CO₂ capture, has a CO₂ uptake capacity of 5.28 mmol/g and CO₂/N₂ selectivity of 122 under the same

conditions. Since post-combustion CO₂ capture materials must operate in the presence of humidity, some of the materials examined here, particularly graphene, may have advantages in this respect over MOFs. Whereas many MOFs including Mg-MOF-74 are not humidity stable, graphene is both hydrophobic and water stable. On the other hand, the rolled architecture of the nanoscrolls may limit the adsorption and desorption kinetics compared to more porous materials such as MOFs. Using molecular dynamics simulations, we found that the full adsorption of CO₂ into the center of nanoscrolls was surprisingly rapid. Moreover, the adsorption rate could be greatly enhanced by the addition of pores into the sheets, albeit with a trade-off with the adsorption capacity. Although idealized nanoscrolls were evaluated in this work, the high performance of the materials suggests that as advances are made in synthesizing nanoscrolls, they should be evaluated for the post-combustion CO₂ capture properties.

4.2 Idealized Carbon-Based Materials Exhibiting Record Deliverable Capacities for Vehicular Methane Storage

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4.2.1 Abstract

Materials for vehicular methane storage (VMS) have been extensively studied, although no suitable material has been found. In this work we use molecular simulation to investigate three types of carbon-based materials, Schwarzites, layered graphenes and carbon nanoscrolls, for use in VMS at adsorption conditions of 65 bar and 298 K, and desorption conditions of 5.8 bar and 358 K. 10 different Schwarzites were tested and found to have high adsorption with maximums at 273 V_{STP}/V but middling deliverable capacities of no more than 131 V_{STP}/V . Layered graphene and graphene nanoscrolls were found to have extremely high CH_4 adsorption of 355 and 339 V_{STP}/V , respectively, when the interlayer distances were optimized to 11 Å. The deliverable capacities of perfectly layered graphene and graphene nanoscrolls were also found to be exceptional with values of 266 and 252 V_{STP}/V , respectively, with optimized interlayer distances. These values make graphene and nanoscrolls the record holders for adsorption and deliverable capacities under VMS conditions.

4.2.2 Introduction

Transportation is one of the largest greenhouse gas production sectors, only behind electricity production.⁴² Although the capture of CO_2 from mobile sources, such as vehicles, is currently impractical, one possible avenue to reduce CO_2 emissions is through the use of alternative fuels, such as natural gas (methane). Natural gas is readily available and is both cheaper and produces less greenhouse emissions than diesel or gasoline.^{43,44} Despite the significant advantages, there are key technological barriers that prevent natural gas vehicles (NGV) from being widely adopted for personal use. The most serious barrier is that in order for NGV to have acceptable ranges, the fuel must be stored in compressed form, which requires large, bulky cylindrical fuel tanks that consume too much trunk space.⁴⁴ What is needed is a low-pressure NG storage technology that would allow for form fitting storage tanks to be created much like today's gasoline fuel tanks. Fuel tanks filled with high surface area nanoporous materials, such as metal-organic frameworks (MOFs), are viewed as a promising technology for high-density, low-pressure storage of NG that could enable widespread adoption of NGV.

Recognizing the barriers for NGV adoption, the U.S. Department of Energy (DoE) set targets for the development of technologies for vehicular methane storage (VMS) through its Methane Opportunities for Vehicular Energy or MOVE program.⁴⁴ This in turn sets the gas storage capacity

targets for nanoporous materials for VMS. The storage capacity, or deliverable capacity, of a material is given by the difference in the material uptake capacities under adsorption and desorption conditions. MOVE set desorption conditions of less than 85 °C (358 K) and greater than 70 psig (5.8 bar) - the inlet pressure of the engine.⁴⁵ The adsorption conditions are not as explicitly stated by MOVE. However, most studies have used a temperature of 298 K and 65 bar.^{46–50} For the material to meet the MOVE target, it must have a volumetric energy density of 9.2 MJ/L. This energy density corresponds to a deliverable capacity of 263 V_{STP}/V of methane. While some studies have used this value as the adsorption capacity target, it is the target for the deliverable capacity of the material.⁴⁶ When computationally evaluating a material's deliverable capacity, the idealized crystal structure is typically used, which does not account for packing loss. A packing loss of 25%, as set by MOVE, therefore gives a deliverable capacity target of 315 V_{STP}/V in this context.

A wide range of porous materials, including MOFs, porous polymer networks (PPNs), zeolitic imidazolate frameworks, and carbon powders, have been examined for their VMS capacities as set by the MOVE program.^{45–49,51} The well-known MOF NU-111⁴⁸ was experimentally measured to have a deliverable capacity of 177 V_{STP}/V under isothermal adsorption and desorption conditions from 65 to 5 bar at 298 K. One of the most widely studied MOFs, HKUST-1,⁵² was determined to have an impressive deliverable capacity of 216 V_{STP}/V from 65 bar and 298 K to 5 bar and 323 K.⁴⁷ Long and coworkers have reported a flexible Co(bdp) MOF with an isothermal deliverable capacity of 197 V_{STP}/V from 65 bar to 5.8 bar at 298 K.⁵¹ One of the widest ranging studies was done by Smit and co-workers, who computationally studied over 3 million unique structures, including both hypothetical and experimentally realized structures. They found that no structure was able to meet the deliverable capacity target set by MOVE, even when considering all methane to be removed (desorption temperature of ∞). They also showed that each the family of material, (i.e. MOFs, PPNs) exhibited a specific region of performance. For example, the uptakes vs deliverable capacities of MOFs all lied within a characteristic region. Although very comprehensive, several classes of materials, both experimentally realized materials and hypothetical ones were not examined in this study. It should be noted that Bhatia and Myers did a study to find the ideal adsorption properties for methane deliverable capacity.⁵³ In that work, they determined the ideal Langmuir constant to give the highest fractional deliverable capacity between

two pressures. Although this work does shed light on the ideal adsorbents for the process, we are more interested in finding materials with the highest absolute deliverable capacity.

In this work, we investigated three classes of carbon-based materials; layered graphenes (LGs), carbon nanoscrolls (CNSs) and Schwarzites. Layered carbon materials with fixed interlayer spacing have been considered for methane storage. Snurr and co-workers studied 6 hypothetical carbon-based systems, with 3 spacings between a lattice of atoms of 8, 12 and 16 Å and determined the largest deliverable capacity to be $190 V_{\text{STP}}/V$. However, pure graphene systems were not evaluated for CH₄ deliverable capacity.⁵⁰ CNSs, first synthesized in 2003,^{19,54} are graphene sheets rolled into papyrus-like structures similar to multi-walled carbon nanotubes, with an example shown in Figure 4.10a. CNS have also been studied for CO₂ uptake capacity^{1,28} and for methane storage,²⁸ but not for use in NGV. These studies show that CNS can have adsorption properties like the best performing MOFs.

Schwarzites are three-dimensional carbon materials whose surfaces are similar to buckyballs except that they contain 7-membered rings, as opposed to the 5-membered rings, which creates negative curvature surfaces.⁵⁵ Over 22 distinct Schwarzite structures have been hypothesized,^{56,57} such as those shown in Figure 4.10b and c. Schwarzites structures have been identified with name codes that contain structural information, such as the number of atoms in a unit cell (C168), the size of rings and how they are oriented (D8bal, P7par), or how a single carbon atom makes up vertices of the rings in the structure (D688, P688). Although amorphous spongy carbons with negatively curved surfaces sometimes referred to as random Schwarzites, have been synthesized,⁵⁸ Schwarzites with regular crystalline structures have not been experimentally realized. Through simulations, Babarao and co-workers compared the CO₂ and CH₄ adsorption capacities of one Schwarzite (C168) up to a pressure of 60 bar at 300 K, and also looked at its ability to selectively adsorb CO₂.⁵⁹ Anderson and co-workers used C168 as a stand in for nanoporous carbon and once again tested for the selective adsorption of CO₂ over CH₄ from temperatures ranging from 308 K to 473 K with pressures up to 16 bar.⁶⁰ In this work, we use molecular simulations to investigate the performance of graphene, carbon CNS made from graphene and Schwarzites as solid sorbents for methane storage in vehicles. We studied both the CH₄ uptake and deliverable capacity for use in vehicles. We determined the optimal geometries of each of these materials and evaluated their VMS capacities at adsorption conditions of 298 K and 65 bar and desorption conditions of 358 K and 5.8 bar. Finally, we compare the results to previously tested materials.

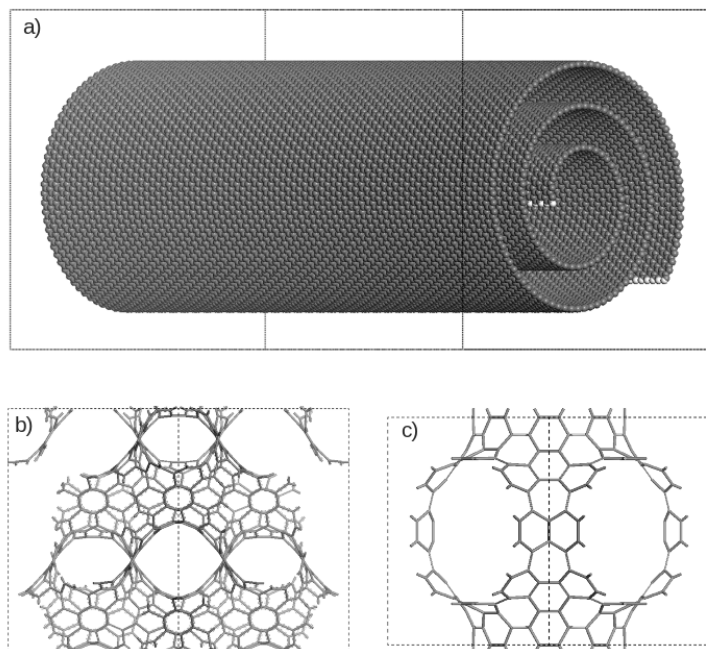


Figure 4.10. a) Image of an idealized graphene-based CNS. Unit cell of the Schwarzite b) C168 and c) P7par.

4.2.3 Methods

For all models, 3-dimensional periodic boundary conditions were used, with unit cells being no less than 12.5 Å along any direction to avoid self-interaction between the guest molecules. A total of 10 distinct Schwarzites were tested and 17 graphenes with interlayer spacings from 4-20 Å in 1 Å increments. Nanoscrolls were tested at various lengths ($l = 200\text{-}3000$ Å), interlayer spacing ($s = 4\text{-}20$ Å), interscroll distances ($d = 4\text{-}25$ Å), with different packing styles (square and hexagonal). These parameters are shown in Figure 4.11. For every nanoscroll the internal diameter was set to 20 Å, which has been shown to be the optimum diameter for structurally stable nanoscrolls.¹⁹ Nanoscrolls were generated by rolling two-dimensional, atom-thick, sheets into Archimedean spirals. These spirals are defined as having a constant interlayer distance, which can be freely set. All gas adsorptions were determined using grand canonical Monte Carlo (GCMC) simulations using an in-house code based on DL_POLY 2 molecular dynamics package²⁹ that has been previously applied to study gas adsorption in MOFs and nanoscrolls.^{1,30,31,33,61} Frameworks atoms positions were frozen for GCMC calculations. Non-bonding interactions were calculated using Lennard-Jones (LJ) potentials. The LJ parameters for the materials were assigned from the universal force field (UFF).³⁴ Parameters for methane guests molecules were developed by Martin

and Siemen to reproduce phase equilibrium as a single point, containing no partial atomic charges.⁶²

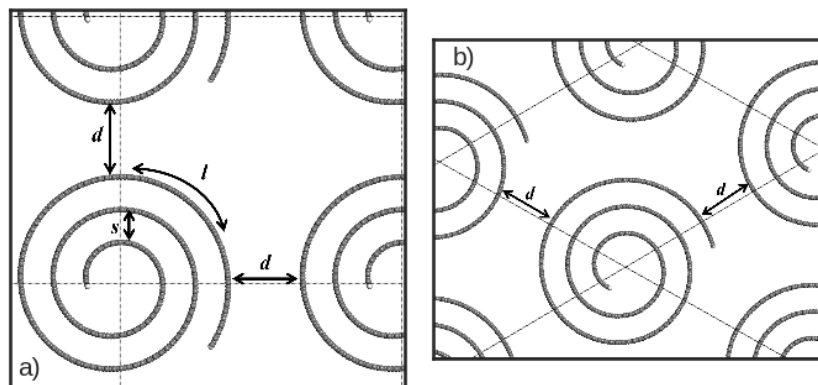


Figure 4.11. a) Square-packed CNSs showing parameters modified during this work of length of scroll (l), interlayer spacing (s), and interscroll distance (d). b) The same CNS in hexagonal-packing model.

Electrostatic interactions were ignored due to the methane model having no associated net charge, dipole, or quadrupole moment. Simulations were performed at pressures up to 65 bars and thus fugacities were used and calculated with the Peng-Robinson equation-of-state.⁶³ For Schwarzites and graphene, GCMC simulations were run for 30,000 cycles, for both the equilibration and the production phases. A cycle consists of N Monte Carlo steps where N is the number of guest molecules present at any given point. For example, if a system adsorbed 100 guest molecules, 3 million steps would be performed for equilibration and a further 3 million steps would be performed for production. When testing nanoscrolls, GCMC simulations were set to 10 million steps for production and 10 million steps for equilibration which is shown to reach equilibration on even the largest of nanoscrolls (Appendix, Figure 4.41). Errors in the uptake and isosteric heats of adsorption were calculated by taking the standard deviation over window averages of the uptake during the production phase of the GCMC simulation. Windows were set to have 500,00 steps per window. Further details about the GCMC simulations are given in the Appendix, Section 4.4.2.

4.2.4 Results and Discussion

We first discuss the natural gas storage capacity of Schwarzites. Several periodic Schwarzite structures have been theoretically constructed, with the most commonly studied being Schwarzite C168. Figure 4.12 shows the methane adsorption capacity of all the tested Schwarzites at 298 K and 65 bar. Schwarzites have high adsorption capacities reaching up to 273 V_{STP}/V for P8bal, which compares well to the uptake capacity of 267 V_{STP}/V at 298 K and 65 bar for HKUST-1.⁶⁴ Figure 4.12 shows the deliverable capacities for all tested Schwarzites. Whereas the calculated

uptake capacities are very high, the calculated deliverable capacities of the Schwarzites are not, with the maximum deliverable capacity being 131 V_{STP}/V for P7par. This is much lower than the MOVE target of 263 V_{STP}/V , and much less than the experimentally determined deliverable capacity of HKUST-1 (216 V_{STP}/V) under similar conditions (a slightly lower desorption temperature of 328 K). As a further point of comparison, we computed the deliverable capacity of HKUST-1 using the same conditions and simulation methodologies as for the Schwarzites and found it to be 210 V_{STP}/V .

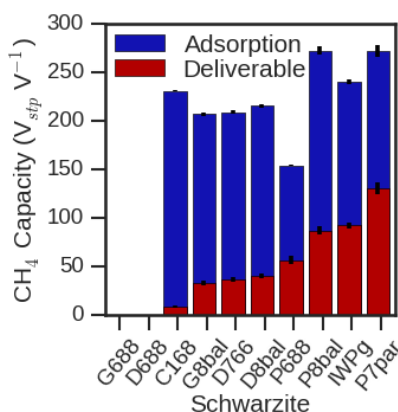


Figure 4.12. Computed CH_4 adsorption (and deliverable) capacity at 298 K and 65 bar (to 358 K and 5.8 bar) of tested Schwarzites ordered in ascending deliverable capacity.

The high adsorption capacities but low deliverable ones of the Schwarzites suggests a strong interaction with the material that is not overcome at the desorption conditions. For example, for P7par, the Schwarzite with the highest deliverable capacity to achieve the MOVE target of 263 V_{STP}/V , the desorption temperature would have to be raised to 728 K. To investigate how strongly held the guests are, we computed the heats of adsorption (HoA) of the Schwarzites and found them to range from 21–38 kJ/mol (Appendix, Table 4.2). Although these are not large compared to the HoAs of other adsorbed guest molecules such as CO_2 , they are generally higher than previously reported HoAs for adsorbed methane on other carbon materials.^{65–67} For comparison, our calculated HoA for methane in HKUST-1 was determined to be 17 kJ/mol. The strong interactions and decreased deliverable capacities in Schwarzites are caused by multiple framework atoms interacting with the guest molecule due to the small pores of the materials. Figure 4.13 shows that as void fraction decreases, the fractional deliverable capacity (deliverable capacity divided by the adsorption capacity) also decreases. Thus, as the void fraction decreases, the density of the material increases giving rise to stronger guest host interactions and lower deliverable capacities.

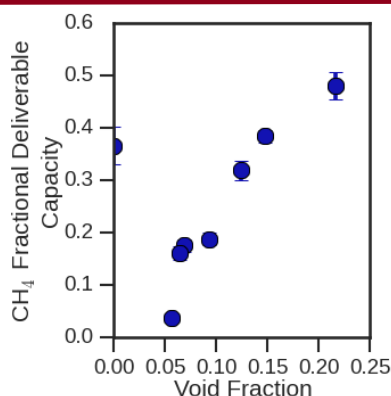


Figure 4.13. Fractional deliverable capacity of tested Schwarzites as a function of void fraction.

An exception to the trend observed in Figure 4.13 is seen with P688 which has no void fraction when using a methane probe radius of 1.8 Å, yet has a 0.40 fractional deliverable capacity. We believe this is since the P688 structure has pores that are so small that it holds the methane molecules weakly that they can be easily desorbed, giving rise to the anomalous deliverable capacity. From the probability distributions, shown in Figure 4.14, we determined that the methane molecules in P688 are on average 3.61 Å away from framework carbon atoms, placing it in the centre of the Schwarzite.. This distance is very close to the 3.58 Å where the LJ interaction energy is zero. Thus, at an average distance of 3.61 Å the methane molecules can adsorb at the adsorption conditions, but when the temperature is raised to that of the desorption conditions, the methane is flushed out. This is corroborated by the fact that if the desorption temperature is kept the same as during the adsorption, the deliverable capacity drops by over 90%, much larger than the other Schwarzites which drop on average by only 50%. In other words, the methane is mostly retained by the material.

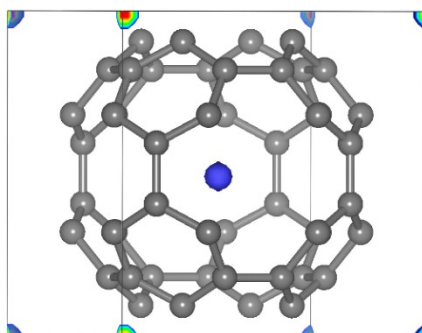


Figure 4.14. Computed CH₄ centre of mass probability distribution at 65 bar and 298 K for P688. Blue indicate regions of low probability and red regions of high probability, respectively. High probability in corners is the centre of other pores when periodic boundary conditions are taken into account.

We now turn our attention to idealized LGs sheets where we examined the methane storage capacities of the materials with interlayer spacings from 4 to 20 Å in 1 Å increments. Figure 4.15 shows both the volumetric adsorption capacity and deliverable capacity of methane as a function of the interlayer spacing. No methane is adsorbed when the spacing is less than 7 Å due to the lack of space. There are clear maxima in the adsorption capacity at interlayer spacings of 7, 11, and 14 Å. Probability distributions from the GCMC simulations shown in Figure 4.16 shows that an interlayer spacing of 7, 11, and 14 Å allow for 1, 2 and 3 well defined layers of methane to form, respectively. The highest uptake achieved occurs at an interlayer spacing of 11 Å where the adsorption capacity was computed to be 355 V_{STP}/V .

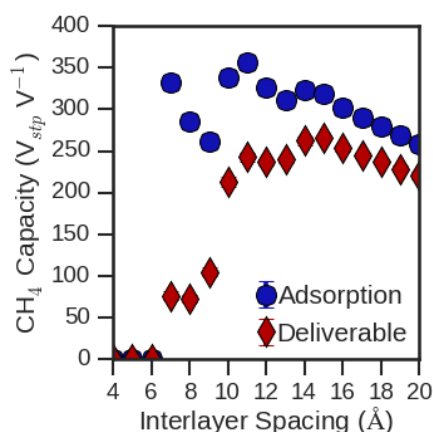


Figure 4.15. Computed CH_4 adsorption capacity (blue circles) of LGs at 298 K and 65 bar and deliverable capacity (red diamond) with the previously mentioned adsorption conditions and desorption conditions of 358 K and 5.8 bar. Error bar are smaller than symbols.

Figure 4.15 reveals that the deliverable capacity also has maxima at the interlayer spacing of 7 and 11 Å with the last maxima being shifted from 14 to 15 Å compared to the maxima in the adsorption capacities. Although the last maxima are shifted, the deliverable capacities at 14 and 15 Å are very close, just as the adsorption capacities at those interlayers spacing are. The maxima observed in the deliverable capacity as a function of the interlayer spacings agree well a previous simulation study by Snurr and co-workers,⁵⁰ who found peaks in the deliverable capacity of LG at 8, 12 and 16 Å spacing. In that study, the desorption conditions were slightly different at 298 K and 5.8 bar in comparison to 358 K and 5.8 bar in this work. They also found that the LG with an interlayer spacing of 16 Å gave the best deliverable capacity of 190 V_{STP}/V . To compare, we computed the deliverable capacity with an interlayer spacing of 16 Å using the same adsorption and desorption conditions used by Snurr and coworkers, and found it to be in excellent agreement - 189 V_{STP}/V .

While the adsorption capacity with an interlayer spacing of 7 Å is high, the deliverable capacity is quite low, at only 76 V_{STP}/V . Again, this implies that the adsorbed methane layer (Figure 4.16a) is held tightly between two graphene layers. The maximum deliverable capacity occurs at an interlayer spacing of 15 Å. The probability distribution with an interlayer spacing of 15 Å is very similar to that shown in Figure 4.16c (14 Å interlayer spacing) in that there are three distinct adsorbed methane layers. The ‘outer’ layers that are adjacent to the graphene sheets are more weakly held than the methane in the 7 Å interlayer spacing system since there is only one graphene sheet, as opposed to two, that the methane strongly interacts. The probability distribution given in Figure 4.16c reveals that the middle-adsorbed methane layer is more weakly held than the layers adjacent to the graphene sheets. The weaker adsorption partially explains the higher deliverable capacity that is observed with the interlayer spacing of 15 Å.

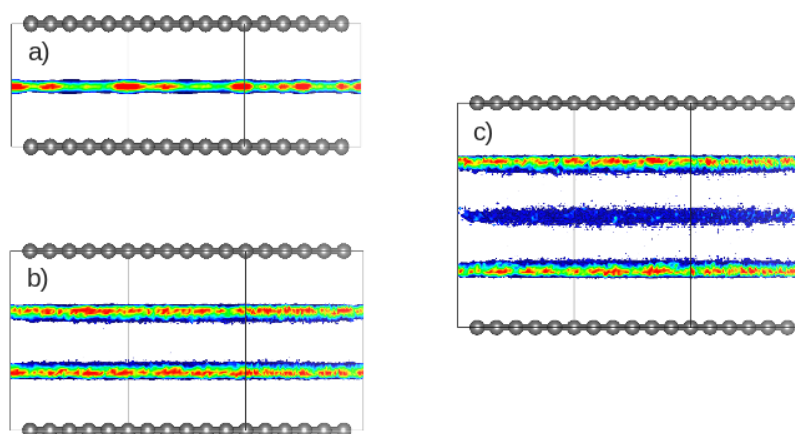


Figure 4.16. Computed CH_4 centre of mass probability distribution at 65 bar and 298 K for graphene with interlayer spacing of a) 7 Å b) 11 Å and c) 14 Å. Blue indicate regions of low probability and red regions of high probability, respectively.

The maximum deliverable capacity of 266 V_{STP}/V for the idealized graphene sheets with an interlayer spacing of 15 Å meets the MOVE target of 263 V_{STP}/V , though this does not consider packing losses. This computed deliverable capacity is better than all the materials tested by Smit and co-workers (over 3 million) making it, to the best of our knowledge, the top hypothetical material for VMS. Of course, LG does not have fixed interlayer spacing, and introducing pillars, such as metal ions,⁶⁸ metal oxides,⁶⁹ or carbon nanotubes,⁷⁰ to hold the layers at fixed distances would lower the uptake capacities since the pillars would occupy space between the layers.

The final material studied for this work is graphene-based CNSs. It should be noted that the work of Peng et. al studied methane storage in CNS.²⁸ In that work they did not look at deliverable capacities, used short nanoscrolls (426 Å), and had limited tuning of their geometric properties.

There are several geometric parameters associated with CNS that we expect to affect the methane uptake. As with graphene, the interlayer spacing of nanoscrolls can be tuned, as well as the length of the nanoscrolls. Furthermore, there are parameters associated with how individual nanoscrolls would pack together to form the solid - the packing arrangement and the interscroll distance. All these geometric parameters are depicted in Figure 4.11. As observed with the LG (Figure 4.15), one would expect the adsorption properties of the nanoscrolls to be highly dependent on the interlayer spacing. Since one can consider a nanoscroll of infinite length to be equivalent to LG, one would also expect to see similar trends in the properties. Figure 4.17 shows the computed adsorption capacity and deliverable capacity of the nanoscrolls as a function of the interlayer spacing. For these simulations, a fixed scroll length of 1600 Å was used with a large 25 Å interscroll distance to isolate the nanoscrolls. As expected, the results are like those obtained for the LG (Figure 4.15). There are maximum adsorption capacities observed at interlayer spacing of 7, 11 and 14 Å, with a gradual decrease in capacity for layer spacing greater than 14 Å. Figure 4.18 shows the probability distributions for methane in the for each of those interlayer spacings, and as seen with LG there are distinct layers created for each increase in spacing. For interlayer spacing below 7 Å, the adsorption capacity is small, but non-zero. The reason for this is that although the interlayer spacing is too small for methane to enter the nanoscrolls, the gas can still adsorb to the outside walls. The deliverable capacity also has three maxima at interlayer spacings of 7, 11 and 15 Å, with an overall maximum occurring at 15 Å. Again, these trends are very similar to those observed with LG.

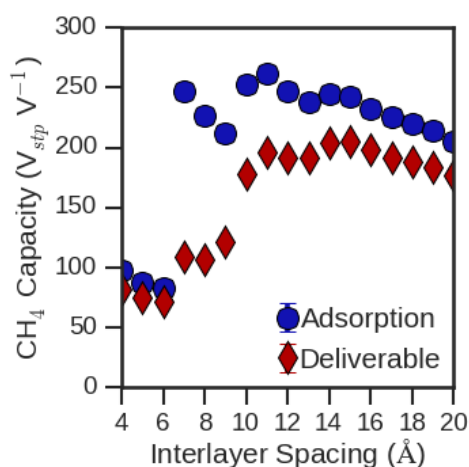


Figure 4.17. Computed CH₄ adsorption (Blue circle) of CNSs at 298 K and 65 bar and deliverable capacity (Red diamond) from adsorption to desorption condition of 358 K and 5.8 bar as a function of interlayer spacing for 1600 Å long nanoscrolls. Error bars are smaller than symbols.

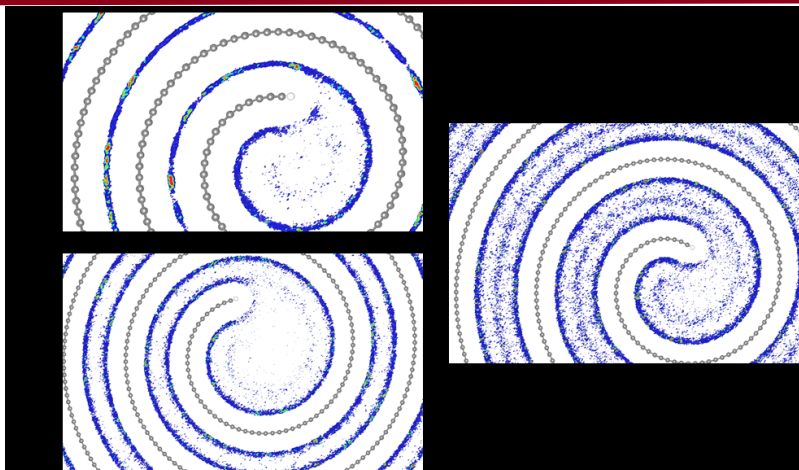


Figure 4.18. Computed CH₄ centre of mass probability distribution at 65 bar and 298 K for carbon nanoscrolls with interlayer spacing of a) 7 Å b) 11 Å and c) 14 Å. Blue indicate regions of low probability and red regions of high probability, respectively.

Next, we examined how the scroll length affects the adsorption properties. We tested 8 nanoscrolls from 200 to 3000 Å in length as isolated nanoscrolls (square packing and interscroll distance of 25 Å) with a fixed interlayer spacing of 11 Å. The results are presented in Figure 4.19. Both the adsorption capacity and deliverable capacity gradually increase and converge to a value as the scroll length increases. This is because as the length of the nanoscroll increases the ratio of the outer layer of the nanoscroll compared to the inner layer decreases, reducing the edge effects where the methane adsorption is weaker. Similar trends in the scroll length were observed for CO₂ uptake in nanoscrolls.¹ We note that the estimated scroll lengths of synthesized CNS is typically in the tens of thousands of Ångstrom range.⁵⁴

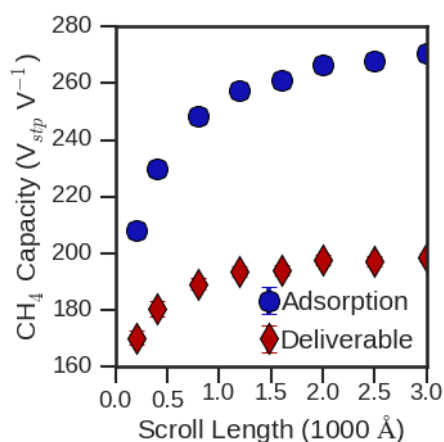


Figure 4.19. Computed CH₄ adsorption capacity (blue circle) and the deliverable capacity (red diamond) as a function of scroll distances for nanoscrolls with interlayer spacing of 11 Å. The adsorption conditions are at 298 K and 65 bar, while the desorption conditions are 358 K and 5.8 bar.

We now examine how the packing arrangement and interscroll distance affects the adsorption properties. Figure 4.20 shows the adsorption and deliverable capacity plotted as a function of the interscroll distance, d , for both a hexagonal and square packing arrangements. It can be seen in all cases that hexagonal packing style results in an increase in both the adsorption and deliverable capacity. Although a square packing arrangement is not likely, and it is well known that a hexagonal packing arrangement is the most efficient arrangement to pack cylinders, Figure 4.20 does show how much the uptake and deliverable capacities are affected by non-ideal packing. The adsorption capacity shows a continual decrease as the interscroll distance increase, while the deliverable capacity does show a peak around 11 Å. Since the inside of the scrolls have a much higher uptake capability compared to the outside of the scrolls and free space one would expect that the adsorption capacity would increase as the packing distance decreases because this increases the density of the nanoscrolls. For the hexagonal packing arrangement, we see a maximum in the deliverable capacity at 11 Å. This suggests that some of the methane adsorbed on the outside of the scrolls at a 11 Å interscroll distance can also easily desorb and is therefore contributing to the deliverable capacity. We expect the relative contribution of the outside of the scroll adsorption to the deliverable capacity to decrease as the scroll lengths get longer.

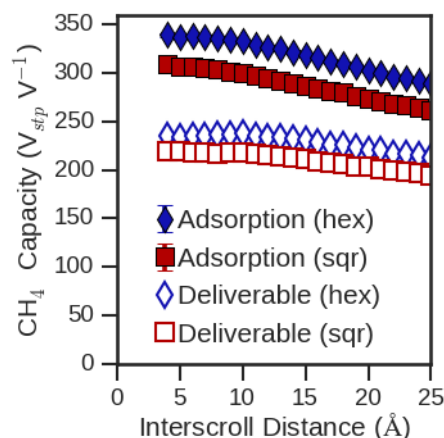


Figure 4.20. Computed CH_4 adsorption (filled) and deliverable capacities (empty) as a function of the interscroll distance for a hexagonal packing (blue diamonds) and square packing (red square) arrangements. Scroll lengths of 1600 Å were used with an interlayer spacing of 11 Å. The adsorption conditions are at 298 K and 65 bar, while the desorption conditions are 358 K and 5.8 bar.

Given that the hexagonal packing arrangement gives the best adsorption properties, we now try to find the set of parameters that give the best overall uptakes and deliverable capacities. Plotted in Figure 4.21 are the a) uptake and b) deliverable capacity plotted as a function of the interscroll distance for interlayer spacing ranging from 7 Å to 16 Å. Interlayer spacing up to 20 Å was tested

(Appendix, Figure 4.42), however they show trends seen in Figure 4.17, where the adsorption and desorption capacity continues to decrease across all interscroll distances tested. Figure 4.21a reveals that the best uptakes are achieved with an interlayer spacing of 11 Å with the smallest interscroll distances. The highest uptake capacity of 339 V_{STP}/V was achieved with an interlayer spacing of 11 Å and an interscroll distance of 4 Å. This is not as high as that computed for LG (355 V_{STP}/V), but it is still exceptional and exceeds the highest adsorption capacity Smit and coworkers found of $\sim 258 V_{STP}/V$.⁴⁶ Figure 4.21b shows deliverable capacities of nanoscrolls with interlayer spacing of 9 Å or smaller not shown, as the results are like those seen in the isolated nanoscrolls and only reach a maximum of 144 V_{STP}/V . The overall maximum deliverable capacity is 252 V_{STP}/V which occurs for an interlayer spacing of 15 Å and interscroll distance of 4 Å, although this is not as high as for LG, (266 V_{STP}/V) it is still one of the highest capacities computed for a hypothetical material. Interestingly, deliverable capacities close to the overall maximum can be achieved with a broad range of interlayer spacings and interscroll distances. For example, deliverable capacities within 5% of the overall maximum can be obtained with interlayer spacing of 14, 15 and 16 Å, with a range of interscroll distances from up to 16 Å. Thus, when targeting materials with the highest capacity, there is some leeway in the interlayer spacing. It is also notable that for the interlayer spacings of 14, 15 and 16 Å the maximum deliverable capacity occurs with the smallest interscroll distances when the scrolls are nearly touching each other. Thus, there is no need to control the interscroll distance to a specific intermediate value, rather the optimal performance is obtained with the highest packing density.

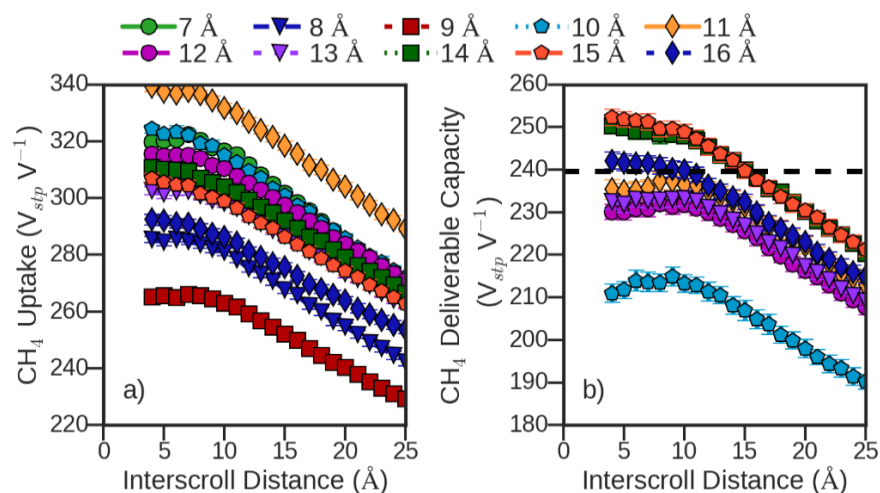


Figure 4.21. a) Computed CH₄ adsorption capacity and b) deliverable capacity as a function of interscroll distances for various interlayer spacing nanoscrolls. Nanoscrolls with length of 1600 Å were used. The adsorption conditions are at 298 K and 65 bar, while the desorption conditions are 358 K and 5.8 bar. Dashed line in b) indicates 95% of maximum deliverable capacity.

