Computer-aided material and process design for ethylene purification from C₂ hydrocarbons

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Abstract

Being a fundamental part of the modern society, the chemical industry produces important chemicals demanded by many downstream industries. However, its production consumes huge amount of energy which takes up approximately 40% of all the industrial energy consumption. For a greener and more sustainable future, the chemical industry must prioritize the development and adoption of innovative technologies and practices aimed at reducing energy consumption and mitigating environmental impact.

As one of the pillars in chemical industries, ethylene (C_2H_4) production has great significance. Despite its small molecular size, ethylene is a valuable basic chemical commodity often used as a precursor for the production of many other important chemicals such as polymers, ethylene oxide, ethylene glycol, etc. Steam cracking is the most widely used ethylene production process. However, steam cracking involves separation processes under harsh and extreme conditions making the production very energy intensive. For instance, cryogenic distillation used to separate C₂ hydrocarbons (C₂H₂, C₂H₄, and C₂H₆) has exceptionally high capital investment and refrigeration energy consumptions. These can be attributed to the C₂ hydrocarbons separation difficulties arise from the molecular similarities and low boiling points (189 K, 170 K, and 184 K), respectively.

Alternatively, novel advanced adsorbent materials metal-organic frameworks (MOFs) displaying high tuneablity and delicately designed molecular binding affinities have emerged, offering a chance to develop new energy efficient separations pathways for C₂ separations. Having been tested at the lab scale, some MOFs (such as TJT-100, NPU-1/2/3, and PCP-FDCA) present excellent adsorptive separation abilities for the simultaneous removal of the ethane and acetylenes impurities from C₂ mixture to obtain polymer grade ethylene product. From the perspective of process intensification in chemical engineering,

one step adsorptive purification is certainly advantageous because it has the energy saving potentials through the integration of multiple adsorption units.

Unfortunately, the iterative and time-consuming experimental processes gravely slow the discovery processes of novel MOF materials. To overcome the obstacle, researchers have employed high-throughput screenings with the aid of computers to assist the discovery process of new materials. High-throughput screening enables a quickly and accurately identification of promising MOF adsorbents with outstanding separation potentials among millions of candidates.

However, high throughput screening is incapable of providing information regarding the process applicability (e.g. in pressure swing adsorption (PSA) processes) of the promising MOFs. Because the high-throughput screening used in most of the previous studies are based on molecular and phase properties. To address the issue, the research paradigm has shifted to the process-performance-based high-throughput screening with a focus on a comprehensive performance evaluation. The key idea is to conduct a multiscale material study not only at the molecular and phase scale but also at the process scale to estimate process feasibility simultaneously. This can be achieved by the incorporation of process modelling into the high-throughput screening framework.

This thesis presents a systematic computational study on the selection of MOFs as adsorbents for ethylene purification from C_2 hydrocarbons. It is structured as follows: Chapter 1 provides a detailed introduction of relevant background knowledge and a review of the state-of-the-art research progress. In Chapter 2, we investigate 4764 MOFs candidates in the experimental validated MOF database at the molecular scale by a high-throughput screening study. A modified evaluation metrics is proposed for an efficient description of the performance of MOFs for the C_2 ternary mixture separation. Accordingly,

two different schemes are proposed, and the best performing MOF adsorbents are identified. The quantitative relationships between MOF structures and adsorption abilities are unveiled. In Chapter 3, we then move on to examine the process feasibility of MOFs in pressure/vacuum swing adsorption processes (P/VSA) through a process performancebased screening study. By combining property-based (selectivity and regenerability) material screening, breakthrough simulation, and P/VSA process optimization, we demonstrate not only the suitability of MOFs for one-step C₂H₄ purification but also their practical applicability in P/VSA processes. The results show that out of the 4764 CoRE MOF candidates, seven MOFs outperform the benchmark TJT-100 in both C₂H₄ purity and recovery for the $5/90/5 C_2H_2/C_2H_4/C_2H_6$ feed mixture. Among the 7 MOFs, OFUCAV has the highest C₂H₄ productivity of 0.158 mol/m³/s and JAVTAC shows the lowest energy consumption of 42.76 kWh/ton C₂H₄, which saves roughly 80% of the cryogenic distillation energy. Moreover, the selected MOFs show better robustness than the benchmark in response to fluctuations of feed composition of the C2 mixture. In Chapter 4, we conclude and summarize the major findings of the thesis and discussed some of the future research directions for MOFs design.

Zusammenfassung

Als fundamentaler Bestandteil der modernen Gesellschaft produziert die chemische Industrie wichtige Chemikalien, die von vielen nachgelagerten Branchen nachgefragt werden. Ihre Produktion verbraucht jedoch eine enorme Menge an Energie, die etwa 40% des gesamten industriellen Energieverbrauchs ausmacht. Für eine grünere und nachhaltigere Zukunft muss die chemische Industrie die Entwicklung und Einführung innovativer Technologien und Verfahren zur Reduzierung des Energieverbrauchs und zur Minderung der Umweltauswirkungen priorisieren.

Die Ethylen (C₂H₄)-Produktion hat als einer der Eckpfeiler der chemischen Industrien große Bedeutung. Trotz ihrer geringen molekularen Größe ist Ethylen eine wertvolle Grundchemikalie, die oft als Vorläufer für die Herstellung vieler anderer wichtiger Chemikalien wie Polymere, Ethylenoxid, Ethylenglykol usw. verwendet wird. Der Steam-Cracking-Prozess ist die am weitesten verbreitete Methode zur Ethylenproduktion. Allerdings umfasst das Steam Cracking Trennverfahren unter extremen Bedingungen, was die Produktion sehr energieintensiv macht. Zum Beispiel erfordert die kryogene Destillation zur Trennung von C₂-Kohlenwasserstoffen (C₂H₂, C₂H₄ und C₂H₆) außergewöhnlich hohe Investitionen in Anlagen und verursacht hohe Kosten des Energieverbrauchs für die Kühlung. Diese Schwierigkeiten bei der Trennung von C2-Kohlenwasserstoffen können auf die molekularen Ähnlichkeiten und die niedrigen Siedepunkte (189 K, 170 K bzw. 184 K) zurückgeführt werden.

Alternativ sind neuartige Adsorptionsmaterialien, sogenannte Metall-organische Gerüststoffe (MOFs), mit hoher Anpassungsfähigkeit und sorgfältig gestalteten molekularen Bindungsaffinitäten verfügbar, die die Möglichkeit bieten, neue energieeffiziente Wege für C₂-Trennungen zu entwickeln. Einige MOFs (wie TJT-100,

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NPU-1/2/3 und PCP-FDCA) haben sich im Labormaßstab als ausgezeichnete adsorptive Trennungsmaterialien für die gleichzeitige Entfernung von Ethan- und Acetylen-Verunreinigungen aus der C₂-Mischung zur Herstellung von Ethylen in Polymerqualität erwiesen. Aus der Sicht der Prozessintensivierung in der Chemietechnik ist eine einstufige adsorptive Reinigung sicherlich vorteilhaft, da sie Potenziale zur Energieeinsparung durch die Integration mehrerer Adsorptionseinheiten hat.

Leider verlangsamen iterative und zeitaufwändige experimentelle Prozesse die Entdeckung neuer MOF-Materialien erheblich. Um dieses Hindernis zu überwinden, haben Forscher Hochdurchsatz-Screenings unter Einsatz von Computern zur Unterstützung des Entdeckungsprozesses neuer Materialien eingesetzt. Hochdurchsatz-Screening ermöglicht eine schnelle und genaue Identifizierung vielversprechender MOF-Adsorbentien mit herausragenden Trennpotenzialen unter Millionen von Kandidaten.

Jedoch ist ein Hochdurchsatz-Screening nicht in der Lage, Informationen zur Prozessanwendbarkeit (z. B. in Druckwechseladsorptionsprozessen (PSA)) der vielversprechenden MOFs bereitzustellen. Denn das Hochdurchsatz-Screening, das in den meisten früheren Studien verwendet wurde, basiert auf molekularen und phasenbezogenen Eigenschaften. Um das Problem zu adressieren, hat sich das Forschungsparadigma hin zu einem prozessleistungsorientierten Hochdurchsatz-Screening mit Fokus auf einer umfassenden Leistungsbewertung verschoben. Die Schlüsselidee besteht darin, eine mehrskalige Materialstudie nicht nur auf molekularer und phasenbezogener Ebene, sondern auch auf prozessualer Ebene durchzuführen, um die Prozessfähigkeit gleichzeitig abzuschätzen. Dies kann durch die Integration von Prozessmodellierung in das Hochdurchsatz-Screening-Framework erreicht werden.

