**Chemistry 4P Project Plan**

**Project Title:** Adsorption-based approach to Helium Recovery from Natural Gas using Metal-Organic Frameworks: A Computational Screening  
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1. Introduction (approx. 500 words)

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. The first reason is that helium is a non-renewable gas, meaning that the supply will run out once all of the Earth’s natural reserves have been tapped. The second reason is that once helium has escaped containment, it leaves the Earth’s atmosphere, becoming lost in space. It often does so due to its small size and the high financial cost of buying a recycler for the vented gas – up to several millions of dollars.3 The severity of the issue was confirmed in 2017 when the European Union added helium to its list of critical raw materials.4 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. To add to this issue, the global demand for helium is expected to rise while the production capacity has reached its limit.

The only useful method for producing of helium is to extract it from specific natural gas fields, i.e., those with a concentration greater than 0.3% are considered economic for extraction. Helium is present in the air at concentrations of 5 ppm,however this concentration is too low to extract a meaningful quantity.5 Conventional methods of helium extraction from natural gas fields involve cryogenic distillation. This process is cost- and energy expensive, requiring extremely low temperatures and high pressure in order to provide an environment suitable for the separation of residual gases like hydrogen and nitrogen.5 New methods designed to extract helium from natural gas in a more efficient process are therefore needed.

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 have gained attention as a molecule capable of adsorbing different gases such as CO­2.6The use of MOFs could be a promising solution to the helium shortage issue.

**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*, **10**, 2022

2. Background (approx. 500 words)

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. Hence, novel adsorption- or membrane-based separation methods are in demand and have been an active area of research in recent years.1

Kadioglu and Keskin performed the first large-scale computational screening of the MOF membranes as the potential materials for He/CH4 separation. In their study, the adsorption and diffusion properties of helium and methane in 139 MOFs were examined *via* the grand canonical Monte Carlo and equilibrium molecular dynamics simulations, considering both the single-component gas as well as the binary CH4/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 CH4/He separation.2

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. 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/N2 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 a useful information on the desired pore size, helium void fraction and surface area of MOF materials.3

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 CH4/N2/He mixture. 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. A maximum separation factor of 152 was observed at temperature of 153 K, a feed pressure of 3 bar, and a permeate pressure of 0.2 bar.4

Helium recovery from the 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.

**References:**

1. T. E. Rufford, K. I. Chan, S. H. Huang and E. F. May, *Adsorp. Sci. Technol.*, 2014, **32** (1), 49-72.
2. O. Kadioglu and S. Keskin, *Sep. Purif. Technol.*, 2018, **191**, 192-199.
3. P. Zarabadi-Poor and R. Marek, *J. Phys. Chem. C*, 2019, **123**, 3469-3475.
4. L. Yu, B. Mayne, M. S. Nobandegani, T. Grekou and J. Hedlund, *J. Membr. Sci.*, 2022, **644**, 120113.

3. Proposal (approx. 500 words)

This project plans to run a computational screening of metal organic frameworks (MOFs) from the Cambridge Structural Database (CSD) to search for suitable structures for the selective adsorption of helium gas over the main components of natural gas reserves, nitrogen and methane.1 Several layers of calculations will be run to reduce the initial ~100000 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.

MOFs that cannot physically adsorb helium 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.

Grand Canonical Monte Carlo simulations2 will be performed through RASPA2 to determine the Henry’s constant for helium, nitrogen and methane adsorption into each MOF that passes through the first phase/s of calculations. These will/may also be performed to determine constants for other noble gases or gases present in natural helium-containing deposits such as ethane and water.

All calculations will be run from the Eddie supercomputer3 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 Marek4 using similar methods on a smaller dataset to both check for concordance and potentially to find helium adsorbing 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)5. 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 helium 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 and from this, a final check can be performed on the MOFs from calculation to determine their viability in replacing existing helium producing systems. 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.