4.2.5 Conclusions

The VMS capabilities of three carbon-based materials, Schwarzites, LG, and CNSs, have been studied with molecular simulation. 10 unique Schwarzites were studied for their adsorption capacities and deliverable capacities at adsorption conditions of 65 bar and 298 K, and desorption conditions of 5.8 bar and 358 K. P7par and P8bal were found to have exceptional adsorption capacities over 250 V_{STP}/V . Unfortunately, all Schwarzites studied were found to have deliverable capacities of less than 150 V_{STP}/V , which is far below the MOVE target of 263 V_{STP}/V . Thus, while some Schwarzites exhibited large adsorption capacities, much of the methane remained adsorbed under the desorption conditions. LG consisting of perfectly flat, infinite sheets of graphene with fixed interlayer spacing were found to have exceptional methane adsorption properties. With an interlayer spacing of 11 Å, LG was computed to have an adsorption capacity of 355 V_{STP}/V at 65 bar and 298 K. The probability distributions of the guest molecules show that two well defined layers of methane form between each layer of graphene sheets. However, the highest deliverable capacity of 266 V_{STP}/V was achieved with an interlayer spacing of 15 Å. In this case, three, weakly bound layers of methane are formed between the graphene layers. Graphene based nanoscrolls were also examined, where the effect of the scroll length, interlayer spacing, scroll distance, and packing arrangement on the adsorption properties examined. The highest deliverable capacity for nanoscrolls with a 1600 Å scroll length was computed to be 252 V_{STP}/V . This was achieved with an interlayer spacing of 15 Å, with a hexagonal packing arrangement with an interscroll distance of 4 Å. For example, deliverable capacities within 5% of the maximum (252 V_{STP}/V) was achieved with a broad range of interlayer spacings (14, 15 and 16 Å) and with a range of interscroll distances up to 16 Å. This suggests there may be some flexibility in the geometries when targeting high capacity nanoscrolls materials.

To our knowledge, the deliverable capacities of CNSs (252 V_{STP}/V) and LGs (266 V_{STP}/V) are the highest computed for any material at conditions relevant to VMS, with the capacity of LGs exceeding the MOVE target of 263 V_{STP}/V . Following a screen of over 3 million materials at the same adsorption conditions (298 K and 65 bar of CH_4) Smit and coworkers found a maximum deliverable capacity of 196 V_{STP}/V for desorption conditions of 5.8 bar at 298 K, and 240 V_{STP}/V for desorption conditions of 5.8 bar at 400 K. Although neither CNS or LG meet the DoE requirement when considering loss due to packing fraction of 315 V_{STP}/V , to the best of our

knowledge these materials provide the highest deliverable methane capacity while staying within the DoE guidelines for vehicular methane storage. These results give new limits for materials to be used for vehicular methane storage. It is important to note that the CNSs and LGs studied here are not structurally stable as the interlayer spacings are fixed. The effect of including pillars, such as adding metal ions between layers, will be the subject of a future study.

4.3 References

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4.4 Appendix

4.4.1 Evaluation of Carbon Nanoscroll Materials for Post-Combustion CO₂ Capture

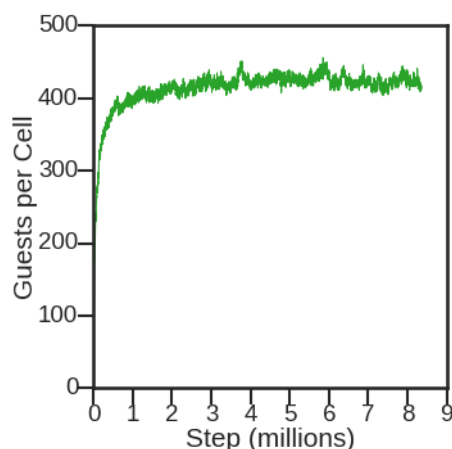


Figure 4.22. Number of CO₂ guest molecules in grand canonical Monte Carlo cell of graphene nanoscroll of 7.3 Å interlayers spacing and 400 Å in length at 313 K and 0.15 bar of CO₂ as a function of the steps. Run was conducted using 10,000 equilibration and 10,000 production cycles that, for this case, gives a total of approximately 8.5 million steps.

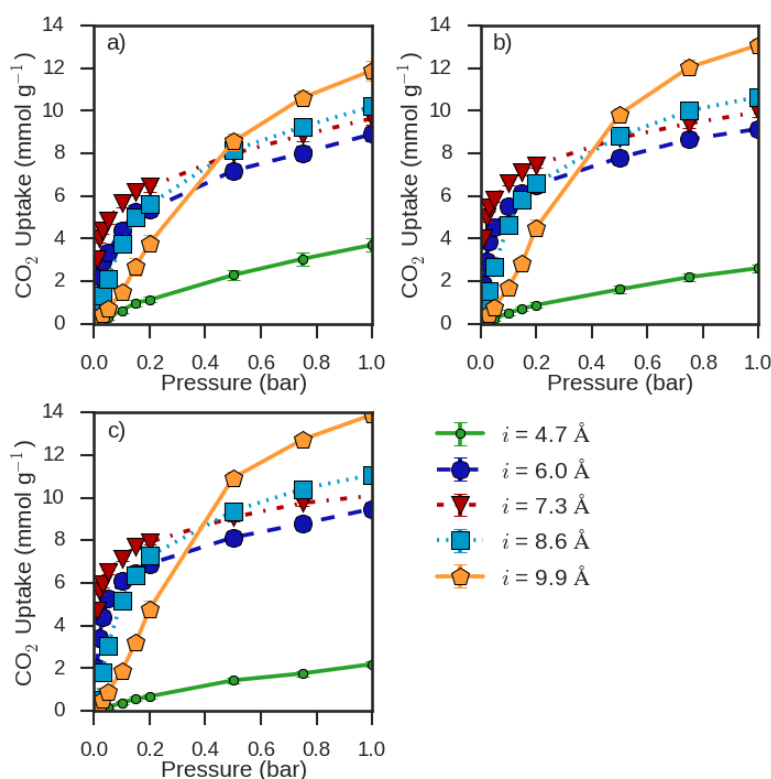


Figure 4.23. CO₂ uptake isotherms of graphene nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 200 Å (b) 300 Å and (c) 400 Å

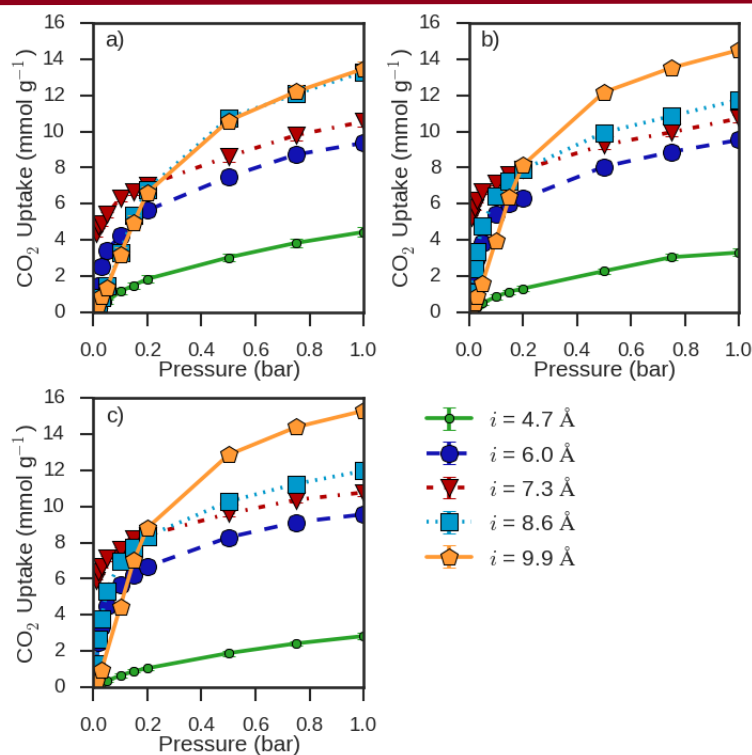


Figure 4.24. CO₂ uptake isotherms of boron nitride nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 200 Å (b) 300 Å and (c) 400 Å

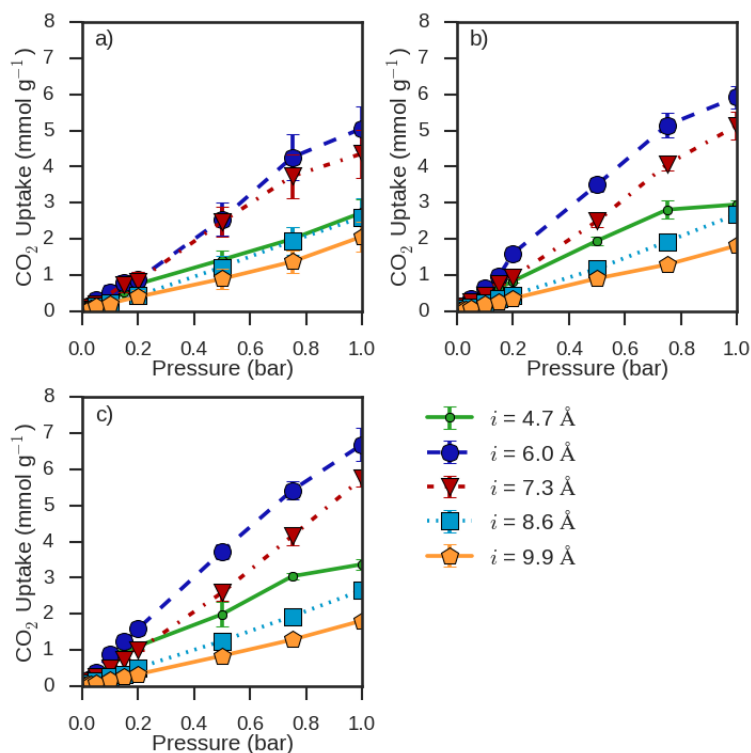


Figure 4.25. CO₂ uptake isotherm of α -graphyne nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 190 Å (b) 300 Å and (c) 400 Å

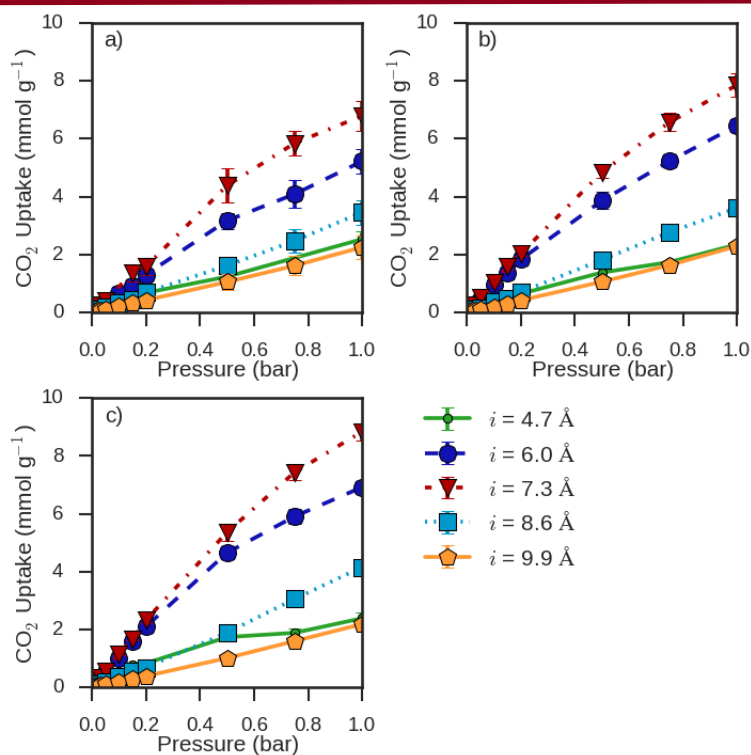


Figure 4.26. CO₂ uptake isotherm of β -graphyne nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 190 Å (b) 300 Å and (c) 400 Å

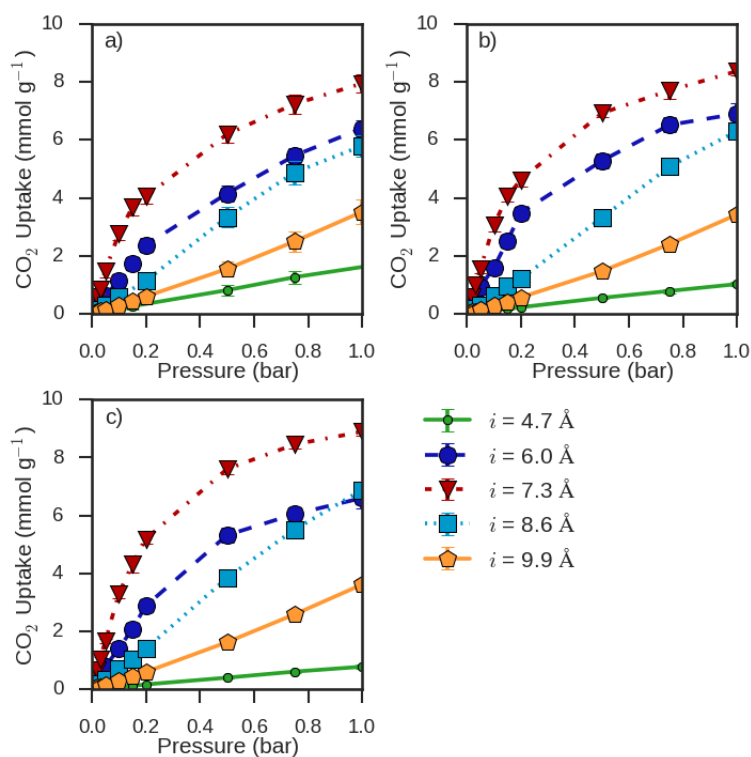


Figure 4.27. CO₂ uptake isotherm of γ -graphyne nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 190 Å (b) 300 Å and (c) 400 Å

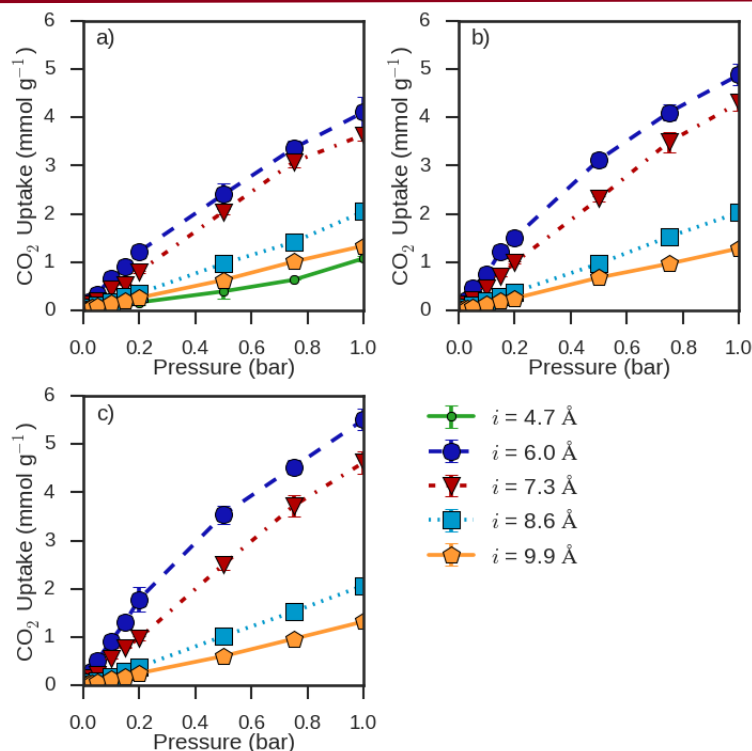


Figure 4.28. CO₂ uptake isotherms of graphene like carbon nitride nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 200 Å (b) 300 Å and (c) 400 Å

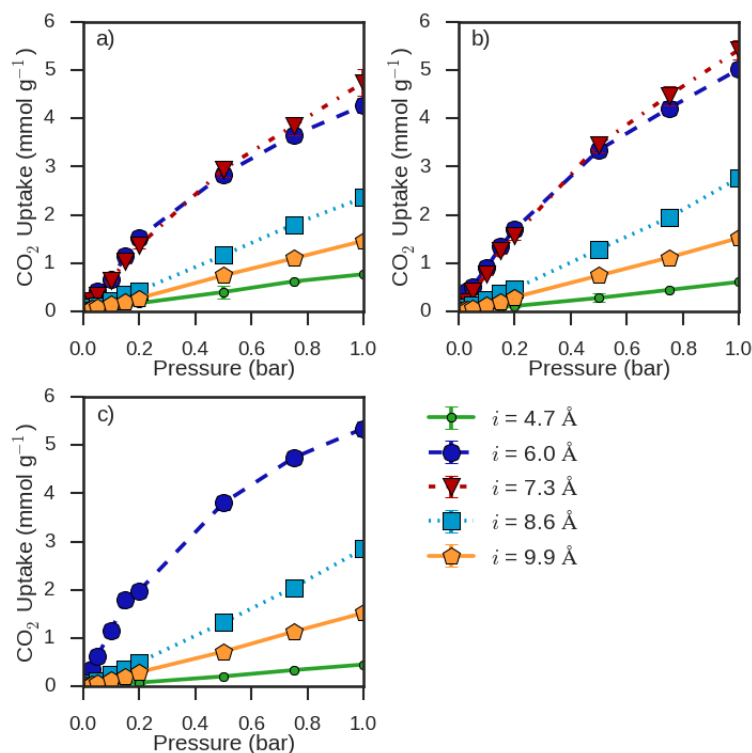


Figure 4.29. CO₂ uptake isotherms of heptazine like carbon nitride nanoscrolls at 313 K at different interlayer spacing (i) at a length (l) of (a) 200 Å (b) 300 Å and (c) 400 Å

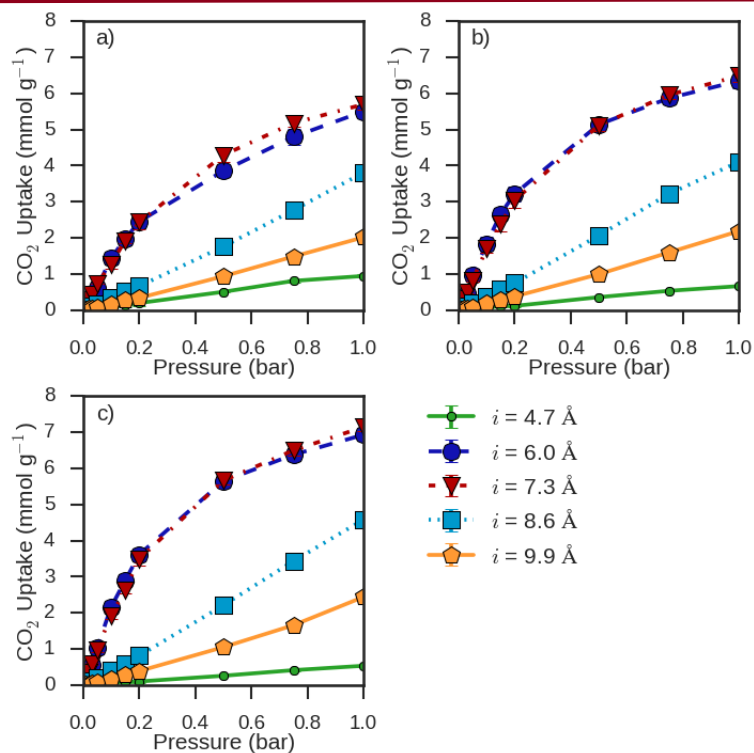


Figure 4.30. CO₂ uptake isotherms of triazine like carbon nitride nanoscrolls at 313 K at different interlayer spacing (*i*) at a length (*l*) of (a) 200 Å (b) 300 Å and (c) 400 Å

Equation 4.1 used to calculate selectivity of from binary component GCMC simulations

$$CO_2/N_2 \text{ Selectivity} = \frac{\frac{CO_2 \text{ Uptake}}{P_{CO_2}}}{\frac{N_2 \text{ Uptake}}{P_{N_2}}} \quad (4.1)$$

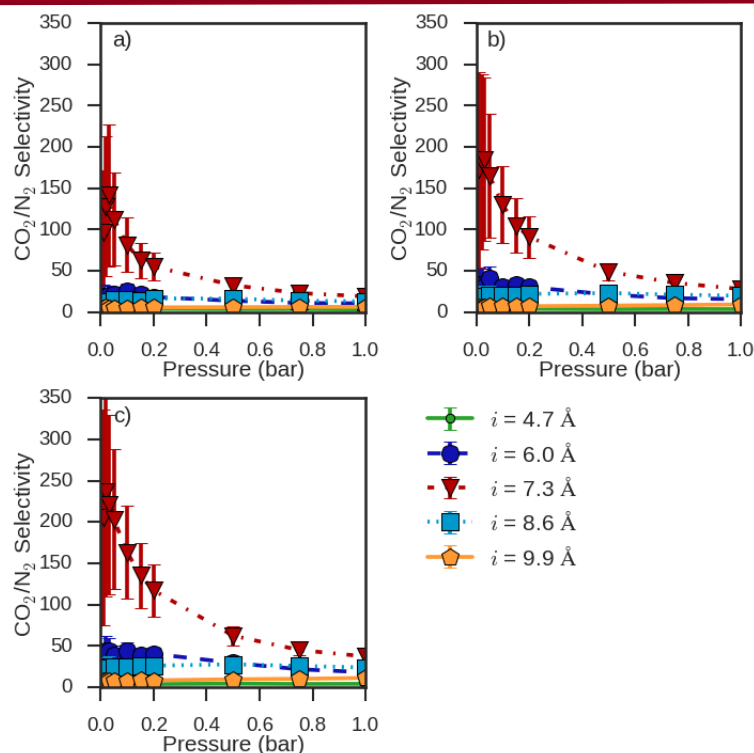


Figure 4.31. CO_2/N_2 selectivity as a function of CO_2 pressure for 1 CO_2 :5 N_2 for graphene NS at 313 K at different interlayer spacing (i) at a length (l) of (a) 200 Å (b) 300 Å and (c) 400 Å

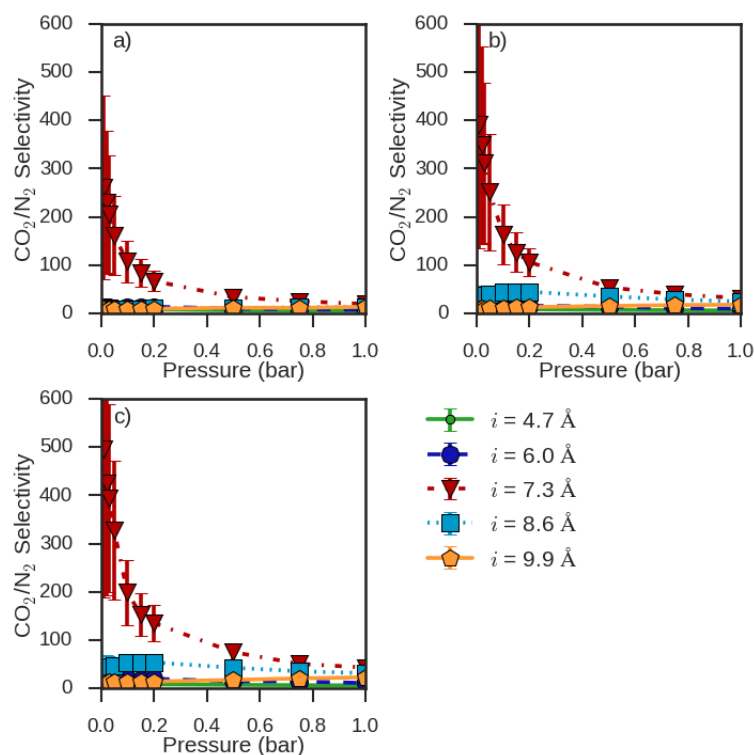


Figure 4.32. CO_2/N_2 selectivity as a function of CO_2 pressure for 1 CO_2 :5 N_2 for boron nitride NS at 313 K at different interlayer spacing (i) at a length (l) of (a) 200 Å (b) 300 Å and (c) 400 Å

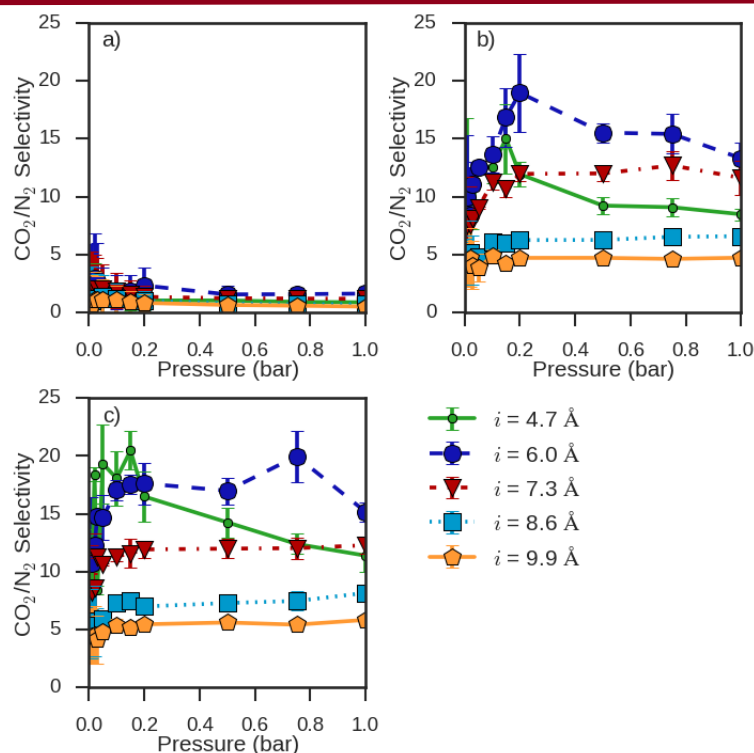


Figure 4.33. CO_2/N_2 selectivity as a function of CO_2 pressure for 1 CO_2 :5 N_2 for α -graphyne NS at 313 K at different interlayer spacing (i) at a length (l) of (a) 190 $\text{\AA}$ (b) 300 $\text{\AA}$ and (c) 400 $\text{\AA}$

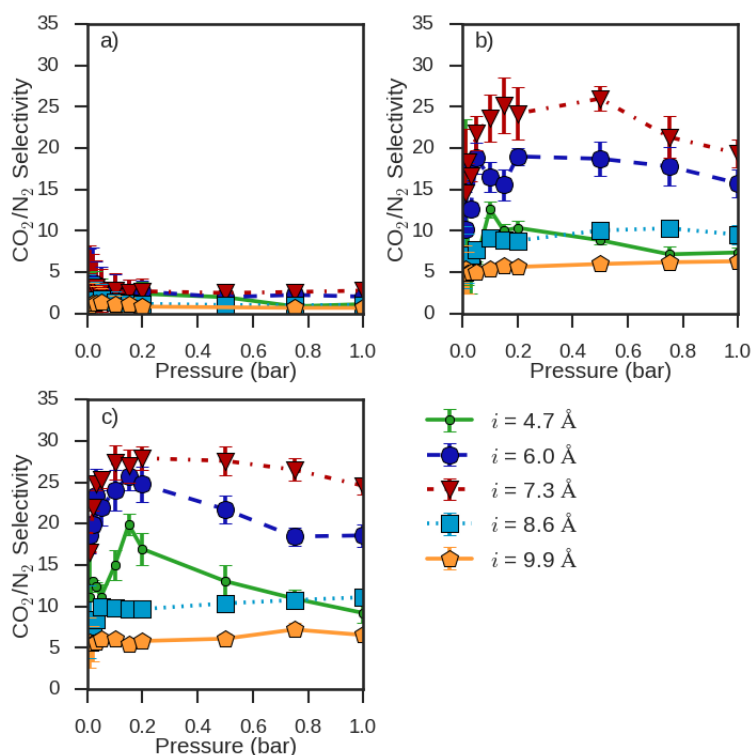


Figure 4.34. CO_2/N_2 selectivity as a function of CO_2 pressure for 1 CO_2 :5 N_2 for β -graphyne NS at 313 K at different interlayer spacing (i) at a length (l) of (a) 190 $\text{\AA}$ (b) 300 $\text{\AA}$ and (c) 400 $\text{\AA}$

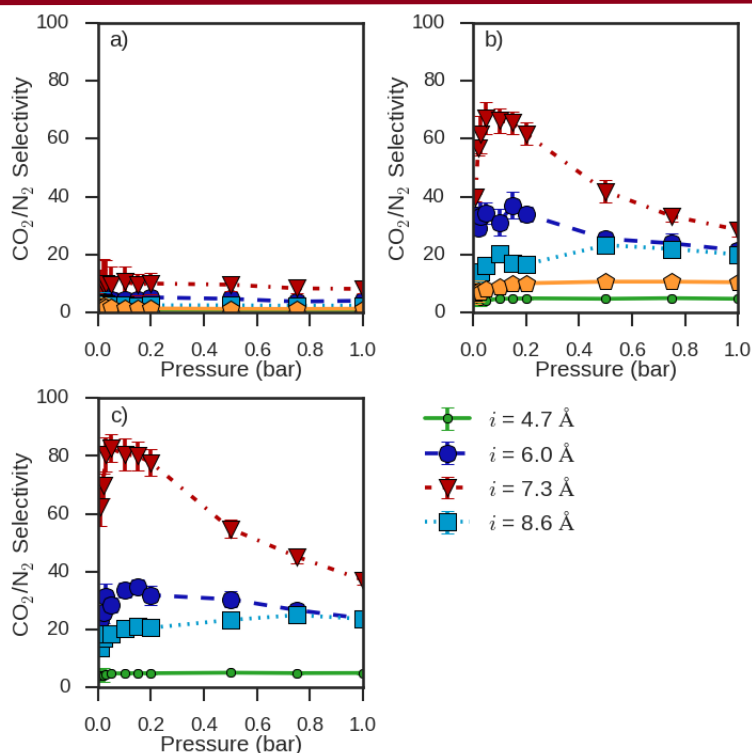


Figure 4.35. CO₂/N₂ selectivity as a function of CO₂ pressure for 1 CO₂:5 N₂ for γ-graphyne NS at 313 K at different interlayer spacing (*i*) at a length (*l*) of (a) 190 Å (b) 300 Å and (c) 400 Å

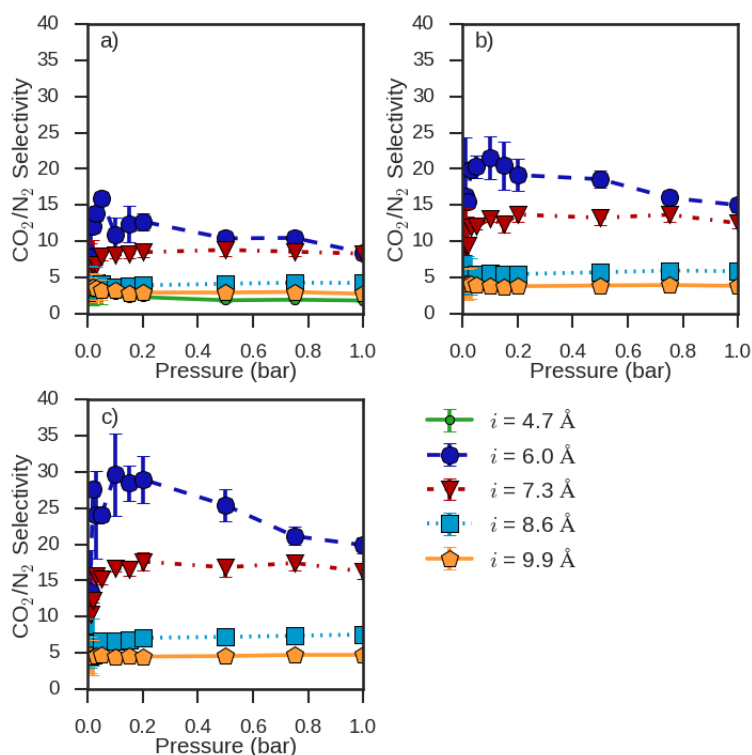


Figure 4.36. CO₂/N₂ selectivity as a function of CO₂ pressure for 1 CO₂:5 N₂ for graphene-like carbon nitride NS at 313 K at different interlayer spacing (*i*) at a length (*l*) of (a) 200 Å (b) 300 Å and (c) 400 Å

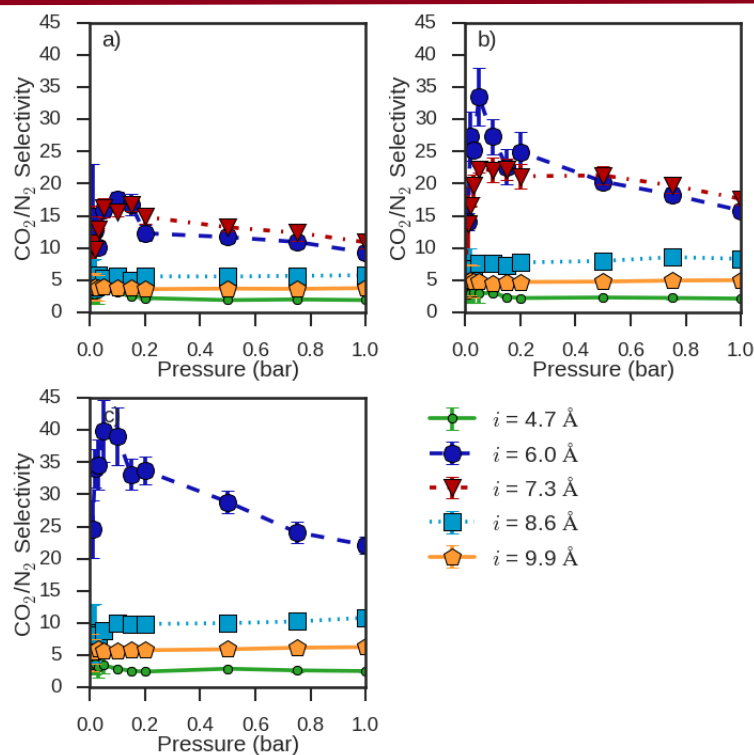


Figure 4.37. CO_2/N_2 selectivity as a function of CO_2 pressure for 1 CO_2 :5 N_2 for heptazine-like carbon nitride NS at 313 K at different interlayer spacing (i) at a length (L) of (a) 200 Å (b) 300 Å and (c) 400 Å.

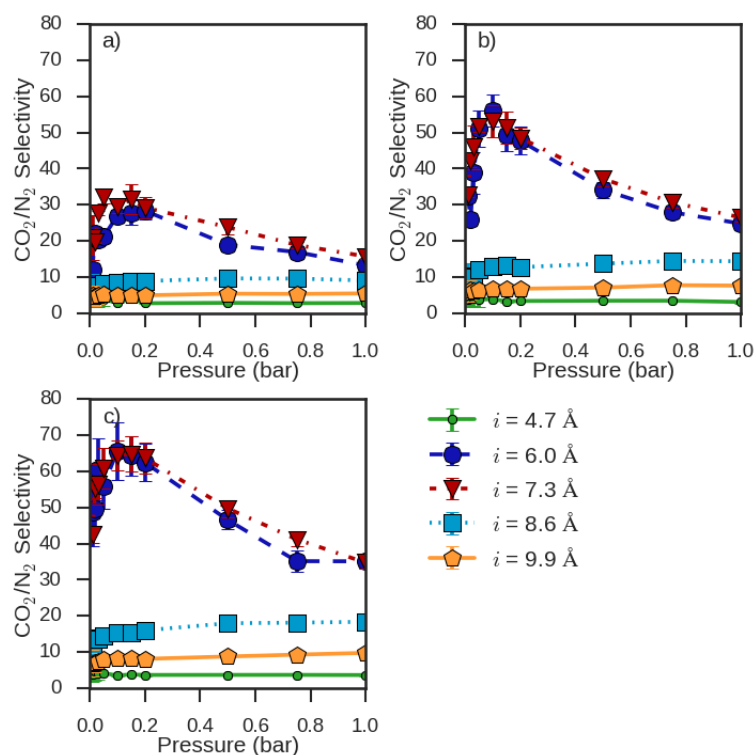


Figure 4.38. CO_2/N_2 selectivity as a function of CO_2 pressure at a ratio for 1 CO_2 :5 N_2 for triazine-like carbon nitride NS at 313 K at different interlayer spacing (i) at a length (L) of (a) 200 Å (b) 300 Å and (c) 400 Å.