Diese Arbeit präsentiert eine systematische computergestützte Untersuchung zur Auswahl

von MOFs als Adsorbentien zur Ethylenreinigung von C2-Kohlenwasserstoffen. Sie ist wie folgt strukturiert: Kapitel 1 bietet eine detaillierte Einführung in relevante Hintergrundkenntnisse und eine Überprüfung des aktuellen Forschungsstandes. In Kapitel 2 untersuchen wir 4764 MOF-Kandidaten in der experimentell validierten MOF-Datenbank auf molekularer Ebene durch eine Hochdurchsatz-Screening-Studie. Es wird eine modifizierte Bewertungsmetrik für eine effiziente Beschreibung der Leistung von MOFs für die Trennung von C2-Ternärgemischen vorgeschlagen. Dementsprechend werden zwei verschiedene Schemata vorgeschlagen, und die am besten abschneidenden MOF-Adsorbentien werden identifiziert. Die quantitativen Beziehungen zwischen MOF-Strukturen und Adsorptionsfähigkeiten werden aufgedeckt. In Kapitel 3 gehen wir dann dazu über, die Prozessfähigkeit MOFs von in Druck-/Vakuumwechseladsorptionsprozessen (P/VSA) durch eine prozessleistungsorientierte Screening-Studie zu untersuchen. Durch die Kombination von eigenschaftsbasiertem (Selektivität und Regenerierbarkeit) Material-Screening, Durchbruchsimulation und P/VSA-Prozessoptimierung zeigen wir nicht nur die Eignung von MOFs für die einstufige C₂H₄-Reinigung, sondern auch ihre praktische Anwendbarkeit in P/VSA-Prozessen. Die Ergebnisse zeigen, dass von den 4764 CoRE-MOF-Kandidaten sieben MOFs den Benchmark TJT-100 sowohl in Reinheit als auch Ausbeute für das 5/90/5 C₂H₂/C₂H₄/C₂H₆-Feedgemisch übertreffen. Unter den 7 MOFs hat OFUCAV die höchste C₂H₄-Produktivität von 0,158 mol/m³/s und JAVTAC zeigt den niedrigsten Energieverbrauch von 42,76 kWh/ton C₂H₄, was etwa 20% des kryogenen Destillationsprozesses entspricht. Darüber hinaus zeigen die ausgewählten MOFs eine hohe Robustheit gegenüber Schwankungen der Zusammensetzung des C2-Gemischs. In Kapitel 4 ziehen wir Schlussfolgerungen und fassen die wichtigsten Erkenntnisse der Arbeit zusammen und diskutieren einige zukünftige Forschungsrichtungen für das Design von MOFs.

Preface

A list of publications connected with this dissertation is given below. The following thesis takes results and approaches from these works, as indicated accordingly.

Chapter 1 section is partially taken from the proceedings chapter of Zhou et al.¹

Chapter 2 on the high-throughput computational screening of metal-organic frameworks for ethylene purification from ethane/ethylene/acetylene mixture is taken from Zhou et al.²

Chapter 3 on the multiscale screening of metal-organic frameworks for one-step ethylene purification in pressure swing adsorption processes is taken from Zhou et al.³

Proceedings chapters used in this dissertation:

[1] <u>Y. Zhou</u>, T. Zhou, K. Sundmacher, In silico screening of metal-organic frameworks for acetylene/ethylene separation, in: S. Pierucci, F. Manenti, G.L. Bozzano, D. Manca (Eds.) *Comput. Aided Chem. Eng.*, Elsevier, 48 (2020):895-900.

Contribution: conceptualization of the study; preparation of software; data analysis, visualization of the data; writing and editing of the draft.

Journal articles used in this dissertation:

[2] <u>Y. Zhou</u>, X. Zhang, T. Zhou, K. Sundmacher, Computational screening of metalorganic frameworks for ethylene purification from ethane/ethylene/acetylene mixture, *Nanomaterials*, 12 (2022):869.

Contribution: conceptualization of the study; preparation of software; data analysis, visualization of the data; writing and editing of the draft.

[3] <u>Y. Zhou</u>, X. Cao, J. Shang, K. Sundmacher, T. Zhou, Multiscale screening of metalorganic frameworks for one-step ethylene purification in pressure swing adsorption processes, *AIChE J.*, 70 (2024):e18544. Contribution: conceptualization of the study; preparation of software; data analysis, visualization of the data; writing and editing of the draft.

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1. Background

The chemical industry has an annual turnover of \$5.7 trillion, approximately 7% of the global GDP as of 2020.³ Its energy usage is even more significant which consumes around 40% of industrial energy. This highlights a pressing need for enhanced energy efficiency and sustainability in chemical industry, as this energy demand constitutes roughly 15% of global energy consumption³ and projections indicate a threefold surge in demand for chemical products by 2050.⁴ The primary contributor to the energy footprint in petroleum chemicals product is the reliance on energy-intensive purification technology, notably cryogenic separation. For a greener and more sustainable future, the chemical industry must prioritize the development and adoption of innovative separation and purification technologies and practices aimed at reducing energy consumption and environmental impact.

1.1. Ethylene production and purification

The production of ethylene (chemical formula C_2H_4) is a crucial process in the petrochemical industry, as three-fourths of petrochemical products are derived from it. The annual production amount in the European union (EU) sums up to around 20,000 kiloton/year (Figure 1-1). Ethylene is a versatile building block for manufacturing many chemicals products. For instance, polyethylene is one of the most widely produced and used plastics globally (Figure 1-1), ethylene dichloride for the manufacture of polyvinyl chloride (PVC) which is another important class of plastics, ethylene oxide which is a widely used medical equipment sterilant, *etc.* Figure 1-1 depicts the annual ethylene production in the EU of the past decades and summarizes downstream chemicals derived from ethylene with their respective market shares.



Figure 1-1: (Top) Ethylene nameplate capacity, production, consumption in EU 15 + Norway + as of 2020 Hungary & Slovakia chart, Turkey is included in 2015 & 2016 data; (Bottom) Ethylene consumption by derivatives in EU15 + Norway + as of 2020
Hungary & Slovakia, LDPE: 25%, LLDPE: 14%, HDPE: 22%, EB: 6%, EO: 12%, EDC: 14%, Others (ethanol, acetaldehyde, EPDM, EVA, VAM & other derivatives): 7%,

adopted from ⁵

Steam cracking is by far the most common technology for ethylene production which involves the thermal decomposition of hydrocarbons in the presence of high temperatures steams. Primary feedstocks for ethylene production are naphtha, ethane, propane, or natural gas liquids, typically obtained from crude oil refining or natural gas processing. These feedstocks are first pretreated and then heated to very high temperatures (typically 750-950°C) in a cracking furnace along with steam. In the furnace, long-chain hydrocarbons break down into smaller molecules, such as ethylene and other valuable by-products. The cracked gas streams exiting the furnace are rapidly cooled and quenched to prevent further side reactions and to stabilize the product stream. The cooled gas streams undergo a series of separation steps so that the target ethylene product can be obtained.

The separation of ethylene from cracked gas streams is a complex process which requires significant energy consumption. Proper sequencing of distillation columns in the separation section affects the consumption of cooling energy and column operating conditions. According to the literature,^{6,7} there are three column sequencing methods for the separation of light olefins from cracked gas: front-end demethanizer, front-end deethanizer, and front-end depropanizer. The first two sequences are very common in the olefin plant separation section and the third method is relatively rare.

In the front-end demethanizer sequencing, demethanizer is the first separation column, as it is shown in Figure 1-2. After drying and chilling, the stream contains a mixture of H₂, CO, and CH₄. The mixture stream is separated first by PSA units to produce high purity H₂. A part of the H₂ product can be used later in the partial hydrogenation of acetylene unit to produce ethylene. The remaining gas mixture (the majority is CH₄) from the top of the demethanizer is recycled back to the furnace as a fuel gas for the burners. The stream coming out of the bottom of the demethanizer column contains heavier hydrocarbons including ethane (C₂H₆), ethylene (C₂H₄) and acetylene (C₂H₂) and C₃₊ components. The

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separation column. The top stream of the deethanizer is sent to the partial hydrogenation reactor to convert acetylene to ethylene and ethane and then loops back to the C_2 splitter for the separation of ethane from the ethylene. Similarly, the bottom stream of the deethanizer column goes into the depropanizer column in which C_3 are separated from C_{4+} components. Propylene and propane are sent to the C_3 splitter and propylene is purified from propane which comes out of the bottom end of the splitter column and is recycled back to the furnace as a fuel gas. In the same manner, C_{4+} stream continues to be forwarded to the debuthanizer column in which a C_4 cut from C_{5+} components can take place. This column sequence is typical in the cracking of liquid hydrocarbons such as light and heavy naphtha and gasoil. However, in the case of ethane cracking, some of the separation sequence due to the presence of lighter products.

In contrast, deethanizer is the first separation column in the front-end deethanizer column sequencing. In such sequencing CO, H₂, CH₄, as well as C₂ is cut from the C₃₊ components. The top stream of the deethanizer column is sent to the demethanizer column where CO, H₂ and CH₄ are separated from C₂. The rest of the column sequence is similar to the front-end demethanizer sequencing. The advantages of this sequencing over the previous one are less cooling energy consumption, lower column height and therefore less capital costs, and less fouling in the column due to relatively lower operating pressures which can prevent undesirable polymerization.



