Chemistry 4P Project Plan

Project Title: Computational Screening of Metal-Organic Frameworks for Helium Recovery

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Introduction:

Helium is the 2nd most abundant element in the universe, existing as a colourless, inert, monoatomic gas. It has many different important applications in the real world, not all of them being obvious. For example, liquid helium is used as a cryogenic coolant in MRI and NMR, providing temperatures low enough for the superconducting magnets to function. In 2016, 30% of helium was used in MRI alone.[1] The gas also has key roles in many other fields. It is used in deep-sea diving air mixtures as it is non-toxic and has no narcotic effect like oxygen and nitrogen do. It is also used in welding as a shielding gas because of its inertness, and as a carrier gas in analytical techniques such as gas chromatography for the same reason.

However, despite helium's abundance in the universe, global supplies are dwindling. There are two reasons for this: the first is that helium is a non-renewable gas, meaning that once all of the Earth's natural reserves have been tapped the supply will run out. The second reason is that helium can easily escape containment due to its small size, and it costs up to several millions of dollars to buy a helium recycler to recapture the vented gas.[2] Once helium escapes containment it leaves the Earth's atmosphere, becoming lost in space forever. The severity of the issue was confirmed in 2017 when the European Union added helium to its list of critical raw materials.[3] Because of helium's many different applications, it is obvious that a shortage would cause many fields, including science and healthcare, to not be able to function normally.

The only useful method for producing helium is to extract it from specific natural gas fields, *i.e.*, those with a concentration greater than 0.3%. Helium is present in the air at concentrations of 0.0005% which is far too low to extract a meaningful quantity.[4] Conventional methods of helium extraction from natural gas fields involve cryogenic distillation. This process requires extremely low temperatures and high pressure in order to provide an environment suitable for the separation of residual gases like hydrogen and nitrogen. Therefore, it is expensive and requires the use of lots of energy.[4] New methods could be designed to extract helium from natural gas which make the extraction process more efficient.

Metal organic frameworks (MOFs) are increasing in popularity as a topic of research. These are crystalline materials made from organic and inorganic building blocks, formed through a process of molecular self-assembly. They are remarkable for their large internal surface area and for the ease of tuning their properties *e.g.* pore size. They have gained considerable attention as a molecule capable of adsorbing different gases such as CO_2.[5] The use of MOFs could be a promising solution to the helium shortage issue due to their high adsorption capacity, as well as their stability when compared to other adsorbents (such as zeolite).

Background

The traditional separation methods for helium recovery from natural gas – such as the most widely used, a cryogenic distillation process followed by pressure swing adsorption – are expensive and energy-intensive.[6] Hence, novel adsorption- or membrane-based separation methods are in demand and have been an active area of research in recent years.

Kadioglu and Keskin performed the first large-scale computational screening of the MOF membranes as the potential materials for He/CH_4 separation.[7] In their study, the adsorption and diffusion properties of helium and methane in 139 MOFs were examined via the grand canonical Monte Carlo (GCMC) and equilibrium molecular dynamics (EMD) simulations, considering both the single-component gas as well as the binary CH_4/He mixtures. Results were compared to the traditional polymer and zeolite membranes, where He selectivity of MOF membranes was found to be lower than most of the conventional membranes, but He permeability of MOF membranes was predicted to be much higher than those of the traditional materials. Three MOF membranes combining the high He selectivity and permeability were identified, suggesting a good alternative material for a membrane-based CH_4/He separation.

A year later, another study on the use of MOFs in helium recovery from natural gas emerged, focused this time mainly on the adsorbent-based approach.[8] 500 MOFs were subject to a several-step computational screening (including GCMC and EMD simulations), leading to 10 structures identified as exhibiting the best performance for the He/N_2 adsorption-based separation. The diffusion-based separation was also assessed, revealing the 10 best MOFs based on their membrane selectivity. Parameters studied included the geometrical properties, dilution and charge effects. The structure-property relationships which were established provided useful information on the desired pore size, helium void fraction and surface area of MOF materials.

Latest research on helium recovery also explores another class of materials – the zeolite-type ultra-thin MFI membranes. L. Yu et al. conducted an experimental study, evaluating the MFI membranes for the separation of equimolar CH_4/N_2/He mixture.[9] Experiments were carried out at different pressures and temperatures, and in all the studied conditions membranes were found to exhibit high separation factor and high flux.

Helium recovery from natural gas remains a very active area of research, and a topic in high demand. Pressing problems of helium deficit require novel solutions and approaches, and thorough studies of potential materials. The previously conducted studies assessed a maximum number of 500 structures which is a very limited number compared to the size of the MOF database and therefore, a study investigating a larger set of MOFs is essential.

Proposal:

This project plans to run a computational screening of MOFs from the Cambridge Structural Database (CSD) to search for suitable structures for the selective separation of helium gas over the main components of natural gas reserves, nitrogen and methane.[6] Several layers of calculations will be run to reduce the initial ~100,000 structures down to ~100 for closer analysis. Characteristics of the final set will be investigated to determine the features of a MOF that may indicate good preferential helium separation. This will build upon previous work done by Zarabadi-Poor and Marek by increasing vastly the number of MOFs analysed by orders of magnitude.[8]

MOFs that cannot physically adsorb natural gas molecules will be initially screened out by calculating pore window sizes and volumes, and other confounding factors such as solvent molecules occupying pores in the crystal structures. These calculations will be performed through the Python scripts that access the CSD for MOF structures.