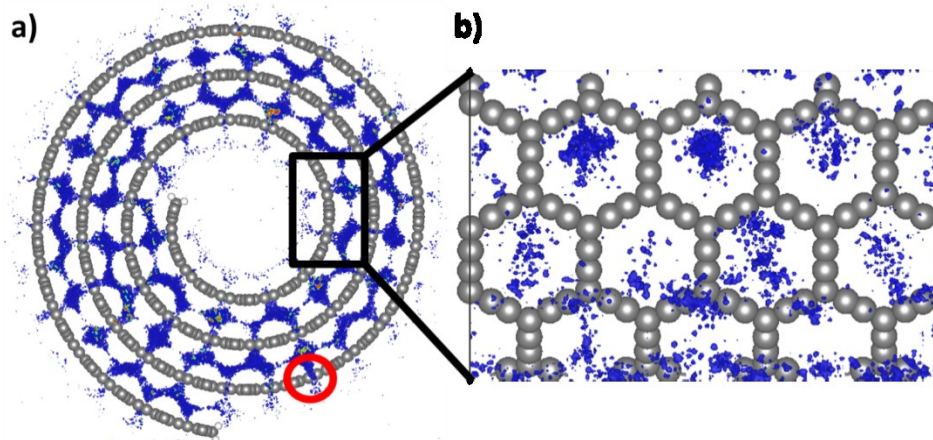


Figure 4.39. CO₂ centre of mass probability distribution plot in optimal length (400 Å) and interlayer spacing (6.0 Å) α-graphyne at for CO₂ uptake at 313 K and 0.15 bar. a) Cross section of nanoscroll with the circle indicating a region of CO₂ probability in a α-graphyne pore. b) Indicated section of nanoscroll viewed parallel to the sheet showing CO₂ probability existing around the pores and diminished probability of being ‘sandwiched’ between carbons of neighboring layers. Blue indicates regions of lower probability and red indicates regions of higher probability.

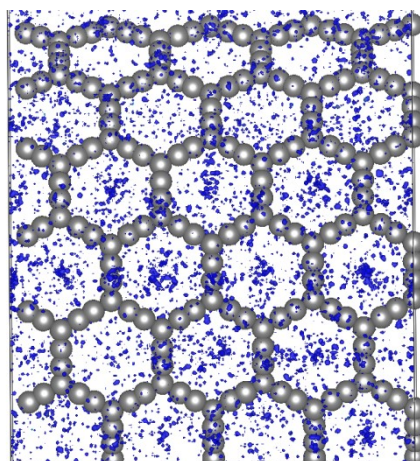


Figure 4.40. CO₂ centre of mass probability distribution plot in optimal length (400 Å) and 7.3 Å interlayer spacing of α-graphyne at for CO₂ uptake at 313 K and 0.15 bar showing CO₂ distributed between the layers and not as concentrated in the pores as for 6.0 Å interlayer spacing nanoscroll.

Data from MD simulations were fit to the exponential decay function of as shown in equation 4.2.

$$D = D_0 e^{-\lambda t} + C \quad (4.2)$$

Where D_0 , λ and C were optimized. Half-lives were then calculated by determining how long it takes for carbon dioxide to travel half the distance between D_0 and C which is shown by equation 4.3.

$$\frac{(D_0 + C)}{2} = D_0 e^{-\lambda t_{1/2}} + C \quad (4.3)$$

When equation 4.4 is rearranged to determine $t_{1/2}$ it is in the form of:

$$t_{\frac{1}{2}} = \ln\left(\frac{2D_0}{D_0 - C}\right)/\lambda \quad (4.4)$$

Table 4.1. Potential parameters for the carbon dioxide, nitrogen and nanoscrolls

Species	Atom	bl (Å)	q (e)	(ϵ/k_b) (K)	σ (Å)
CO ₂	C	0.0	0.6512	29.932	2.7450
	O	1.1490	-0.3256	85.664	3.0170
N ₂	N	0.5500	-0.4820	39.966	2.4549
	CoM	0.0	0.9640	0	0
Nanoscroll	C	-	Variable ($\sim -0.1 - 0.02$)	52.838	3.4309
	H	-	Variable ($\sim 0.05 - 0.2$)	22.142	2.5711
	B	-	Variable ($\sim 0.2 - 0.4$)	90.581	3.6375
	N	-	Variable (~ -0.4)	34.722	3.2607

Note: bl Is distance of the atom to the molecular mass center.

Lorentz-Berthelot mixing rules were used to determining parameters between atoms of different types.

4.4.2 Idealized Carbon-Based Materials Exhibiting Record Deliverable Capacities for Vehicular Methane Storage

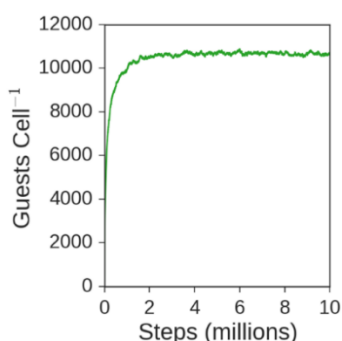


Figure 4.41. Number of CH₄ guest molecules in grand canonical Monte Carlo cell of an isolated graphene nanoscroll 20 Å interlayer spacing and 3000 Å in length at 298 K and 65 bar of CH₄ as a function of the steps. This is the most highly adsorbing structure based on number of guest molecules, and by the end of the equilibration period (10 million steps), equilibrium is reached.

Table 4.2. Heats of adsorption of CH₄ in studied Schwarzites that had non-zero adsorption, at the adsorption condition of 298 K and 65 bar. Errors are windowed standard deviation from GCMC.

Schwarzite	Heat of Adsorption (kJ/mol)
C168	21.4 +/- 0.3
G8bal	24.9 +/- 0.4
D766	21.8 +/- 0.4
D8bal	24.7 +/- 0.4
P688	38.0 +/- 0.4
P8bal	29.3 +/- 0.6
IWPg	23.2 +/- 0.7
P7par	25.1 +/- 0.7

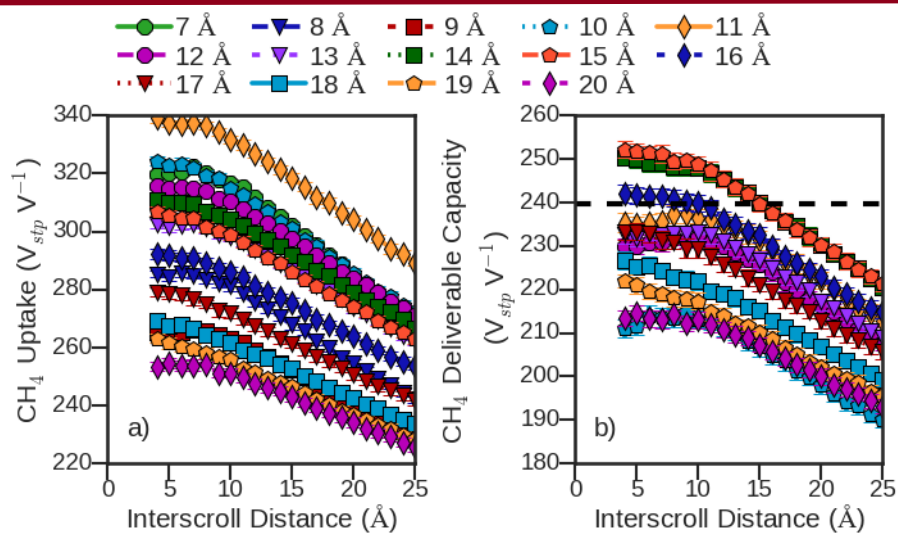


Figure 4.42. a) Computed CH₄ adsorption capacity and b) deliverable capacity as a function of interscroll distances for various interlayer spacing nanoscrolls. Nanoscrolls with length of 1600 Å were used. The adsorption conditions are at 298 K and 65 bar, while the desorption conditions are 358 K and 5.8 bar. Dashed line in b) indicates 95% of maximum deliverable capacity.

5 Split Charge Equilibration for MOFs

In this chapter I present work on the Split Charge Equilibration (SQE) parameterization I performed. The writing of the SQE code was done by Dr. Carlos Campana. The rest of the presented work in this manuscript was my own research, from creation of the testing and validation sets, development of the genetic algorithm, the parameterization, and subsequent analysis. This chapter was adapted with permission from *The Journal of Physical Chemistry C*, Volume 121, Issue 1, Pages 903-910 in 2017.¹ Copyright 2018, American Chemical Society. Formatting of the manuscript has been changed to maintain similar style to the rest of the thesis, however all content is the same as the original publication. Changes include the layout of the manuscript, numbering of sections, and figures, and combining the works cited list of the main text and appendix.

Split-Charge Equilibration Parameters for Generating Rapid Partial Atomic Charges in Metal- Organic Frameworks and Porous Polymer Networks for High-Throughput Screening

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5.1 Abstract

The split-charge equilibration (SQE) method was parameterized to reproduce the quantum mechanical, electrostatic potential (ESP) in an atomistically and topologically diverse training set of 559 metal-organic frameworks (MOFs) and 45 porous polymer networks (PPNs). The training set contained a total of 17 elements and 31 unique element-element bonds, 13 inorganic SBUs, 101 organic SBUs and 30 functional groups. Split-Charge Equilibration MOF Electrostatic-Potential-Optimized, or SQE-MEPO, method was validated against a set of 585 (520 MOFs and 65 PPNs) that were not part of the training set by comparing the derived ESP to the quantum mechanical ESP and comparing the computed CO₂ uptakes and heats of adsorption at both low (0.15 bar) and high pressures (10 bar). For this large validation set, the SQE-MEPO ESP deviated from the QM ESP by 30% less than other parameterized charge determination methods with a mean absolute deviation (MAD) of 6.47 mHartree compared to the next closest method with a MAD of 9.53 mHartree. When comparing the CO₂ uptakes and heats of adsorption calculated with SQE-MEPO charges compared to charges best fit to reproduce the QM ESP, SQE-MEPO was found to have a Pearson and Spearman correlation coefficients of >0.95 at both low and high pressures. SQE-MEPO allows for rapid charges to be generated for MOFs that provides DFT quality electrostatic interactions when simulating adsorption properties that are ideal for high throughput screening.

5.2 Introduction

Metal-organic Frameworks (MOF)²⁻⁴ are a class of materials most noted for their nanopores and the tunability of the pore chemistry. The tunability of the chemistry of MOF pores has made them a prime candidate for use in gas separation and storage.⁵⁻⁸ MOFs have found particular interest as an energy-efficient sorbent for use in carbon capture and storage (CCS)⁹⁻¹¹ due to their easy-on, easy-off physisorption, high CO₂ adsorption capacity, and high CO₂/N₂ selectivity at low partial pressures. To aid in the discovery of high-performing materials, there have been numerous computational studies that have evaluated MOFs for CO₂ adsorption properties using grand canonical Monte Carlo (GCMC) simulations.¹²⁻¹⁸ In these simulations, framework-guest interactions are statistically evaluated to determine the adsorption properties. Due to the number of calculations required, parameterized force fields are typically used to calculate both the van der Waals (i.e., Lennard-Jones) and electrostatic interactions, the latter of which are typically

calculated using a fixed partial atomic charge approximation. While the parameters used for the van der Waals interactions are relatively transferable from one system to another, the partial atomic charges need to be evaluated for each structure. Charges that are fit to reproduce the electrostatic potential (ESP) of quantum mechanical (QM) calculations are most often used within the fixed charge approximation. Typically, the charges are derived from a molecular density functional theory (DFT) calculation of the individual MOF building units^{19–22} or a periodic DFT calculation of the entire MOF.²³

The development of algorithms to build hypothetical MOFs from libraries of structural building units (SBUs) have resulted in the ability to screen hundreds of thousands to millions of materials for their gas adsorption properties. Performing first principles DFT calculations on these many materials is intractable, and so researchers have turned to rapid charge generation methods that only take seconds to perform. The most popular of these is the Charge Equilibration (QEq) method of Rappé-Goddard.^{24,25} QEq is an empirical method that uses defined atomic hardness and electronegativity parameters for each atom type to define an energy expression in terms of the atomic charges. The energy expression is given in equation 5.1, where Q_i , κ_i , and χ_i are the partial atomic charge, atomic hardness and electronegativity for the atom i , respectively, is minimized.

$$E_{QEq}(\mathbf{Q}) = \sum_i \left(\chi_i Q_i + \frac{1}{2} \kappa_i Q_i^2 \right) + \sum_{i,j>i} Q_i Q_j J_{ij}(r_{ij}) \quad (5.1)$$

The second term in equation 5.1 is the distance dependent electrostatic potential, J , between the charges on atoms i and j . This is a standard $1/r_{ij}$ Coulomb potential between point charges that is modified to be dampened at very short distances. In this work, we use the electrostatic potential, J_{ij} , of Verstraelen *et al.*²⁶, as detailed in the Appendix.

In the context of MOFs, Sholl and co-workers⁶ looked at a total of 500 MOFs and examined them for CO₂/N₂ used the QEq with the parameters taken from the Open Babel software.²⁷ Wilmer *et al.* studied structure-property relationships of CO₂ in over 130,000 hypothetical MOFs,²⁸ where they used their extended QEq (EQEq) method to derive the charges for each MOF.²⁹ In previous work we developed a set of parameters for QEq, known as MOF Electrostatic Potential Optimized (MEPO).³⁰ MEPO-QEq was trained to reproduce the REPEAT²³ ESP fitted charges from periodic DFT calculations of 543 hypothetical MOFs and further validated by examining the CO₂ adsorption in 693 hypothetical MOFs not found in the training set. The MOFs used in both the training and validation set were carefully selected to be diverse in their SBUs and the range of CO₂

adsorption values. In that work, the parameters for a total of 10 elements were parameterized to minimize the difference between the ESP of the REPEAT charges and the ESP derived from the MEPO-QEq charges. The MEPO-QEq charges were found to outperform both standard QEq and EEq charges in accurately reproducing CO₂ adsorption properties such as the uptake and the heats of adsorption when compared to those determined by REPEAT charges.²⁹ Recently MEPO-QEq parameters were used to screen over 4700 experimental MOFs for gas adsorption,¹⁸ evaluate carbon nanoscrolls post-combustion carbon capture,³¹ used for training machine learning tools^{32,33} and used as a benchmark.^{34,35} Even with a thorough parameterization, the QEq method has its limitations such as limited transferability based on its training set.³⁶

Mueser and coworkers developed what can be considered an extension of the QEq model that overcomes many of its shortcomings called the split-charge equilibration (SQE) method.³⁷ In the SQE method, an energy expression is defined in terms of split-charges, q_{ij} , that are associated with each covalent bond. Partial atomic charges are then obtained from the split-charges from as shown in equation 5.2, where the split-charge represents the charge that flows from atom j to atom i and the sum is over all atoms bonded to atom i .

$$Q_i = \sum_j q_{ij} \quad (5.2)$$

As a generalization of the atomic hardness and electronegativity, additional bond hardness, κ_{ij}^b , and bond electronegativity, χ_{ij}^b , parameters are introduced in the SQE energy expression given in equation 5.3, where the second term is the QEq energy expression given in terms of the atomic charges defined by equation 5.1.

$$E_{SQE}(\mathbf{q}) = \sum_{i,j>i} \left(\chi_{ij}^b q_{ij} + \frac{1}{2} \kappa_{ij}^b q_{ij}^2 \right) + E_{QEq}(\mathbf{Q}) \quad (5.3)$$

By setting either the bond or atomic parameters to zero, it is seen that the SQE model encompasses both the QEq and the atom-atom charge transfer (AACT)³⁸ models, respectively. Although the SQE method has been applied and trained on small organic molecules,³⁹ and simple periodic systems such as silicates,²⁶ to the best of our knowledge the SQE method has not been used for more complex materials, such as MOFs.

In this work, we present a set of SQE parameters that were fit directly to reproduce the quantum mechanical ESP on a diverse set of 559 hypothetical MOFs. To further extend the applicability of the parameters we included 45 hypothetical porous polymer networks (PPN).⁴⁰ PPN are 3D

periodic structures similar to MOF with nanopores and tunability but they do not contain any metals. These parameters were then tested on a set of 520 MOFs and 65 PPNs, which were not used in the training set. Our parameterization, which we term SQE-MEPO (Split-charge equilibration - MOF electrostatic potential optimized) was found to be the most accurate empirical method for determining ESPs in these nanoporous materials. These results were validated by comparing results the CO₂ uptakes and heats of adsorption from GCMC to GCMC calculations using DFT derived charges. SQE-MEPO can allow greater accuracy when performing high-throughput screening of these materials.

5.3 Methods

The training and validation sets used in this work were chosen to be large and contain a diverse number of chemical environments to be as transferable as possible. The training and validation training sets consisted of MOFs generated in a similar manner to those used in our previous study.³⁰ These MOFs were created from a geometric approach, where the inorganic and organic SBUs were connected by pre-defined parameters. In this work, the structures used were extended to include MOFs with a much greater diversity of network topologies constructed from a graph-theoretical topology based builder⁴¹ and hypothetical porous polymer networks (hPPNs). All MOFs came from in-house databases while all PPNs were taken from work by Martin *et al.*⁴⁰ The MOFs were chosen to have a wide range of inorganic and organic SBUs and functional groups. More specifically, the training set included 559 MOFs and 45 PPNs for a total of 604 unique structures. 13 inorganic SBUs, 101 organic SBUs and 31 functional groups were used to construct the MOFs in the training set with 81 different network topologies. The 45 PPNs were functionalized with a total of 19 unique functional groups that were also used in the set of MOFs. Our validation set included a total of 585 structures not found within our training set, with 520 MOFs and 65 PPNs. The MOFs in the validation set were constructed from 13 inorganic SBUs, 95 organic SBUs, and 32 functional groups with 82 different topologies. The PPNs were functionalized with a total of 21 functional groups. Both training and validation sets had the same 17 elements and 31 bond types, in approximately equal proportions as shown in Figure 5.1, with the order as shown in Table 5.1. Structures were functionalized using an in-house code that replaces symmetrically determined hydrogen atoms. All structures, and a breakdown of atom and bond types, are given in the Appendix.

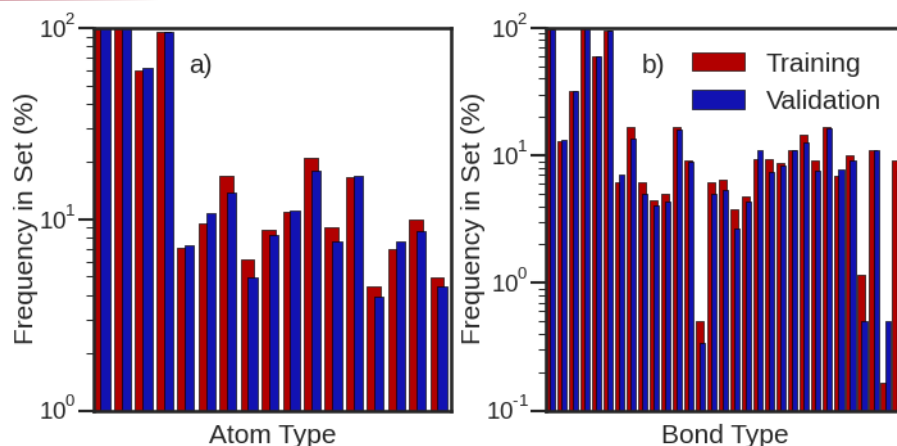


Figure 5.1. Comparison of the frequency of each (a) Atom and (b) Bond type in the training and validation sets. The order of the atom and bond types are the same as those in Table 5.1.

All structures, including the hypothetical PPNs, were geometrically optimized with the universal force field (UFF)⁴² that we have implemented into the GROMACS software package.⁴³ The UFF was found to unphysically distort the inorganic SBUs, so the bonds and bond angles involving all metal centers were fixed. After geometry optimization, a single point QM calculation on each material were performed with VASP^{44–46} using the PBE functional⁴⁷ and a plane wave cut-off energy of 520 eV. The gauge corrected DFT-derived ESPs were used to calculate the REPEAT partial atomic charges²³ for each structure. The CO₂ adsorption properties were determined using an in-house GCMC⁴⁸ based upon DL_POLY 2 molecular dynamics package⁴⁹ which has been previously applied to study gas adsorption in MOFs.^{5,9,13} Guest-framework interactions were calculated using LJ potentials for repulsive steric and attractive dispersion interactions, while point charge approximation was used for electrostatic interactions. The LJ parameters for the frameworks were assigned from the UFF,⁴² while the CO₂ parameters and partial atomic charges were developed by Garcia-Sánchez.⁵⁰ Further details about the GCMC simulations can be found in the Appendix.

The SQE method uses two parameters for each element i , the electronegativity, χ_i , and the hardness κ_i . Additionally, each bond type (e.g. H-C, C-O), between element i and element j has an associated electronegativity, χ_{ij} , and hardness, κ_{ij} . It should be noted that the bond electronegativity between atoms of the same element (ex. C-C) is set to 0. All SQE parameters were simultaneously fit to minimize the average of all the structures' mean absolute difference between the ESP resulting from the SQE charges and the ESP from a periodic DFT calculation of the material (the QM ESP) on a set of real space grid points. Unlike our previous work which fit

parameters to reproduce the ESP from the REPEAT fitted charges, in this work, the parameters were directly fit to the gauge-modified²³ QM ESP. Each structure's grid was a uniformly spaced 0.2 Å along the cell vectors. Only grid points that were between one and two van der Waals radii of atoms were considered valid and used for fitting. The ESP due to the point charges was calculated using the Wolf summation,⁵¹ which was found to be as accurate as the Ewald summation⁵² while being significantly more efficient.⁵³ A custom genetic algorithm (GA), similar to that used in our previous work,³⁰ was used to fit all the SQE parameters simultaneously. The GA started by creating multiple sets of randomly generated parameters, collectively known as a generation, that were then evaluated for how closely they reproduced the QM ESP. The new generation was formed by using a roulette wheel selection algorithm choose two individuals from the generation to act as a parent to new individuals by a mating algorithm. The mating algorithm would take a random value for each parameter that was between the values of the parameter of both the parents' parameter. Subsequent mutations were allowed that would alter a parameter $\pm$ 30% of the value. The GA was considered converged when the top performer remained the same for ten generations. Following the application of the GA, a local grid search of each parameter was performed to refine the fit.

5.4 Results and Discussion

In this work, we optimized SQE parameters for 17 elements and 31 bond types. However, 5 of the bonds were between the same element for which the bond electronegativity is set to 0, thereby giving a total of 91 parameters that were optimized. The radii used in this work were 1.5 times the covalent bond radii for each element from OpenBabel,²⁷ except hydrogen which was set to three times the radius as proposed by Verstraelen *et al.*³⁹ The radii determine when the conventional Coulomb potential, J_{ij} , is damped at close range. The optimized SQE-MEPO parameters are given in Table 5.1, along with the original MEPO-QEq parameters. The training and validation sets used in this work contain more atom types than the original MEPO-QEq parameterization. As a result, QEq parameters from OpenBabel were used in this work for the atom types not available in the original MEPO-QEq work. We note that although the atomic hardness and electronegativity parameters have the same theoretical origin in QEq and SQE, they are not fully equivalent as the bond parameters can influence them. Moreover, it can be shown that the atomic electronegativities in the SQE method can be accounted for with the new combined bond electronegativity parameters.³⁹

Table 5.1. MEPO QEq and SQE-MEPO parameters.

MEPO-QEq			SQE-MEPO		SQE-MEPO					
Atom	χ_i (eV)	κ_i (eV)	χ_i (eV)	κ_i (eV)	Bond	χ_{ij} (eV)	κ_{ij} (eV)	Bond	χ_{ij} (eV)	κ_{ij} (eV)
H^a	4.53	13.89	2.44	17.27	H-C	-0.05	4.27	N-Zn	-2.50	33.50
C	5.43	11.71	4.32	11.84	H-N	-0.68	0.39	O-Al	0.42	25.66
N	6.69	13.24	6.56	11.11	H-O	-1.52	1.30	O-S	2.56	4.10
O	8.71	17.14	12.36	27.16	C-C	0	1.10	O-V	3.65	29.74
F	6.42	22.26	9.91	30.04	C-N	-0.17	3.55	O-Co	3.92	21.69
Al^a	4.06	7.18	1.97	4.54	C-O	-0.44	3.42	O-Ni	2.99	27.09
S	3.37	10.18	4.92	11.80	C-F	0.13	12.18	O-Cu	4.88	23.53
Cl	5.82	14.55	6.23	35.48	C-S	-0.46	15.26	O-Zn	4.38	14.15
V	4.09	8.43	4.82	14.04	C-Cl	0.24	0.49	O-Zr	0.85	38.55
Co^a	4.11	8.35	4.88	8.24	C-Br	1.39	33.74	O-Cd	3.07	13.62
Ni^a	4.47	8.41	2.52	7.82	C-I	0.38	18.95	F-V	0.07	0.32
Cu	5.43	6.94	6.89	9.32	N-N	0	17.20	Co-Co	0	40.80
Zn	3.70	8.93	8.25	6.05	N-O	0.14	1.64	Ni-Ni	0	10.37
Br	5.69	17.52	9.29	12.34	N-S	-2.42	13.05	Cu-Cu	0	39.79
Zr^a	3.40	7.10	2.14	10.57	N-Co	0.29	41.90			
Cd^a	5.03	7.91	3.79	8.45	N-Ni	1.31	9.03			
I	5.43	11.44	6.25	18.12	N-Cu	-0.96	25.95			

^aParameters taken from OpenBabel²⁷ software as they were not fit in MEPO-QEq work.

Here we compare the performance the SQE-MEPO charges to the REPEAT²³ ESP fitted charges, and those of MEPO-QEq.³⁰ Previously, MEPO-QEq was shown to outperform other QEq parameterizations including one with the extended QEq method. As a result, we use the MEPO model as a baseline for comparisons in this work. The REPEAT results are considered the target as they are the charges that best reproduce the QM ESP. We additionally compare the results to the case where all charges are set to zero to examine the sensitivity of the charges on the calculated property. We first examine how well each model reproduces the QM ESP on grid points for both the training and validation set of materials. Given in Figure 5.2a are the mean absolute deviations (MADs) between the QM ESP and the ESP of a given charge model (i.e. MEPO-QEq, REPEAT) for each member of the training set where the materials are left to right ordered from lowest to highest MAD. Figure 5.2b shows the same for the validation set. Figure 5.2 shows that for both the training and validation set, the REPEAT charges perform the best, with the performance of the SQE-MEPO model lying roughly midway between the MEPO-QEq and REPEAT models. The

exception to this is for the first 15 structures of the training set, where the MADs using the MEPO model are lower than those of the SQE-MEPO model. On the other hand, the SQE-MEPO model out performs the MEPO-QEq model by ~30% when averaging over the training and validation set as shown in Table 5.2. Also, given in Table 5.2 are the MADs from the QM ESP that captures 90% of the training or validation set. What this number represents is that if we consider the top 90% of structures in the training set based on MAD, that the maximum MAD for SQE-MEPO is 8.9 mHartree, while it is 15.3 mHartree for MEPO-QEq.

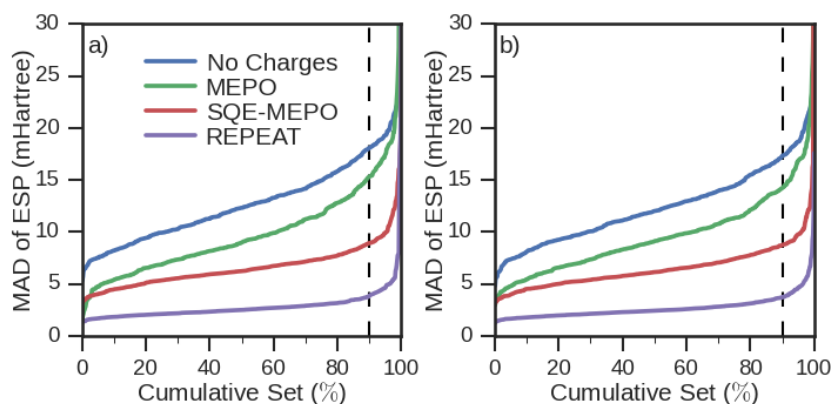


Figure 5.2. MAD between the QM ESP and the ESP calculated from different charge models for each member of the (a) training set and (b) validation set sorted from smallest to largest MAD. The dashed line corresponds to 90% of the set. The y-axis maximum was set to 30 mHartree

Table 5.2. Statistics of the MADs of ESPs for the various charge generation methods to the QM ESP in mHartree.

Charge Model	Training Set		Validation Set	
	mean	max at 90% ^a	mean	max at 90% ^a
no charges	12.80	18.1	12.39	17.2
MEPO-QEq	9.96	15.3	9.53	14.0
SQE-MEPO	6.63	8.9	6.47	8.7
REPEAT	2.87	3.9	2.66	3.7

^amax at 90% is the maximum MAD of ESPs from the smallest 90% of MADs of ESPs for that set and method

To further validate the results of SQE-MEPO model we have looked at CO₂ adsorption properties calculated with GCMC simulations and compared them to the same properties calculated with the REPEAT charges. CO₂ has a non-negligible quadrupole moment⁵⁴ of -13.4×10^{-40} C m² and therefore we expect the electrostatic interactions to be important for determining the CO₂ adsorption properties. For example, for the CO₂ model we used, when partial atomic charges are placed on the nuclear centers to reproduce the experimental quadrupole moment, the magnitude of the charges are -0.326 e and $+0.652$ e on the O and C atoms, respectively.⁵⁰ Therefore, we expect the electrostatic interactions to be important for determining

the CO₂ adsorption properties. To corroborate the effect of the quadrupole moment, we also compare the results to those obtained with no charges to evaluate the sensitivity of the results to the charges. Figure 5.3 and Table 5.3 compare the adsorption properties calculated with the various charge models compared to those determined with the REPEAT charges. Figure 5.3a and Figure 5.3c, graphically compares the CO₂ uptake values (0.15 bar and 298 K) for the various charge models with the REPEAT results for the training and validation sets, respectively. Visual inspection reveals that the SQE-MEPO model performs the best, with a small systematic under estimation of the CO₂ uptake compared to the REPEAT results for both the training and validation set. Also, the CO₂ uptake values in both the training and validation set span a large range from 0 mmol/g to almost 7 mmol/g. Table 5.3 shows that Pearson correlation (least squares) coefficient for SQE-MEPO is ~0.95 for both the training and validation set, while it is ~0.90 for MEPO-QEq. Similar results are obtained with the Spearman rank correlation coefficients. It is notable that the MEPO-QEq model does not perform significantly better than using no charges at all in terms of linear correlation of ranking. At the same time, one should keep in mind that the MEPO-QEq model was not parameterized to either the training or validation set used in this work. The heats of adsorption (HoA) are not as sensitive to the charge model as the uptakes are as shown in Figure 5.3b and Figure 5.3d. For example, with the validation set, the Pearson correlation coefficient is with no charges is 0.894. Nonetheless, the SQE-MEPO model performs the best of all models for reproducing the results obtained from the REPEAT charges. As noted, the SQE-MEPO model systematically under-estimates the CO₂ uptake, with the best-fit line for the uptake having a slope of $m=0.85$ for the training set and 0.87 for the validation set. The same is true for the HoA, where the SQE-MEPO gives best fit slopes of $m=0.95$ for both the training and validation sets. This was also seen with MEPO-QEq as well which is what was observed when MEPO-QEq parameters were developed. The lines of best fit for SQE-MEPO are the closer to the ideal value of 1 than MEPO-QEq in all cases, except in the case of training set HoA. The reason its slope is lower is because MEPO-QEq over predicted a few of HoAs, causing an increase in the slope.

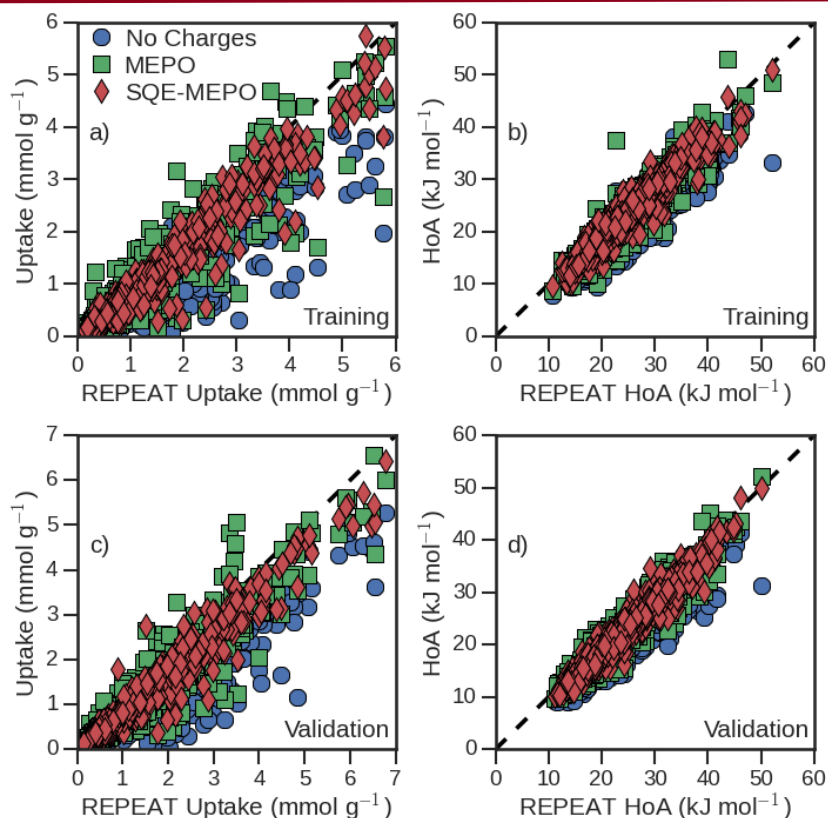


Figure 5.3. Comparison of adsorption properties calculated with different charge models to those calculated with DFT derived REPEAT charges at 0.15 bar CO₂ and 298 K for (a) CO₂ uptake and (b) heats of adsorption with the training set and (c) CO₂ uptake and (d) heats of adsorption with the validation sets. The dotted black line shows the ideal correspondence.

Table 5.3. RMSDs, Slopes, Pearson and Spearman rank order coefficients for CO₂ uptake and HoA at 0.15 bar CO₂ and 298 K computed with no charges, MEPO-QEq, and SQE-MEPO compared with values determined with REPEAT charges for training and validation sets.

Set	Charge Model	CO ₂ Uptake				CO ₂ HoA			
		RMSD (mmol/g)	Slope	Pearson (R ²)	Spearman (R ²)	RMSD (kJ/mol)	Slope	Pearson (R ²)	Spearman (R ²)
Training	no charges	0.769	0.628	0.863	0.842	4.420	0.869	0.874	0.887
	MEPO-QEq	0.503	0.829	0.876	0.873	2.858	0.957	0.889	0.890
	SQE-MEPO	0.407	0.845	0.938	0.932	2.278	0.944	0.932	0.930
Validation	no charges	0.755	0.652	0.877	0.873	4.389	0.871	0.894	0.909
	MEPO-QEq	0.466	0.855	0.900	0.910	2.654	0.935	0.910	0.913
	SQE-MEPO	0.363	0.866	0.956	0.954	2.198	0.953	0.946	0.946

The performance of the SQE-MEPO charges for reproducing the CO₂ adsorption properties at low pressure are relevant for post-combustion CO₂ capture, there is also interest high pressure adsorption of CO₂ for processes such as pre-combustion CO₂ capture.⁵⁵ Figure 5.4 and Table 5.4 compares the calculated adsorption properties of REPEAT charges to the various other charge models, at a CO₂ pressure of 10 bar at 298 K. Figure 5.4a and c show comparison of the CO₂

uptake capacities for the training and validation sets, respectively. In both cases, it can visually be seen that SQE-MEPO outperforms the other charge validation schemes. This is further confirmed by Table 5.4, which shows the root mean squared deviation (RMSD), Slopes, Pearson and Spearman-Rank correlation of the training and validation sets. Compared to the low-pressure adsorption results, the difference in performance of the SQE-MEPO and MEPO-QEq models at high pressure is much less. This is because at high pressure, both the geometry of the MOF and the CO₂-CO₂ interactions play a larger role in determining the adsorption compared to the CO₂-framework electrostatic interactions. It should be noted RMSDs presented in Table 5.4 are all higher than those presented in Table 5.3, due to the uptake capacity being much greater at the higher pressure, spanning from 0 to ~35 mmol/g. Once again, the HoAs for both the training and validation set, shown in Figure 5.4b and d respectively, are not as charge sensitive as the CO₂ uptake capacity. SQE-MEPO was found to still perform the best out of any of the charge models, which is supported by the smaller RMSDs and larger Pearson and Spearman coefficients. The SQE-MEPO model continued to under-estimate the CO₂ uptake, with slopes of $m=0.93$ and 0.91 for the training and validation sets respectively. This trend was also seen in for the HoAs, which had slopes of $m=0.94$ and 0.96 for the training and validation sets. The values of these slopes are similar to those found for MEPO-QEq suggesting the differences in the two charges is not as impactful at high pressures, as it was at low pressures.