Figure 1-2: The conventional block flow diagram of naphtha cracking olefin plants. Orange box are the cracking related processes steps, and the trapezoid shape represents a compressor. Blue box are the hydrocarbon separation processes and rectangles denote distillation columns with inlet steams coming in from the middle of the tower and outlet streams coming out of the top and bottom of the column. The red line highlights the C_2 separator and the produced C_2H_4 . The figure is adopted from the literature^{6,7}

In both sequences, the splitting of C_2 hydrocarbons is the key problem. Due to the fact that C_2H_4 has a very low boiling point (169.5 K), the current practice for the design of C_2 splitter uses primarily cryogenic distillation. As a separation/purification unit operation, cryogenic distillation performs the separation of gas/liquid mixtures by exploiting vapor-liquid equilibrium under extremely low temperature. The extremely low temperature means huge refrigeration energy consumption, thus making it a very energy demanding separation/purification technology. On top of that, the low relative volatility between ethane and ethylene (which is about 1.2, due to molecular similarities) makes the splitting even more energy intensive. As is known, distillation separation difficulties arise significantly as relative volatility approaches 1. For the C_2 splitting, a large number of distillation trays and high reflux ratios are required, which are also contributors to the

increase of total energy consumption. The separation of ethylene from cracked gas consumes approximately 15% to 20% of the entire ethylene production process energy.⁸ The removal of C_2H_2 from ethylene product is the other challenge. Because C_2H_2 can irreversibly deactivate catalysts in downstream processes. For example, during stereoregular polymerization of ethylene, it rapidly poisons the Ziegler-Natta catalysts therefore sharply decreases the productivity of polyethylene. Current state-of-the-art method for the removal of C_2H_2 is catalytic selective hydrogenation. In selective acetylene hydrogenation, there are two major competing reaction pathways: hydrogenation to produce ethylene/ethane and oligomerisation leading to the formation of 1,3-butadiene and larger hydrocarbons.⁹ Ideally by the design of suitable catalysts which promote the former reaction pathway while inhibit the latter, acetylene can be removed. However, the synthesis of high selective catalyst remains a great challenge. Especially, how to prevent the formation of 'green oil' which generally results in catalyst deactivation due to hydrocarbon accumulation on the catalyst surface¹⁰ still needs to be further studied.

To address the difficulties in C₂ splitting, we propose a one-step direct purification of ethylene from C₂H₄ and C₂H₆ using physical adsorption as an alternative to the current energy intensive hydrogenation/cryogenic distillation strategy. Such strategy is attractive for (i) it is a process intensification eliminating the need of additional reactor design by replacing the reaction-separation with one combined single separation unit. (ii) Adsorptive separation becomes competitive when the relative volatility of the key components is less than about 1.25.¹¹ For purification systems involving light gases, adsorption is generally considered more favorable than distillation in terms of energy efficiency and total costs.¹¹ By switching distillation-reaction to adsorption separation, potential energy consumption can be saved. However, such objective is only achievable with a suitable adsorbent materials selection as well as processes design.

1.2. Gas separation via adsorption

Adsorption is a surface phenomenon where gas molecules are attracted and adhere onto the surface of a solid material. This attraction occurs due to various forces such as van der Waals forces, electrostatic interactions, or chemical bonding between the gas molecules and the surface of the solid. The former two types of interactions can be categorized as physical adsorption while the latter involving electron transfer is considered chemical adsorption or chemisorption. Similar to distillation, the fundamental mechanism of adsorption is the principle of thermodynamic equilibrium. At equilibrium conditions, all of the intensive state variables such as temperature, surface tension, and chemical potentials between the bulk phase and the adsorbed phase are equal for all species. The thermodynamic equilibrium between the bulk phase and the adsorbed phase can be quantitative described by adsorption isotherms which measure the variation in the amount of adsorbates with the change in pressure at constant temperatures. There are many different types of isotherms each suitable in its unique application domain, interested readers are advised to refer to the comprehensive introduction by Ruthven.¹¹

With a basic understanding of adsorption thermodynamics, since 1960s many chemical engineers had begun to explore the potential of adsorption in the separation of gaseous mixtures. The earliest and the most notable examples was the separation of air. Milton first developed and invented synthetic zeolites also known as molecular sieves.¹² This class of adsorbents was known to be able to preferentially adsorb nitrogen over oxygen from air. Later on Skarstrom¹³ and Guerin de Montgareuil and Domine¹⁴ introduced efficient pressure-swing cycles and applied the process for air separation and achieved significant improvements on separation energy. The example of air separation demonstrates that the selection of suitable materials and design of fit process are two key ingredients to the successful industrial application.

1.2.1. MOFs as adsorbent materials for C₂ hydrocarbons separation

Generally speaking, there are two types of microporous materials for adsorption, i.e. the ordered and unordered ones. Most of the traditional adsorbents such as silica gel $(SiO_2 \cdot nH_2O)$, activated alumina (Al_2O_3) , and activated carbon, belong to the unordered category, which means the manufacturing process controls the distribution of micropore size and mean micropore diameters. On the other hand, ordered porous materials such as crystalline aluminosilicates also known as zeolites (M(AlO₂)(SiO₂)_x(H₂O)_y), and metalorganic-frameworks (MOFs) have well-designed microporous structures. The assembly of ordered frameworks is of great interest to scientist because of the potential in fulfilling specific and cooperative functions.¹⁵ In particular, the chemistry of MOFs has attracted attention as it provides an extensive number of crystalline materials with high stability, tunable metrics, organic functionality and porosity.¹⁶ MOFs are comprised of metal ions or clusters coordinated with organic ligands. For a comprehensive overview of metal ions and organic ligands and synthetic techniques, readers are recommended to refer to the literature.¹⁶ They are known for the characteristic porous networks which result in large surface areas and high permanent porosity. Besides, MOFs have fine-tuned pore chemistry which enables selective bindings of target molecules. Owing to these excellent properties, MOFs are considered as ideal adsorbent materials in gas separation/purification.

Over the past two decades, adsorptive separation on metal-organic frameworks (MOFs) has been considered of having great potential in delivering the challenge of energy-efficient C₂ separations.³ Many MOFs were reported with great selectivity for ethylene in binary systems (i.e. C_2H_4/C_2H_2 , C_2H_4/C_2H_6 , CO_2/C_2H_4 and etc.). For instance, some of the representative MOFs are Cu-BTC¹⁷, ZIF-8¹⁸, Fe₂(dobdc)¹⁹, and NOTT-300²⁰, M₂(*m*-dobdc) (M = Mn, Fe, Co, Ni; *m*-dobdc^{4–} = 4,6-dioxido-1,3-benzenedicarboxylate)²¹. A detailed list of MOFs for the separation of C₂ binary mixtures can be found in Table 1-1.

But the design of one step C₂H₄ purification adsorbents remained challenging, due to not only the molecular similarity between C2 hydrocarbons also the complex multicomponent adsorption environment.²²⁻²⁵ A number of novel materials were designed to address the challenge by means of various separation mechanisms such as customizing specific interaction sites. For example, Hao et al. proposed a robust MOF, TJT-100, which had a trinuclear $Co_3(\mu_3-OH)(O_2C)_4$ cluster and was linked by DCPN (DCPN = 5-(3',5'dicarboxylphenyl) nicotinate)) ligands. TJT-100 was proven to be able to simultaneously trap C₂H₂ and C₂H₆ with the formation of C-H···O electrostatic interactions while maintaining an unfavorable interaction between C₂H₄ and the framework.²⁶ Furthermore, Xu et al. designed a Th-azole network MOF (Azole-Th-1). It had a UiO-66-type structure with a *fcu* topology built upon a Th₆ secondary building unit and a tetrazole-based linker. They showed that owing to the strong van der Waals interaction between ethane and Azole-Th-1. At 100kPa and 298K, the synthesized MOF achieved a C₂H₄ purity over 99.9% and a productivity of 1.34 mmolg⁻¹ for separating the (9:1:90 $C_2H_6/C_2H_2/C_2H_4 v/v/v$) ternary mixture.²⁷ Inspired by another MOF belonging to the same Zr cluster-based UiO family (UiO-67), Gu et al. introduced Lewis basic sites and built a C₂H₆-selective MOF (UiO-67-(NH₂)₂).²⁸ They reported that with suitable pore confinement and the amino groups decorated functional surfaces, exceptional performance was acquired in the breakthrough experiments of the mixture (1/49.5/49.5 C₂H₂/C₂H₄/C₂H₆) and obtained a 0.55 mmolg⁻¹ productivity at ambient conditions. Similarly, Sun et al. customized two ethane-selective MOFs (PCP-FDCA and PCP-IPA-NH₂) with C₂H₂ and CO₂ binding sites. They discovered that due to the electrostatic interaction between the specific binding sites FDCA and C₂H₂, one-step purification of C₂H₄ from the ternary mixture (1:1:1 C₂H₆/C₂H₄/C₂H₂) was achieved with a productivity of 0.20 mmolg⁻¹.²⁹ Wang et al. reported a robust MOF [Zn-(BDC)(H₂BPZ)]·4H₂O with methyl-decorated non-polar pores. They discovered that this MOF was able to produce high purity ethylene for mixtures of various C₂ ratios, because of the methyl-rich nonpolar system with accessible O/N adsorption sites.³⁰ Wang et al. synthesized new MOFs(UPC-612 and UPC-613) based on the modification of a stable ftw topological Zr-MOF(MOF-525). A cyclopentadiene cobalt functional group was introduced, leading to increasing host-guest interactions. It was demonstrated that in breakthrough experiments both MOFs were able to produce 99.9% purity ethylene for an equimolar mixture and UPC-612 had a 0.47 mmolg⁻¹ productivity.³¹ Similarly, Cao et al. reported an ultra-microporous sorbent Zn-atz-oba³², which enabled selective adsorption of C_2H_2 , C_2H_6 and CO_2 over C_2H_4 due to the binding sites that lie in the confined region enclosed by four atz linkers and three oba linkers. They also demonstrated through breakthrough experiments that Zn-atz-oba could produce polymer-grade C_2H_4 from the equimolar ternary C_2 mixture in a single step with a productivity of 0.106 mmol/g. Moreover, Mukherjee et al. reported two isostructural aminopyrazine-linked hybrid ultramicroporous materials i.e., SIFSIX-17-Ni and TIFSIX-17-Ni, which had the ability to purify polymer-grade C_2H_4 from a ternary equimolar mixture of C_2H_2 , C_2H_4 and CO_2 under ambient conditions with the productivities of 7.2 and 15.8 cm³/g, respectively.³³ The high affinity towards both gases impurities could be attributed to the unique co-adsorption binding sites induced by the presence of amino groups.