Widom insertion calculations[10] will be performed to determine each MOF's Henry's constants for helium, nitrogen and methane, to approximate adsorptive behaviour for each MOF that passes through the first phase of calculations. Time permitting, GCMC simulations[11] will be performed to calculate full isotherms for the best performing MOFs.

All calculations will be run from the ECDF Linux Compute Cluster (Eddie) supercomputer[12] due to the strenuous computational requirements for processing a dataset as large as the Cambridge Structural Database. Results will be compared with the 2019 paper from Zarabadi-Poor and Marek[8] using similar methods on a smaller dataset to both check for concordance and potentially to find helium separating MOF structures that were not previously characterised.

Results from calculations will also be compared to literature experimental results, when possible, through use of the NIST database of novel and emerging adsorbent materials (DNEM)[13]. This database contains isotherms and information on the adsorbent properties of a range of MOFs, and can provide empirical backing to support any observations made from our simulations.

Additionally, MOF properties relevant to their thermal stability will be investigated to identify potential problems with industrial use of the most highly selective MOFs. Factors that may cause a MOF to break down or otherwise not function in the conditions required for bulk helium production will be identified. From this, a final check can be performed on the MOFs from

calculation to determine their viability in replacing existing helium producing systems. Those to be investigated include the presence of solvent molecules in the MOF structures and the average bond strengths.

The environmental cost to the production of high selectivity MOFs will also be investigated against current helium production to further prove or disprove their potential viability. To accomplish this, each element will be given a range of parameters - including financial cost, geographic source and toxicity - that estimate the environmental impact and MOFs will thus be judged based on a score produced from their composition.

Resources required

The Eddie supercomputer will be used to perform Monte Carlo simulations, implemented in the RASPA suite of codes, eg. computing Henry's constants via the Widom insertion method in RASPA. This High performance computing (HPC) facility consists of over 7000 Intel® Xeon® cores with up to 3 TB of memory available on a single computer node. The CSD will provide the dataset of the MOFs studied (over 100,000 MOFs) and data allowing to calculate their properties such as pore volumes, densities, surface areas, limiting pore diameters (LPDs) and largest cavity diameters (LCDs). The NIST website provides data on different adsorbent/adsorbate isotherms to compare computational results with experimental ones. For the best-performing MOFs, GCMC simulations will also be performed to obtain the full adsorption isotherm data.

Cost per core hour: £0.02.

The Eddie supercomputer has 7,000 cores but only one will be used.

Assuming an estimated time of a week processing time (50 hours), approximate cost would be: £1.00.

Organisation

Task	Name	5	6	7	8	9	10
Pre-selection of MOFs for further study (based on pore size, solvent content, void space etc.)	W						
Henry's constant calculation for the pre-selected MOFs in the CCDC using the Widom insertion method	W, A						
Comparison of predictions of molecular simulations with the experimentally available data for He adsorption isotherms of several MOFs	A						
Calculation of the amount of gas adsorbed for selected MOFs (based on Henry's constant calculations) using GCMC simulations	W, A						
Determination of the best-performing MOFs for He recovery based on calculations	W, A						
Comparison of calculated best-performing MOFs with the literature	A						
Determining the structure-property relationship for the best-performing MOFs reported in the literature	W						
Study of the structure-property relationship of best-performing MOFs found and comparison with the literature	W, A						
Writing of a code to allocate an environmental score to each MOF based on their elemental composition	J						

Writing of a code to allocate a financial cost to each MOF based on their elemental composition	S						
Computation of the best-performing MOFs into the code to plot their cost vs environmental impact vs effectiveness	J, S						
Writing a code to estimate the stability of MOFs (eg. solvent content, bond strength)	J, S						
Computation of the best-performing MOFs for He recovery to assess their stability	J, S						

References

1. J.E. Hamak, *U.S. Department of the Interior, U.S. Geological Survey, Minerals Yearbook,* 2016.
2. *Helium should be recycled*, Nature, 2017, **547**, 6.
3. A. King, *Helium and rubber added to EU critical raw materials list,* RSC Chemistry World, 2017 (accessed Oct 04, 2022).
4. A. J. Kidnay and W. Parrish, *Fundamentals of Natural Gas Processing*, CRC Press, Boca Raton, FL, 2019.
5. T. Jia, Y. Gu, F. Li, *J. Environ. Chem. Eng*, 2022, 10.
6. T. E. Rufford, K. I. Chan, S. H. Huang and E. F. May, *Adsorp. Sci. Technol.*, 2014, **32** (1), 49-72.
7. O. Kadioglu and S. Keskin, *Sep. Purif. Technol.*, 2018, **191**, 192-199.
8. P. Zarabadi-Poor and R. Marek, *J. Phys. Chem. C*, 2019, **123**, 3469-3475.
9. L. Yu, B. Mayne, M. S. Nobandegani, T. Grekou and J. Hedlund, *J. Membr. Sci.*, 2022, **644**, 120113.
10. K. Binder, *Rep. Prog. Phys.*, 1997, **60**, 487-559.
11. D. J. Adams, *Mol. Phys.*, 1975, **29 (**1), 307-311.
12. Edinburgh University Information Services, https://www.ed.ac.uk/information-services/research-support/research-computing/ecdf/high-performance-computing, (accessed October 2022).
13. National Institute of Standards and Technology database of novel and emerging adsorbent materials, https://adsorption.nist.gov/isodb/index.php#home, (accessed October 2022).