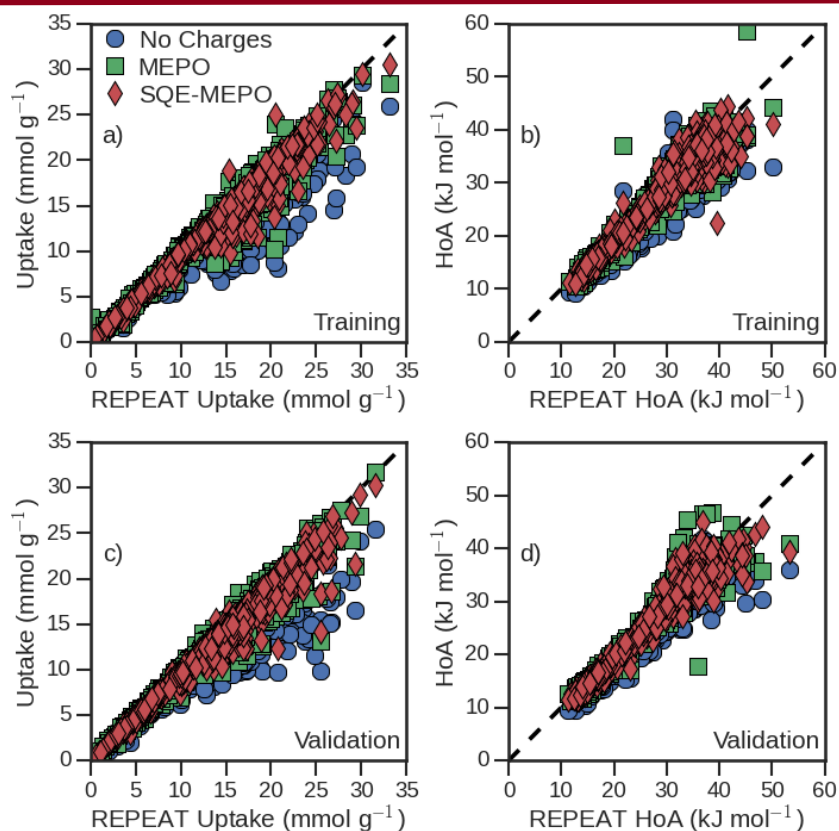


Figure 5.4. Comparison of adsorption properties calculated with different charge models to those calculated with DFT derived REPEAT charges at 10 bar CO₂ and 298 K for (a) CO₂ uptake and (b) heats of adsorption with the training set and (c) CO₂ uptake and (d) heats of adsorption with the validation sets. The dotted black line shows the ideal correspondence.

Table 5.4. RMSDs, Slopes, Pearson and Spearman rank order coefficients for CO₂ uptake and HoA at 10 bar CO₂ and 298 K computed with no charges, MEPO-QEq, and SQE-MEPO compared with values determined with REPEAT charges for training and validation sets.

Set	Charge Model	CO ₂ Uptake				CO ₂ HoA			
		RMSD (mmol/g)	Slope	Pearson (R ²)	Spearman (R ²)	RMSD (kJ/mol)	Slope	Pearson (R ²)	Spearman (R ²)
Training	no charges	3.280	0.773	0.862	0.845	3.829	0.914	0.889	0.829
	MEPO-QEq	1.858	0.899	0.940	0.929	2.670	0.958	0.909	0.856
	SQE-MEPO	1.416	0.926	0.968	0.962	2.347	0.944	0.929	0.884
Validation	no charges	3.302	0.761	0.856	0.885	3.568	0.931	0.912	0.866
	MEPO-QEq	1.669	0.911	0.946	0.943	2.555	0.963	0.922	0.891
	SQE-MEPO	1.525	0.909	0.962	0.962	2.226	0.960	0.944	0.900

5.5 Conclusions

In this work, we developed a robust set of split-charge equilibration parameters, termed SQE-MEPO, for rapidly generating partial atomic charges in MOFs and PPNs that was fit to reproduce the ESP of first principles QM calculations. These parameters were developed and trained on over

600 unique structures that included 13 inorganic SBUs, 101 organic SBUs, and 31 functional groups that cover 17 elements, 31 unique bond types, and 81 different network topologies. SQE-MEPO was validated on a total of 585 structures not part of the training set. SQE-MEPO charges were found to reproduce the ESP within the pores of the validation set materials significantly better than a similarly fit parameterization of the QEq method known as MEPO-QEq. On average, over the whole validation set, the MAD between the DFT ESP and those resulting from the SQE-MEPO charges was approximately 30% smaller than those resulting from the MEPO-QEq charges. The method was further validated by evaluating the CO₂ uptake and heats of adsorption from GCMC simulations at both low and high pressure. The adsorption properties determined with the SQE-MEPO charges were found to be in excellent agreement with those determined using DFT derived ESP fitted charges, with a Pearson and Spearman Rank correlation of 0.93 or higher. This is notable since SQE-MEPO was trained to reproduce the DFT derived ESP and not the CO₂ uptake and HoA properties directly. The CO₂ uptakes determined by SQE-MEPO were found to slightly under-predict those determined with the DFT derived charges, although this was also noted with MEPO-QEq. SQE-MEPO is a robust method for rapidly generating partial atomic charges that accurately reproduces the DFT derived ESP in nanoporous materials that are ideal for high throughput screening.

5.6 References

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5.7 Appendix

5.7.1 Dampened Coulomb Potential

As taken from the work of Verstraelen *et al.*²⁶ we used the electrostatic potential as shown in equation 5.4.

$$J_{ij}(r_{ij}) = \frac{\text{erf}(\alpha_{ij}r_{ij})}{r_{ij}} \quad (5.4)$$

Which corresponds to the interaction potential between two Gaussian charge distribution $g(\mathbf{r})$ given by equation 5.5:

$$g_i(\mathbf{r}) = \left(\frac{1}{2\pi R_i^2} \right)^{\frac{3}{2}} e^{-\frac{(\mathbf{r}-\mathbf{r}_i)^2}{2R_i^2}} \quad (5.5)$$

Where $\mathbf{r}_i$ is the position of atom i and the parameter R_i , can be viewed as the effective radius of atom i . The α_{ij} parameter can be calculated by equation 5.6:

$$\alpha_{ij} = \left(\frac{1}{2R_i^2 + 2R_j^2} \right)^{\frac{1}{2}} \quad (5.6)$$

5.7.2 Breakdown and Training Validation Sets

The training set consisted of a total of 604 structures and the validation set had a total of 585 structures. The breakdown of element types and the number of cifs they appeared in are shown in Table 5.5. Likewise, the number of breakdown of bonds is shown in Table 5.6. The functional groups and number of structures they were attached to is given in Table 5.7. The MOFs comprised 559 and 520 of the structures in the training and validation sets respectively, with the topologies shown in Table 5.8. All structures are available in the zip files.

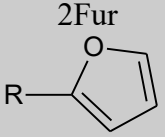
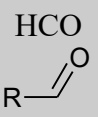
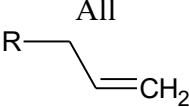
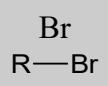
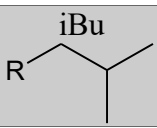
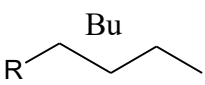
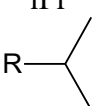
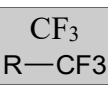
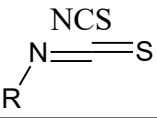
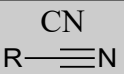
Table 5.5. Parameterized elements and the number of cifs they appeared in for both the training and validation sets.

Element	Training	Validation	Element	Training	Validation	Element	Training	Validation
H	595	582	S	101	80	Zn	100	98
C	604	585	Cl	37	29	Br	27	23
N	362	358	V	53	48	Zr	42	45
O	575	557	Co	66	65	Cd	60	51
F	43	43	Ni	126	105	I	30	26
Al	57	63	Cu	55	45			

Table 5.6. Parameterized bonds and the number of cifs they appeared in for both the training and validation sets.

Bond	Trainin g	Validatio n	Bond	Trainin g	Validatio n	Bond	Trainin g	Validatio n
H-C	593	581	N-N	101	96	O-Co	66	65
H-N	78	79	N-O	55	52	O-Ni	87	73
H-O	192	186	N-S	3	2	O-Cu	55	45
C-C	604	585	N-Co	37	30	O-Zn	100	98
C-N	362	357	N-Ni	39	32	O-Zr	42	45
C-O	571	549	N-Cu	23	16	O-Cd	60	51
C-F	37	42	N-Zn	29	26	F-V	7	1
C-S	101	80	O-Al	57	63	Co-Co	66	65
C-Cl	37	29	O-S	56	44	Ni-Ni	1	3
C-Br	27	23	O-V	53	48	Cu-Cu	55	45
C-I	30	26						

Table 5.7. Functional groups attached to structures, and the number of structures each functional group was attached to in both the training and validation sets. Functional Group column contains both the name and a drawing of the functional group. The functional group attaches the structure on the 'R' shown in the drawing.

Functional Group	Training	Validation	Functional Group	Training	Validation
 2Fur	1	2	 HCO	18	21
 All	2	2	 I	30	26
 Br	27	23	 iBu	0	2
 Bu	1	5	 iPr	1	2
 CF ₃	7	11	 Me	16	13
 Cl	35	26	 NCS	14	13
 CN	39	53	 NH ₂	28	26
COH	14	18	N(Me) ₂	7	9

$\text{R}-\text{CHO}$			$\text{R}-\text{N}$		
COMe $\text{R}-\text{C}(=\text{O})\text{Me}$	19	13	NO_2 $\text{R}-\text{N}(\text{O})_2$	52	50
$\text{CO}(\text{NH}_2)$ $\text{R}-\text{C}(=\text{O})\text{NH}_2$	7	5	OAc $\text{R}-\text{O}-\text{C}(=\text{O})\text{Me}$	5	7
$\text{CO}(\text{OEt})$ $\text{R}-\text{C}(=\text{O})\text{OEt}$	15	12	OEt $\text{R}-\text{O}-\text{CH}_2\text{CH}_3$	9	11
$\text{CO}(\text{OH})$ $\text{R}-\text{C}(=\text{O})\text{OH}$	21	22	OH $\text{R}-\text{OH}$	55	52
$\text{CO}(\text{OMe})$ $\text{R}-\text{C}(=\text{O})\text{OMe}$	18	12	OMe $\text{R}-\text{CH}_3$	33	33
Et $\text{R}-\text{CH}_2\text{CH}_3$	5	6	Pr $\text{R}-\text{CH}_2\text{CH}_2\text{CH}_3$	1	2
F $\text{R}-\text{F}$	28	23	SMe $\text{R}-\text{S}-\text{Me}$	18	20
H $\text{R}-\text{H}$	24	25	SO_3H $\text{R}-\text{S}(=\text{O})_2\text{OH}$	54	40

Table 5.8. Topologies of hypothetical MOFs in the training and validation sets.

Topology	Training	Validation	Topology	Training	Validation	Topology	Training	Validation
acs	30	16	lni	0	2	tfz	8	4
apo	1	0	lnj	1	0	tfz-d	4	6
baa	1	1	lon	1	1	the	4	1
bba	1	0	mcn	0	2	tsb	1	0
bbf	0	1	mer	0	1	ttp	1	0
bbg	1	0	mfj	0	1	ttu	0	1
bbr	0	1	mjb	0	2	ttx	1	0
bbv	1	0	moc	0	2	ttz	1	0
bcu	75	70	mot-e	2	0	ubt	42	45
bel	0	1	muo	2	2	ukk	2	0
cdl	0	1	nbo	0	3	umy	1	0
cdm	1	0	neb	0	1	unb	0	1
cds	0	1	npo	0	1	unc	0	2
crb	1	1	ofp	1	0	une	1	0
crs-d	1	0	pcu	17	27	ung	1	0
cus	0	1	pte	1	2	unh	0	2
cut	1	0	pth	1	0	uni	0	1
dme	9	5	ptr	2	1	unj	0	2
doh	1	0	pts	1	1	unn	0	1
eed	0	1	qdl	1	0	uoc	0	1
fjh	1	0	rna	3	6	uod	1	0
flu	5	3	sbr	0	1	uop	0	1
fof	1	0	sda	1	0	uov	0	1
fry	0	3	sit	2	1	uow	1	0
fsb	0	1	sni	1	0	utj	1	3
fsc	89	72	soc	2	0	vby	1	1
fsd	3	1	sod	0	1	wbl	0	1
fsf	3	0	spl	1	1	wmi	0	1
fsg	1	1	sra	110	111	xai	2	1
fsi	1	0	sto	2	2	xat	2	0
fsn	0	1	stp	1	1	xax	5	2
gar	1	0	stx	1	2	xay	1	1
hms-e	1	0	tbo	1	0	xbe	8	2
hst	2	0	tfb	1	0	xbi	2	0
ins	4	2	tfc	4	2	xbl	0	1
irl	41	49	tfg	0	2	xbv	1	0
ith-d	2	2	tfh	1	1	ylf	2	1
Jea	8	5	tfj	0	2	yug	0	1
Jeb	4	1	tfl	0	1	zul	0	3
Jph	0	1	tfm	1	0	zyg	1	0
Kea	0	1	tfo	11	7			

5.7.3 GCMC Methods

Grand Canonical Monte Carlo (GCMC) simulations were performed using an in-house developed code base upon DL_POLY 2 molecular dynamics package⁴⁹ that has been previously applied to study gas adsorption in metal-organic frameworks.^{5,9,13,56} The atomic positions of the structures were fixed in the simulations. Non-bonding interactions were calculated using Lennard-Jones (LJ) potentials and electrostatic interactions calculated with partial atomic charges. The LJ parameters for the nanoscrolls were assigned from the universal force field (UFF)⁴² and partial atomic charges were assigned by the various methods described in the work. Parameters for the CO₂ guest molecules were developed by Garcia-Sánchez *et al.* to reproduce adsorption in zeolites.⁵⁰ Gas adsorption were performed at 298 K at both 0.15 bar and 10 bar of CO₂. Fugacities were calculated using the Peng-Robinson equation of state.⁵⁷ GCMC simulations were run for 30,000 cycles, for both the equilibration and the production phases. A cycle consists of N Monte Carlo steps where N is the number of guest molecules present at any given point.

6 Optimization of Parasitic Energy

In this chapter, I present work done on the optimization of the parasitic energy of structures for post-combustion carbon capture. Part of this chapter is adapted with permission from *The Journal of the American Chemical Society*, **2017**, 139, 1734-1737 for which I was a co-first author.¹ Copyright 2018, American Chemical Society. That work was done in collaboration with the Ramanathan group from the Indian Institute of Science Education and Research Pune (IISERP). In that work, they performed the synthesis and experimental testing of the material, while I performed adsorption isotherm modelling, computational simulation of gas adsorption, and the optimization of the parasitic energies. It was through these simulations that the material was identified as high-performing for post-combustion CO₂ capture. Some additional work in this chapter, like the optimization of the PE for the Computation-Ready Experimental (CoRE) database, was used in part for a publication currently being worked for submission as of the time of writing this thesis. For this chapter, all the presented work was done by me. It should be noted that when the work was published, an older version of the parasitic energy was used, which caused differences in the numerical results, and slight changes in the rankings. At the time of writing this chapter, all the results and analysis were performed using the most recent version of the parasitic energy.

6.1 Abstract

Metal-Organic Frameworks (MOFs) have attracted significant attention as solid sorbents in pressure and temperature swing gas separation for their potential in low-energy Post-Combustion Carbon Capture (PoCCC). The parasitic energy (PE) is a physically motivated figure of merit to estimate the energetic (and by extension monetary) cost of a carbon capture system. In this chapter, I present my work using the PE to guide the discovery of optimal solid sorbents for PoCCC. Using experimentally derived adsorption isotherm models (AIMs) parameters for CO₂ and N₂ adsorption data of 43 porous structures, we found that a nickel isonicotinate based ultra-microporous MOF, **IISERP-MOF2**, had the lowest PE reported to date (823.4 kJ/kg CO₂), outperforming the PoCCC benchmark MOF, Mg-MOF-74 (947.8 kJ/kg CO₂). The PE was optimized for each structure in the Computation-Ready Experimental (CoRE) MOF database, using computational gas adsorption data. It was found that no CoRE MOF was able to outperform **IISERP-MOF2**, with the lowest PE reaching 833.2 kJ/kg CO₂, although a total of 144 were found to have PEs lower than Mg-

MOF-74. Finally, 581 CoRE MOFs were selected and functionalized using a library of 28 common functional groups, to create a total of 152,722 functional MOFs (fMOFs). Ten of these fMOFs were found to have PEs lower than **IIERP-MOF2**, with the lowest reaching 749 kJ/kg CO₂. An analysis was done on the functional groups, and it was found that NH₂, OH, and HCO are over-represented in the absolute lowest PEs of the fMOFs.

6.2 Introduction

The primary emission source of CO₂ is from burning fossil fuels for energy production.^{2,3} In the long term, these emissions would be reduced by replacing fossil fuels with cleaner alternative energy sources such as wind or solar. However, global energy demand is increasing, with an upsurge in power plants burning fossil fuels to fulfil that need. One potential way to reduce their CO₂ emissions in the meantime is to employ Carbon Capture and Storage (CCS).⁴⁻⁶ The idea behind CCS is to capture CO₂ selectively and permanently store it, typically deep underground. It has been estimated that 70% of the cost of CCS is due to the separation of the CO₂ from the flue gas due to its low concentration, 10-15% CO₂ to 75-86% N₂.⁷ Overall, this separation process can cause a decrease of 30% in the plant's power production.⁴ In the case of the Boundary Dam power plant in Saskatchewan,⁸ it has been estimated that adding a CCS unit has tripled the cost of the electricity. The increased cost is not only due to the capital cost of constructing the CCS unit but also due to the energy that must be diverted to run the CCS unit. This energy penalty for running a CCS unit is known as the parasitic energy (PE). Current solvent based CCS units, such as the Boundary Dam facility, have PEs that are too high for CCS to be implemented on a larger scale.

As mentioned in Chapter 1, one of the primary reasons the PE for PoCCC is currently so high is because current technology uses liquid amines for the separation.^{9,10} During the regeneration process, the aqueous amine solution is heated up to temperatures of 120°C to break the chemical bond formed between the amine and the CO₂.¹¹ This is highly energy intensive for two reasons: 1) the liquid water has a high heat capacity requiring much energy to raise the temperature, and 2) chemical bonds between the CO₂ and amines need to be broken. For this reason, solid sorbents with easy-on-easy-off physisorption have been developed as an energetically favourable alternative.¹²⁻¹⁴ Solid sorbents are already used industrially for some gas separation processes, such as for natural gas purification where CO₂ is removed from a methane-rich stream using zeolites.^{15,16} This has led to the study of nanoporous materials, such as Metal-Organic Frameworks

(MOFs),^{17–19} or Porous Polymer Networks (PPNs),^{20,21} for use in gas separation as well. When looking at PoCCC, MOFs have been considered in part due to their favourable properties such as high CO₂ adsorption and high CO₂/N₂ selectivities.^{22,23}

For coal-burning power plants, the typical flue gas is at 323 K,⁵ with a CO₂ concentration of 10–15%²⁴ and the majority of the remaining gas being N₂. This makes some gas adsorption properties, such as the CO₂ adsorption or the CO₂/N₂ selectivity, easy to determine for a MOF due to the relatively uniform flue gas composition at the adsorption conditions. The PE is more difficult to determine because the desorption conditions also needs to be simulated. However, there can be significant variation in the desorption conditions as well as the composition of the gas under these conditions. In a PSA system, where the pressure is reduced to remove adsorbed CO₂, the choice of the desorption pressure is not intuitive. The more the pressure is lowered, the more CO₂ is removed, although it comes with an added cost to run the vacuum to that pressure. The trade-off is different for each structure, and as such, there has been work to optimize the desorption conditions of multiple MOFs.^{13,14,25,26} Highly sophisticated engineering models have also been used to optimize the desorption process, where an entire PSA system is modelled, as seen in the work by Haghpanah *et al.*²⁵ In these models a PSA system is broken into separate sections, and the gas adsorption process is propagated through time, allowing the system to adsorb and desorb the gas. Such simulations are discussed further in Chapter 8. Although these methods can tell us much about how a structure will perform in a PSA system, they require a great amount of computational power and become impractical when screening thousands of structures. The work by Huck *et al.* also looks at optimizing the process conditions;¹³ however, simple calculations (equations 1.12–1.18) were used which only require results calculated from Grand Canonical Monte Carlo (GCMC) simulations. The PE is evaluated for each desorption condition, and the lowest PE is chosen as representative of that structure. To the best of my knowledge, even this streamlined method has only been performed on tens of structures at most.

In this chapter, I present my work on the high-throughput optimization of the PE of MOFs. This is done by first optimizing the PE of both named structures first presented by Huck¹³ and then the Computation-Ready Experimental (CoRE)²⁷ MOF database. For the MOFs from Huck, experimental gas adsorption data, in the form of adsorption isotherm model (AIM) parameters, were used, while the gas adsorption for the CoRE database was simulated using an in-house GCMC code. The PE was evaluated for each structure using a single adsorption condition and

multiple desorption conditions, with the desorption condition that gave the lowest PE chosen as the optimal condition. Finally, select MOFs from the CoRE database were functionalized using a small library of 28 common functional groups. Using the GCMC methodology, each functionalized MOF was evaluated for the PE, with the functionalization and desorption condition that gave the lowest PE chosen as the representative.

6.3 Methods

6.3.1 Gas Adsorption of Named MOFs

In the initial stages of the work, we compare our results to previous results. In 2014, Huck *et al.* compiled a list of experimentally derived Langmuir AIM parameters for CO₂ and N₂ adsorption of over 40 materials including MOFs, Zeolites, and PPNs.¹³ For CO₂ parameters, these were either single- or dual-site models, while N₂ adsorption was always fit to a single site model. To keep consistent with Huck's methods, we considered adsorption to occur at 313 K and 0.14 bar of CO₂ and 0.86 bar of N₂, while desorption occurred at 333 K from pressures ranging from 0.01 to 0.5 bar, where 99% is CO₂ and 1% N₂. The desorption temperature was elevated to account for the heat generated due to the adsorption of guest molecules on the frameworks. The values given by Huck were given at temperatures of 298 K, although the Langmuir constant, K_{Hij} , is a temperature dependent value. Equation 6.1 is a version of the van't Hoff equation showing how the K_{Hij} for a guest i at binding site j is related to its heat of adsorption, Δh_{ij} , temperature, T , gas constant, R , and a fitted constant, A . By using these values, the K_{Hij} was changed by fitting the A value and then altering the temperature to the desired value. This process was unnecessary for **IISERP-MOF2**, as our experimental collaborators gave us gas adsorption data for the CO₂ and N₂ at 313 and 333 K. For **IISERP-MOF2** at each temperature, the CO₂ data was fit to a dual-site Langmuir model and a single-site Sips model for the N₂. These parameters were used in Ideal Adsorbed Solution Theory (IAST),²⁸ as implemented by Simon *et al.*²⁹ to calculate the gas adsorption of gas mixtures.

$$\ln(K_{Hij}) = A - \frac{\Delta h_{ij}}{RT} \quad (6.1)$$

6.3.2 Gas Adsorption of CoRE Database MOFs and Functional Variants

The CoRE database²⁷ (as presented in Chapter 3) was used for this work. In addition to the CoRE MOFs, select CoRE MOFs were functionalized using a small library of 28 common

functional groups which are given in the Appendix (Table 6.2). Only MOFs with 3 or fewer unique hydrogen atoms that were connected to carbon atoms were chosen for functionalization. To determine the number of unique hydrogen atoms, an in-house developed code was used that identifies unique organic linkers and hydrogen atoms within a MOF. We only considered hydrogen atoms that were directly attached to carbon atoms as they are historically the most commonly functionalized, and there are many techniques designed for this.³⁰ For MOFs that had 1 or 2 unique hydrogen atoms, all possible functional group combinations were created. For MOFs with 3 unique hydrogen atoms, every unique combination of 2 functional groups was created. This was done to keep a reasonable level of synthetic feasibility as well as for ease of computational testing.

For the CoRE MOFs and fMOFs, atomic positions were geometrically optimized using the Universal Force Field (UFF)³¹ and the GROMACS software package.³² It was found by a previous Woo lab member that the UFF causes unphysical distortion of the inorganic SBUs of MOFs, so all bond lengths and angles involving metal centres were fixed during optimization with the force field. After atomic position optimization, the partial atomic charges were calculated using the Split-Charge Equilibration (SQE)³³ method using SQE-MEPO³⁴ parameters described in Chapter 5. Gas adsorption properties were calculated using our in-house developed GCMC code. The adsorption and desorption conditions were the same as described in Section 6.3.1. Framework atomic positions were frozen during GCMC simulations, and the guest molecules were held rigid. Intermolecular interactions were calculated using the Lennard-Jones (LJ) 12-6 potential for van der Waals interactions and Ewald summation for the electrostatic interactions. The LJ parameters for framework atoms were taken from the UFF.³¹ García-Sánchez developed the LJ parameters and partial atomic charges for the CO₂ guest molecule to replicate CO₂ adsorption in zeolites,³⁵ and the N₂ parameters were developed in-house and are given in the Appendix of Chapter 3 (Table 3.1). All simulations were run for a total of 30,000 equilibration cycles and 30,000 production cycles. A cycle is N GCMC steps, where N is the number of guest atoms in the simulation cell at a given time. The results, including error bars and heats of adsorptions, were calculated using 50,000 step window averaging.

6.3.3 Optimization of Parasitic Energy

PEs were calculated using equations 1.12-1.18. PEs were calculated with the adsorption condition held constant but with different desorption pressures. The desorption temperature was

held constant at 333 K, which is similar to that done by Huck *et al.*¹³ The reasoning behind this choice of desorption temperature is that the adsorption of the guest molecules will cause the temperature of the PSA system to rise, therefore increasing the temperature by 20 K. The desorption pressures we tested varied from 0.01 to 0.5 bar. The desorption condition which gave the lowest PE was chosen as the representative value. This process was done for each structure tested.

6.4 Results and Discussion

6.4.1 Parasitic Energy Optimization of Names MOFs

Initially, I looked to replicate the PE calculations from Huck *et al.*¹³ This was done to verify our PE calculations and that the results matched Huck's, with the results presented in Figure 6.1. Our results show good correspondence to those presented by Huck, having a slope of 0.9808, a correlation coefficient of 0.997, and a Spearman correlation coefficient of 0.981. It should be noted that for this analysis, the y-intercept was forced to be 0. Deviations from a perfect 1-to-1 fit could be from multiple sources: 1) Huck used a competitive isotherm model, while I used IAST to calculate the binary mixture gas adsorption, 2) the desorption pressures tested were not listed by Huck, so I constructed my own set, 3) they used proprietary software to simulate the pressurization step and 4) Huck used a value of 0.35 for the packing loss, while I used a value of 0.25, in line with other researchers' work.^{36–38} From this analysis the lowest PE was found to be for Mg-MOF-74, the same result as Huck;³⁹ however, our value for the PE was 736.4 kJ/kg CO₂ compared to 727 kJ/kg from Huck. To provide some context for the presented PEs using a similar analysis, a state-of-the-art power plant integrated with a liquid amine PoCCC unit is estimated to have a PE of 1060 kJ/kg CO₂,^{4,12} while a coal-burning power plant that is retrofitted for a liquid amine is estimated to have a PE of 1327 kJ/kg CO₂.

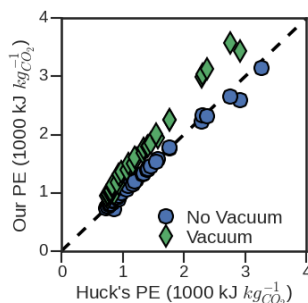


Figure 6.1. Comparison of the optimized PE calculated in this work vs the optimized PE calculated by Huck *et al.* for 42 materials. The blue circles were found by optimizing the PE without the vacuum term while the green diamonds were optimized with the vacuum energy.

It is noted that in the calculations of the PE by Huck there is no energy contribution for the evacuation of guest molecules, where the pressure is reduced from atmospheric pressure (1 bar) to as low as 0.01 bar. The system is placed under vacuum, which contributes to the energetic cost. They reasoned that the compressor that could be used to pressurize the heavy stream to transport conditions (150 bar),^{4,12,40,41} could be used to create a vacuum simultaneously. Upon discussion with process engineers who specialize in PSA gas separations, the energetics of applying the vacuum should be explicitly considered. This is noted in our version of the PE equation given in equation 1.12 and 1.15.¹ The PEs, including the vacuum energy, are also given in Figure 6.1. The line of best fit (when the intercept is set to 0) shows a good correlation with Huck's PE of a correlation coefficient of 0.9962 and a Spearman rank coefficient of 0.991, which are comparable to when the vacuum portion was not included. The slope was higher with the vacuum (1.2697) because the vacuum portion increased the PE on average by 29.8%. The rest of the work in this chapter will use the PE with the vacuum term.

When including the vacuum term, the lowest PE was found to be from a material known as mmen-CuBTTRi (m-CuB),⁴² with a PE of 898.4 kJ/kg CO₂, compared to Mg-MOF-74, which was 947.8 kJ/kg CO₂. Huck did note the low PE of m-CuB in their work, which they attributed to m-CuB being a functionalized material, essentially tuned for low PE. In their work, m-CuB has the second lowest PE of 752 kJ/kg CO₂ compared to 727 kJ/kg CO₂ for Mg-MOF-74. The reason that m-CuB performed better than Mg-MOF-74 when the vacuum term was applied is that m-CuB has an optimal desorption pressure of 0.2 bar, compared to 0.1 bar for Mg-MOF-74. By elevating the desorption pressure, although less CO₂ is removed, less energy is spent during the vacuum and pressurization phases. Mg-MOF-74 is known to have a strong affinity for CO₂, even at low concentrations,²² and therefore needs to have a low desorption pressure to remove enough CO₂ to make the process viable. If the desorption pressure were set to 0.2 bar, Mg-MOF-74 would have a PE of 1005 kJ/kg CO₂. Although there are many reasons why different materials have different optimal desorption pressure, one reason that we noted is the CO₂ adsorption of m-CuB is affected by the small (20 K) temperature change more than Mg-MOF-74. This is evident when looking at the CO₂ Henry's constants (calculated by equation 6.1), where m-CuB had a drop of 70.6% compared to 57.8% for Mg-MOF-74. This drop is tied to the HoA of the materials, which is 53 kJ/mol for m-CuB and 37.36 kJ/mol for the first binding site of Mg-MOF-74. m-CuB is the 2nd

highest HoA, while Mg-MOF-74 is the 13th highest HoA, meaning there are other properties besides the HoA that contribute to their low PEs.

In collaboration with the Ramanathan Group from the Indian Institute of Science Education and Research Pune (IISERP), I calculated the optimal PE of their newly synthesized nickel-isonicotinate **IISERP-MOF2** (shown in Figure 6.2) for PoCCC.¹ To calculate the PE, the Ramanathan group provided experimental CO₂ and N₂ adsorption data at 313 K and 333 K. The CO₂ data was fit to a dual-site Langmuir AIM (equation 1.1); however, the N₂ data was fit to a single-site Sips AIM (equation 1.2). This was done because the Langmuir AIM was found not to reproduce the experimental N₂ adsorption data well. Further details about the fittings, as well as the fitted AIM parameters and figures, are given in the Appendix of this chapter (Section 6.7.1). Using the same methods as our previous analysis (Section 6.4.1), the PE for **IISERP-MOF2** was optimized and found to give a PE of 823.4 kJ/kg CO₂, which is 8.3% lower than m-CuB and 13.8% lower than Mg-MOF-74. As of writing this thesis, this is the lowest PE noted for any material calculated using this methodology.¹ When looking at the results, it was found that the Langmuir constants decrease 72.2% over the 20 K drop, making it a more substantial drop than for m-CuB. In addition to having a low PE, **IISERP-MOF2** has other properties that make it suitable for PoCCC, such as water stability, and minimal loss of performance during cycling in humid gas streams, to name a few.¹

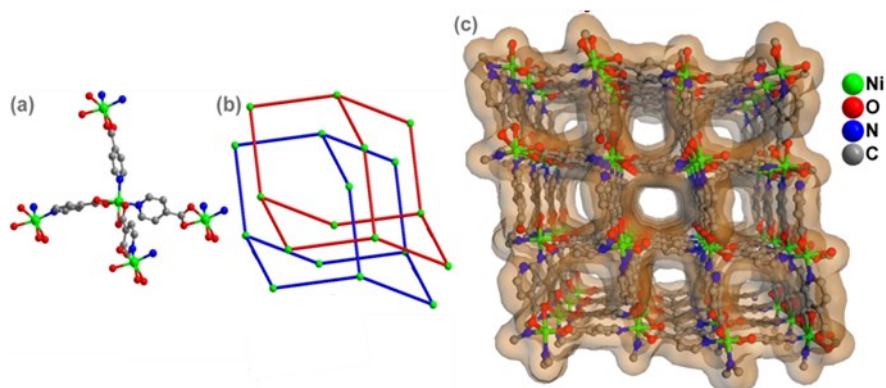


Figure 6.2. a) Building unit of **IISERP-MOF2**, showing the Ni centre and isonicotinate ligands. b) 2-fold interpenetration present in **IISERP-MOF2** diamondoid structure, with only Ni (green spheres) centres shown. c) **IISERP-MOF2** with the Connolly surface representation (probe radius=1.4 Å).

When looking at why **IISERP-MOF2** outperformed all other MOFs, it was found that no traditional gas adsorption metric made it outstanding. When looking at the properties for all 42 structures tested, **IISERP-MOF2** has the 16th highest CO₂ adsorption capacity, 6th highest CO₂/N₂ selectivity, 20th highest CO₂ working capacity, the 4th highest CO₂ purity, and the 27th lowest CO₂

heat of adsorption. One metric that **IISERP-MOF2** was the best at was the N₂ uptake, which showed minimal N₂ uptake at flue gas conditions. Although it stands out in that one category, something that should be mentioned is that **IISERP-MOF2** is consistently one of the best performing materials in all categories. Looking at the average ranking of all these categories, **IISERP-MOF2** has the 3rd best average ranking of the 42 tested materials. Two functionalized PPNs, PPN-CH₂TAEA and PPN-CH₂DETA, had the best and 2nd best average rankings of all tested structures on these criteria. **IISERP-MOF2** is unique, however, because of its desorption pressure which is 0.3 bar, compared to the 0.05 bar for the two PPNs. The reason why these 2 structures need such low desorption pressures could be attributed to their CO₂ affinity, specifically their Langmuir constants, which are 12.8 and 22.2 times larger than Mg-MOF-74. When considering the desorption pressure, it was found that **IISERP-MOF2** was the only structure with the pressure above 0.2 bar at a value of 0.3 bar. Having a high desorption pressure was not the only factor in determining if a structure would have a low PE, as the lowest PE structures could have low desorption pressures. For example, PPN-CH₂TAEA has an optimized desorption pressure of 0.05 bar, while it has the 6th lowest PE, outperforming 11 materials with higher desorption pressures. This shows that simple gas adsorption metrics such as the CO₂ uptake or CO₂/N₂ selectivity may not be good predictors of whether a material will have a low PE or not. It takes a combination of both material and process properties to evaluate a material's potential.