Apart from the modifications of binding sites to increase specific host-adsorbate interactions, researchers also devised MOFs with tailor-made pore structures to capture target adsorbate molecules. For instance, Zhu et al. reported a series of new MOFs (NPU-1/2/3), which had 9-connected nodes based on a hexanuclear metal cluster [Mn₆(μ_3 -O)₂(CH₃COO)₃]⁶⁺ and a *pacs* topology, with different linker ligands. They revealed that the dual cage nature of NPU-1 enabled one step production of polymer-grade ethylene from an equimolar mixture at ambient conditions.³⁴ Another class of MOF known as anion-pillared MOF emerged as another promising one step separation MOFs. Zhang et al. reported an anion-pillared hybrid ultramicroporous material CuTiF₆-TPPY. Its 4,6-connected *fsc* framework exhibited semi-cage-like 1D channels sustained by porphyrin rings and TiF₆⁻² pillars.²² Dynamic breakthrough experiments confirmed the direct purification of ethylene of 99.9% purity from the mixture (1/9/90 C₂H₂/C₂H₆/C₂H₄) under

ambient conditions. In addition to the efforts in the design of delicate adsorbent to perform one step purification, Chen et al. introduced the concept of synergistic sorbent separation technology (SSST) to enable high-purity ethylene production from the ternary mixture.³⁵ In the SSST, three benchmark sorbents (SIFSIX-3-Ni, TIFSIX-2-Cu-i, and Zn-atz-ipa) were selected for CO₂, C₂H₂, and C₂H₆ removal, respectively. Owing to the synergy, they successfully demonstrated that for the purification of the (1:1:1:1 CO₂/C₂H₂/C₂H₄/C₂H₆) mixture, this technology yielded 99.9% of ethylene purity and a working capacity of 0.14 mmolg⁻¹.

Due to the length limitation, it is impractical to enumerate all the related MOFs in details, especially those for binary separations. Instead, a comprehensive summary of the state-of-the-art MOFs for C₂ separations is given here in Table 1-1. The list includes the above-mentioned one-step C₂ separations MOFs as well as MOFs for the binary C₂ separations such C_2H_2/C_2H_4 , C_2H_4/C_2H_6 and reverse separation of C_2H_6/C_2H_4 under various mixture conditions.

Table 1-1: Summary of surface areas, pore volumes, adsorption uptakes (at 1 bar unless otherwise specified) and IAST selectivity of state-of-the-art adsorbents for light C₂ hydrocarbons separations (C₂H₂/C₂H₄, C₂H₄/C₂H₆, C₂H₆/C₂H₄, and C₂H₂/C₂H₄/C₂H₆)

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	C2H2 uptake (mmol/g)	C ₂ H ₄ uptake (mmol/g)	C ₂ H ₆ uptake (mmol/g)	Sads (C2H4/C2H6)	S_{ads})(C ₂ H ₂ /C ₂ H ₄)	T)(K)	Ref.
HKUST-1	2139.1ª	0.763		4.76°	1.31°	3.63 ^b		296	36
CoMOF-74	1448.5ª	0.515	0.130 ^e	6.68°, 7.93°	1.04°	6.45 ^b	1.62 ^d	296	36
MgMOF-74	1668.5ª	0.607	0.148°	5.41°, 6.59°	0.96°	5.63 ^b	2.23 ^d	296	36
FeMOF-74		0.626		6.71°	0.62°	10.79 ^b		318	36
PCN-16	2809.7ª	0.999		0.22°	0.08°	2.77 ^b		296	36

Table 1-1 (continued)

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	C2H2 uptake (mmol/g)	C2H4 uptake (mmol/g)	C2H6 uptake (mmol/g)	Sads (C2H4/C2H6	Sads ;)(C2H2/C2H4	T)(K)	Ref.
PCN-250	1470 ^h	0.564		4.22	5.21	0.52 ^b		298	37
NOTT-102	3590.1ª	1.281		2.22°	0.70 ^c	3.17 ^b		296	36
UTSA-20	1894.1ª	0.675	0.071°	2.95°, 4.57°	1.51°	1.96 ^b	1.53 ^d	296	36
UTSA-33a	1024.1ª	0.367	0.044 ^e	2.64 ^e			1.64 ^d	296	36
UTSA-34a	937.0ª	0.334	0.036 ^e	2.28 ^e			1.58 ^d	296	36
UTSA-34b	1532.6ª	0.542	0.052 ^e	3.59 ^e			1.42 ^d	296	36
UTSA-35a	875.0ª	0.313	0.045 ^e	2.17 ^e			2.07 ^d	296	36
MOF-505	1703.7ª	0.609	0.068°	4.67 ^e			1.45 ^d	296	36
NaX	950.0ª	0.280		3.37°	0.42°	8.01 ^b		296	36
NaETS-10				2.99°	0.20 ^c	14.78 ^b		296	36
NOTT-300	1370 ^h	0.433	6.34	4.28	0.85	48.7 ^b	2.30 ^f	293	20
M'MOF-3a	237 ⁱ , 110 ^j	0.164	1.9	0.4			24.03 ^f , 34.17 ^d	295	38
TJT-100	890 ^h , 1077 ^a	0.39	5.67	4.37	4.70	0.83 ^k	1.8 ^d	273, 298	26
TIFSIX-14-Cu-i	425 ^h		3.78	1.41			229 ^d	298	39
TIFSIX-2-Cu-i	685 ^h		4.1					298	40
TIFSIX-17-Ni	237.6 ^j		~3.2	~0.2	~0.15		670.9 ^f	298	33
SIFSIX-2-Cu-i	503 ^h		4.02	2.19			44.54 ^d , 41.01 ^f	298	25
SIFSIX-2-Cu	1881 ^h		5.38	2.02			6.0 ^d , 4.95 ^f	298	25

Table 1-1 (continued)

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	C2H2 uptake (mmol/g)	C2H4 uptake (mmol/g)	C2H6 uptake (mmol/g)	Sads (C2H4/C2H6	S _{ads})(C ₂ H ₂ /C ₂ H ₄)	T)(K)	Ref.
	11 7 0h		0.50	4 11			10.63 ^d ,	200	25
SIFSIX-1-Cu	11/8"		8.50	4.11			8.37 ^f	298	25
	o s oh		2 (1	0.04			8.82 ^d ,	•••	25
SIFSIX-3-Zn	250 ⁿ		3.64	2.24			13.72 ^f	298	25
	acob		2.20	1.75			5.03 ^d ,		25
SIFSIX-3-N1	368 ⁿ		3.30	1.75			5.98 ^f	298	25
SIFSIX-17-Ni	229.2 ^j		~3.2	~0.15	~0.10		506.4^{f}	298	33
GeFSIX-2-Cu-i (ZU-32)	467 ^j	0.25	116 ⁿ	64.0 ⁿ			67 ^d	298	41
GeFSIX-14-Cu-i									41
(ZU-33)	424	0.24	119 ⁿ	22"			1100 ^a	298	
	970 ^h		4.27	1.66			10.72 ^d ,	206	25 42
UTSA-100a		0.399					19.55 ^f	296	25,42
UTSA-280	331 ^h			2.5	0.098	>10000 ^b		298	43
UTSA-30a	592.1 ^h ,603. 8 ^a	0.259	~2.3	~2.0	~2.0			296	44
UTSA-60a	484 ^h ,500 ^a		3.12	2.05			$\sim 6^d$	296	45
UTSA-67a	1137 ^h	0.47	5.13	2.81			5-6 ^d	296	46
	577 ^h ,		2.4	2.5	2.0	1.6	10 ^d ,	200	47
UISA-220	825ª		~3.4	~2.5	~2.0	~1.6°	8^{f}	298	47
	311 ^j ,	0.1.6	2.8,	0.04,			. 10000f	298,	18
U1SA-300a	444 ⁱ	0.16	3.4	0.04			>10000	273	10
ITQ-55				1.28 ¹	0.76 ^m	90 ^b		303	49

Table 1-1 (continued)