**References:**

1. T. E. Rufford, K. I. Chan, S. H. Huang and E. F. May, Adsorptive Science and Technology, 2014, 32, 1, 49-72
2. D. J. Adams, Molecular Physics, 1975, 29, 1, 307-311
3. Edinburgh University Information Services, https://www.ed.ac.uk/information-services/research-support/research-computing/ecdf/high-performance-computing, (accessed October 2022)
4. P. Zabradi-Poor and R. Madek, Journal of Physical Chemistry, 2019, 123, 6, 3469-3475
5. National Institute of Standards and Technology database of novel and emerging adsorbent materials, https://adsorption.nist.gov/isodb/index.php#home, (accessed October 2022)

4. Resources required

The ECDF Linux Compute Cluster (Eddie) supercomputer will be used to perform grand canonical Monte Carlo (GCMC) simulations, implemented in the RASPA suite of codes. Theis High performance computing (HPC) facility consists of over 7000 Intel® Xeon® cores with up to 3 TB of memory available on a single compute node. They will be used to compute adsorption isotherms of various gases in different MOFs. The Cambridge Structural Database (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). They will allow to study the API (Absorbance Performance indicator) of various MOFs structure, based on their selectivity, working capacity, and adsorption enthalpy. The NIST website provides data on different adsorbent/adsorbate isotherms to compare computational results with experimental ones. Henry’s constants will be computed using the Widom insertion method in RASPA.

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

The data costs £175.00 per TB. It is estimated that 50GB will be used. This will amount to roughly £8.75 spent on storage.

5. Organisation

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| **Task** | **Name** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
| 1. Project plan draft | W, A, J, S |  |  |  |  |  |  |  |  |  |  |
| 2. Project plan final | W, A, J, S |  |  |  |  |  |  |  |  |  |  |
| 3. Analysing the best-performing MOFs for He/N2 separation given in the literature |  |  |  |  |  |  |  |  |  |  |  |
| Pre-selection of MOFs for further study (based on pore size, solvent-free structures etc.) |  |  |  |  |  |  |  |  |  |  |  |
| Calculation of pore volumes, densities, surface areas, limiting pore diameters (LPDs) and largest cavity diameters (LCDs) of pre-selected MOF structures |  |  |  |  |  |  |  |  |  |  |  |
| Comparaison with the MOFs from the literature, finding similarities/differences |  |  |  |  |  |  |  |  |  |  |  |
| Computation of Henry's constants using the Widom insertion method for pre-selected MOFs |  |  |  |  |  |  |  |  |  |  |  |
| Comparaison of predictions of molecular simulations with the experimentally available data for He permeability of several MOF membranes |  |  |  |  |  |  |  |  |  |  |  |
| Sustainability analysis to determine stability under extraction conditions (pressure, temperature) |  |  |  |  |  |  |  |  |  |  |  |
| Calculation of the selectivity, working capacity, and adsorption enthalpy of pre-selected MOFs |  |  |  |  |  |  |  |  |  |  |  |
| Calculation of the different API for pre-selected MOFs |  |  |  |  |  |  |  |  |  |  |  |
| Calculation of the amount of gas adsorbed using grand canonical Monte Carlo (GCMC) simulations |  |  |  |  |  |  |  |  |  |  |  |
| Identification of the best-performing MOFs for He separation from natural gases based on computational data aquired |  |  |  |  |  |  |  |  |  |  |  |
| Study of the structure/property relationship of best-performig MOFs |  |  |  |  |  |  |  |  |  |  |  |
| Study of the recovery of He after separation |  |  |  |  |  |  |  |  |  |  |  |
| Environmental impact of best-performing MOFs synthsis and usage |  |  |  |  |  |  |  |  |  |  |  |
| Comparaison of the selectivity of the MOFs vs traditionally used adsorbants |  |  |  |  |  |  |  |  |  |  |  |
| Comparaison of the financial and energy cost of using the identified best-performing MOFs |  |  |  |  |  |  |  |  |  |  |  |

6. Appendices