6.4.2 Parasitic Energy of the CoRE Database

After finding that **IISERP-MOF2** outperformed all the structures from the Huck work,¹³ the CoRE database was screened using a similar analysis. As the CoRE database does not have experimental gas adsorption data (specifically CO₂ and N₂) for every structure, GCMC calculations were performed at the same conditions as those for the named MOFs in the previous section. Although in Chapter 3, the experimentally determined atomic positions and REPEAT⁴³ partial atomic charges were used for the CoRE database, to keep these calculations consistent with ones performed later, the atomic positions of the CoRE structures were geometrically optimized using the UFF³¹ as implemented in the GROMACS software package.³² After atomic position optimization, the SQE method using SQE-MEPO parameters was used to assign partial atomic charges. The choice to optimize atomic positions with UFF and use SQE charges was made to

keep these results consistent with the next section, which required high-throughput screening techniques.

Figure 6.3 shows the optimal PE from altering the desorption pressure as a function of a static 0.05 bar PE. Before optimization, the lowest PE was found to be 990 kJ/kg CO₂, and after optimization, the lowest PE was found to be 833.2 kJ/kg CO₂. The optimization process was found to have a median decrease in the PE of 4.5% or 54.3 kJ/kg CO₂. What is interesting to note is that the largest percentage decrease in PE was found for MOFs which had low absolute PE after optimization. This is especially evident when considering the 100 materials with the lowest PEs after optimization, which had a median decrease of 11.0% or 112.4 kJ/kg CO₂, more than double the overall results. The MOF with CSD RefCode YAZFOW⁴⁴ was found to have the lowest PE after optimization (833.2 kJ/kg CO₂), although it was not able to outperform **IISERP-MOF2** (823.4 kJ/kg CO₂). YAZFOW is an indium-based MOF which has already been found to be highly selective for CO₂ over N₂ and CH₄. It was also found to have water stability, confirmed by soaking YAZFOW in distilled water for three days, as well as in boiling water for one day. A total of 23 MOFs had lower PEs than m-CuB (898.4 kJ/kg CO₂) and 144 MOFs lower than the typical benchmark MOF for PoCCC, Mg-MOF-74 (947.8 kJ/kg CO₂). It is worth mentioning that 1181 (34.0 % of the CoRE database) structures outperformed the state-of-the-art liquid amine plants (1060 kJ/kg CO₂),²⁴ and 2301 (66.3 %) outperformed a retrofitted amine capture plant (1327 kJ/kg CO₂).¹² Although no MOF has a lower PE than **IISERP-MOF2**, there is potential that some of these MOFs may have other properties that would make them useful for PoCCC. These could include chemical stability and adsorption kinetics, which cannot be assessed by the computational tools used in this work. This work shows that even simplistic process optimization is needed to see the actual potential of a MOF for a gas separation process.

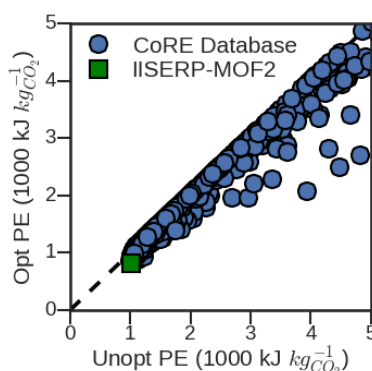


Figure 6.3. PE calculated from GCMC results for the CoRE database with optimized desorption pressure as a function of the PE when desorption was set to 0.05 bar. The green square represents **IISERP-MOF2**.

As in Chapter 3, data analysis was performed to see if simple metrics could be related to the optimized PE. In this analysis, a total of 77 descriptors were used, including the 47 from Chapter 3. 6 of the new descriptors are the optimized CO₂ and N₂ working capacities (gravimetric and volumetric), optimized purity, and the fixed PE. The choice to use the optimized gas adsorption properties was made to try and find any relationship with the optimized PE, although as the process is already optimized, the answer would be known. The remaining 24 descriptors were the following FoMs: CO₂ regenerability (equation 6.2), Adsorbent Performance Score (APS) (equation 6.3),⁴⁵ Adsorption Figure of Merit (AFM) (equation 6.4),⁴⁶ Sorbent Selection Parameter (SSP) (equation 6.5),⁴⁷ Separation Potential (SP) (equation 6.6),⁴⁸ Adsorbent Performance Indicator (API) (equation 6.7),⁴⁹ and Isotherm Separation Parameter (ISP) (equation 6.8). The ISP used in this work is a modified version proposed by Rege and Yang⁵⁰ to work for dual-site Langmuir AIMs, where their model was made for single-site Langmuir AIMs. The API has 3 variables (A, B, and C) which are used to tune the API for different applications, and for this work, we used values of 1, 1, and 1, respectively, to represent general purification, and 0.5, 2, and 1 for a bulk separation. These values and their associated cases were the values originally used by Wiersum *et al.* when they proposed the API.⁴⁹ Each metric has already been used to evaluate materials, and to the best of my knowledge, this is the most systemic collection of FoMs used to study materials for gas separation. Any FoM that could be affected (APS, AFM, SP, and API), both gravimetric (mmol/g) and volumetric (V_{STP}/V), were calculated and used in the analysis. All FoMs, besides SP, were calculated at both the fixed and optimized desorption pressure.

$$Regenerability = 100\% \frac{q_{CO_2}^a}{\Delta q_{CO_2}^a} \quad (6.2)$$

$$APS = S_{CO_2, N_2} \Delta q_{CO_2}^a \quad (6.3)$$

$$AFM = \Delta q_{CO_2}^a \frac{(S_{CO_2, N_2}^a)^2}{S_{CO_2, N_2}^d} \quad (6.4)$$

$$SSP = \frac{\Delta q_{CO_2}^a (S_{CO_2, N_2}^a)^2}{\Delta q_{N_2}^a S_{CO_2, N_2}^d} \quad (6.5)$$

$$SP = q_{CO_2}^a \frac{p_{N_2}}{p_{CO_2}} - q_{N_2}^a \quad (6.6)$$

$$API = \frac{(S_{CO_2, N_2} - 1)^A \Delta q_{CO_2}^a{}^B}{(\Delta H_{oA_{CO_2}})^C} \quad (6.7)$$

$$ISP = \frac{\Delta q_{CO_2}^a (\sigma_{CO_2}^1 k_{CO_2}^1 + \sigma_{CO_2}^2 k_{CO_2}^2)}{\Delta q_{N_2}^a (\sigma_{N_2}^1 k_{N_2}^1 + \sigma_{N_2}^2 k_{N_2}^2)} \quad (6.8)$$

Every metric had its Spearman R^2 value calculated when compared to the optimal PE. As expected, the single best metric was the PE from the fixed desorption pressure, with an R^2 of 0.980. The next best Spearman correlations were the bulk separation APIs using the fixed desorption values, both with gravimetric (R^2 0.942) and volumetric (R^2 of 0.939) values. This is somewhat expected because the API is a combination of relevant parameters for the PE, including the selectivity, the heat of adsorption, and working capacity. What is surprising is that the fixed desorption APIs give the best Spearman correlation and not the optimized value APIs (R^2 of 0.877 for both gravimetric and volumetric). The reason why the fixed value APIs gave better correlations than the optimized values were investigated, with no satisfactory answer found. The API still requires multiple GCMC calculations, which can be computationally expensive, so it would be advantageous if geometric properties, which are more rapidly calculated, could be used. The best Spearman ranking for geometric values was with the largest pore in the structure, which was found to be an R^2 of 0.031. This shows that the considered geometric values are unable to predict the optimized PE, although this is not surprising as Fernandez *et al.* needed to use more advanced geometric descriptors (like atomic-property weight radial distribution functions) to predict the CO_2 adsorption capacity at flue gas conditions.⁵¹ It would then be assumed that to predict a more complicated property, like the PE, more advanced descriptors might be needed. Another surprising result was that the optimized purity was found not to be as strongly correlated (R^2 of 0.786) when compared to the purity and PE correlation found during the Chapter 3 screening (R^2 of 0.895). The reason for the decrease in correlation is because in the screening done in Chapter 3, the desorption pressure is held constant making the vacuum and pressurization terms (equations 1.15 & 1.16, respectively) single variable terms that are inversely proportional to the purity. This is substantial as the sum of the vacuum and compression terms account for an average of 79.6% of the total PE when the desorption pressure is fixed, and 77.0% when optimized. When optimized, the p_d changes based on the material, reducing the impact of the purity on the PE. An interesting value is the SP (R^2 of 0.846), as it is the highest correlated value which did not require any information about the desorption conditions, and therefore only needs a single GCMC calculation.

Overall it was found that simple process optimization at the GCMC can be used to minimize the PE, with overall decreases of PEs of 4.5% or 54.3 kJ/kg CO₂. The decrease is more pronounced for structures with low PEs, where the median decrease can be as high as 11.0% or 112.4 kJ/kg CO₂. It should be noted that no CoRE MOF was able to outperform **IISERP-MOF2** in terms of optimized PE. After this, I tried to determine the relationships between 77 descriptors and the optimized PE. It was found that the bulk separation API, using values from the fixed desorption pressure, was the best single descriptor, with Spearman ranks of 0.942 and 0.939 for gravimetric and volumetric respectively. This might allow a simple filter to remove potentially bad materials without the need to perform the optimization procedure done here.

6.4.3 Parasitic Energy of the Functionalized CoRE Database

Finally, I looked at the effect that functionalization had on the PEs of selected MOFs from the CoRE database. In previous work, it has been found that functionalization can change, and therefore tune, the property of a MOF for a given application.^{52–54} In one example by Biswas *et al.*, 1,4-benzenedicarboxylate linkers were experimentally functionalized with six different functional groups.⁵⁵ It was found that depending on which functional group was used; the CO₂ adsorption could nearly triple from 2.1 to 5.9 mmol/g at 1.0 bar. Functionalization was computationally mimicked by using an in-house code that replaces hydrogen atoms of the MOF with functional groups from a given library. The code essentially works by functionalizing the linker of a MOF and then having those functionalized linkers be used as the organic SBUs during a MOF's synthesis. More details about the functionalization code and the functional group library are given in the Appendix (Section 6.7.2). From the MOF symmetry standpoint, this means that the crystal symmetry may be different from pre-functionalization, shown in Figure 6.4. The functionalized MOF (fMOF) should be able to be made without needing to control the placement of the functional groups, as it is done randomly, like during synthesis.

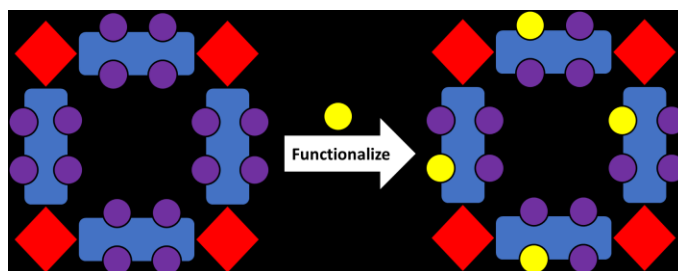


Figure 6.4. Cartoon representation of functionalizing a structure using our in-house code, CliSwitch. Inorganic SBUs (red diamonds), organic SBUs (blue rectangles), hydrogen atoms (purple circles), and a functional group (yellow circle) are shown. Symmetry is lost with addition of the functional group.

A simple test was done by repeating the functionalization on 12 unique MOFs, and it was found that for most MOFs, the average difference in CO₂ adsorption when functionalized differently could be attributed to the error in the GCMC calculations. By this, I mean that the difference in adsorption between materials functionalized with the same group was smaller than the error of the GCMC calculations. Details and results of the test are shown in the Appendix (Section 6.7.3). For this work, only 2 functional groups were placed in a MOF at a given time. This was done to provide realistic synthetic targets. Similarly, only MOFs that contain 3 or fewer unique hydrogen atoms were considered for this work. There were 581 MOFs that had up to and including 3 unique functionalization sites that when functionalized would give 816,213 unique functional group combinations. Of the 816,213 unique combinations, only 152,722 combinations were viable from a steric point of view. These were all created and tested.

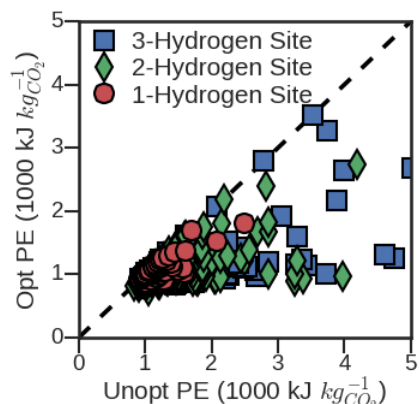


Figure 6.5. The optimal PE of CoRE found by altering functionalization and desorption conditions as a function of the optimal PE of the CoRE MOF from altering desorption conditions. Results are section based on the number of unique hydrogen sites for functionalization: 1-site (red circle), 2-sites (green diamond), and 3 sites (blue squares).

Figure 6.5 shows the impact of functionalization on the PE of a material where the PE is compared to the base structure (Unopt) and the MOF with the functional groups optimized (Opt PE). It was found that the median decrease of PE due to functionalization was 161 kJ/kg CO₂ or 14.3%, which is more than the 54.3 kJ/kg CO₂ or 4.5% associated with the optimization of just the desorption pressure. This makes sense as functionalization changes the chemical composition of the pores and can alter a MOF's adsorption properties.⁵⁶ The lowest PE, 749 kJ/kg CO₂, after functionalization, came from a MOF with a CSD RefCode of IKEBUV01,⁵⁷ when functionalized with NHMe and Me. In addition to the single best fMOF, 9 other MOFs outperformed **IISERP-MOF2**, of which 8 were derived from IKEBUV01. Looking at the results as a function of the number of unique hydrogen sites, it was found that increasing the number of possible hydrogen

sites also increased the degree at which functionalization affected it, with the median decrease of PE increasing from 5.9%, 10.7%, and 21.2% as the number of functionalization sites increased from 1 to 3 sites. The reason for this seems to be evident when looking at Figure 6.5, where both 2- and 3-site MOFs were likely to have structures with large unoptimized PEs, and could, therefore, decrease by a more substantial amount.

As in the previous section, data analysis was performed where the 77 descriptors were used to find relationships with the optimized PEs. This work was performed on not only the base 581 CoRE MOFs but on all 152,722 functionalized MOFs. When looking at the Spearman correlation, once again the strongest correlation of the optimized PE was with fixed desorption PE (R^2 of 0.979). After that, the next highest correlation was with the bulk separation version of the API using the fixed desorption values (R^2 0.954). This is not surprising as it is the same result found for the full unfunctionalized database. When examining geometric descriptors that could be used to rank the performance of PE, the highest Spearman correlation R^2 was found to be only 0.11 for the volumetric surface area calculated using a helium (1.0 Å) probe. Once again this shows that single geometric descriptors are insufficient to predict the optimized PE of materials.

Another result of interest would be to see which functionalizations most affected the results. For this study, Adjusted Residuals (A_{ij}) (equation 6.9) were used to study how often the functional groups appeared in the top performing functionalized MOFs. Adjusted residuals work by splitting a data set into different categories, in this case, top performing and bottom performing structures. For each category, the amount of each functional group is tallied to see how often each functional group i is observed in each category j to determine the Observed value O_{ij} . After tallying, an expectation value, E_{ij} , can be calculated (equation 6.10) for each functional group-category combination which is based on ratios. From there the A_{ij} is calculated by equation 6.10, which indicates how many standard deviations the observed values are from the expected value. For this work, a more positive value means the functional group is observed more often than expected in the top performers, while a more negative value means the functional group is observed less than expected in the top performers. A value of 0 means the functional group showed up as often as expected. These values are not based on any chemical intuition and are entirely based on statistics.

$$AR_{ij} = \frac{O_{ij} - E_{ij}}{\sqrt{E_{ij} * \left(1 - \frac{E_{ij}}{\sum_i O_{ij}}\right) * \left(1 - \frac{E_{ij}}{\sum_j O_{ij}}\right)}} \quad (6.9)$$

$$E_{ij} = \sum_j o_{ij} \frac{\sum_i o_{ij}}{\sum_i \sum_j o_{ij}} \quad (6.10)$$

For this work, two different targets were used to separate the results into categories: the first being the absolute lowest 10% of PEs as a target, and the second target being the largest 10% decrease in the PE, with the results shown in Figure 6.6. For the lowest absolute PEs, the most over-represented functional groups were NH_2 , OH , and HCO . The reason why these functional groups are over-represented is beyond the scope of this work. A potential reason may be that these functional groups have areas of positive and negative electrostatic potential, which favourably interact with the quadrupolar nature of CO_2 . For the largest PE percent decrease, the over-represented functional groups were found to be OPr, OPre, Ph, and Pr. A preliminary assessment as to why these functional groups overperform would be that it is based on their space filling nature, as they are the largest in the library (compared to something like fluoride). When looking at those MOFs which had the largest percentage decrease in PE, it was noticed that large, bulky functional groups gave the largest decrease. What the two analyses had in common was that the most under-represented functional groups were the halogens. Once again, the exact reason why these halogens are under-represented in the top performers is outside the scope of this work. The best reasoning would be that in the case of achieving the lowest absolute PE, halogens only add a concentrated negative electrostatic potential. This would adversely interact with the negative charge associated with the oxygen atoms of the CO_2 , potentially reducing its performance. In the case of the lowest percentage decrease of PE, this is reasonable as the halogens are some of the smallest functional groups in the library, which contrasts with the space-filling hypothesis of the over-represented functional groups.

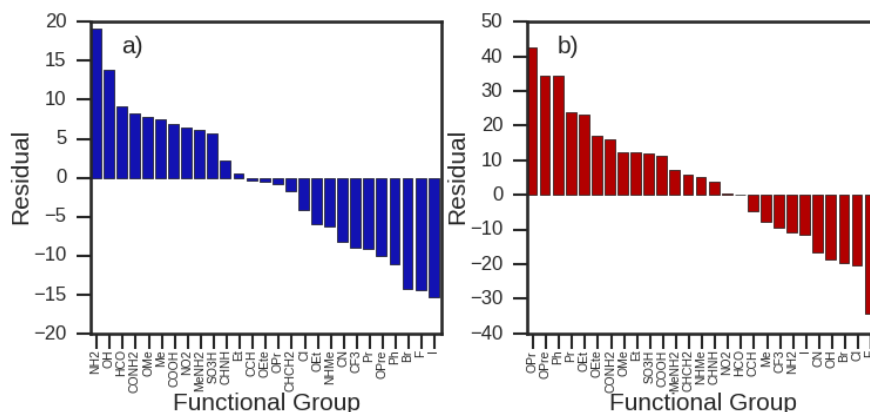


Figure 6.6. Residuals of functional groups from the screening of the functionalized CoRE for desorption optimized PE when looking at a) the lowest 10% of absolute PEs and b) the largest 10% of PE decrease.

Although the studied fMOFs do show promise for PoCCC based upon the optimized PEs, it should be noted that there are potential issues. Although there are examples and methods to functionalize MOFs, both pre- and post-synthetically,^{30,58,59} there is no guarantee that the structure will be able to be synthesized in that fashion. Additionally, like all computationally derived structures, even through functionalization there is potential that the structure may not be stable for other reasons, such as mechanical or chemical stability.

6.5 Conclusions

Solid sorbents were optimized for PoCCC based on their PE. Using CO₂ and N₂ adsorption data of 42 experimentally tested solid sorbents, it was found that **IISERP-MOF2** had the lowest PE of 823.4 kJ/kg CO₂, compared to the next lowest, m-CuB, of 898.4 kJ/kg CO₂. **IISERP-MOF2** was close to the reasonable minimum energy, discussed in Section 3.7.4, of a PSA system of 624.6 kJ/kg CO₂. The PE by altering the desorption pressure for 3468 MOFs from the CoRE database and found a median decrease of 54.3 kJ/kg CO₂ or 4.5%. It was found that although no CoRE MOF outperformed **IISERP-MOF2**, 1181 outperformed state-of-the-art amine CO₂ capture systems, 144 outperformed Mg-MOF-74, and 23 outperformed m-CuB. In the final study, 581 of the CoRE MOFs were chosen and functionalized using a library of 28 functional groups giving 152,722 fMOFs that were sterically viable. The structures were tested, and a total of 10 structures were found to have lower PEs than **IISERP-MOF2**, with the lowest structure reaching a PE of 749 kJ/kg CO₂. It was found that the absolute lowest PE fMOFs had an over-representation of the NH₂, OH, and HCO functional groups, while the most significant decrease in PE occurred when using large functional groups such as OPr, OPre, and Ph. It was found that halogen were the most under-represented functional groups in the top performers.

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6.7 Appendix

6.7.1 IISERP-MOF2 Fitting

IISERP-MOF2 was fit to AIMs using data provided by collaborators at IISER Pune. CO₂ data was fit to dual-site Langmuir models, while N₂ data was fit to a single-site Sips model. The saturation capacities and the heterogeneity constants were kept consistent between the temperatures, while the Henry's constant could change. This was done by performing a least square fit simultaneously on both isotherms while optimizing for the saturation capacities, heterogeneity parameter, the Henry constants at 313 K and the ratio of Henry's constants between 313 K and 333 K. The experimental data along with the fitted AIMs are given in Figure 6.7a) and b) for CO₂ and N₂ respectively. Fitted parameter values are given in Table 6.1.

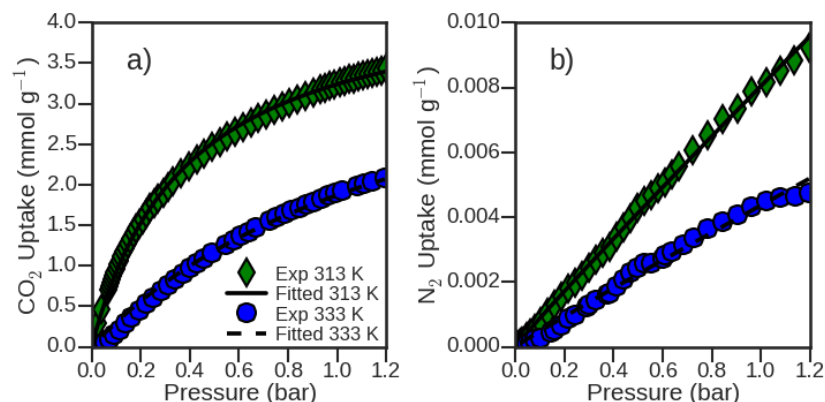


Figure 6.7. Experimentally derived a) CO₂ and b) N₂ adsorption data for **IISERP-MOF2** at 313 K (green diamonds) and 333 K (blue circles). Lines represent the fitted adsorption isotherm models.

Table 6.1. Adsorption Isotherm Model parameters for 1 at the adsorption and desorption conditions for CO₂ and N₂. CO₂ was fit to Dual-Site Langmuir and N₂ was fit to Sips.

Parameter	CO ₂				N ₂		
	σ_1 (mmol/g)	k_{H1} (bar ⁻¹)	σ_2 (mmol/g)	k_{H2} (bar ⁻¹)	σ (mmol/g)	k_H (bar ⁻¹)	N
Adsorption	0.641	2.827	3.861	2.527	4.997	1.257×10^{-3}	0.963
Desorption		0.783		0.700		6.654×10^{-4}	

6.7.2 Structure Functionalization

An in-house developed program was used to functionalize the structures and was the one used for one of our published papers.⁶⁰ In that work, the program, known as CliSwitch, would determine similar hydrogen atoms based upon the names of the hydrogen atoms in Crystallographic Information File (CIF). This limited the functionalization to modifying each CIF file, which was

time-consuming and not intuitive. Additionally, to maintain a level of synthetic feasibility, hydrogen atoms across an organic SBU were kept similar across organic linkers, which is explained in more detail in Chapter 7. For this work, CliSwitch was modified to work 1) in a high-throughput way and 2) to functionalize MOFs in a way that mimics MOF synthesis.

An updated version of CliSwitch is used which works by reading in a structure and determining the organic SBUs by cutting apart structures at the metal-organic bond. The bonding information of each organic SBU is then compared against each other, and similar SBUs are grouped. From the bonding information, the symmetry of each linker could be determined, and from that, similar hydrogen atoms were determined. For example, Benzene-1,4-dicarboxylic acid (BDC), shown in Figure 6.8, contains 4 unique hydrogen atoms, all of which are viewed as similar. When functionalizing MOFs, if there is symmetry within an organic SBU, a random choice is made as to which hydrogen atom is the H1 atom, and from that choice, the rest of the organic linker is functionalized. Concerning the shown BDC linker, any one of the 4 hydrogen atoms can be viewed as H1, so if the structure was functionalized with fluoride at an H1 position, and ammonia at the H3 position, there are 4 possible outcomes, which are shown in Figure 6.8. For every linker in the structure, this process is repeated, randomly choosing which hydrogen atom is the H1 if there are symmetrical hydrogen atoms to H1. As the choice of how each SBU is functionalized is random, regarding its symmetry, if the functionalization fails due to steric hindrance, the process is repeated a maximum of 30, or until the structure is created, whichever comes first. The functional groups that are used in this work are given in Table 6.2.

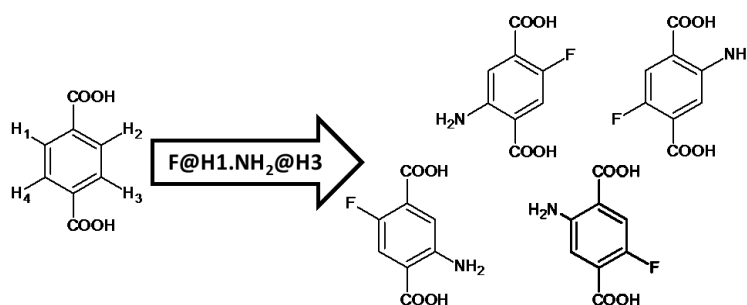


Figure 6.8. Possible functionalization of BDC with fluoride at H1 and ammonia at H3.

Table 6.2. Functional Groups used in the functionalization part of this work.

Functional Code	Structure	Functional Code	Structure	Functional Code	Structure
Br		OEtc		H	
CF ₃		OMe		I	
CHNH		OPre		MeNH ₂	
CN		Pr		NHMe	
COOH		CCH		OEt	
F		CHCH ₂		OH	
HCO		Cl		OPr	
Me		CONH ₂		Ph	
NH ₂		Et		SO ₃ H	
NO ₂					

6.7.3 Functionalization Tests

To verify the accuracy of functionalizing the structures, tests were performed on 12 MOFs: **IISERP-MOF2**,⁶¹ bio-MOF-11,⁶² HKUST-1,⁶³ IRMOF-16,⁶⁴ Mg-MOF-74,³⁹ MIL-47,⁶⁵ MIL-53Cr,⁶⁶ MIL-88B,⁶⁷ MOF-5,⁶⁸ MOF-70,⁶⁹ SBMOF-1,⁷⁰ and UiO-66.⁷¹ Each structure was functionalized with 28 unique functional groups (shown in Table 6.2), placing them in the H1 position found by the in-house program, with each functionalization happening a total of 30 times. As the program randomly functionalizes the structure, by repeating the same functionalization, a new structure could be created as the functional groups can be placed in different positions. The repetition allows for an analysis of the impact of functionalizing the same structure in different ways and how that impacts its properties such as gas adsorption. In this work, CO₂ adsorption at flue gas conditions was used and calculated the same way as all the work in the main text. By

nature, GCMC calculations are random, so to account for the impact of the different functionalizations on this, the differences in CO₂ uptakes were compared to the average standard deviations of the CO₂ uptake. This was done by comparing the average relative standard deviation of functionalizations (across all functional groups), against the average relative error of the GCMC calculations for each base MOF. The error in the GCMC calculations was calculated as the standard deviation of the window averages of each GCMC calculation. The results are given in Table 6.3.

For most of the tested base MOFs, the difference in CO₂ uptake found from the functionalization could mainly be attributed to the error from the GCMC. This is seen by the average difference in functionalization being smaller or close to the average error of the GCMC calculation. The MOF with the most notable difference is MOF-70 where the average difference from functionalization is more than double the average GCMC error. Overall, the results show that this functionalization method does give consistent enough results for first screening, although further testing should be done for the hit materials. As a note, the MIL-53Cr errors are so high due to the low absolute CO₂ uptake that ranged from 0 to 0.078 mmol/g.

Table 6.3. Difference in CO₂ adsorption at 298 K and 0.15 bar when using the same functionalization for 12 unique MOFs, compared to the average error (standard deviation of window averaging) of the GCMC calculations. Values are relative values to the averages.

Material	Difference in Functionalization (%)	Error in GCMC Calculation (%)
IISERP-MOF2	1.79	2.78
bio-MOF-11	5.14	8.95
HKUST-1	7.64	6.58
IRMOF-1	4.03	7.06
Mg-MOF-74	5.06	7.23
MIL-47	7.89	6.44
MIL-53Cr	55.00	52.90
MIL-88	12.15	8.64
MOF-5	3.32	6.04
MOF-70	10.97	5.39
SBMOF-1	1.97	2.78
UiO-66	4.86	5.85

7 Metal-Organic Framework Functionalization Genetic Algorithm

In this chapter, I present work on the Metal-Organic Framework Functionalization Genetic Algorithm (MOFF-GA). The development and utilization of MOFF-GA was primarily performed by me. I was also the primary author of the manuscript. A Postdoc of the group, Dr. Thomas Daff, assisted in the development of the program, and a summer student, Sarah Piotrkowski, helped test and optimize MOFF-GA. This work was originally published in *Science Advances*, Volume 2, Issue 11, Page e1600954 in 2016 for a special issue on “Materials by Design.”¹ Copyright 2016, Science AAAS. Formatting of the manuscript has been changed to maintain similar style to the rest of the thesis; however, all content is the same as the original publication. Changes include the layout of the manuscript, numbering of sections, numbering of the figures, and combining the works cited list of the main text and appendix. It should be noted that this work was performed using a different equation to calculate the parasitic energy than what was seen in the previous chapters, which is detailed in the appendix of this chapter. Additionally, this work was completed before the parameterization of the SQE method, as outlined in Chapter 5, and therefore the QEq method was used with MEPO parameters.²

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Materials Design by Evolutionary Optimization of Functional Groups in Metal-Organic Frameworks

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7.1 Abstract

A Genetic Algorithm (GA) has been developed that efficiently optimizes a desired physical or functional property in Metal-Organic Frameworks (MOFs) by evolving the functional groups within the pores. The approach has been used to optimize the CO₂ uptake capacity of 141 experimentally characterized MOFs at conditions relevant for post-combustion CO₂ capture. A total search space of 1.65 trillion structures was screened and 1035 derivatives of 23 different parent MOFs were identified as having exceptional CO₂ uptakes of >3.0 mmol/g (0.15 atm, 298 K). Many well-known MOF platforms were optimized with some, such as MIL-47, having their CO₂ adsorption increase by more than 400%. The structures of the high performing MOFs are provided as potential targets for synthesis.

7.2 Introduction

Metal-Organic Frameworks (MOFs) are a novel class of materials composed of metal clusters and polydentate organic linkers or secondary building units (SBUs) that self-assemble to form crystalline porous networks.^{3,4} MOFs have garnered significant attention for a wide range of applications, such as gas separation and storage,^{5,6} catalysis,⁷ and proton conducting membranes.⁸ The breadth of applications is largely due to their highly tunable nature. An enormous array of metal clusters and organic groups can be combined to form a nearly limitless number of MOFs with diverse functional properties. These properties can be further tuned by altering the functional groups within the MOF.

Functionalization has been shown to have a dramatic effect on the properties of a MOF. For example, Deng *et al.* synthesized a MOF-5 variant with 3 different functional groups and found it to have a 400% increase in selectivity for CO₂ over CO when compared to the unfunctionalized parent MOF.⁹ Using density functional theory (DFT) to guide their design Froudakis and coworkers found the addition of a chosen functional group to increase CO₂ adsorption significantly in IRMOF-8.¹⁰ There has also been a desire to increase the complexity of functionalizations.⁶ For example, Cohen and coworkers have developed versatile post-synthetic methodologies and applied them to functionalize IRMOF-3 with 5 different functional groups (in this work we consider -H as a distinct functional group)¹¹ while Yaghi and coworkers have synthesized MOFs with as many as 9 different functional groups.⁹

Determining the optimal groups to functionalize a MOF for an application can be challenging and sometimes non-intuitive. For example, Shimizu and co-workers¹² synthesized an amine functionalized zinc triazole-oxalate MOF and found it to have excellent low-pressure CO₂ uptake. The group then synthesized a related MOF in which the oxalate anions were replaced with phosphate thereby giving more amine groups per metal center. Despite having a similar pore size, and a higher amine density, a significant decrease in CO₂ uptake was observed demonstrating the complexity involved when tuning a MOF's properties via functionalization.¹³ If 40 functional groups were considered, there would theoretically be 6.25 million (40⁴) distinct functional group combinations possible. Such a search space would be impossible to explore experimentally and would be challenging to screen exhaustively computationally for most properties, particularly if a quantum mechanical calculation is required in the screening process.

Genetic Algorithms (GAs), which are inspired by Darwinian evolution, have been used in efficient optimization of large and complex search spaces where an exhaustive search would be impractical. GAs have been used in computational materials science for a range of applications¹⁴ including *ab initio* crystal structure prediction.¹⁵ Deem and co-workers recently developed a genetic algorithm to optimize a MOFs properties and showed optimization for methane deliverable capacity and surface area.^{16,17} In their work, they use a large precursor library of commercially available molecules to create new organic linkers, which are combined with a set of metal SBUs to form MOFs. A GA is used to optimize the construction of new organic linkers and their combinations with metal SBUs for a given property of the MOF. As pointed out by the authors, there could be difficulties in synthesizing the MOFs with the created linkers¹⁶ since there is no guarantee the SBU's will self-assemble to form a stable crystalline structure with the proposed structure. This often the criticism directed towards hypothetical materials that are proposed *in silico*. In order to improve the synthetic viability, in this work we have developed a GA to be used with experimentally realized structures and focuses only on optimizing the functionalization of materials. The premise is that modifying existing stable MOFs where the functional groups can be installed either in a pre- or post-synthetic fashion will enhance the synthetic viability of the predicted materials. We demonstrate that a specialized GA can efficiently evolve the functional groups in MOFs to optimize a desired property such that only a fraction of the search space needs to be sampled. MOFF-GA (MOF Functionalization GA) as we will term it, has tailored mating and mutation routines, along with GA parameters that have been optimized to recover the highest

performing MOFs in the search space as potential targets for synthesis. The GA has been validated on a diverse set of 48 MOFs whose complete search space has been evaluated. We further applied MOFF-GA to optimize the CO₂ uptake of 141 experimentally characterized MOFs at conditions relevant to post-combustion CO₂ capture (0.15 atm and 298 K) and have identified hundreds of potentially high performing targets for synthesis.

MOFF-GA has 13 GA parameters, such as the population size and mutation rates that were optimized to give the highest best find rate and the number of top 50 MOFs recovered, while minimizing the number of unique MOFs sampled. Three different properties (CO₂ uptake, surface area, and parasitic energy (PE) computed on an assortment of MOFs were used to optimize the parameters. As a result, we consider the default MOFF-GA parameters to be fairly generalized and robust. Full details of the parameterization, implementation, and other computational details are given in the Methods Section and the Appendix. We only highlight a few important features here. The first challenge of successfully applying a GA to the specific problem is to define a suitable chromosome representation of the search space in which desirable traits can be inherited. In this work, the functionalizable sites that are equivalent are first identified and numerically labeled as shown in Figure 7.1a) for the organic SBUs of ZBP. In this work, equivalent functionalization sites are determined from symmetry and refer to those that will enable the SBUs to be reversed (or rotated) to give a structure with the same connectivity. This equivalence is utilized to maintain a level of synthetic feasibility. The chromosome in MOFF-GA is simply the sequence of equivalent functionalization sites and their associated functional groups. Figure 7.1b) gives an example of a chromosome for ZBP. When creating a structure, MOFF-GA performs a partial conformation search to determine if the functionalization is sterically feasible. If it is not, then, the structure is discarded thereby causing the mechanism that created the chromosome to repeat until a viable structure is made. All structures are geometry optimized with the universal force field (UFF)¹⁸ (including cell vectors) to alleviate steric clashes during functional group insertion. CO₂ adsorption properties were determined from GCMC simulations using the UFF force field and *ab initio* fitted MEPO-QEq charges² for the framework atoms.