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	C2H2 uptake (mmol/g)	C2H4 uptake (mmol/g)	C2H6 uptake (mmol/g)	Sads (C2H4/C2H6	S _{ads})(C ₂ H ₂ /C ₂ H ₄	T)(K)	Ref.
Zeolite 5A	457-600 ^h			2.45	1.72	4.5 ^b		303	50
PAF-1-SO ₃ Ag	783 ^h			4.06	2.23	27 ^b		296	51
MIL-101-Cr				3.26,	1.47,	9.7 ^b ,		296,	50.50
SO ₃ Ag	1374 ⁿ ,1253 ⁿ	n		4.32	1.22	16 ^b		303	52,53
Fe ₂ (<i>m</i> -dobdc)	1295 ^h			7.0	6.0	25 ^b		298	21
Fe ₂ (O ₂)(dobdc)	1073 ^h			~2.36	~3.06	0.22 ^b		298	54
Azole-Th-1	983 ^h			3.6	4.5	1.46 ^b		298	27
Zn-atz-ipa	650 ^h		1.82	1.64	1.65	0.58 ^b	0.85^{f}	298	35
	710.7 ^h ,	0.287	2.77,	2.03,	2.05,	0.78 ^b		298,	22
Zn-atz-oba	783.1ª		4.19	2.81	2.70		1.43 ^t	273	32
UiO-66-ADC	556 ^h			1.7	1.6	0.55 ^b		298	55
UiO-67	2815 ^h	1.25	2.09	2.13	3.05	0.67 ^b	1.07 ^d	296	28
UiO-67-(NH ₂) ₂	2022 ^h	0.8	5.9	4.32	5.32	0.58 ^b	2.1 ^d	296	28
NUS-36	79.1 ^h			1.5	1.0	4.1 ^b		298	55
Mg-gallate	559 ^j			3.0	0.26	37.3 ^b		298	56
Ni-gallate	424 ^j			1.97	0.28	16.8 ^b		298	56
Co-gallate	475 ^j			3.37	0.31	52 ^b		298	56
MAF-49				~0.16	~1.39	0.11 ^b		316	57
$Cu(Qc)_2$	240 ^j ,290 ⁱ	0.11		0.78	1.85	0.29 ^b		298	58
Cu(ina) ₂	228 ^j ,260 ⁱ	0.10		1.90	1.99	0.77 ^b		298	58
ZU-62-Ni									
(NbOFFIVE-2-Ni-	. 585 ⁱ	0.22	3.0	0.8			37.2 ^d	298	59

Table 1-1 (continued)

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	C2H2 uptake (mmol/g)	C2H4 uptake (mmol/g)	C2H6 uptake (mmol/g)	Sads (C2H4/C2H6	S _{ads})(C ₂ H ₂ /C ₂ H ₄)	T)(K)	Ref.
NKMOF-1-Ni	382 ^h		~2.48	~1.93	~2.08		~1000 ^d , ~40 ^g	298	60
CPL-1	414 ^j		2.07	0.31			26.8 ^d	298	61
CPL-2	495 ^j		3.13	~1.8			12.0 ^d	298	61
CPL-5	523 ^j		3.01	~1.8			6.0 ^d	298	61
[Zn- (BDC)(H ₂ BPZ)]·4 H ₂ O	906.5 ^h , 1332.1 ^a		~4.08, ~5.46	~3.00, ~4.00	~3.32, ~4.40	0.45 ^b	1.6 ^f	298,273	30
MOF-525	3116.7 ^h		3.89	3.28	4.42	~0.45 ^b	$\sim 2.2^{\mathrm{f}}$	273	31
MOF-525(Co)	2934.3 ^h		3.68	2.86	3.18	~0.55 ^b	$\sim 0.1^{\mathrm{f}}$	273	31
UPC-612	2016.8 ^h		5.25	4.72	6.47	~0.68 ^b		273	31
UPC-613	853.2 ^h		4.26	3.40	3.65	~0.65 ^b	$\sim \! 1.5^{\mathrm{f}}$	273	31
ELM-12 (Cu(bpy) ₂ (OTf) ₂)		0.138	~2.3	~1			14.8 ^d , ~30 ^f	298	62
NPU-1	1557ª, 1396 ^h	0.47	5.10, 6.92	4.20, 5.67	4.50, 5.66	0.75 ^b	1.4 ^f	298,273	34
NPU-2	1844 ^a , 1580 ^h	0.66	3.99, 6.98	3.42, 5.42	4.42, 6.02	0.65 ^b	1.25 ^f	298,273	34
NPU-3	2133ª, 1834 ^h	0.77	2.54, 5.15	2.19, 4.12	3.33, 5.46	0.31 ^b	1.32 ^f	298,273	34
CuTiF ₆ -TPPY	685ª	0.32	3.62	2.42	2.82	0.47 ^ь , 0.47°	5.03 ^d , 5.47 ^f	298	22
PCP-FDCA	542 ^j	0.17	4.39	3.08	3.17	0.60 ^b	4.82^{f}	298	29

Table 1-1 (continued)

Adsorbent	Surface area (m ² /g)	Pore volume (cm ³ /g)	C2H2 uptake (mmol/g)	C2H4 uptake (mmol/g)	C2H6 uptake (mmol/g)	Sads (C2H4/C2H6	S _{ads})(C ₂ H ₂ /C ₂ H ₄	T)(K)	Ref.
PCP-IPA-NH ₂	387 ^j	0.13	2.01	1.80	1.94	0.45 ^b	1.0^{f}	298	29
JNU-1	818 ^h		~2.65					298	63
JNU-2	1219 ^h	0.56		~3.57	4.19	0.62 ^b		298	64
ZJU-30a	228 ^h		~2.14	~1.80	~1.94			298	65
ZIF-4	300 ^h	0.38		2.2	~2.3	0.45 ^b		293	66
ZIF-7				~1.8	~1.8			298	67
ZIF-8	1844 ^h			~1.5	~2.5				68
Mg ₂ (dhtp)	1420 ^h			~7.0	~5.6				68
Co ₂ (dhtp)	763 ^h			~4.5	~4.0				68

Table 1-1 (continued)

a. Langmuir surface area calculated from N₂ adsorption at 77 K.

b. IAST calculated adsorption selectivity of an equimolar C_2H_4/C_2H_6 mixture at $p_1 = p_2 = 50$ kPa

c. IAST calculated uptakes (mol/L) in an equimolar C_2H_4/C_2H_6 mixture at $p_1 = p_2 = 50$ kPa

d. IAST calculated adsorption selectivity of an (1/99 mol/mol) C_2H_2/C_2H_4 mixture at $p_1=1$ kPa, and $p_2=99$ kPa

e. IAST calculated uptakes (mol/L) in an (1/99 mol/mol) C_2H_2/C_2H_4 mixture at $p_1 = 1$ kPa, and $p_2 = 99$ kPa

f. IAST calculated adsorption selectivity of an equimolar C_2H_2/C_2H_4 mixture at $p_1 = p_2 = 50$ kPa

g. IAST calculated uptakes (mol/L) of an equimolar C_2H_2/C_2H_4 mixture at $p_1 = p_2 = 50$ kPa

h. BET surface area calculated from N_2 adsorption at 77 K.

i. Langmuir surface area calculated from CO₂ adsorption at 195 K.

j. BET surface area calculated from CO₂ adsorption at 195 K.

k. IAST calculated adsorption selectivity of an (99/1 mol/mol) C_2H_4/C_2H_6 mixture at $p_1 =$ 99 kPa, and $p_2=1$ kPa

1. at 0.45 bar

m. at 0.6 bar

n. pure component adsorption uptakes (cm³ gas /cm³ adsorbent) at 1.01 bar and 298 K

o. IAST calculated adsorption selectivity of an (90/10 mol/mol) C_2H_4/C_2H_6 mixture at $p_1 = 90$ kPa, and $p_2 = 10$ kPa

Despite the progress, the biggest hinderance to the identification of novel MOF materials experimental synthesis is the time-consuming experimental process. Usually. the experimental synthesis relies heavily on expert experiences. But as is known expert experiences are often built on a few specific structures and it becomes less inefficient when handling vast varieties of MOF structures. Also, since one of the most notably characteristics of MOFs is its gigantic combinatorial design space, the labor-intensive individual inspection of MOF structures one by one becomes a daunting task and in reality, often impractical. Besides, expert experiences also face the transferability problem. This means whenever a different separation system needs to be investigated, our previous synthetic knowledge about MOFs' functionality becomes uncertain. Therefore, there is an urgent need for a tool which can address these issues and help accelerate the experimental discovery processes.

1.3. High-throughput computational screening of novel adsorbent materials

High-throughput computational screening of materials is the tool which can reliably assist

in advancing the synthesis of novel materials, and thus significantly reducing the required time in experiments. As illustrated in Figure 1-3, the high-throughput screening of MOFs for adsorption separation consists of four steps 1) preparation of MOF database with activated MOFs structures (solvent molecules removed and electron charge distributions computed); 2) performing molecular simulations, i.e. grand canonical Monte Carlo (GCMC) simulations to obtain equilibrium adsorption loadings; 3) analysis and assessment of MOF performances based on selection criteria for adsorption.



Figure 1-3: The flow of high-throughput computational screening approach.

1.3.1. MOF Database

hMOF database

The large-scale computational screening requires a computation-ready database with the crystallographic information for each structure. In 2011, a hypothetical MOF (hMOF) database was first proposed by Wilmer et al.⁶⁹ The idea was to generate new or hypothetical MOFs by recombining building blocks derived from crystallographic data of previously reported experimental synthesized MOFs. To facilitate the recombination, atoms were grouped into the building blocks which could then combine with each other provided that the geometry and chemical composition local to the point of connection was

the same as that in crystallographically determined structures. The construction of hypothetical MOFs was carried out in an enumerative and stepwise manner, see Figure 1-4. Although hMOF database had attained a significantly large number of MOF candidates (137,953), it suffered from the lack of chemical variety in metal nodes and linker types due to the use of limited number of 102 building blocks. Such characteristic of the database made it less ideal for conducting computational screening despite the huge number of candidates.