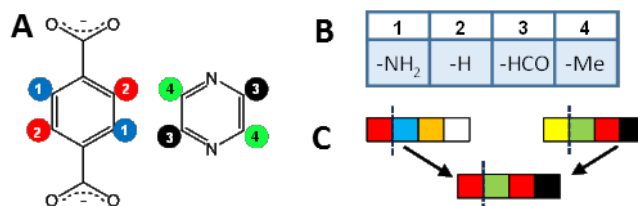


Figure 7.1. Chromosome Representation and Mating. a) The organic SBUs of the MOF ZBP with the functionalizable positions highlighted. b) Example chromosome of ZBP. c) Schematic of the one-cut mating process.

7.3 Results

To demonstrate a typical GA run, we optimized the four functional groups in ZBP for CO₂ uptake capacity at 0.15 atm, 298 K. In this work, we used 28 common functional groups (Table 7.11), which for ZBP's four functional groups there are theoretically 614,656 combinations possible. However, only 96,156 combinations were found to be sterically viable. This number is small enough that the CO₂ uptake of all viable structures has been calculated to validate the GA. It should be noted that before the optimization it is not known which combinations are sterically viable and, as a result, the GA is still searching the complete search space of 614,656 combinations.

Figure 7.2 shows the progress of a typical MOFF-GA run in which the CO₂ uptake capacity is optimized in the MOF ZBP. The average CO₂ uptake capacity of the population (size = 113) and the uptake capacity of the best individual, are plotted as a function of the generation. Figure 7.2 reveals that the fittest individual in the population rapidly increases and does not improve after 7 generations. In this run, MOFF-GA does find the global optimum, which has an exceptional uptake of 4.2 mmol/g – a 4.8-fold increase over the parent MOF.

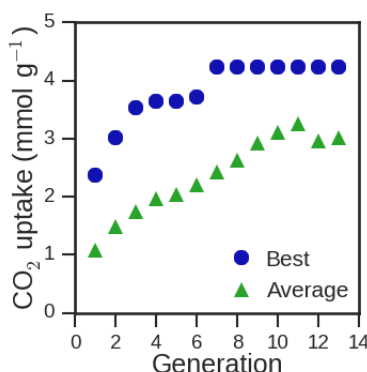


Figure 7.2. MOFF-GA Results. Population average and best individual CO₂ uptake (0.15 atm, 298 K) as a function of the generation during a MOFF-GA run for the optimization of the MOF ZBP. The generation zero uptake is that of the unfunctionalized MOF.

Given in Table 7.1 are relevant per-run optimization statistics based on 1000 GA runs on ZBP with different random seeds. The ‘best find rate’ provides the percentage of GA runs that locate the true global optimum. The average rank of the top MOF from a GA run is given as ‘rank of best’, where the closer to 1, the better. The ‘number of top 50’ refers to the average number of the top 50 MOFs the GA can locate in a run. The ‘structures sampled’ gives the average number of viable structures (and percentage of all possible viable structures) that are sampled in each run. In practice, GAs are typically run multiple times (3-5) on the same problem with different random seeds. If one were to run MOFF-GA 5 times to optimize the functional groups of ZBP for CO₂ uptake capacity, it would find the top ranked structure 99.9% of the time and recover 33 of the top 50 MOFs on average while only sampling a total of 4,553 unique structures.

Table 7.1. MOFF-GA results for ZBP. Averaged statistic of 1000 GA runs for the functional group optimization of ZBP for different properties. The percentage of Structures Sampled column is a fraction of the total number of sterically viable structure (96,156).

Property Optimized	Best Find Rate (%)	Rank of Best	Number of Top 50	Structures Sampled	Functional Groups of Best
CO ₂ uptake at 0.15 atm CO ₂ , 298 K	81	1.6	20.9	1069 (1.1%)	HCO, H, HCO, CH=CH ₂
Volumetric Surface Area	68	1.9	19.8	1263 (1.31%)	H, H, OPr, H
Parasitic Energy	67	2.5	14.7	1519 (1.6%)	NO ₂ , H, OH, HCO

Large surface areas are often desired in nanoporous materials. Table 7.1 shows the optimization statistics of ZBP for the purely geometric property of the volumetric surface area. In this case, the best find rate of the GA is not as favorable. We attribute this to the fact that the optimal solutions can be single large functional groups such as propyl ether, or multiple smaller functional groups possessing similar areas. Although the best find rate is not as favorable, the average rank and number of top 50 found are similar to those found for the CO₂ uptake optimization. In pragmatic terms, finding the single best functionalization is not as important as finding a number of the top candidates.

Multi-property fitness functions can also be optimized. To demonstrate this, we optimize the PE, which gives the energetic cost of CO₂ capture under specific adsorption and desorption conditions.^{19,20} It can be defined in terms of the uptake capacities of CO₂ at the adsorption (0.15 atm, 298 K) and desorption conditions (0.7 atm, 413 K), the heats of adsorption, the CO₂/N₂

adsorption selectivity, and the latent heat capacity of the MOF. All of these quantities can be evaluated with the same GCMC simulations used to calculate the CO₂ uptake, with the exception of the heat capacity which we fix to a typical value of 1.0 kJ/kgK. The PE can have opposing terms similar to that found in multi-objective optimizations that must be balanced during the optimization. Specifically, a high CO₂ uptake capacity is often associated with a high binding energy or heat of adsorption (HoA), and while a high uptake is good for the PE, a high HoA is detrimental to it. Table 7.1 reveals that the PE is more challenging for MOFF-GA to optimize than either the CO₂ uptake capacity or the surface area for ZBP. Nevertheless, the optimization metrics are still quite favorable and running MOFF-GA 5 times would recover the best performing structure 99.0% of the time and 33 of the top 50 MOFs on average.

To examine how broadly applicable MOFF-GA is to a variety of MOFs and different sized search spaces, we have optimized the PE of a diverse set of 48 experimentally characterized MOFs. The averaged optimization metrics for 25 two-site and 18 three-site MOFs are given in c while the metrics for MOFs with four or more sites are given individually. The complete search space for all systems has been evaluated (297,125 viable, 19 million in total) for validation purposes.

Table 7.2. MOFF-GA results for PE. Averaged statistics of 1000 GA runs for the functional group optimization of MOFs for parasitic energy. Viable structures are the total number of sterically viable structures. The percentage in Structures Sampled column is an average if the fraction of the total number of viable structures.

MOF	Sites	Viable Structures	Best Find Rate (%)	Rank of Best	Number of Top 50	Structures Sampled (%)
2-site: average of 25 MOFs (alternate GA parameters)	2	361	93 (70)	1.1 (1.6)	43.0 (25.8)	67.8 (32.0)
3-site: average of 18 MOFs	3	4149	76	1.6	28.7	22.9
MEKDUC*	4	5808	75	1.6	29.4	9.9
UTEXAT* (4 of 5 sites)	4	20825	84	1.3	34.0	4.3
FUNBEW-Br*	4	32215	31	5.9	8.6	3.8
UTEXAT*	5	33072	90	1.2	20.3	2.8

*Cambridge Structural Database identifier.

2-site MOFs, which have a theoretical search space size of 784, were tested to see if the GA would apply to small search spaces (<1000). Table 7.2 reveals that the optimization metrics are excellent, except that the GA on average samples 68% of the viable structures in a single run. Thus, it only makes sense to run the GA once, but this does not result in a significant reduction of

sampling compared to a complete scan. Since the GA parameters were optimized using test sets with large search spaces, we re-optimized the GA parameters using only 2-site MOFs. The optimization metrics with this alternate set of GA parameters is given in parenthesis in Table 7.2. With the 2-site GA parameters, the number of unique structures sampled is halved, but there is also a notable reduction in the best find rate from 93% to 70%. In some scenarios, it may be of value to apply MOFF-GA on small search spaces, for example, when optimizing a property that is very time consuming to evaluate such as non-linear optical properties that require expensive first principles calculations. In such a case, running MOFF-GA once with the 2-site parameters would sample only a third of the search space while still recovering many of the top candidates (on average 26 of the top 50, with the best rank of 1.6).

18 unique 3-site MOFs, which each has a total search space size of 21,952, have been optimized where it was found that the number of viable structures ranged from 1,054 to 17,514. On average, a single MOFF-GA run would sample 23% of the viable structures with the best find rate of 76%. Since one typically has an idea of the theoretical search space size beforehand, one could run the GA 2 or 3 times for searches whose size is $< 20,000$. Using the averaged statistics, running the GA twice would sample ~40% of the viable structures, but would have a 95% chance of finding the top performer. Again, in some usage scenarios, sampling only 40% of the search space would result in worthwhile time savings compared to an exhaustive systematic search.

The benefit of applying the GA becomes clear with four-site and larger search spaces. Provided in Table 7.2 are the optimization metrics for 4 and 5 site MOFs for which we have performed a full scan of the search space. If we include ZBP (Table 7.1), the number of viable structures ranges from 5,808 to 96,156. The optimization statistics are generally very good, and applying MOFF-GA 5 times, will only sample a fraction of the total search space while having a high probability of recovering the top performing structures. Even with the MOF FUNBEW-Br, which had the lowest optimization statistics found in this study, the application of the GA would be beneficial. Specifically, if one were to apply MOFF-GA 5 times, one would still recover the top performing structure 84% of the time, while sampling only 16% of the entire viable search space. Additionally, after 5 GA runs, on average one would recover 27 of the top 50 structures, providing many targets for synthesis.

MOFF-GA has been applied to optimize the CO₂ uptake capacity of an additional 93 experimentally characterized MOFs, including several MOFs whose search space is too large to evaluate completely ($>1.7 \times 10^7$). Including the 48 MOFs used to validate MOFF-GA, Figure 7.3 plots the optimized CO₂ uptake of 141 MOFs compared to the CO₂ uptake of the unfunctionalized parent structure. Although a small fraction of MOFs sees little to no improvement (mostly small pore MOFs), there is on average a 3.4-fold increase in CO₂ uptake upon functional group optimization. We highlight a few well-known MOFs such as MIL-47 and HKUST-1, which show considerable improvement. With the addition of one functional group the uptake of MIL-47 increases by 2.74 mmol/g. Additionally, 1035 functionalized structures from 23 different parent MOFs were predicted to have a CO₂ uptake capacity over 3 mmol/g at 0.15 atm, 298 K. This is deemed high performing for these conditions especially considering that none of the parent MOFs possess open metal sites, which can enhance the CO₂ uptake through chemisorption (but also make them prone to water degradation). Interestingly, the aldehyde (-HCO) functional group and not the amine group was the most common substituent in the MOFs with uptakes >3 mmol/g. Moreover, of these high performing MOFs, 85% have only 1-3 different non-hydrogen functional groups, which enhances the prospect that the MOFs identified could be synthesized. At this point, the practical application of MOFF-GA involves constructing a hypothetical structure and computing the properties. Consequently, the screening results are vulnerable to similar issues as other large-scale virtual screening studies in that the structures predicted may be impossible to synthesize or be structurally different from those made in the lab.^{21,22} However, since the structures identified in this work are derived from experimentally characterized MOFs, they may be more synthetically accessible compared to purely hypothetical MOFs.

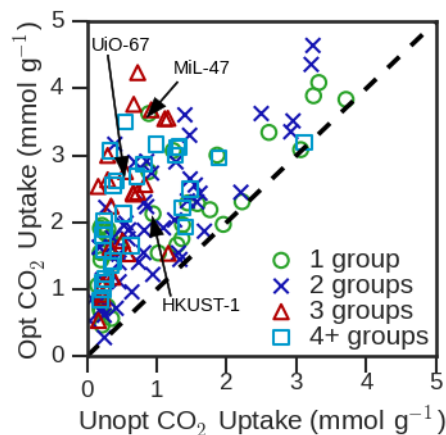


Figure 7.3. CO₂ uptake at 0.15 atm, 298 K for 141 experimentally characterized MOFs whose functional groups have been optimized with MOFF-GA compared to the uptake of the unfunctionalized parent MOF (dashed line). Data point symbols denote the number of unique, non-hydrogen functional groups in the best structure.

7.4 Discussion

Functionalization has always been considered a principal avenue for improving the functional properties of MOFs. In this work, we have developed a customized GA to identify the most favorable functionalizations of a parent MOF as to optimize a desired functional and/or physical property. MOFF-GA as we term it, has been validated on a diverse set of 48 MOFs with a range of search space sizes. We demonstrate that MOFF-GA can locate the best structures while sampling only a small fraction of the search space. MOFF-GA is particularly powerful when applied to large search spaces but can still be beneficial when applied to small search spaces (<1000), particularly if the property being optimized is time consuming to evaluate. The CO₂ uptake of 141 experimentally characterized parent MOFs have been optimized resulting in 1035 functionalized derivatives of these MOFs being identified with exceptional uptakes of >3 mmol/g at 0.15 atm, 298 K. All these structures are provided in the Appendix to allow researchers to browse and identify potential synthetic targets. In total, the CO₂ uptake of 581,278 unique structures has been calculated to screen a search space of over 1.64 trillion structures. Over 20 well-known MOFs were optimized for CO₂ uptake, with MIL-47 reaching nearly a 4 mmol/g capacity upon functionalization. Although some of these structures may be challenging or even impossible to synthesize, the approach yields many high-performing structures which can then be examined by researchers to identify the best potential synthetic targets. MOFF-GA demonstrates an efficient method for predictive high performance materials design that should be applicable not only to

MOFs but to the functionalization of other classes of materials such as covalent organic frameworks and porous polymer networks.²³

7.5 Methods

Our GA follows most of the same procedures as other GAs. An initial set of individuals are randomly created, the number of members of the set is known as the *population*. A set of individuals at a given time is known as a generation. All individuals in the generation are evaluated for their fitness, such as CO₂ uptake. The next generation is constructed from the previous one with mating and mutation mechanisms. Our GA employs elitism which carries forward a fraction of the top performing individuals from one generation into the next generation with no modification. The fraction of top performers carried forward is known as the elite. The *population size* and the *elite fraction* are adjustable parameters of the optimization algorithm.

Another challenge in applying a GA involves developing mating and mutation schemes that allow the desirable traits to be passed onto subsequent generations while still allowing for a broad sampling of the search space. In MOFF-GA, the mating scheme used consists of cutting the chromosome of each parent at the same point and combining opposite sides of the chromosome from each parent to form the child chromosome. The cut-position is determined randomly, and the process is shown schematically in Figure 7.1. A similar two-cut mating scheme is also utilized.

After mating occurs to create a new generation, each individual has a chance, governed by the *mutation rate* parameter, to undergo a mutation. Two mutation mechanisms are utilized in MOFF-GA. The first is a swap mutation, where two randomly chosen functional groups of a chromosome are exchanged. The second mutation involves randomly replacing one group by either a similar (i.e. methyl for ethyl) or a dissimilar functional group, where the choice of similar or dissimilar is chosen randomly according to the *similarity probability* parameter. The higher the *Similarity Probability* the more likely a chemically similar functional group will be chosen. Chemical similarity was determined by 3 properties, the electrostatic potential (ESP), the van der Waals Potential (VdWP), and steric hindrance. For all functional groups, the groups were aligned as if attached to a benzene ring, and all of the properties were calculated on identical 3D grids. ESPs were calculated using charge equilibration (QEq) atomic charges on the functional group with a point charge probe. The VdWPs were calculated using a Lennard-Jones potential and a carbon probe. Steric hindrance was decided with a binary output using the VdWP. If the VdWP at a grid

point was 0 or greater it was set as sterically unavailable and assigned a value of 1. If the VdWP was below 0 it was sterically available and assigned a value of 0. To calculate the similarity between two functional groups we used a continuous Tanimoto coefficient,²⁴ which returns a score from 0 (maximum dissimilarity) to 1 (the same) for any pair of groups. The value of each property at each grid point was used to evaluate the Tanimoto coefficient. For each pair functional groups, the calculated Tanimoto coefficient was used to determine if the pair was similar or dissimilar using a *similarity threshold* parameter.

During the optimization process, once the top performing individual has remained constant for a set number of generations (currently 3), MOFF-GA enters a stagnation phase. During the stagnation phase MOFF-GA uses 3 methods to create new individuals: mutating the best; random creation; and normal mating. When mutating the best, individuals are created which differ from the best performer by one functional group only. All combinations of these individuals are created randomly over stagnant generations and tested for their performance. A fraction of the population each generation, determined by the *best mutated* parameter, is reserved for these individuals. Random creation, during the stagnation adds completely randomly made individuals each generation of the stagnation phase. The amount of randomly created individuals each generation is set by the *random mutated* parameter. The remaining population are created using the normal mating scheme.

MOFF-GA has two convergence criteria that must be met before the optimization is stopped. The first is the top performing individual must stay the same for a certain number of generations (currently 5). The second is that all individuals created in the aforementioned stagnation phase which differ by only one functional group from the top performer must have been tested. Once these two criteria have been met MOFF-GA is considered complete.

Full details of MOFF-GA are given in the Appendix, along with a full description of all 13 GA parameters, their optimized values, and details of how the parameters were optimized.

Gas adsorption calculations were performed using an in-house Grand Canonical Monte Carlo (GCMC) code based on DL_POLY 2 molecular dynamics package.²⁵ Non-bonding interactions were calculated with a Lennard-Jones potential utilizing parameters for the framework atoms taken directly from the UFF¹⁸ with Lorentz-Berthelot mixing rules for cross-terms. Electrostatics were based on partial atomic charges calculated by charge equilibration using the MEPO-QEq

parameters,² which were fit to reproduce the electrostatic potential obtained from REPEAT atomic partial charges.²⁶ The CO₂ molecules were modeled using the force field developed by García-Sánchez *et al.*²⁷ and the N₂ molecules were modelled using the TraPPE force field parameters.²⁸

All GCMC simulations consisted of 30000 cycles of equilibration and 30000 cycles of production. One cycle consists of a N of trial moves where N is equal to the number of guest molecules in the system at that time. All simulations included random insertion, deletion, and translation moves of molecules with equal probabilities. Atoms in the framework were held fixed at their crystallographic positions. A LJ cut-off distance of 12.5 Å was used for all simulations and a supercell is constructed for each structure that satisfies the minimum image criterion. The Ideal gas law was assumed when computing the chemical potential in the grand canonical ensemble.

7.6 References

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7.7 Appendix

7.7.1 Details of the Genetic Algorithm

7.7.1.1 Genetic Representation

Genetic Algorithms (GAs) are built upon the genetic representation, or chromosome, of the system. For MOFF-GA we were interested in optimizing the functional groups on the organic linker, also known as a secondary building unit (SBU). The hydrogen atoms of the SBU are labelled in order to identify each unique functionalization site. Sites which would heavily increase synthetic difficulty if functionalized, such as those on the nitrogen of aniline, were ignored. The functionalized SBU could then be represented by the functional groups attached to each labelled site which we call the Functional Group Code (FGC). The example in Figure 7.4 shows the labelled sites H1, H2, H3 on the SBU and the FGC F@H1.Cl@H3 which indicates that site H1 is functionalized with a fluoride group and H2 is functionalized with a chloride group. For unfunctionalized sites the label is omitted from the FGC. The combination of parent MOF and FGC uniquely identify each functionalized MOF.

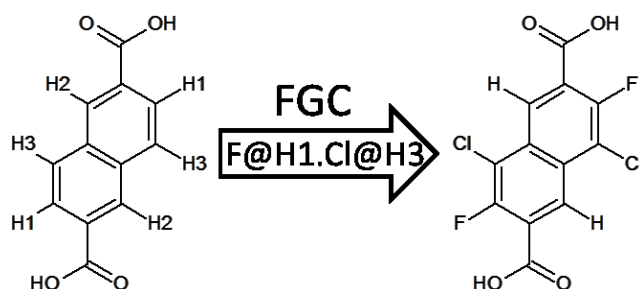


Figure 7.4. Example of the application of a Functional Group Code to the unfunctionalized SBU of the Parent MOF.

7.7.1.2 General Procedure

Our GA follows most of the same procedures as other GAs. An initial set of individuals are randomly created, the number of members of the set is known as the *Population*. A set of individuals at a given time is known as a generation. All individuals in the generation are evaluated for their fitness, such as CO₂ uptake. The next generation is constructed from the previous one with mating and mutation mechanisms. Our GA employs elitism which carries forward a fraction of the top performing individuals from one generation into the next generation with no modification. The fraction of top performers carried forward is known as the *Elite*. The top performers are monitored until they converge on a result. Several parameters, (described in Section

2) are used to tune the performance of the whole procedure.

7.7.1.3 Mating Scheme

Most of the individuals in a generation are created by a mating mechanism. Mating is an important part of how a GA works as it ensures the new generation inherits favourable traits of the parents.

7.7.1.4 Choosing Parents

In order to create the new generation with higher performing individuals the top performers from the previous generation need to be selected. We use a single metric, x , that measures the performance of the material, such as the CO₂ uptake or PE. We then define a scaling function, $s(x)$, which favours the higher performing individuals. The scaling functions will differ based on the optimizing property, as shown in Table 7.3. PE, for example, used a scaling function that favoured smaller energies as we want to minimize the property. The CO₂ uptake scaling function is used to place more weight on higher uptake materials. This is done as the range of CO₂ uptake within a generation can be limited. An exponential function will give the higher performing individuals a higher weight during parent selection.

Table 7.3. Scaling functions used for fitness

Property	Scaling Function
CO₂ Uptake	$s(CO_2Uptake) = e^{CO_2Uptake}$
Gravimetric Surface Area	$s(SA) = SA$
Parasitic Energy	$s(P_E) = \frac{1}{P_E}$

In equation 7.1 the i^{th} individual of the population has its scaled performance, $s(x_i)$, normalized to the entire population. For the entire population, this creates a set which sums to 1 with no individual going below 0. These values are able to be used in a selection process known as fitness proportionate selection, or more commonly, roulette wheel. The roulette wheel technique allows any member of the generation to be selected at random based on its weight. The higher the weight the more likely it will be chosen.

$$Weight(x_i) = \frac{s(x_i)}{\sum_{n=1}^{pop_n} s(x_i)} \quad (7.1)$$

The roulette wheel works by randomly selecting a random number between 0 and 1. The weight

of each individual are then added, in descending order, until the cumulative weight is greater than the random number. The individual that caused the cumulative weight to go beyond the random number is selected as a parent. This process is repeated for a second parent. If both parents are the same individual both parents are reselected. This allows the new generation to come up with new, untested individuals to test. Once both parents are chosen they are mated by either a 1 or 2-cut mating scheme. There is a random choice for selecting between the 1 and 2-cut schemes which is known *Single Cut Rate*. The larger the *Single Cut Rate* the more likely the 1-cut mating scheme will occur.

7.7.1.5 1-cut mating scheme

In the 1-cut mating scheme, the chromosomes of both parents are cut at a single, randomly selected position and complementary pieces from the two parents are combined. This process is shown in Figure 7.5. The selection of the first and second portion is also randomly selected with an equal chance.

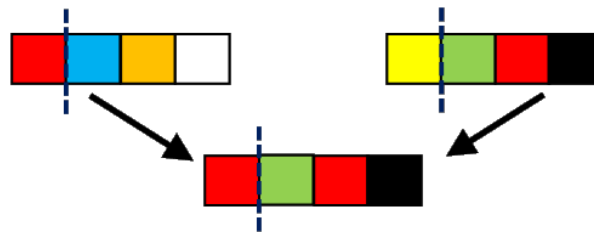


Figure 7.5 Schematic of 1-cut mating process

7.7.1.6 2-cut mating scheme

The 2-cut mating procedure is similar to that of the 1-cut mating scheme however two unique locations are chosen. The two locations are chosen at random and must not be the same. There is an equal chance for each parent to provide the middle slice or the outer slices. These sections are then joined together to form the new child, as seen in Figure 7.6.

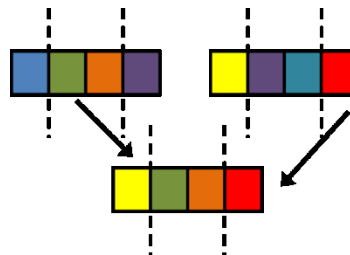


Figure 7.6. Schematic of 2-cut mating process

7.7.1.7 Mutations

After mating occurs, the new child undergoes mutation. MOFF-GA used two distinct mutations, Type 1 and Type 2 Mutations (described below). The number of mutations a single child can have is equal to the number of functional positions plus 1. Type 1 Mutation can occur once during the mutation process. Type 2 Mutation can occur at every functional position during the mutation process. The rate that mutations occur is known as the *Mutation Rate*. This single value controls how often all mutations occur in MOFF-GA. We have also included a biasing scheme that prefers selection of functional groups that appear more often in high performing members (Described later).

7.7.1.8 Type 1 Mutations

The first mutation is known as a swapping mutation. This mutation will swap the functional groups of two randomly chosen functionalization sites. If the two functional groups are identical, then the mutation completes even though there is no effective change in the chromosome. The mutation is schematically shown in Figure 7.7.

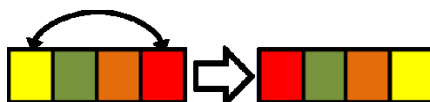


Figure 7.7. Schematic of swapping mutation

7.7.1.9 Type 2 Mutations

The second mutation is a replacement mutation which changes the functional group at a single functional position. The mutation can occur at every functional group in the chromosome, with a probability given by the *Mutation Rate*, potentially creating a fully random chromosome from the parents. If a functional group position is selected for mutation by the *Mutation Rate* a subsequent choice is made of whether to replace it with a chemically similar or dissimilar functional group. The choice of similar or dissimilar is chosen randomly according to the *Similarity Probability* parameter. The higher the *Similarity Probability* the more likely a chemically similar functional group will be chosen.

Chemical similarity was determined by 3 properties, the Electrostatic Potential (ESP), the van der Waals Potential (VdWP), and steric hindrance. For all functional groups, the groups were aligned as if attached to a benzene ring, and all of the properties were calculated on identical 3D grids which were larger than the largest functional groups. ESPs were calculated using charge

equilibration (QEq) atomic charges on the functional group with a point charge probe. The VdWPs were calculated using a Lennard-Jones 6-12 potential with universal force field (UFF) parameters¹⁸ and a carbon probe. Steric hindrance was decided with a binary output using the VdWP. If the VdWP at a grid point was 0 or greater it was set as sterically unavailable and assigned a value of 1. If the VdWP was below 0 it was sterically available and assigned a value of 0.

To calculate the similarity between two functional groups we used a continuous Tanimoto coefficient. The Tanimoto coefficient is a pairwise similarity measure shown in equation 7.2. In Tanimoto calculations, two functional groups (A and B) have paired components, i , compared to calculate the overall similarity. For our chemical similarity, the components used were the value of each property at each grid point. The similarity is a normalized value that ranges 0 (maximum dissimilarity) to 1 (the same).

$$Tanimoto(A, B) = \frac{\sum_i A_i B_i}{\sum_i A_i A_i + \sum_i B_i B_i - \sum_i A_i B_i} \quad (7.2)$$

Using the Tanimoto coefficients two unique sets are created for every functional group, the chemically similar and dissimilar sets. These are created by assigning a *Similarity Threshold Value*. This single value is used to discriminate between chemically similar and dissimilar functional groups for each combination. If the Tanimoto coefficient for two functional groups is less than the *Similarity Threshold Value* they are classified as dissimilar while if they higher they are similar.

7.7.1.10 Biased Functional Group Selection

When MOFF-GA is initialized all chemically similar (or chemically dissimilar) functional groups have an equal probability of being selected during Type 2 Mutation. The Biased Functional Group (BFG) function makes functional groups that appear more often in high performing members have a greater chance of being selected during Type 2 Mutation. Similarly, it will make functional groups which continually appear in low performing individuals and have a lower chance of selection. This process is controlled by 3 unique parameters known as the *Weighting Cut*, the *Weighting Cut-Off* and the *Weighting Change*. The *Weighting Cut* is the fraction of top (bottom) individuals that are considered as the top (bottom) performers in the function. The *Weighting Cut-Off* will determine how often a single functional group needs to appear in the top (bottom) performers for its weighting to be changed. Finally, the *Weighting Change* will determine how

much to add (subtract) from the weighting of the functional group. The initial weighting for every functional group is set to 50 and is limited to never drop below 1. During selection of functional groups the weighting of a functional group describes the probability of it being selected. For example, if two functional groups, A and B, have weightings of 50 and 1 respectively then functional group A will be selected 50 times more often than functional group B.

7.7.1.11 Stagnation

Once the top performing individual has remained constant for a set number of generations, determined by *Stagnation*, MOFF-GA enters a stagnation phase. During the stagnation phase MOFF-GA uses 3 methods to create new individuals: mutating the best; random creation; and normal mating. When mutating the best, individuals are created which differ from the best performer by one functional group. All combinations of these individuals are created randomly over stagnant generations and tested for their performance. A fraction of the population each generation, determined by the *Best Mutated* parameter, is reserved for these individuals. Random creation, during the stagnation adds completely randomly made individuals each generation of the stagnation phase. The amount of randomly created individuals each generation is set by the *Random Mutated* parameter. The remaining population are created using the normal mating scheme.

7.7.1.12 Convergence

The endpoint of MOFF-GA is based on convergence criteria since the GA cannot know when and if it has found the best individual. Once the criteria are met, the GA will finish. For MOFF-GA there are two convergence criteria. The first is the top performing individual must stay the same for a set amount of generations known as the *Convergence*. The second is that all individuals which differ by only one functional group from the top performer must have been tested. Once these two criteria have been met MOFF-GA is considered complete.

7.7.1.13 GA Parameters

The GA has 13 unique parameters which can be modified. All parameters are mentioned in the GA detail (Section 7.7.1). Table 7.4 lists all parameters and their effects on MOFF-GA.

Table 7.4. Description of the MOFF-GA optimization Parameters.

Property	Description
Population	Number of individuals within a single generation
Elite	Fraction of best performing individuals carried over to next generation
Single Cut Rate	Probability of performing a 1-cut vs 2-cut mating during mating process
Mutation Rate	Probability of a Type 1 Mutation or Type 2 Mutation at each functional position occurring
Similarity Threshold Value	Similarity threshold value for determining chemically similar and chemically dissimilar functional groups
Similarity Probability	Probability of mutating with a chemically similar functional group vs chemically dissimilar functional group
Weighting Cut	Fraction of top and bottom individuals used during weighting change
Weighting Cut-off	Number of ties a single functional group needs to be in the Weighting Cut fraction for a Weighting Change to occur
Weighting Change	Value of weight change for a functional group if 'Weighting Cut-Off' is achieved (Initial for all functional groups is weight of 50)
Stagnation	Number of generations of the same top performer before stagnation phase begins
Best Mutated	Fraction of individuals during stagnation that are similar to the top performer
Random Mutated	Fraction of individuals during stagnation that are randomly created (Not from mating)
Convergence	Minimum number of generations of the same top performer before convergence is achieved

7.7.2 Parameter Optimization

7.7.2.1 Genetic Algorithm Performance Index (GAPI)

There are many ways to rank the performance of a GA, such as how often it finds the top performer, or how many individuals are tested. We developed a term known as the genetic algorithm performance index (GAPI) to rank the performance of MOFF-GA by a single number. GAPI (equation 7.3) combines three unique MOFF-GA performance properties: 1) how often the top performer is found (Best Find Rate), 2) the number of the top 50 performing individuals found, and 3) how many unique individuals are tested. These were selected with the idea of wanting MOFF-GA to find the top performer, many good performers, and to do so with testing as few unique individuals as possible (reduce the computations). These are built on having a high best find rate, a high amount of the top 50 MOFs found, as well as few individuals tested as possible.

$$GAPI = S_{BFR} + S_{Top\ 50} + S_{Unique} \quad (7.3)$$

S_{BFR} , $S_{Top\ 50}$ and S_{Unique} are transformation functions which convert the best find rate, amount of top 50 found and amount of unique MOFs tested respectively. As we felt no single performance

property was more important, we constrained each function to lie between 0 and 1. This allowed every performance property an equal opportunity to contribute to the overall GAPI. We decided not to use simple weighting or scaling functions as each performance property was non-linear. For example, if we consider two unique cases of MOFF-GA, one where 0 of the top 50 performers are recovered and one where 35 are recovered. Increasing from 0 to 10 of the top 50 performers should have a larger effect on GAPI than increasing from 35 to 45. This is reasonable as it is more important to improve the first amount of performance parameters rather than to fully maximise a property. By applying a more complex transformation function, such as the sigmoidal function shown in equation 7.4, we could both scale the properties appropriately and capture the non-linear effects.

$$S_i(x) = \frac{K}{1 + A * e^{-r*x}} + C \quad (7.4)$$

Sigmoidal functions can be easily fit to scaled, non-linear data due to high flexibility of parameters. First, we needed to define scale the values of x . Using the absolute value for BFR or amount of unique used would cause the bottom term to nearly disappear. We scaled all performance properties to lie between 0 and 1. For best find rate and top 50 recovered this was done by normalizing values to the maximum (100 and 50 respectively). The scaling for the amount unique MOFs tested was found by first subtracting the amount of chemically similar (differing from the top performer by one functional group) and then taking the inverse (equation 7.5). The amount of chemically similar MOFs is removed because these need to be tested by the convergence criteria. This would make the amount of unique MOFs less the chemically similar ones the absolute minimum that could be tested.

$$\text{Scaling Unique MOFs} = \frac{1}{\text{Unique MOFs} - \text{Chemically Similar}} \quad (7.5)$$

By setting equation 7.4, to 0 and 1 at the lowest and highest possible values for x respectively, we could rearrange for K and C in terms of A and r . This constrained the function to go between 0 and 1 over the range for all possible values of x regardless of the values of A and r . Each transformation function could then be fit by using only A and r and would still remain within the 0 to 1 range.

The final thing necessary before the fitting could actually occur was to define the remaining data points. These were objectively selected values chosen from *a priori* knowledge of how MOFF-GA worked. The values, seen in Table 7.5, were selected based on a scale of performance.

Low Function Value (0.2) would be known as a ‘very bad’ performance, while a high Function Value, such as 0.9, would be a ‘very good’ performance. The Function Values of 0 and 1 correspond to the worst and best performances respectively.

Table 7.5. Values used to fit transformation function (equation 7.4) of performance properties.

Function Value	BFR (%)	Top 50 Recovered	Unique MOFs	Unique MOFs (2-sites)
0	0	0	Infinite	730
0.2	10	3	3000	350
0.4	30	8	2200	250
0.6	50	14	1600	180
0.8	80	24	1100	90
0.9	95	37	500	30
1	100	50	1	1

Using the sigmoidal function, we respected both range from 0 to 1 of the Function Values as well as the non-linearity of the MOFF-GA’s performance. By having the constrained range all GAPI’s would lie between 0 (worst) and 3 (best). This allowed a quick understanding of how MOFF-GA performed during those trials. The non-linearity of the sigmoidal functions allowed each property to be treated uniquely as previously mentioned. This is most evidently seen during parameter optimization if one performance property reached a ‘very good’ (0.9) performance while the others were at ‘bad’ (0.4) levels. It would be more beneficial, and potentially easier, to improve the two ‘bad’ properties than to try to maximise the one already at ‘very good’.

Table 7.6 shows two sets of Unique MOFs values, one for 2-site MOFs and one for larger site (3+ site) MOFs. The amount needed for 2-site MOFs is significantly smaller than the large search space MOFs. This is best seen that for a large site MOF a ‘very good’ performance was set to 500 unique MOFs tested. For a 2 site MOF, 500 individuals would be almost all possible MOFs (784) and would make MOFF-GA unnecessary. This did not allow a good range for the amount of unique MOFs used, and therefore a second transformation function for the amount of unique MOFs tested is used when 2-site MOFs are considered.

All equations were fit using the SciPy package in python. As mentioned only the values of A and r were fitted. Table 7.6 shows values used for each transformation function. R^2 is also shown for each transformation function. The 2-site Unique MOFs transformation function had the smallest R^2 at 0.942. Figure 7.8-Figure 7.11 shows the transformation functions for each performance property with the values they were fitted against.

Table 7.6. Fitted values used in equation 7.4 for each performance properties. R^2 values are calculated using Table 7.5 values.

Property	X	A	r	K	C	R ²
BFR (%)	BFR (%) / 100	−0.992	0.00376	−0.0226	3.015	0.986
Top 50 Recovered	Top 50 Recovered / 50	−1.732	−1.340	0.841	1.150	0.999
Unique MOFs	1 / (Unique – Chemically Similar ^a)	8.352	4174.663	1.120	−0.120	0.984
Unique MOFs (2-Site)	1 / (Unique – Chemically Similar ^a)	3.239	308.689	1.471	−0.4712	0.942

^aChemically Similar refers to the number of MOFs which differ from the top performer by 1 functional group.

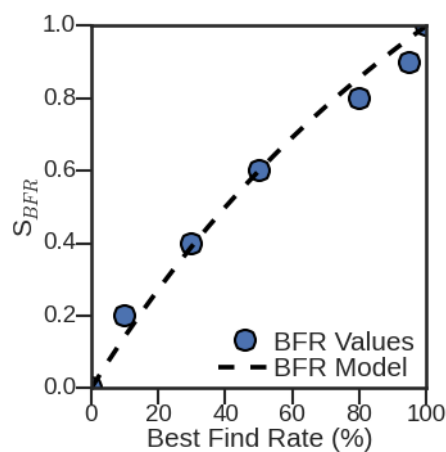


Figure 7.8. Fitted transformation function (Black dashed line) used in GAPI for best find rate. Blue circles are points used to fit equation.

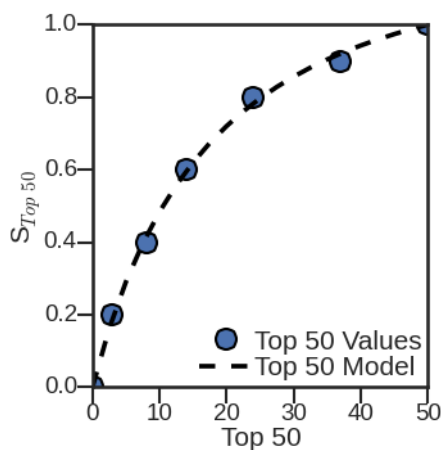


Figure 7.9. Fitted transformation function (Black dashed line) used in GAPI for top 50 performers recovered. Blue circles are points used to fit equation.

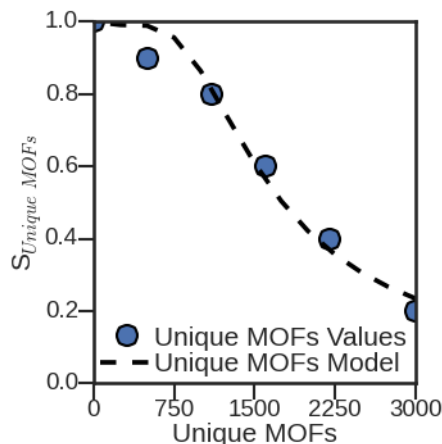


Figure 7.10. Fitted transformation function (Black dashed line) used in GAPI for Unique MOFs tested for large search space (3+ site) MOFs. Blue circles are points used to fit equation.

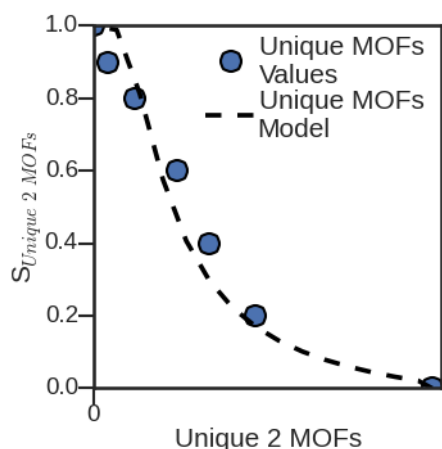


Figure 7.11. Fitted transformation function (Black dashed line) used in GAPI for Unique MOFs tested for 2-site MOFs. Blue circles are points used to fit equation.

7.7.2.2 Optimization Sets

To find the 13 optimal MOFF-GA parameters (Section 7.7.1.13), a test set of 7 different MOFs was used: OCIHIS,²⁹ bio-MOF-11,³⁰ IRMOF-6,³¹ MITSEO,³² IRMOF-16,³¹ UTEXAT,³³ and $\text{Zn}_2(1\text{-}4\text{-benzenedicarboxylate})_2(\text{pyrazine})$, ZBP. For each of these MOFs, the complete search space was evaluated for the three properties: CO_2 uptake at 0.15 atm and 298 K, gravimetric surface area, and the PE (Section 7.7.6). Table 7.7, details the size of the search space for each of the seven MOFs used to optimize the GA parameters. In this work, three sets of MOFF-GA parameters were developed, one for large search spaces (4+-site parameters), one for small search spaces (3-site parameters) and one for very small search spaces, which we call the 2-site GA parameters. To find the optimal parameters for large search spaces, the MOFs ZBP and UTEXAT, which have 4 or more functionalization sites, were used. To find a general and robust set of MOFF-

GA parameters, the aggregate GAPI was optimized for all 3 properties, for these 2 MOFs simultaneously. For small search spaces, the same was performed with the 2 MOFs: MITSEO, IRMOF-16. The GA parameters were also optimized for very small search spaces with the 3 MOFs: OCIIHS, Bio-MOF-11 and IRMOF-6.

Table 7.7. Sterically viable structures for training MOFs

Functional Positions	Total Possible Structures	MOF	Viable Structures
2	784	OCIIHS	621
		Bio-MOF-11	629
		IRMOF-6	644
3	21,952	MITSEO	14,293
		IRMOF-16	17,514
4	614,656	ZBP	96,156
5	> 17 million	UTEXAT	36,501

7.7.2.3 MOFF-GA Parameter Optimization

A variety of methods could have been used to optimize the 13 GA parameters; however, we opted to use a GA. As not to confuse it with the MOFF-GA, we will term the GA used to optimize the MOFF-GA parameters, pGA. The structure of pGA is similar to MOFF-GA, where the 13 parameters are their values are used to make up the pGA chromosome (parameter set). Each generation of pGA consisted of 25 unique parameter sets. The convergence criteria of pGA was set to the top performing parameter set remaining constant for 10 generations.

To optimize the parameters, the fitness function used was the sum of the GAPIs for all MOFs in each set (4+-site, 3-site and 2-site), for all three properties (CO₂ uptake, surface area, and PE). To evaluate the GAPI, MOFF-GA was ran 100 times for each MOF, for each property. From those trials the best find rate, the average of the top 50, and number of unique individuals sampled were determined. To ensure high performing parameter sets pGA was run a total of 5 times on each MOF set.

7.7.2.4 Parameter Set Performance

Each set of GA parameters were optimized on a subset of the MOFs with complete search spaces. A subset was selected for parameter optimization due to the computational expenses. There was a total of 50 MOFs (25 2-site, 20 3-site and 5 4+-site) which had a complete area scan completed for the 3 properties. As we only optimized the parameters on the subset of all available MOFs, we tested each of top 5 parameter sets from the parameter optimization.

The total of 10 parameter sets found from small and large search space optimization were tested on both small and large search spaces. It was thought for small and large space MOFs there could be a single robust parameter set that would perform well on all of them. This was thought because values between the small and large space parameter sets were relatively close and could potentially be transferable. The values for the very small search spaces were significantly different than the other parameter sets and were treated differently. We then tested the 5 parameter sets determined from very small search space optimization only on the very small search space MOFs. The parameter sets were tested by performing 100 runs of MOFF-GA, for each property, for each MOF. For each property, the 100 trials were used to calculate a GAPI. The sum of all GAPIs was used as the determining factor for performance.

It was found the 2nd best parameter set from the large search space optimization worked best on all MOFs with 3 or more sites, for all properties. We chose this parameter set as default parameters for MOFF-GA. For MOFs with 2-sites it was found the best parameter set from the optimization was the top performing parameter set on very small search spaces. This parameter set was then referred to as 2-site parameters. The exact values for each parameter set and their ranges during optimization are shown in Table 7.8.

7.7.3 MOFF-GA Parameter Values

Table 7.8. Parameters used by MOFF-GA that were optimized. The range is given along with the ideal determined values for 3+ and 2 Site MOFs.

Property	Min.	Max.	Default (3+ Sites) Parameters	2-Site Parameters
Population	10	400	113	27
Elite	0	0.5	0.272	0.478
Single Cut Rate	0	1	0.958	0.415
Mutation Rate	0	1	0.446	0.298
Similarity Threshold Value	0	0.9	0.312	0.538
Similarity Probability	0	1	0.305	0.417
Weighting Cut	0	0.5	0.419	0.201
Weighting Cut-off	0	20	2	1
Weighting Change	0	50	24	18
Stagnation	0	5	3	1
Best Mutated	0	1 – Elite	0.038	0.256
Random Mutated	0	1 – (Elite + Best Mutated)	0.064	0.036
Convergence	Stagnation + 1	Stagnation + 5	5	2

7.7.4 Structure Preparation and Construction

MOFs were found from the Cambridge Structural Database (CSD). MOFs were cleaned in Materials Studio. Cleaning involved removing guest/solvent molecules, removing disorder from the framework and assigning symmetry. Symmetry was assigned by Materials Studio and used as a basis for the number of functional sites on the SBUs.

For some MOFs, the symmetry of the SBUs was greater than the MOF's overall symmetry. An example of this idea is seen in Figure 6.8. In this example, the SBU on the left would be the symmetry determined by Materials Studio. By modifying the names of the hydrogen atoms within the CIF an artificial symmetry was imposed on the SBU. This does not change the symmetry within the CIF but does affect how the MOF is functionalized. If two hydrogen atoms have the same name they were seen as symmetrical by our functionalization program.

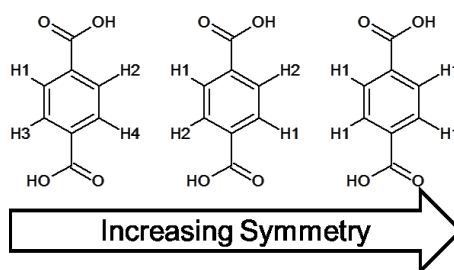


Figure 7.12. SBU with increasing internal symmetry

All functionalized SBUs found at the higher symmetry can be found at the lower symmetry. These artificial symmetries were placed on the SBUs to increase synthetic feasibility. At the lower symmetry SBUs, if all synthetic positions contain different functional groups it could be difficult to synthesis both the SBU and the MOF. Additionally, the higher symmetry limits the search space as the size is defined by the number of symmetrical positions raised to the number of functional groups available. Although the low symmetry SBU could reach the same functionalizations as the highly symmetrized SBU it is not always guaranteed. For these reasons, we have included the same MOFs at different levels of SBU symmetry.

Functionalization of MOFs was carried out using an in-house program, *Fapswitch*. *Fapswitch* works by first identifying symmetrical atoms in the MOF. Using the FGC (Figure 7.4) functional groups are placed sequentially into the MOF. *Fapswitch* ensures that there are no steric collisions from the inserted functional groups by doing a simple conformational search. Combinations of functional groups are rejected if atoms fall within a factor of the atom's Van der Waals radius. A factor of $2^{(1/6)}$ of the VdW radius was used as this ensures that the VdW potential of any inserted

atom is 0 or lower in a Lennard-Jones 12-6 potential. For each site, the functional group is inserted, aligned with the structure using the minimum energy configuration when attached to a benzene ring. All inserted atoms are tested for overlap. If there is steric overlap the group is rotated about the bond to the structure incrementally until there is no overlap. If a complete rotation is completed without finding a configuration with no overlap, that FGC is rejected. The procedure is repeated for all sites in the MOF and all codes in the FGC.

To relax the induced stresses, all MOFs had their geometries optimized with UFF as implemented in the General Utility Lattice Program (GULP), version 4.0.³⁴ Bonding information was included in the generation of the structures and passed to the optimizer.

7.7.5 Molecular Simulations

Gas adsorption calculations were performed using an in-house Grand Canonical Monte Carlo (GCMC) code based on DL_POLY 2 molecular dynamics package.²⁵ Non-bonding interactions were calculated with a Lennard-Jones potential utilizing parameters for the framework atoms taken directly from the UFF¹⁸ with Lorentz-Berthelot mixing rules for cross-terms. Electrostatics were based on partial atomic charges calculated by charge equilibration using the MEPO-QEq parameters,² which were fit to reproduce the electrostatic potential obtained from REPEAT atomic partial charges.²⁶ The CO₂ molecules were modeled using the force field developed by García-Sánchez *et al.*²⁷ and the N₂ molecules were modelled using the TraPPE force field parameters.²⁸

All GCMC simulations consisted of 30000 cycles of equilibration and 30000 cycles of production. One cycle consists of a N of trial moves where N is equal to the number of guest molecules in the system at that time. All simulations included random insertion, deletion, and translation moves of molecules with equal probabilities. Atoms in the framework were held fixed at their crystallographic positions. A LJ cut-off distance of 12.5 Å was used for all simulations and a supercell is constructed for each structure that satisfies the minimum image criterion. The Ideal gas law was assumed when computing the chemical potential in the grand canonical ensemble.

Geometric properties were calculated with Zeo++³⁵ using helium probe of 1 Å to determine the solvent accessible surface areas and pore sizes.

7.7.6 Parasitic Energy

The PE is a term to describe the energy needed to remove CO₂ from a solid sorbent. PE is a

combinatorial term which has information from adsorption conditions and desorption conditions. For adsorption conditions, we used flue gas conditions (298 K with 0.15 bar CO₂ and 0.75 bar N₂), while desorption conditions were at increased temperature and decreased pressure (413 K with 0.70 bar CO₂ and 0.01 bar N₂).

PE is broken into two terms, the thermal contribution (Q) and the work of compression (W_{Comp}). Q (equation 7.6) contains the energy necessary to raise the temperature of the system and disrupt the host-guest interactions. It is seen that Q contains the heat capacity of the adsorbent being used. Determining the heat capacity of a material can be a computational expensive calculation to run. In this study, we used a constant heat capacity for all materials of 1 kJ/kgK. This was chosen as it was average value over a range of similar solid sorbents from a previous study.³⁶ W_{Comp} (equation 7.7) is the energy necessary to change the pressure during desorption process as well as to compress it for transport conditions (313 K and a total of 150 bar).

$$Q = \frac{\Delta T(C_p + \sum_i^{gas} C_i q_i^a)}{\Delta q_{CO_2}} + \frac{\sum_i^{gas} \Delta h_i^a q_i^a - \Delta h_i^d q_i^d}{\Delta q_{CO_2}} \quad (7.6)$$

$$W_{\text{Comp}} = R \left\{ T_{\text{comp}} \left| \ln \left(\frac{p_c}{p_d} \right) \right| + T_{de} \left| \ln \left(\frac{p_d}{p_a} \right) \right| \right\} \sum_{i=1}^{gas} \frac{\Delta q_i}{\Delta q_{CO_2}} \quad (7.7)$$

PE (equation 7.8) adds the thermal contribution and work of compression, while considering energy recovery from the desorption process. The terms that make up Q , W_{Comp} , and PE are described in Table 7.9.

$$PE = 0.75 \eta_{T_{\text{final}}} Q + W_{\text{comp}} \quad (7.8)$$

Table 7.9. Terms used in PE with a brief description.

Term	Description
ΔT	Change in temperature from adsorption to desorption conditions
C_p	Heat capacity of adsorbent (1 kJ/kgK)
C_i	Heat capacity of the gas i
$q_i^{a(d)}$	Amount of gas i adsorbed at adsorption (desorption) condition
$\Delta h_i^{a(d)}$	Heat of adsorption of gas i as adsorption (desorption) condition
Δq_i	Working capacity of a gas i
$T_{C(d)}$	Temperature at compression (desorption) condition
$P_{c(d)(a)}$	Pressure at compression (desorption) (adsorption) condition
$\eta_{T_{\text{Final}}}$	Carnot efficiency of steam generator (0.18)

7.7.7 Top Performing Structures

Provided in Table 7.10 are a list of all MOFs found CO₂ uptake greater than 3 mmol/g at flue gas conditions. Parent MOFs are the unfunctionalized base structure with their SBUs given. For

each high performing functionalization, the CO₂ uptake and the FGC are given. Figure 7.4 shows how the FGC works by changing the parent MOF's SBUs into the functionalized SBUs. For simplicity if a functional position is a hydrogen atom than it is not omitted in the FGC. The details of the functional groups, such as name and structure, are given in Table 7.11.

Table 7.10. Functionalized MOFs with CO₂ uptake greater than 3 mmol/g with the corresponding functional groups. A blank Functional Group Code means the unfunctionalized Parent MOF.

Table 7.10 omitted due to space as it is 28 pages. The table can be found online at DOI: 10.1126/sciadv.1600954

Table 7.11. Details of Functional Group Codes and their associated structure. X is the bonding position to the MOF.

Functional Group Code	Name	Structure	Functional Group Code	Name	Structure
Br	Bromo	X—Br	CCH	Ethynyl	X—
CF₃	Trifluoromethyl	X—	CHCH₂	Ethenyl	X—
CHNH	Methanimine	X—	Cl	Cloro	X—Cl
CN	Cyano	X—	CONH₂	Amide	X—
COOH	Carboxylic Acid	X—	Et	Ethyl	X—
F	Fluoro	X—F	H	-	X—H
HCO	Aldehyde	X—	I	Iodo	X—I
Me	Methyl	X—	MeNH₂	Methanamine	X—
NH₂	Amine	X—NH ₂	NHMe	Methylamine	X—NH—
NO₂	Nitro	R—	OEt	Ethoxy	X—O—
OEte	Ethenyloxy	X—O—	OH	Hydroxyl	X—O—H
OMe	Methoxy	X—O—	OPr	Propoxy	X—O—
OPre	2-Propenyloxy	X—O—	Ph	Phenyl	X—
Pr	Propyl	X—	SO₃H	Sulfonic Acid	X—

8 Combined Atomistic-Macro Scale Pressure Swing Adsorption Optimization

The work presented in this chapter was a collaborative effort between myself, a Ph.D. candidate Thomas Burns from the Woo lab, and the research group of Arvind Rajendran from the University of Alberta, which included graduate students Kasturi Nagesh Pai and Gokul Subraveti. For this work, I was responsible for the computational gas adsorption calculations, parameterizing the adsorption isotherm models for each structure, filtering structures based on their properties, writing and running the genetic algorithm for the process condition optimizations, and performing all data analysis presented for this chapter. Our collaborators, from the University of Alberta, were responsible for the development of the process simulator code. Thomas Burns, from the Woo lab, was responsible for modifying and compiling the process simulator code, performing the grid search of process conditions on each material, and selecting MOFs to be optimized for the genetic algorithm. As of the time of writing this thesis, part of this work is incorporated into a manuscript submitted for publication.

8.1 Abstract

Post-Combustion Carbon Capture (PoCCC) is a key approach in the world's efforts to reduce Greenhouse Gas (GHG) emissions. To perform PoCCC, materials which selectively adsorb CO_2 can be used to remove the CO_2 from the flue gas of power-plants. So far in this thesis, work has been done on finding materials for gas separations like PoCCC using metrics derived from equilibrium-based adsorption calculations or experiments. In this chapter, detailed process simulations of a pilot scale Pressure Swing Adsorption (PSA) system are run to provide a more realistic and holistic view of how each material would perform for PoCCC. Atomistic Grand Canonical Monte Carlo simulations were performed to evaluate the CO_2 and N_2 gas adsorption properties of a database of experimentally realized MOFs. After filtering the original 3468 MOFs in this database, 1212 structures were evaluated for their PSA performance with detailed process simulations using a grid search of process conditions. 162 of the most promising MOFs were then selected, along with an additional 49 materials for which experimental isotherms were available, to have their process conditions fully optimized with a genetic algorithm. The PSA process conditions were optimized in order to maximize the CO_2 purity, recovery, and productivity while minimizing the parasitic energy (PE) of CO_2 capture. From the optimization of the 211 structures,

202 of them were able to meet the US DoE recovery and purity targets of capturing at least 90% of the CO₂ at a minimum purity of 95%. 193 of the 202 MOFs had PEs lower than the solvent-based plants (1060 kJ/kg CO₂). Machine learning was then applied to the results to see if various metrics, such as the adsorption or geometric properties of the material, could be used to predict if a material would meet the purity/recovery targets. However, no useful relationships could be found between 90 metrics and PSA performance of the materials.

8.2 Introduction

Throughout this thesis so far, I have discussed finding ideal materials for use in gas separation processes. There are many ways to determine what the ideal material is, and any metric discussed in Chapter 1 could be used, among others. The main problem with any single metric mentioned so far is that they do not give a complete picture of how a material will perform in a real gas separation process. Gas separations systems are complicated dynamic processes and as a result, the materials used in them likely need to be evaluated using multiple metrics including those that contain the kinetics of adsorption. As previously mentioned in Chapter 1, 3, & 6 achieving a low parasitic energy (PE) is an important target, tied with having a high CO₂ purity, which is also essential since the U.S. Department of Energy (DoE) has set a target purity of 95%.¹ As shown in Chapter 3, the minimum theoretical PE is achieved when the absolute amount of CO₂ that is recovered tends to 0. In practical applications, a significant recovery is beneficial to have as much impact on greenhouse gas (GHG) emissions as possible. According to the DoE, a total of 90% of the CO₂ should be recovered from post-combustion flue gas.² For this chapter, we will use the term Purity/Recovery target or “PRT.” For example, the DoE target of 95% purity and 90% recovery will be given as the “95/90”-PRT. One additional practical quantity for PoCCC is the productivity, which is the amount of CO₂ captured per m³ of material per second (mol CO₂ / m³ s). The higher the productivity, the less sorbent material is needed to capture the CO₂, which in turn will lead to lower capital costs (building the Pressure Swing Adsorption systems) and lower overall cost of CO₂ capture.

One limit of our GCMC simulations is that they only provide equilibrium adsorption data of a material. The dynamic or kinetics of gas adsorption are not predicted from these simulations. This means a property such as productivity, which are time-based quantities, cannot be accurately estimated from GCMC simulations alone. Equilibrium adsorption properties of a material also

cannot be used to estimate the purity or recovery accurately using the material.³ In the previous work presented in this thesis, I used the equilibrium properties but had to assume a 100% recovery to estimate the purity of gas separation. Finally, the PE calculations used in my previous work (and those of others) were relatively simplistic and only provided rough estimates.

In this chapter, I present work done in collaboration with the Rajendran group from the University of Alberta, to evaluate the performance of sorbent materials for post-combustion carbon capture (PoCCC) using detailed PSA process simulations. This was done by using the Computation-Ready Experimental (CoRE)⁸ MOF database, and by computationally modelling CO₂ and N₂ adsorption properties, and determining the required adsorption isotherm model (AIM) parameters for the process simulations. In addition to the CoRE database, a total of 49 structures with experimentally determined AIM parameters were also studied. A Genetic Algorithm (GA) was used to optimize the performance of some of the structures further. An analysis was done to see if the conventional metrics, such as CO₂ uptake or selectivity, or figures of merit (FoMs), such as the Adsorbent Performance Score (APS), or the simplistic PE, could be related to their performance determined from the process simulations. To the best of my knowledge, this is the first time that the atomistic-scale of GCMC simulations has been combined with the macro-scale PSA process simulations to screen materials.

8.3 Methods

8.3.1 Isotherm Modelling and Parameterization

The entire CoRE database had CO₂ and N₂ isotherms modelled using an in-house GCMC code. During the GCMC calculations, the atomic framework positions were frozen, and all guest molecules were rigid. Interatomic interactions were calculated using the Lennard-Jones (LJ) 12-6 potential (equation 2.6) to describe the van der Waals terms and the Ewald summation (equation 2.10) to account for electrostatic terms. For framework atoms, the LJ parameters were taken from the Universal Force Field (UFF)⁹ while the partial atomic charges were calculated using the REPEAT method.¹⁰ REPEAT partial atomic charges were fit to a gauge-modified quantum mechanical derived electrostatic potential from the *Vienna Ab-Initio Software Package* (VASP),^{11,12} using the PBE Functional^{13,14} with a planewave cut-off of 400 eV. The CO₂ parameters used were derived by García-Sánchez *et al.*¹⁵, and the N₂ parameters were developed in-house¹⁶ and are given in Chapter 3. The GCMC simulations were performed for 30,000

equilibration cycles followed by 30,000 production cycles. A single cycle is N GCMC steps, where N is the number of guest molecules in the system at any given time. GCMC calculations were performed at 298 K using 16 pressures ranging from 0.01 to 1.2 bar, using the Peng-Robinson equation of state to calculate the fugacities.¹⁷

Each gas adsorption isotherm was fit to dual-site Langmuir (DSL) AIMs and used in all PSA simulations. The GCMC derived heats of adsorption (HoA) were used to calculate site potentials, ΔU , as well as Langmuir constant, $b_{i,j}$, using equations 8.1 and 8.2, respectively. The Langmuir constants used in this work ($b_{i,j}$) are different from the previously used constant ($K_{i,j}$) because they are in units of m^3/mol and work on concentrations (C_i) and not the pressure (p_i). The reason for using the concentration-based values is because the PSA simulator code was written to work in terms of concentrations, not pressures. The version of the DSL used in the PSA code is given in equation 8.3. The final value needed for the PSA simulator is the perfect crystal density, ρ_{cry} , calculated from the Crystallographic Information File. The PSA simulator requires the material density that accounts for the loss due to the binder. This is known as the ρ_{bind} and is calculated by multiplying ρ_{cry} by 0.75, which is a value given by our collaborators.

$$\Delta U = \text{HoA} - RT \quad (8.1)$$

$$b_{i,j}^T = b_{i,j}^0 e^{\frac{-\Delta U}{RT}} \quad (8.2)$$

$$\sigma(C, i) = \sum_j \frac{\sigma_{i,j}^s b_{i,j}^T C_i}{1 + b_{i,j}^T C_i} \quad (8.3)$$

8.3.2 Pressure Swing Adsorption Simulator

The PSA simulator used in this work was based on a four-cycle PSA system as shown in Figure 8.1. These four phases are the adsorption, blow-down, evacuation, and re-pressurization phases. As the development of the PSA simulator was performed by Haghpanah and co-workers⁶ and was primarily the responsibility of the uAlberta co-workers, only a brief description of how it works is given here, with full details given in their published works.^{3,4,6} To explain how the simulations work, I will describe them using a 1 m PSA column, oriented like Figure 8.1, with the flue gas entering from the bottom. The PSA simulator works as a finite volume simulation with the column packed with a solid sorbent. The inlet gas mixture enters the column from the bottom of the column at a temperature, T_{ads} , and flows from the bottom of the column to the top with the flow rate, V_0 . The PSA simulator breaks the column in 20 sections where the gas passes from one end to the

other. Instantaneous lateral diffusion of the gas across each section is assumed. The material is also assumed to be formed onto a binder, causing the crystal density to drop by 25%. Ideally, the heavy stream (CO_2 rich stream for PoCCC) adsorbs onto the material, allowing the light stream (N_2 rich stream for PoCCC) to pass freely. The system adsorbs the gas for a set amount of time, t_{ads} , after which the inlet stream is diverted into another column. For the original column, a vacuum is applied to the top of the column to start the blow-down phase. The blow-down phase lowers the PSA system to a pressure, p_{bd} , for a set amount of time, t_{bd} . Breakthrough experiments show light stream fronts typically travel ahead of the heavy stream front, as the heavy stream is adsorbed to the gas scrubber.^{18–20} This is accounted for in the PSA simulation by applying a force equal to the blow-down pressure at the top of the column. The point of the blow-down phase is to remove the light stream (N_2), to create a further purified heavy stream (CO_2). Afterwards, a force is applied to the bottom of the column to simulate the further reduction of the pressure to p_{ev} . This force is applied for a set time (t_{ev}) which is known as the evacuation phase. The final step of the PSA simulator is the re-pressurization phase. This phase occurs by using the same composition as the light phase that exited from the blow-down phase, which is N_2 rich and forcing it into the system from the top, with force equal to 1 bar of pressure. The cycle of four steps (adsorption, blow-down, evacuation and re-pressurization) is repeated until the mass balance is achieved, or a maximum number of cycles is reached. For the PSA simulator, mass balance is defined when the amount of CO_2 and N_2 moles that leave the system is within 2% of the moles that enter the system. Assumptions and constant parameters are given in the Appendix.

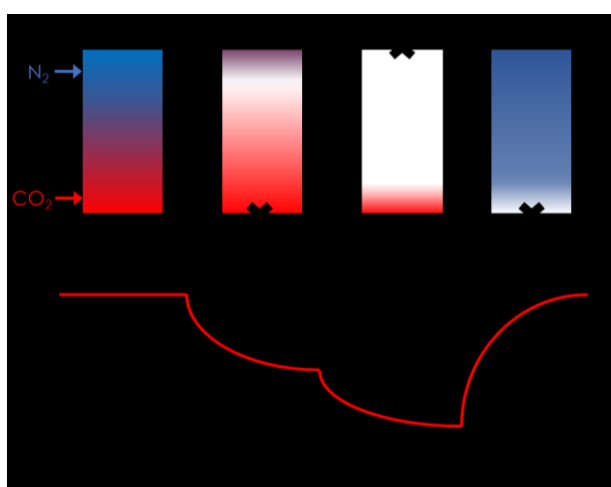


Figure 8.1. Representation of the 4-stage Pressure Swing Adsorption cycle used in this work with the corresponding pressure graph.

There are many parameters involved in the PSA simulator, such as the length column, internal diameter, and particle porosity to name a few. In this work, we assumed that the system remained the same and only the adsorbent was changed. This meant that only adsorbent specific parameters were changed, such as the isotherm parameters, the density of the material, and heat capacity to name a few. The densities and AIM parameters are easily calculable using simulation techniques from the Woo lab and were calculated for each material. It has been established that for Zeolite-13X, the kinetics of adsorption onto the structure is controlled by macro diffusion, and not diffusion into the pores, so diffusion properties may only have a minor effect.²¹ The diffusion properties used the values of Zeolite-13X as they are a good approximation. For the experimental structures taken from the work by Huck,²² the associated heat capacities were available, so those values were used. For all structures, if the value of a property was unavailable, values calculated for Zeolite-13X were used, which is similar to what our collaborators have done previously.³ These properties included the heat capacities and kinetic properties such as diffusion coefficients.

The PSA simulator uses the AIM parameters to determine the amount adsorbed for each type of gas. This is done by using the Competitive Isotherm Model (CIM) as described in Chapter 1. All isotherms used in the PSA simulations were fit to DSL AIMs. As DSL AIMs have two binding sites, a choice needs to be made as to how they interact. For example, Ritter described combination rules for binary interaction,²³ where the DSL binding sites are first ordered by the size of the adsorption constant ($b_{j,i}^0$). A larger adsorption constant means a stronger interaction with the guest. Perfect Positive (PP) interaction is when the strong adsorption sites interact with strong sites, and weak with weak. For example, equation 8.4 shows PP interaction for the CO₂ guest, where the subscript 1 denotes the site with the larger adsorption constant, and 2 is the site with the smaller adsorption constant. Using the adsorption constant as an indication of site strength is the approximation that Huck *et al.* also used in their work.²² Although there are other binary interactions, such as Perfect Negative (PN) where the weak sites of one species interact with the strong sites of the other species, in this work PP interactions were used for all gas adsorption calculations.

$$\sigma(C, CO_2) = \frac{\sigma_{CO_2,1}^s b_{CO_2,1}^T C_{CO_2}}{1 + b_{CO_2,1}^T C_{CO_2} + b_{N_2,1}^T C_{N_2}} + \frac{\sigma_{CO_2,2}^s b_{CO_2,2}^T C_{CO_2}}{1 + b_{CO_2,2}^T C_{CO_2} + b_{N_2,2}^T C_{N_2}} \quad (8.4)$$

8.3.3 Optimization of Process Condition for Each Material

Once the CoRE materials were filtered based on structure and performance (described later), they were tested using a grid-search. For the grid search, four parameters were held constant, and the remaining three varied over 10 values, for a total of 1000 points. All the process input parameters are given in Table 8.1. For the grid search, the T_{in} , t_{bd} , and p_{ev} were held constant to 298.15 K, 30 s, and 0.03 bar respectively. The t_{ads} ranged from 30 to 120 s in 10 s intervals, p_{bd} ranged from 0.06 to 0.15 bar in 0.01 bar intervals, and the V_0 ranged from 0.01 to 0.09 in 0.01 intervals. The time of blow-down, t_{bd} , was treated somewhat differently and was fixed to be 10 seconds larger than the t_{ads} value. The choice of ranges and which ones to hold constant were chosen by our collaborators and based on their previous work optimizing process conditions. The grid-search was done as a collaborative effort by me and a Woo lab colleague, Thomas Burns.

Table 8.1. Process parameters that PSA-GA optimized, as well as the ranges they could optimize over.

Process Parameter	Symbol	Optimization Range	Unit
Temperature of adsorption	T_{ads}	293.15-328.15	K
Feed velocity	V_0	0.1-2	m/s
Time of adsorption	t_{ads}	20-200	s
Blow-down pressure	p_{bd}	0.03-0.15	bar
Time of blow-down	t_{bd}	20-50	s
Evacuation pressure	p_{ev}	0.01-0.06	bar
Time of evacuation	t_{ev}	20-200	s

To further optimize the process input parameters, an in-house developed GA was used. This GA was a modified version of the GA used in the development of the SQE-MEPO parameter set²⁴ discussed in Chapter 5. The set of parameters were treated as a list of values, and when mating the value for the child, was chosen to be between a random value between the parents' values. The GA optimized all seven process parameters simultaneously, which are given in Table 8.1 along with the ranges they were optimized over. The GA tried to simultaneously optimize the four process criteria, by use of a scaled distance function shown in equation 8.5. In the equation x^b , the best value that could be achieved, x^w , was set as the worst value for the process criteria, with those values given in Table 8.2. The values for purity and recovery come from the DoE guidelines for the worst, and the maximum possible value for the best. Although it is possible for values to go below the x^w value (purities lower than 95% for example), the fitness function becomes exponentially more punitive the further away it goes. The x^b value for the PE was to be the theoretical minimum value when looking at the thermodynamic minimum and compression, as

discussed in Chapter 3. The remaining three values, x^w for PE, and the x^b and x^w for productivity, were chosen based on preliminary results from the PSA simulations. One of the highest productivities found was 2.5 mol / m³s and therefore a larger value, 3.5 mol/ m³s, was chosen to ensure that the limit would not be hit. Finally, the x^w values for the productivity and PE were chosen to ensure one value did not dominate during preliminary testing.

$$fit = \sum \left(\frac{val - x^b}{x^b - x^w} \right)^2 \quad (8.5)$$

Table 8.2. PSA process criteria, and the best and worst values that were used in equation 8.5 to calculate the fitness.

Process Criteria	x^w	x^b	Unit
Purity	95	100	%
Recovery	90	100	%
Productivity	0.5	3.5	mol / m ³ s
Parasitic Energy	900	486	kJ/kg CO ₂

8.3.4 Random Forests

In this chapter, machine learning was performed using Random Forest (RF) classifiers, which are collections of multiple Decision Tree (DT) classifiers. DTs are branching models for decisions where descriptors are used in each branch to classify a candidate solution (CS). RFs work by having a CS that is classified by multiple DTs, and the result is the classification that appears most often. For example, if an RF contained 11 DTs, and 6 of the DTs indicated a material would meet the “95/90”-PRT and the other 5 said it would not, the RF would say the material would meet the PRT. To create an RF in this work, first, all relevant data was randomly split in ratios of 90:10 to create the RF training and testing sets respectively. The RF training set was the data that was used in order to train each of the DTs. For this work, an RF consisted of 11 DTs, with the tree depths ranging from 1 to 10 nodes.

To train the DTs, first, the RF training set was randomly split into two sets. These were the DT training and validation sets, which had 90% and 10% of the RF training sets, respectively. Using the sklearn module³² for Python, the DTs were trained, going from depths of 1 to 10 nodes. What this meant is that the same training and validation sets were used to create 10 DTs of increasing depth. The process of splitting the RF training set and DT training set was repeated until each tree depth had a total of 11 DTs.