Figure 1-4: Visual summary of the hypothetical MOF-generation strategy. a, Crystal structures of existing MOFs were obtained from X-ray diffraction data (a, left) and subsequently divided into building blocks (a, middle) that then could be recombined to form new, hypothetical MOFs (a, right). b,The recombination process occurs by stepwise addition of building blocks (i), which are attached at their connection sites (purple Xs).
Building blocks are also connected across periodic boundaries (ii, hashed circles indicate mirror images). The process repeats (iii to iv) until all connection sites are utilized. An interpenetrated MOF may be generated if enough space exists (v, black circles indicate atoms belonging to one of two interpenetrated frameworks). Grey, red, blue and turquoise spheres represent carbon, oxygen, nitrogen and zinc atoms, respectively. Hydrogen atoms are omitted for clarity. The figure is adopted from the literature⁶⁹

ToBaCCo database

Another database known as Topologically Based Crystal Constructor (ToBaCCo)⁷⁰ came into existence in 2017. Based on the knowledge that topology-based design is central to the development of new MOFs in the lab analogous to the experimental synthesis process, ToBaCCo implemented a top-down approach to the construction of new MOF database based on topological blueprints. MOF components were split or merged into supramolecular building blocks to allow for the assembling in predefined topological blueprints. ToBaCCo had been used to construct a set of 13512 MOFs in 41 different topologies. However, the algorithm in ToBaCCo was not able to check for generated MOF structure integrity such as atom overlapping, thus these structures need to undergo further optimizations before applications in molecular simulations. Despite that, researchers demonstrated the success of ToBaCCo in finding new MOFs for cryo-adsorbed hydrogen storage.⁷¹ Compared to the hMOF database, MOFs generated by ToBaCCo had better diversity in chemistry as well as in topology. But since they were both derived from computation algorithms, the MOFs' experimental synthesizability was in doubt.

CoRE MOF database

Cambridge Structural Database (CSD) is currently the world's largest databank storing small molecule crystal structures reported by experiments. By 2019 the database has grown to over a million structures. Most of the experimentally reported crystal structures in CSD have the problem of containing solvent molecules or disordered atoms, which must be removed prior to computational screening. Computation-ready experimental (CoRE) MOF database⁷² addresses the issue by providing a comprehensive set of porous MOF structures that are immediately suitable for molecular simulations. As illustrated in Figure 1-5, for the preparation of the CoRE MOF database, a chemical bond analysis is first carried out to eliminate non-MOFs structures from the CSD database. Then through the examination of the bonded components of molecular graphs, 3D frameworks are detected

from their 1D or 2D counterparts. Finally, cleaning protocols, which involve the retention of charge balancing ions and solvent removal followed by pore characterization, are conducted to get the final MOFs structures. Although the CoRE MOF database contains totally only 4764 candidates which are less than hMOF or ToBaCCo, it is derived directly from experiments. This guarantees that all the candidate MOFs are experimentally viable and there is no structural integrity problem. Besides, the distinctive sources of experiments lead to a large chemical diversity which also makes it a suitable basis for high-throughput screenings.



Figure 1-5: Schematic illustration of the CoRE MOF database construction. Chemical bond analysis was performed using the CCDC Conquest program, 3D framework detection and pore characterization were performed using the Zeo++ Open Source
 Software, and cleaning protocols were implemented in Python using the ASE and SciPy libraries. All structures in the CoRE MOF database have pore-limiting diameters (PLDs) >2.4 Å. The figure is adopted from the literature⁷²

1.3.2. Molecular simulation

Molecular simulation is the core of high-throughput screening. It is a powerful tool which can help us examine adsorption phenomena at the molecular level. The principles of molecular simulations are simple. A system is modeled by describing the interactions between the atoms. An appropriate molecular simulation technique is used to link these interactions at the molecular level to macroscopic quantities that are accessible experimentally.⁷³ For example, in a system of *N* particles that interact via an intermolecular pair potential u(r). The configuration of the system can be denoted by $\Gamma^N = r_1, r_2, ..., r_N$, where r_i is the vector describing the position of particle *i*. The total energy of the system can be calculated by the following equation:

$$U(\Gamma^N) = \sum_{i>j} u(r_{ij})$$
(1.1)

where r_{ij} is the geometric distance between particles *i* and *j*, and u(r) is the potential energy between two particles. For adsorption, since we are interested in the prediction of adsorption loadings of adsorbates in the presence of pressure change, we wish to link the potential energy somehow to the equilibrium loading. Experimentally, the most common practice for the measurement of adsorption loading is to put an adsorbent in a container that contains gases. The gases are kept at constant temperature and pressure or partial pressures in the case of a mixture. In equilibrium, the adsorbed gas molecules have the same temperature and chemical potential as the molecules in the container. In principle, one can imitate the experimental setup by the simulation of adsorbents and the gas molecules in a similar container. However, such system is not convenient to simulate, instead material scientists turn to use the grand canonical ensemble, where the temperature, volume, and chemical potentials are imposed. This ensemble can be easily investigated in a grand canonical Monte Carlo (GCMC) simulation. The input of the simulation is the temperature and chemical potential of the molecules in the reservoir and the average
number of adsorbed molecules is the outcome of the simulation. The key to a successful Monte Carlo simulation lies very much in the generation of statistically independent configurations. Statistical thermodynamics assumes that if we simulate a system at constant temperature sufficiently long, the probability that we find a particular configuration is given by the Boltzmann distribution.

$$P_{NVT}(\Gamma^N) \propto e^{-\frac{U(\Gamma^N)}{k_B T}}$$
(1.2)

where k_B is the Boltzmann constant, and U is the intermolecular potential. In a Monte Carlo simulation, a Markov chain consists of a sequence of configurations, where the probability of finding a particular configuration in this chain is given by the Boltzmann equation. In practice, such a chain is generated by performing attempts to generate a new configuration, for example, by displacing a randomly selected particle and accepting or rejecting this move according to an appropriate acceptance rule. This acceptance rule can be derived from the condition of detailed balance

$$acc(o \rightarrow n) = \min\left(1, e^{-\frac{U(n) - U(o)}{k_B T}}\right)$$
 (1.3)

This equation shows that the probability of accepting/ rejecting depends on the energy difference between the old (o) and the new (n) conformation. The most computational expensive part in a Monte Carlo simulation is the calculation of energy differences. GCMC has proven as the most effective molecular simulation method in predicting gas adsorption equilibrium in porous materials over the decades.

GCMC in RASPA

RASPA is a force-field-based molecular simulation tool that focuses on MC simulations of porous materials clays, carbon nanotubes, zeolites, and MOFs. It was developed by a collaboration among Northwestern University, the University of Amsterdam, the University Pablo de Olavide, and the University of Delft.⁷⁴ It has the capability to simulate

adsorption isotherms efficiently. Customized MC moves such as insertion and deletion are used in the μ VT ensemble to equilibrate the system at the fixed value of the chemical potential. In general, a RASPA simulation of isotherms consists of the following steps 1) preparation of Crystallographic Information Files (cif) for MOF structures; 2) force field definition 3) defining gas adsorption molecules; 4) defining MC parameters in raspa files; 5) performing simulation.

For example, suppose we want to simulate the adsorption isotherm of C_2H_4 in HKUST-1. The MOF structure file of HKUST-1 can be acquired from the CoRE MOF database. Based on the cif file, we then recompute partial charges of the framework through the charge equilibrium calculation using the EQeq method. The final structure must be checked to ensure that it's charge neutral, which means that a net zero charge on the framework should be observed since we have not introduced any free cations or anions into the structure. Figure 1-6 is an example of the MOF structure file with assigned partial charges.