8.4 Results and Discussion

Before any large scale screening, I initially tested the full process optimization on eight experimentally characterized materials: Mg-MOF-74,²⁵ Zeolite-13X,²⁶ UTSA-16,²⁷ CALF-20,²⁸ SION-66, SION-67, mmen-CuBTtri (m-CuB),²⁹ and **IISERP-MOF2**.¹⁸ Mg-MOF-74 is often promoted as being a high-performer for PoCCC, while Zeolite-13X is currently used industrially for CO₂ scrubbing for natural gas purification. UTSA-16 is a MOF that was previously examined by the Rajendran Lab with full process simulations and found to be high performing.³ CALF-20 is a MOF patented by the Shimizu group at the University of Calgary, whose CO₂ uptake capabilities were found to be nearly unaffected by water up to 40% relative humidity. **IISERP-MOF2** is a MOF synthesized by the Ramanathan group that we had previously identified as having a low PE of PoCCC using a simple model for the PE (Chapter 3). m-CuB was found to be amongst the highest performing materials based on the simple model of the PE. The MOFs SION-66 and SION-67 were synthesized by the Stylianou group of EPFL and have binding sites identified by the Woo lab for ideal CO₂ adsorption.³⁰ The process conditions were optimized for each material using the GA a minimum of four times. Compared to the high throughput screening (vide infra), the process conditions for these 8 materials were optimized for various combinations of process performance parameters, such as the Purity/Recovery or the Productivity/Energy. As a result, many PSA simulations were performed for each MOF. For example, for **IISERP-MOF2**, over 135,000 different process conditions were simulated.

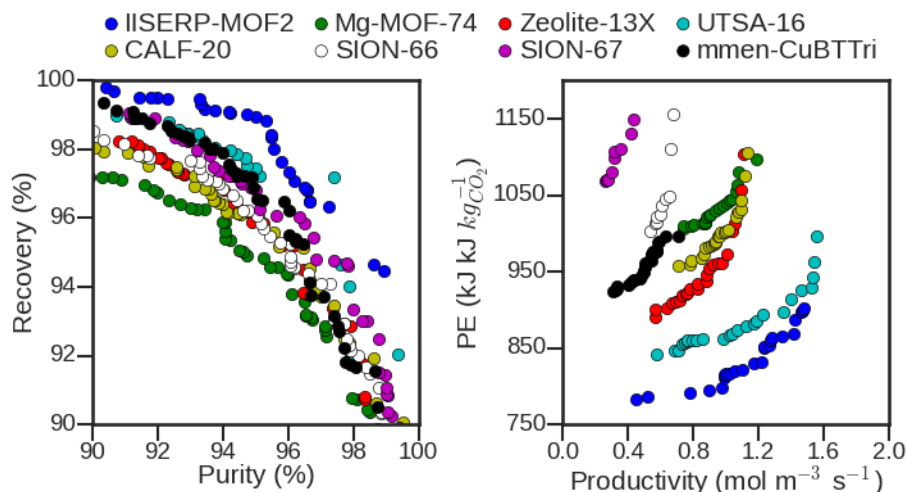


Figure 8.2. Pareto fronts were constructed from GA data for a) Purity-Recovery and b) Productivity-PE. The Productivity-PE data is constructed with points that meet the “95/90”-PRT.

Figure 8.2a shows the Purity-Recovery Pareto fronts for each material, which shows the antagonistic relationship between purity and recovery. In other words, in order to recover more CO₂ from the flue gas, a trade-off is made where the outlet stream will not be as pure. From this work, it was found that **IISERP-MOF2** had the best performance in terms of purity and recovery. Given that Mg-MOF-74 is often reported as the benchmark MOF to beat in terms of PoCCC, it was found to be the worst performing of the eight materials evaluated. This low performance of Mg-MOF-74 can be attributed to its high N₂ adsorption. When looking at the Henry's constant at 298 K, the N₂ value for Mg-MOF-74 was 0.23 bar⁻¹, which is roughly twice as much as the next closest MOF, CALF-20 of 0.12 bar⁻¹. **IISERP-MOF2**, which showed the best performance, had the lowest N₂ adsorption constant of 0.0013 bar⁻¹, nearly 200 times smaller than Mg-MOF-74. Once a material can reach the DoE purity-recovery targets, it is then important to minimize the cost. As mentioned previously, the cost of CO₂ capture is associated with both productivity and the PE. The productivity/PE Pareto fronts are shown in Figure 8.2b for all eight materials, with all shown points meeting the "95/90"-PRT. In this case, the ideal material would maximize productivity while simultaneously minimizing PE. Once again, **IISERP-MOF2** was found to be the highest performer, while Mg-MOF-74 was among the worst materials, along with SION-66 and SION-67. Although these simulations do consider more than the GCMC results from previous chapters, there are additional considerations for the materials. Other properties to consider would be the stability of materials, how a MOF performs in the presence of water, and the cost of synthesis, all of which are beyond the scope of this work.

The study was expanded to looking at MOFs from the CoRE database. Since adsorption data under the PSA conditions examined here are not available for these MOFs, we used atomistic GCMC simulations to evaluate them. A set of heuristic filters were used to reduce the number of structures to be screened with full process simulations. The CoRE database contained 77 elements, with many containing metals that were either rare or toxic. Thus, only MOFs which contained the following elements were screened: H, Li, B, C, N, O, F, Na, Mg, Al, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Br, Zr, Cd, Sn, and I. Some concessions were made in this filter in that elements that are widely used in the MOF community, such as V, were included. The density of the material was also used as a filter, like MOFs with low densities that would have low productivities, according to our engineering collaborators. 1150 kg/m³ was considered low density, and any MOF with lower crystal densities were removed. There were 3468 CoRE MOFs examined before the

filters; however, 1124 MOFs were removed due to low density, while 1362 were removed due to filtered elements. This left a total of 1212 MOFs from the CoRE database that were screened. Single component isotherms of CO₂ and N₂ were modelled from pressures of 0.01 to 1.2 bar and fit to DSL AIMs. In addition to those MOFs, 49 structures with experimental CO₂ and N₂ adsorption isotherm parameters were tested. Those included the eight structures mentioned previously, with the remaining 41 obtained from Huck, for which experimental adsorption data is available.²² For the remainder of this chapter, these 49 structures will be known as the experimental structures, because their AIM parameters were fit to experimental data. Overall, a total of 1261 structures were screened using full process simulations.

Process optimizations were performed on the 1261 materials using a grid search of process conditions. Materials which all process simulations failed from the grid search (meaning their performance would be very poor), were removed from further screening. This left 1180 structures, for which the grid search provided a total of 1.026 million process simulation points. The PE and productivity of these points are presented in Figure 8.3. It was found that when considering all MOFs, there is a tendency for the process points to favour low PE values, with 45% of all points from 840 unique structures having PEs less than that of a state-of-the-art liquid amine plant (1060 kJ/kg CO₂).³¹ Next, a filter was applied to remove points which did not meet “92/87”-PRT. A lower PRT was chosen for the filter, as the grid search is a course optimization method, and if the parameters were further optimized, there is a possibility that the structure will meet the “95/90”-PRT. Only 50,972 points, or 5.0% of all grid points from 680 structures, were able to meet the “92/87”-PRT, of which 45,570 points from 611 structures had PEs less than 1060 kJ/kg CO₂. The reason for the increase in the ratio of low-PE points (45.0 to 89.4%) is because purity is highly tied to the PE, meaning removing low purity points would disproportionately remove high-PE points. A similar analysis was performed looking at the productivity of the processes, shown in Figure 8.3b). The distribution showed many peaks and valleys, which is particularly evident in the “92/87”-PRT points. There appears to be 10 potential peaks, which is due to the discretization of the flow rate, V_0 , in the grid search. Figure 8.4a) shows the relationship between the flow rate and productivity, and that as the flow rate increases, the productivity does as well. The only other correlation between parameters and performance was between the blowdown pressure (p_{blow}) and the PE shown in Figure 8.4b), which shows that when the blowdown pressure increases, the PE decreased.

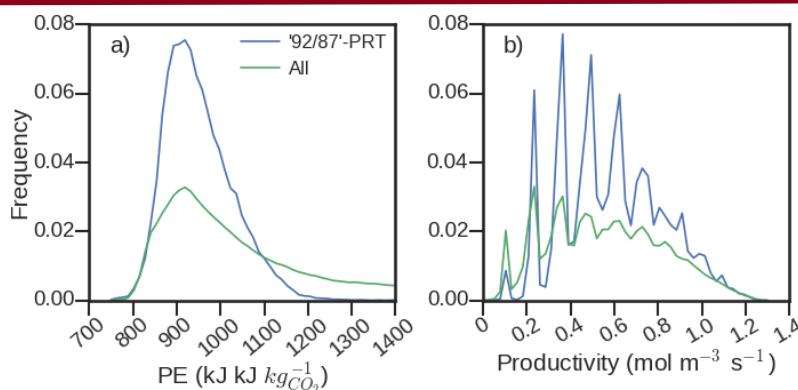


Figure 8.3. Frequency histograms of the a) PE and b) productivity of the results from the filtered CoRE database and experimental results. The green line represents when all points are considered, and the blue line represent points that reach the “92/87”-PRT.

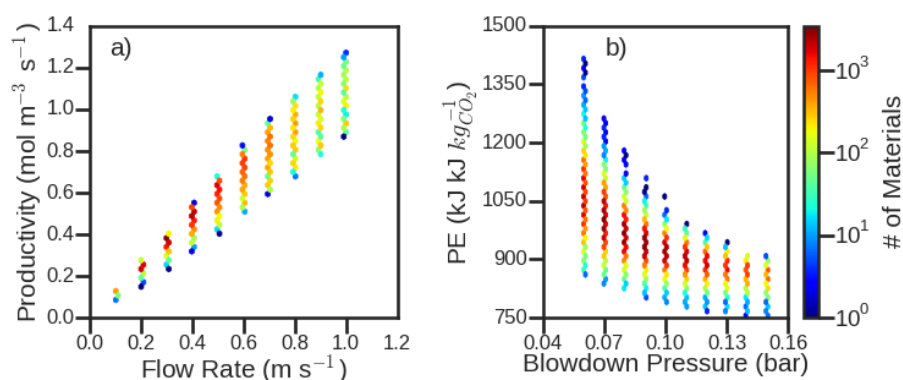


Figure 8.4. Heatmaps of grid search points reaching “92/87”-PRT for a) the productivity vs the flow rate and b) the PE vs the blow-down pressure.

After performing the grid search, all seven process parameters (shown in Table 8.1) were optimized using the in-house developed GA. As optimizing the parameters for all 1180 structures would be too costly, the grid-search data was used as a screen for the best-performing structures. All 49 experimental structures were optimized, of which 18 met the “95/90”-PRT, 14 failed that PRT but met the “92/87”-PRT, and the remaining 17 were unable to meet even the “92/87”-PRT. From the 1131 CoRE MOFs that returned grid-search results, 274 structures that met the “95/90”-PRT were ranked according to their PE, and the lowest 140 structures were selected for full process optimization. Finally, structures which did not meet the “95/90”-PRT but met the relaxed “92/87”-PRT were also ranked by their PE, with the 22 structures with the lowest PE from this group selected for further process optimization. Those 22 structures that did not meet the PRT were chosen for further optimization to see if it would be possible to meet the “95/90”-PRT after optimization. For this work, the PE was used as the primary metric for selecting materials for full process optimization because there are benchmark values of the PE from liquid amine scrubbing

systems. Although productivity could have also been used as a metric for selecting the materials, benchmark values here are not available, and directly correlating the productivity to the plant size or cost is a difficult problem. Altogether a total of 211 structures were optimized by the GA, and the process conditions of each structure were optimized a minimum of 4 times. For these optimizations, the fitness function given in equation 8.5 with fixed parameters given in Table 8.2 was minimized. A strict “95/90”-PRT was imposed on all materials which resulted in 9 of the 211 materials being discarded. Of those 9, only 1 material was from the CoRE MOFs, while 8 were from the experimental structures. None of those 8 experimental structures were able to meet even the relaxed “92/87”-PRT from grid search data, so it is not surprising that they were unable to meet the strict “95/90”-PRT. Figure 8.5 shows the improvement of the fitness function from the best point from the grid to the best point found by using the GA data for the remaining 202 structures, where all points were shown to meet the “95/90”-PRT. It should be noted that 44 structures were unable to meet the “95/90”-PRT from the grid search, so their grid search results are ignored in the figures and analysis.

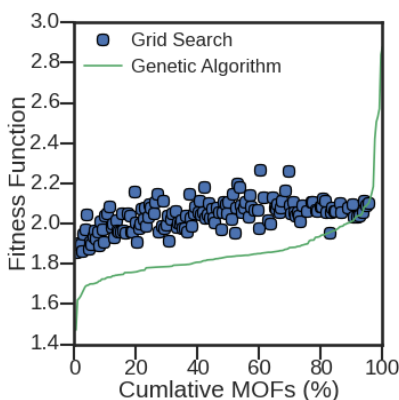


Figure 8.5. Lowest fitness function values (equation 8.5) for each MOF when using grid search (blue circles) and GA (green line) data. All points meet the “95/90”-PRT. Arranged in ascending order of GA fitness. If a grid search result did not meet “95/90”-PRT, its results were ignored.

The fitness value for each structure improved when optimized using the GA, although the degree of improvement was different for each MOF. For the 158 structures which had both grid search and GA data, it was found that the purity and recovery, Figure 8.6a and b respectively, showed only moderate improvement on average: 1.47% and 1.24%. A few structures (<10) had a decrease in their purities or recoveries after optimization, although they did increase performance in either the PEs or productivities. It was interesting that after optimization the PE only improved in 85 structures (54%), as seen in Figure 8.6c. The largest improvement overall was found in the

productivity (Figure 8.6d), which increased on average by 97.5%. The reason why the productivity might have the largest improvement is that both purity and recovery for both the grid-search and GA data were forced to be high with the “95/90”-PRT. The purity is correlated to the PE due to the compression, so if a cut-off was applied for high CO₂ purity, this would also force the PEs to be high-performing in those materials. This meant that the productivity was the only parameter not specifically filtered for in the grid-search results, so it would have the most significant potential for improvement. After GA optimization of all the materials, **IISERP-MOF2** was still seen as the best material, noted by the lowest fitness function. Although **IISERP-MOF2** was the best material for both the recovery and PE (93.6% and 875 kJ/kg CO₂, respectively), as with the analysis of Chapter 6, I attribute this to the overall performance of **IISERP-MOF2**. The next highest recovery was 93.3%, and the next lowest PE was 887 kJ/kg CO₂, which are very close values to **IISERP-MOF2**. When looking at the average rank of all four performance values, **IISERP-MOF2** had the best average rank of 10 compared to 21.25 for the next best material UTSA-16.

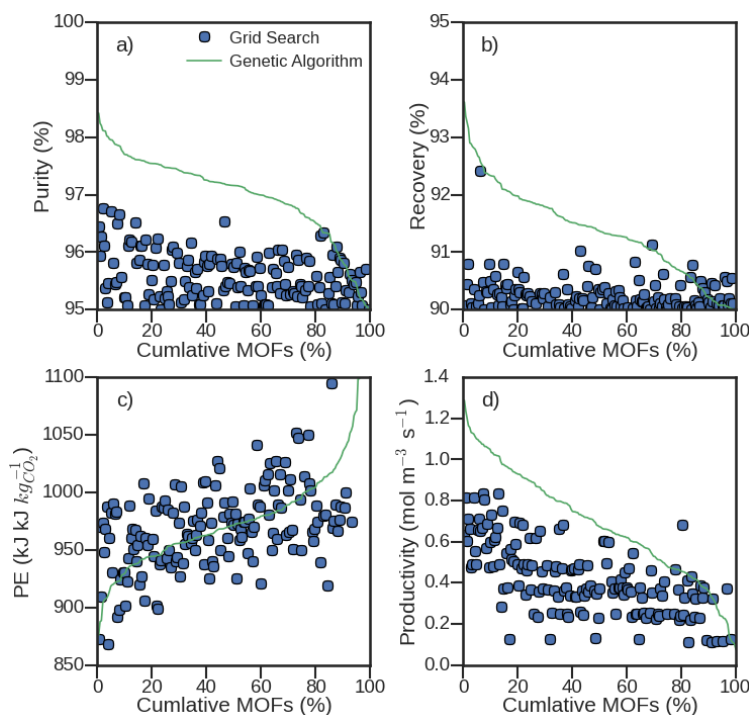


Figure 8.6. Performance targets: a) Purity, b) Recovery, c) PE, and d) Productivity for each structure. Data is taken from the best fitness function (equation 8.5) for grid search (blue line) and GA (green line) data. MOFs are ordered from best-to-worst performance target from the GA data.

Full optimization of the process conditions using the GA can identify high-performance materials, but it is computationally intensive. For this reason, developing machine learning models can be a way to expedite the process. There has already been an effort to try and relate material

level properties to the PSA performance;⁷ this was done using advanced machine learning methods like artificial neural networks on a limited number of structures, up to 74. A simpler method would be to use easily calculable metrics such as geometric or gas adsorption properties, or related FoMs, and directly relate it to the PSA performance. There are many possible ways to rank or classify data from the PSA analysis, so separate analyses were performed to determine 1) if a structure can reach the “95/90”-PRT from grid search and 2) determining if a GA optimized MOF that meets the “95/90”-PRT would be in the top half of performers according to the fitness function. If relationships were able to be made, it would mean that some PSA simulations can be skipped while still identifying the high-performance materials with high accuracy. A total of 90 descriptors were used in this analysis, including the 77 mentioned in Chapters 3 & 6. The remaining 13 included the optimized PE, as well as the 3 parameters for each of the four binding sites ($\sigma_{i,j}$, $b_{i,j}^0$, and $b_{i,j}^{298}$). The site potentials, $\Delta U_{i,j}$, was ignored, as it is a modified version of the HoA (equation 8.1) and they are already included. For the RF analysis, of the 1180 MOFs which were tested using PSA simulations, only 1131 were considered. This is because the 49 experimental structures were removed due to having no geometric data associated with them because they do not have an associated crystallographic information file (CIF). Of these 1131 structures, 274 were able to meet the “95/90”-PRT based on the grid optimization of process conditions. Furthermore, 161 of 1131 structures had GAs performed on them and were split into two equally sized groups for high (81) and low (80) performing structures, according to the fitness function.

The first machine learning models were trained on the grid search data to determine whether a material, if given the 90 previously mentioned descriptors, could meet the “95/90”-PRT. There are many ways to determine which model is the best, but for this work, the Matthews Correlation Coefficient (MCC) was used.³³ The MCC was chosen as it is a single number that has been shown to be good at describing the efficacy of a classifier, especially when the data is unbalanced.³⁴ This is the case here where only 274 structures out of 1131 meet the “95/90”-PRT. The MCC ranges from 0 (random classification) to 1 (everything properly classified). RFs, where the DTs had depths of 2 or 4, were found to have the highest MCC scores of 0.2 for the RF training set. To give a sense of what an MCC of 0.2 means, one RF classified a group of materials which met the “95/90”-PRT, although it only contained 3 of the 45 materials that met the “95/90”-PRT. These are inaccurate models that cannot accurately determine if a material will meet the “95/90”-PRT.

We next developed an RF to predict whether a GA optimized material would be in the upper or lower half of the GA optimized fitness function, given in equation 8.5. In this case, a total of 161 structures were used for training, with 81 used as “high-performance” and 80 as “low-performance.” With a dataset of 161 structures and DT depths of 8 or more (2^8 is 256), it could be expected that an RF should be able to classify CS perfectly. The problem with this type of classification—and any machine learning on small datasets—is the likelihood that the model would overfit to the training data. This means that although the model could classify the training set, it would be highly specific to that data and could not be used on a different set. This is seen as some DT training sets had MCCs as high as 0.650, while the MCC for the RF test set was 0.13. Perhaps with more data, a more robust RF could be created; however, based on that performance and the results from the “95/90”-PRT predictions, it is unlikely that a larger training set will make it a predictive model. What I conclude is that the collection of 90 descriptors used in this work are unable to be used as predictors for PSA performance and that PSA simulations are needed to understand their potential.

8.5 Conclusions

In this chapter, I presented results where detailed process simulations of a PSA system have been combined with atomistic simulations to give realistic estimates of the performance of a material in a real gas separation system. Gas adsorption isotherms were determined from GCMC simulations for all MOFs from the CoRE database. After removing the most poorly performing materials, detailed process simulations were run on 1261 of the original 3468 CoRE MOFs using a grid search of process conditions. From this grid search, the 162 of the CoRE MOFs with the best PEs along with 49 materials with experimental adsorption data, were evaluated with the process simulations in more detail. More specifically, the process conditions of these materials were fully optimized with a genetic algorithm that I developed to either minimize the PE or maximize the productivity while maintaining the “95/90”-PRT of CO₂ capture. It was found that **IIERP-MOF2** was the best MOF for PoCCC when considering the balance of productivity and PE. With realistic estimates of a material’s performance from compute-intensive process simulations, we next tried to determine if any easily calculated metrics of a material could be correlated with its performance as determined by the detailed process simulations. A total of 90 metrics that included geometric and adsorption properties of a material and composite figures of

merit were examined. Using a Random Forrest classifier, a commonly used machine learning method, a classifier could not be constructed that could accurately predict if a material would meet the “95/90”-PRT based on the 90 metrics. Thus, all the commonly used metrics used to evaluate the performance of a material for CO₂ capture, are not good predictors of their real-world performance. As such, detailed process simulations need to be performed.

8.6 References

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8.7 Appendix

8.7.1 PSA Constant Parameters

Table 8.3. Parameters used in the PSA simulator

Parameter	Value	Unit
Column length	1	m
Inner column radius	0.1445	m
Outer column radius	0.1620	m
Column void fraction	0.37	-
Particle voidage	0.35	-
Tortuosity	3	-
Column wall density	7800	kg m ⁻³
Specific heat capacity of gas	1010.6	J kg ⁻¹ K ⁻¹
Specific heat capacity of adsorbent	1070	J kg ⁻¹ K ⁻¹
Specific heat capacity of adsorbed phase	1010.6	J kg ⁻¹ K ⁻¹
Specific heat capacity of column wall	502	J kg ⁻¹ K ⁻¹
Fluid viscosity	1.72 x 10 ⁻⁵	kg m ⁻¹ s ⁻¹
Molecular diffusivity	1.3 x 10 ⁻⁵	m ² s ⁻¹
Adiabatic constant	1.4	-
Effective gas thermal conductivity	0.09	J m ⁻¹ K ⁻¹ s ⁻¹
Thermal conductivity of column wall	16	J m ⁻¹ K ⁻¹ s ⁻¹
Inside heat coefficient	8.6	J m ⁻² K ⁻¹ s ⁻¹
Outside heat transfer coefficient	2.5	J m ⁻² K ⁻¹ s ⁻¹
Universal gas constant	8.314	m ³ Pa mol ⁻¹ K ⁻¹
Vacuum pump efficiency	72	%
Compressor efficiency	85	%
Flue gas pressure	1	bar
Ambient temperature	298.15	K

8.7.2 PSA Simulator Assumptions

The constitutive transport equations were obtained based on the following assumptions:

- Bulk gas flow was represented by the axially dispersed plug flow model
- Gas-phase obeys ideal gas law
- Particle size was assumed constant for all MOFs
- Solid-phase mass transfer was described using a linear driving force (LDF) model. Just as is the case for Zeolite-13X pellets. Mass transfer in the crystals is assumed to be fast and resistance is controlled by molecular diffusion in macropores.
- No radial gradients for concentration, temperature and pressure along the column
- Darcy's law accounts for frictional pressure drop along the column in the axial direction
- Thermal equilibrium exists between the gas-phase and solid-phase inside the column
- The outer surface of the column is maintained at a constant temperature and heat transfer occurs across the column wall
- The particle properties and bed voidage are uniform across the column

9 Conclusions and Future Work

9.1 Conclusions

All the work performed in this thesis was motivated by the general goal of aiding in materials discovery for gas adsorption and separation processes. This was done with the use of high-throughput screenings, concentrated case studies, and machine learning (particularly Genetic Algorithms). This work was done in a way to provide both high-performing “hit” materials as well as to provide a broader understanding of the performance of MOFs and other porous structures for use in gas storage and separation.

In Chapter 3, I investigated the gas storage and separation capabilities of the Computation Ready Experimental (CoRE)¹ database. The processes studied were vehicular methane storage (VMS), post-combustion carbon capture (PoCCC), and landfill gas separation (LGS). The gas adsorption properties, including uptakes, working capacities, selectivities, and parasitic energies (PEs) were calculated using results from Grand Canonical Monte Carlo (GCMC) simulations and REPEAT² partial atomic charges derived from Density Functional Theory (DFT). I found that only 2 MOFs were able to surpass the needed 0.5 g/g deliverable capacity target needed for VMS, and furthermore, no MOF was able to pass the volumetric target of 265 V_{STP}/V .³ The highest performing MOF from this screening had a volumetric uptake of 239 V_{STP}/V , which makes it the best performing MOF for this process to date. For PoCCC, although multiple gas adsorption properties could be considered, the main property of interest is the PE. The screening found that 68 CoRE MOFs have lower PEs than the benchmark MOF, Mg-MOF-74 (1028 kJ/kg CO₂), and 2417 MOFs outperformed a retrofitted liquid amine PoCCC (1327 kJ/kg CO₂) plant. Finally, in Chapter 3, the CoRE database was screened for LGS. The purity of the light stream is vital as the CH₄ will be utilized for a fuel source, so the screening examined both the purification energy (Pfe) and CH₄ purity of the light stream. Accounting for these two factors, it was found that a total of 2107 outperformed Zeolite-13X, which is currently used commercially for the process. A collection of 5 CoRE MOFs was identified that form a Pareto front CH₄ purity and Pfe. That means that these 5 MOFs can all be the top performer, depending on the trade-off of CH₄ and Pfe.

In Chapter 4, I studied carbon materials for both PoCCC and VMS. Only Carbon Nanoscrolls (CNSs) were studied for PoCCC, while CNSs, graphenes, and Schwarzites were studied for VMS. In the case of PoCCC, it was found that CNSs perform quite well after we optimized the type of

the CNS, the interlayer spacing, and the length of the scroll.⁴ Having a graphene-based CNS that had an interlayer spacing of 7 Å and having a 400 Å long scroll would give values of 7.7 mmol/g for uptake and 135 for selectivity. A boron nitride nanoscroll of similar lengths would have an uptake of 8.2 mmol/g and a CO₂/N₂ selectivity of 153. These values compare well with the high-performing MOFs and zeolites of Mg-MOF-74 and Zeolite-13X. Mg-MOF-74 had a 5.28 mol/g uptake and 122 CO₂/N₂ selectivity while Zeolite-13X had 2.5 mmol/g uptake and 114 CO₂/N₂ selectivity using similar conditions. CNSs with larger holes, such as α -graphyne, allowed for the quick uptake of gas in between the layers. When looking at VMS, CNSs were unable to meet the volumetric deliverable capacity set by the U.S. DoE.⁵ By optimizing the interscroll distance, interlayer distance, and packing style, graphene CNSs were found to give the highest CH₄ deliverable capacity of 252 V_{STP}/V. This could not outperform the best layered graphene (266 V_{STP}/V), although it was better than the best Schwarzite (150 V_{STP}/V). The deliverable capacities of CH₄ for both the optimized CNS and layered graphene are the highest for any material to the best of my knowledge. It should be noted, though, that for CNSs that the calculations did not include any pillars that would be needed to maintain the interlayer spacing. Considering this, the work of this chapter still helps push the limits of what is possible for VMS, since to the best of our knowledge this is the highest deliverable capacity found for any material. As some of these materials may be considered ideal CH₄ adsorption platforms, the DoE target of 330 V_{STP}/V may be unobtainable by any material.

In Chapter 5, I presented my work on creating a Split Charge Equilibration method⁶ (SQE-MEPO) specifically parameterized to reproduce the electrostatic potential fitted partial atomic charges in MOFs.⁷ SQE is a generalization of the popular Charge Equilibration (QEq)⁸ method that is known for rapidly generating charges for various purposes. The SQE method is just as rapid as the QEq method but should provide more “accurate” charges in part because it has more parameters that can be fit. This work is an extension of previous work done in the Woo lab creating a QEq parameter set for MOFs called MEPO (MOF Electrostatic-Potential Optimized).⁹ In the original MEPO work, only 11 parameters were optimized, whereas my work involved fitting an additional 37 parameters. Moreover, further improvements were made to the methodology by directly fitting the method to the DFT derived electrostatic potential. In the original MEPO methodology, charges were fit to the electrostatic potential generated from the REPEAT partial atomic charges. The new SQE-MEPO parameters were found to better reproduce the QM ESP,

with an average mean absolute deviation of 6.63 mHartree, compared to 9.96 mHartree for MEPO-QEq. The CO₂ adsorption values were then tested using the different charge calculation methods. It was found that the SQE-MEPO charges outperformed those of the MEPO method. More specifically, when comparing the CO₂ adsorption calculated using DFT derived REPEAT charges, SQE-MEPO gave a root mean squared deviation of 0.363 mmol/g for the validation set compared to the MEPO method which gave an RMSD of 0.466 mmol/g. When looking at the Spearman rank correlation coefficients, SQE-MEPO gave an $R^2 = 0.954$ compared to 0.900 for MEPO. In other words, SQE-MEPO can more accurately rank the order of the CO₂ adsorptions compared to MEPO.

Chapter 6 focused on examining a more holistic metric for evaluating the performance of MOFs for post-combustion CO₂ capture. The parasitic energy (PE) is a single figure of merit that estimates the energy required to capture the CO₂ using the material in a pressure swing or temperature gas separation unit and compress it to 150 bar for transport. In this chapter, the PEs of several materials were first examined using available experimental adsorption isotherm data. It was found that the material **IISERP-MOF2**, synthesized by the Ramanathan group at the Indian Institute of Science Education and Research (IISER) Pune, was found to have the lowest PE, with a value of 823.4 kJ/kg CO₂.¹⁰ The next lowest PE was that of mmen-CuBTTri (m-CuB) with 898.4 kJ/kg CO₂. The approach was then expanded by computationally screening the CoRE database of approximately 3500 MOFs and optimizing each material's desorption pressure to minimize the PE. It was found that no CoRE MOF outperformed **IISERP-MOF2**, although 23 MOFs outperformed m-CuB. A subsection of 581 MOFs from the CoRE database were functionalized in order to minimize their PE. Using a library of 28 common functional groups, 150,000 functionalized MOFs were constructed and evaluated for their CO₂ gas separation capabilities. Functionalization of the 581 parent MOFs lead to the PE of the materials dropping on average by 161 kJ/kg CO₂ or 14.3%. Functionalization identified 9 materials with PEs lower than **IISERP-MOF2**, with the lowest having a PE of 749 kJ/kg CO₂. It was found that the functional groups NH₂, OH, and HCO were commonly found functional groups in MOFs with the absolute lowest PEs.

In Chapter 7, I presented work on a genetic algorithm (GA) known as the Metal-Organic Framework Functional GA (MOFF-GA).¹¹ MOFF-GA is a program I developed to determine how to functionalize a MOF's pores in order to optimize a chosen property. Determining the best

functionalization of a material can be challenging because of the number of potential functional group combinations. For example, using a library of 30 functional groups, there are more than 800,000 unique functional group combinations available to a MOF with 4 unique functionalization sites. It was found that MOFF-GA could identify high performing functional group combinations without sampling all possible combinations. A test case was done where 22 MOFs with 3 to 5 functionalizable sites were each optimized a total of 1000 times. It was found that on average a single run of the GA would find the single best structure 74.9% of the time, with 27.6 of the top 50 functionalizations being recovered, while testing only 19.7% of the total structures. In practice, the GA would be run multiple times—up to 5 times for a single structure—which would increase all those statistics, as noted with FUNBEW-Br, which only found the single best structure 31% of the time. However, if the GA was run 5 times, that number would increase to 84%, with the number of structures sampled increasing from 3.8% to 16%. MOFF-GA was then applied to a total of 141 base MOFs (including 43 that were used for validation), and it was found that on average a MOF could increase its CO₂ adsorption by 340% through functionalization. When examining all of the functionalized MOFs constructed, 1035 were found to have exceptional CO₂ uptake at flue gas conditions (CO₂ uptake > 3 mmol/g). Of those 1035, 85% of the MOFs were found to have 3 or fewer functional groups, making them potentially synthetically viable. MOFF-GA showed potential to be an efficient way to tune porous structures for a given application.

Chapter 8 highlights work done in collaboration with the process engineering group of Dr. Arvind Rajendran at the University of Alberta. Here, our group's atomistic simulations of gas adsorption were integrated with the detailed process simulations of pressure swing adsorption (PSA) gas separation systems developed by the Rajendran group. This allowed us to perform detailed process optimizations on an unprecedented number of materials, which provide more accurate PE estimates. There was a total of 1632 materials screened where the various process conditions, such as the adsorption time and desorption pressure, were optimized in order to minimize the PE while maintaining the “95/90”- Purity Recovery Target (PRT). Following full process optimizations using a GA, only 202 materials were found to be able to meet the “95/90”- PRT with **IISERP-MOF2** having the lowest PE of all materials screened. Since the optimization of process conditions is very time consuming, we applied machine learning methods to determine if any common adsorption metrics or geometric features of a MOF could be used to predict if a

material would meet the “95/90”-PRT. Using a random forest decision tree machine learning model, an accurate classifier could not be constructed.

This suggests that full process simulations are required to properly assess the performance of a material for post-combustion CO₂ capture.

9.2 Future Work

In Chapter 3, I presented my work in screening the CoRE database for only 3 processes: VMS, PoCCC, and LGS. There are many other potential applications that the materials could be screened for, such as coal mine methane separation, nuclear reprocessing, oxyfuel separation or pre-combustion carbon capture to name a few. As this version of the CoRE database already has REPEAT partial atomic charges calculated for it, the results from additional screenings should be relatively quick while also giving high accuracy values.

Chapter 4 looked at gas storage and separation for CNSs and other carbon-based materials. In this work, we examined idealized materials in which the interlayer spacing was artificially fixed. However, in a real material, the interlayer distances would have to be maintained by pillars, such as ions or a particular size. Future work is needed to examine the gas adsorption where realistic models of the pillars are used. The pillars would have a complex effect on the gas adsorption properties, so finding the ideal linker would be a non-trivial task. After determining these linkers, experimentally validating the gas adsorption properties and studying for other properties of interest (like stabilities and kinetics) would be the next step.

SQE-MEPO parameters generated in Chapter 5 are a step forward from the previous QEq parameters but could still be refined. Future work regarding SQE-MEPO might be to apply atom typing to help refine the results. It was found in the Woo lab that MEPO did not appropriately work when it came to the SO₃H functional group, and so atom typing was employed where the oxygen and sulphur atoms of SO₃H were parameterized differently compared to if they were in other parts of the framework. Another potential avenue for future work is to look at developing SQE parameters for charged frameworks. An additional interesting avenue would be to apply SQE for charged materials. Charged materials made up approximately 10% of the unfiltered CoRE database, as well, there has been work done in the Woo lab to create a hypothetically charged MOF database. Applying high-throughput screening techniques like SQE would help better understand these systems. However, using SQE on charged frameworks may lead to complications as the

parameterized nature may lead to the charge becoming delocalized across a large portion of the structure.

Chapter 7 focuses on the development of a genetic algorithm (MOFF-GA) to optimize the functionalization of MOFs that was initially applied to identify high performing materials for post-combustion CO₂ capture. However, MOFF-GA can be applied to optimize MOFs for virtually any process as long as the property of interest can be computed. One process that is currently being investigated in the Woo lab is the optimization of MOFs for landfill gas separations, where CO₂ is removed from a methane-rich gas stream. It would be important to synthesize high performing materials in order to validate the methodology. As of writing this thesis, this is indeed being investigated by our experimental collaborators in the lab of Dr. Muralee Murugesu, with Gabriel Brunet and Dr. Shyamapada Nandi.

In Chapter 8, detailed process simulations of a PSA gas separation unit were performed. In a PSA system, the pressure is lowered to desorb the gas that is adsorbed by the MOF. It has been suggested that one could improve the efficiency of PoCCC by using heat generated by the power plant to desorb the gas, in what is called temperature swing adsorption (TSA). One important extension of the work initiated in this chapter would be to extend the detailed process simulations to a combined pressure and temperature swing adsorption system to explore the limits of using MOFs for energy efficient CO₂ capture.

In work presented in Chapter 8, process conditions were optimized to give the lowest PE of CO₂ capture. However, the PE only accounts for the operational costs, not the capital costs of CO₂ capture. Future work should scale up the simulations to industrially sized columns so that accurate estimates of the number of columns, pumps, and the amount of MOF required, can be determined. These quantities will then be used to calculate the capital costs and therefore to estimate total costs of CO₂ capture with MOFs. The work of Farooq, who has recently developed a framework for costing CO₂ capture in PSA systems, could be used as a starting point.¹² The ultimate goal is to identify existing materials or design new materials at the molecular level that are optimized for large scale PoCCC.

9.3 References

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