data_CuH2(C3O2)2	H 0.73407 0.50556 0.73407	0.136994	C 0.02349 0.56939 0.56939	0.6513	C 0.02865 0.70129 0.56877	0.002077	O 0.12528 0.97974 0.50868	-0.553008
symmetry space group name H-M 'P 1'	H 0.0263 0.73407 0.50556	0.136994	C 0.74292 0.61334 0.61334	-0.139565	C 0.70129 0.02865 0.70129	0.002077	O 0.97974 0.12528 0.3863	-0.553009
cell_length_a 18.58840033	H 0.73407 0.0263 0.73407	0.136994	C 0.83773 0.56939 0.56939	0.651299	C 0.56877 0.02865 0.70129	0.002077	O 0.97974 0.50868 0.12528	-0.553008
_cell_length_b 18.58840000	H 0.50556 0.0263 0.73407	0.136994	C 0.61334 0.74292 0.61334	-0.139565	C 0.70129 0.70129 0.02865	0.002077	O 0.12528 0.3863 0.97974	-0.553009
cell length c 18.58840000	H 0.73407 0.73407 0.0263	0.136994	C 0.56939 0.83773 0.56939	0.651299	C 0.02865 0.56877 0.70129	0.002077	O 0.50868 0.97974 0.3863	-0.553009
_cell_angle_alpha 60.00000000	H 0.0263 0.50556 0.73407	0.136994	C 0.61334 0.0304 0.61334	-0.139566	C 0.70129 0.70129 0.56877	0.002077	O 0.3863 0.12528 0.50868	-0.553008
_cell_angle_beta 60.00000059	H 0.73407 0.73407 0.50556	0.136994	C 0.56939 0.02349 0.56939	0.6513	C 0.56877 0.70129 0.70129	0.002077	O 0 12528 0 50868 0 3863	-0.553009
_cell_angle_gamma 59.99999980	H 0.50556 0.73407 0.73407	0.136994	C 0.0304 0.61334 0.74292	-0.139566	C 0.70129 0.02865 0.56877	0.002077	0 0 97974 0 3863 0 50868	-0 553009
symmetry_Int_Tables_number 1	H 0.73407 0.0263 0.50556	0.136994	C 0.02349 0.56939 0.83773	0.651299	C 0.02865 0.70129 0.70129	0.002077	0.0.3863.0.97974.0.12528	-0 553009
_chemical_formula_structural CuH2(C3O2)2	H 0.0263 0.73407 0.73407	0.136994	C 0.74292 0.61334 0.0304	-0.139566	C 0.70129 0.56877 0.02865	0.002077	0 0 50868 0 12528 0 97974	0.553008
chemical_formula_sum 'Cu12 H24 C72 O48'	H 0.73407 0.50556 0.0263	0.136994	C 0.83773 0.56939 0.02349	0.651299	C 0.29871 0.43123 0.97135	0.002077	0 0 50969 0 2962 0 97974	0.553000
_cell_volume 4541.62256967	H 0.26593 0.49444 0.9737	0.136994	C 0.38666 0.38666 0.9696	-0.139566	C 0.43123 0.29871 0.29871	0.002076	0 0 2962 0 50969 0 12529	0.553009
_cell_formula_units_Z 12	H 0.49444 0.26593 0.26593	0.136994	C 0.43061 0.43061 0.97651	0.6513	C 0.29871 0.97135 0.43123	0.002077	0 0.3003 0.30000 0.12320	-0.333009
loop_	H 0.26593 0.9737 0.49444	0.136994	C 0.38666 0.38666 0.25708	-0.139565	C 0.97135 0.29871 0.29871	0.002077	0 0.97974 0.12526 0.50868	-0.555008
_symmetry_equiv_pos_site_id	H 0.9737 0.26593 0.26593	0.136994	C 0.45061 0.45061 0.16227	0.051299	C 0.97135 0.43123 0.29871	0.002077	0 0.12528 0.97974 0.3863	-0.553009
_symmetry_equiv_pos_as_xyz	H 0.9737 0.49444 0.26593	0.136994	C 0 16337 0 97651 0 43061	0.651300	C 0.29871 0.29871 0.97135	0.002077	0 0.50868 0.97974 0.12528	-0.553008
1 'x, y, z'	H 0.26593 0.26593 0.9737	0.136994	C 0.9696 0.25708 0.38666	0.031233	C 0.43123 0.97135 0.29871	0.002077	0 0.3863 0.12528 0.97974	-0.553009
loop_	H 0.49444 0.9737 0.26593	0.136994	C 0 97651 0 16227 0 43061	0.651299	C 0.29871 0.29871 0.43123	0.002076	O 0.97974 0.50868 0.3863	-0.553009
_atom_site_type_symbol	H 0.26593 0.26593 0.49444	0.136994	C 0 9696 0 38666 0 25708	-0 139566	C 0.29871 0.43123 0.29871	0.002076	O 0.12528 0.3863 0.50868	-0.553009
_atom_site_fract_x	H 0.26593 0.49444 0.26593	0.136994	C 0.97651 0.43061 0.16227	0.651299	C 0.97135 0.29871 0.43123	0.002077	O 0.50868 0.12528 0.3863	-0.553009
_atom_site_fract_y	H 0.9737 0.26593 0.49444	0.136994	C 0.25708 0 38666 0 9696	-0.139566	C 0.29871 0.97135 0.29871	0.002077	O 0.3863 0.97974 0.50868	-0.553009
_atom_site_fract_z	H 0.26593 0.9737 0.26593	0.136994	C 0.16227 0.43061 0.97651	0.651299	C 0.43123 0.29871 0.97135	0.002077	O 0.97974 0.3863 0.12528	-0.553009
_atom_site_charge	H 0.49444 0.26593 0.9737	0.136994	C 0.38666 0.9696 0.38666	-0.139566	O 0.49132 0.6137 0.02026	-0.553009	O 0.12528 0.50868 0.97974	-0.553009
Cu 0.43356 0.56644 0.0 0.910425	C 0.61334 0.61334 0.0304	-0.139566	C 0.43061 0.97651 0.43061	0.6513	O 0.6137 0.49132 0.87472	-0.553009	O 0.6137 0.49132 0.02026	-0.553009
Cu 0.56644 0.43356 0.0 0.910425	C 0.56939 0.56939 0.02349	0.6513	C 0.38666 0.25708 0.38666	-0.139565	O 0.02026 0.87472 0.49132	-0.553008	O 0.49132 0.6137 0.87472	-0.553009
Cu 0.0 0.0 0.43356 0.910424	C 0.61334 0.61334 0.74292	-0.13956	5C 0.43061 0.16227 0.43061	0.651299	O 0.87472 0.02026 0.6137	-0.553009	O 0.87472 0.02026 0.49132	-0.553009
Cu 0.0 0.0 0.56644 0.910424	C 0.56939 0.56939 0.83773	0.651299	C 0.25708 0.38666 0.38666	-0.139565	O 0.49132 0.02026 0.87472	-0.553008	O 0.02026 0.87472 0.6137	-0.553009
Cu 0.43356 0.0 0.0 0.910424	C 0.0304 0.74292 0.61334	-0.139565	C 0.16227 0.43061 0.43061	0.651299	O 0.6137 0.87472 0.02026	-0.553009	O 0.02026 0.49132 0.87472	-0.553009
Cu 0.56644 0.0 0.0 0.910424	C 0.02349 0.83773 0.56939	0.651299	C 0.9696 0.38666 0.38666	-0.139566	O 0.02026 0.49132 0.6137	-0.553009	O 0.87472 0.6137 0.02026	-0.553009
Cu 0.0 0.43356 0.56644 0.910425	C 0.74292 0.0304 0.61334	-0.139565	C 0.97651 0.43061 0.43061	0.6513	O 0.87472 0.6137 0.49132	-0.553009	O 0.49132 0.02026 0.6137	-0.553009
Cu 0.0 0.56644 0.43356 0.910425	C 0.83773 0.02349 0.56939	0.651299	C 0.38666 0.9696 0.25708	-0.139566	O 0.49132 0.87472 0.6137	-0.553009	0 0 6137 0 87472 0 49132	-0.553009
Cu 0.43356 0.0 0.56644 0.910425	C 0.61334 0.0304 0.74292	-0.139566	C 0.43061 0.97651 0.16227	0.651299	O 0.6137 0.02026 0.49132	-0.553009	0 0 87472 0 49132 0 6137	-0.553009
Cu 0.56644 0.0 0.43356 0.910425	C 0.56939 0.02349 0.83773	0.651299	C 0.38666 0.25708 0.9696	-0.139566	O 0.02026 0.6137 0.87472	-0.553009	0 0 0 0 0 0 2 0 6 1 3 7 0 4 9 1 3 2	-0 553009
Cu 0.0 0.56644 0.0 0.910424	C 0.61334 0.74292 0.0304	-0.139566	C 0.43061 0.16227 0.97651	0.651299	O 0.87472 0.49132 0.02026	-0.553009	0 0 6137 0 02026 0 87472	-0.553009
Cu 0.0 0.43356 0.0 0.910425	C 0.56939 0.83773 0.02349	0.651299	C 0.56877 0.70129 0.02865	0.002077	O 0.3863 0.50868 0.97974	-0.553009	0 0 49132 0 87472 0 02026	-0.553009
H 0.50556 0.73407 0.0263 0.136994	C 0.0304 0.61334 0.61334	-0.139566	C 0.70129 0.56877 0.70129	0.002077	O 0.50868 0.3863 0.12528	-0.553009	0 0.45152 0.0/4/2 0.02026	-0.555009

Figure 1-6: Crystallographic Information File file of HKUST-1 in RASPA

Then, molecular modellings of adsorbate molecules need to be chosen. Here the TraPPE model is selected to define C_2H_4 molecule. It contains critical constant parameters about C_2H_4 , such as critical temperature, pressure, and acentric factor. The C_2H_4 molecule is

modeled symmetrically by pseudo atoms groups denoted CH_2 -sp₂, therefore the number of atoms is two and the number of groups is one. The bond between the two pseudo atom groups CH_2 -sp₂ is considered rigid and the bonding distance is set to 1.33 Angstrom. Figure 1-7 shows the molecular definition file for C_2H_4 molecules in RASPA.

```
# critical constants: Temperature [T], Pressure [Pa], and Acentric factor [-]
282.35
5041800.0
0.0866
# Number Of Atoms
# Number Of Groups
# Alkane-group
flexible
# number of atoms
# atomic positions
0 CH2_sp2
1 CH2_sp2
# Chiral centers Bond BondDipoles Bend UrayBradley InvBend Torsion Imp. Torsion Bond/Bond Stretch/Bend Bend/Bend Stretch/Torsion Bend/Torsion
IntraVDW IntraCoulomb
0 1 0 0
                               0 0 0
                                                   0
                                                        0
                                                                 0 0
                                                                                   0
                                                                                           0
                                                                                                0
                                                                                                         0
# Bond stretch: atom n1-n2, type, parameters
0 1 RIGID_BOND 1.33
# Number of config moves
0
```

Figure 1-7: Molecular definition file for ethylene in RASPA

The forcefield parameters are defined as pairs of the atomic interactions (Figure 1-8). For all single atoms, their Lennard-Jones (LJ) potentials can be represented by two parameters. Totally there are 107 single atomic LJ parameters defined, which can be combined in pairs to calculate the cross-interactions pairwise parameters according to the Lorent-Berthelot mixing rule. The general cutoff rule is set to be shifted and tail corrections are not computed.

# general rule for shifted vs truncated	Fm	lennard-jones 6.04 2	2.93 Pm	lennard-jones	4.53 3.16	H C2H2 none
shifted	Fr	lennard-jones 25.16 4.	.37 Po	lennard-jones 1	163.52 4.20	# general mixing rule for Lennard-Jones
# general rule tailcorrections	Ga	lennard-jones 208.836 3.90	0481 Pr	lennard-jones 5	.03 3.21	Lorentz-Berthelot
no	Ge	lennard-jones 190.69	3.81 Pt	lennard-jones 4	0.25 2.45	Lorente bertilelot
# number of defined interactions	Gd	lennard-jones 4.53 3	.00 Pu	lennard-jones 8	8.05 3.05	
107	н	lennard-iones 7.64893 2.84	642 Ra	lennard-jones 2	203.27 3.28	
# type interaction, parameters. IMPORTANT	HF	lennard-iones 36.23 2	.80 Rb	lennard-jones 2	20.13 3.67	
Ac_ lennard-jones 16.6 3.10	Ha	lennard-iones 193.71	2.41 Re	lennard-jones 3	33.21 2.63	
Ag_ lennard-jones 18.1159 2.80455	Ho	lennard-iones 3.52 3	.04 Rh	lennard-jones 2	26.67 2.61	
Al lennard-Jones 155.998 3.91105	He	lennard-iones 10.9 2.64	Rn	lennard-jones 1	124.78 4.25	
Am lennard-jones 7.04 3.01		lennard-iones 170 57 4	01 Ru	lennard-jones 2	28.18 2.64	
Ar lennard-jones 119.8 3.34	In	lennard-iones 301 428 3 976	608 S	lennard-jones 173.1	107 3.59032	
As_ lennard-jones 155.47 3.77	Ir	lennard-iones 36.73 24	53 Sb	lennard-jones 225.	.946 3.93777	
At lennard-jones 142.89 4.23	K	lennard-iones 17.61 3	40 Sc	lennard-jones 9.5	6117 2.93551	
Au_ lennard-jones 19.62 2.93	Kr	lennard-iones 166.4 3.636	Se	lennard-jones 1	46.42 3.75	
B lennard-jones 47.8058 3.58141		lennard-jones 855 3	14 Si	lennard-Jones 155.9	998 3.80414	
Ba lennard-jones 183.15 3.30	La	lennard-iones 12.58 2	18 Sm	lennard-jones	4.03 3.14	
Be_ lennard-jones 42.7736 2.44552	Lu.	loppard-jones 20.63 3	24 Sn	lennard-jones 2	285.28 3.91	
Bi lennard-jones 260.63 3.89	Lu_	lonnard ionor 5.52 20	Sr Sr	lennard-jones 1	18.24 3.24	
Bk lennard-jones 6.54 2.97	A.d.	lennard iones 5.55 2.0	Ta Ta	lennard-jones 4	10.75 2.82	
Br_ lennard-jones 186.191 3.51905	Ma	loppard ioner 55 9574 3 6	0141 Tb	lennard-jones 3	3.52 3.07	
Clennard-jones 47.8562 3.47299	Mg_	lennard iones 6 54195 2.6	2705 TC	lennard-jones 2	24.15 2.67	
Calennard-jones 119.75 3.03	NIN_	lennard inner 20.10	272 Te	lennard-jones 200.	281 3.98232	
Cd_ lennard-jones 114.734 2.53728		lennard-jones 20.10	Z./Z Th	lennard-jones 1	13.08 3.03	
Ce lennard-jones 6.54 3.17	N_	lennard-jones 38.9492 3.26	256 Ti	lennard-jones 8.55	5473 2.8286	
Cf_ lennard-jones 6.54 2.95	Na_	lennard-jones 15.09 2	2.66 TI	lennard-jones 34	42.14 3.87	
Cl lennard-jones 142.562 3.51932	Ne_	lennard-jones 21.1352 2.88	5918 Tm	lennard-jones	3.02 3.01	
Cm_ lennard-jones 6.54 2.96	ND_	lennard-jones 29.69	2.82 U	lennard-jones 1	1.07 3.02	
Co_ lennard-jones 7.04507 2.55866	Nd_	lennard-jones 5.03 3	18 V	lennard-jones 8.0	5151 2.80099	
Cr_ lennard-jones 7.54829 2.69319	NO_	lennard-jones 5.53 2	.89 W	lennard-jones	33.71 2.73	
Cu_ lennard-jones 2.5161 3.11369	NI_	lennard-jones 7.54829 2.52	481 Xe	lennard-jones 221.	.0 4.1	
Cs_ lennard-jones 22.64 4.02	Np_	lennard-jones 9.56 3	.05 Y	lennard-jones 3	6.23 2.98	
Dy_ lennard-jones 3.52 3.05	0_	lennard-jones 48.1581 3.03	315 Yb_	lennard-jones 1	114.72 2.99	
Eu_ lennard-jones 4.03 3.11	Os_	lennard-jones 18.62 2	2.78 Zn_	lennard-jones 62.3	3992 2.46155	
Er lennard-jones 3.52 3.02	P_	lennard-jones 161.03 3.697	23 Zr_	lennard-jones 34.7	221 2.78317	
Es_ lennard-jones 6.04 2.94	Pa_	lennard-jones 11.07 3	.05 CH2_sp	2 lennard-jones	93.0 3.685	
Flennard-jones 36.4834 3.0932	Pb_	lennard-jones 333.59	3.83 CH3_sp	3 lennard-jones 9	98.0 3.75	
Fe lennard-jones 6.54185 2.5943	Pd_	lennard-jones 24.15 2	2.58 C C2H2	lennard-jones 5	7.875 3.8	

Figure 1-8: Forcefield definition file in RASPA

Finally, we can define the MC simulation script in RASPA (Figure 1-9). The total number of initialization and equilibration cycles is set to be 20000. After the completion of initialization and equilibration, the simulation goes into the production stage where properties of the systems are recorded for later computation of the properties of interest, (e.g. equilibrium loadings). We then specify the systems temperature to 300 K and the operating pressures to be ranging from 100 Pa to 1 MPa. The choice of the types and probabilities of MC moves is also critical to the final outcome. Here we apply four types of MC moves namely translation, rotation, reinsertion and swap moves. These four types of MC move is set with an equal probability. With all these being set, we can now run the GCMC simulation and obtain the equilibrium loadings of C₂H₄ at different pressure levels. But how to interpreter these outputs by RASPA remains a question. In the next section 1.3.3, we will briefly review some of the reported selection criteria for adsorbent materials.

SimulationType MC NumberOfCycles 20000 NumberOfInitializationCycles 20000 PrintEvery 100 RestartFile no Forcefield SelfDefined Cutoff 12 Framework 0 FrameworkName HKUST-1 UseChargesFromCIFFIle yes UnitCells 2 2 2 HeliumVoidFraction 0.75 ExternalTemperature 300 ExternalPressure 1e2 1e3 1e4 1e5 1e6 component 0 MoleculeName C2H4 MoleculeDefinition TraPPE FugacityCoefficient 1 IdealGasRosenbluthWeight 1 TranslationProbability 1 RotationProbability ReinsertionProbability 1 SwapProbability 1 CreateNumberOfMolecules 0

Figure 1-9: GCMC simulation input file in RASPA

1.3.3. Adsorbent selection criteria

Adsorption selectivity (S_{ads}) is the most widely used metric to evaluate gas separation performances of adsorbents at the adsorption condition. Due to the simple and intuitive definition, it has been proven effective in many high-throughput screening studies for assessing MOFs' separation performance. For mixture component adsorptions, selectivity is defined as the ratio of the adsorptive component uptake q of the more strongly adsorbed gas component i to the uptake of other gas species j divided by their respective bulk compositions at a predetermined pressure:

$$S_{ads} = \frac{q_i y_j}{q_j y_i} \tag{1.4}$$

However, the derivation of adsorption selectivity is a time-consuming procedure because of the involvement of a mixture adsorption calculation. For better efficiency, researchers compute instead pure component selectivity at infinite dilution condition. It is defined as the ratio of the Henry's constants $K_{\rm H}$ of single component gas species extrapolated at zero loading as follows:

$$S_{0,ads} = \frac{K_{H,i}}{K_{H,j}} \tag{1.5}$$

Interestingly, when the system is close to the ideal condition, the substitutive computation can yield a fairly good approximation and vastly reduce computational costs.⁷⁵⁻⁷⁷ In fact, infinite dilution selectivity $S_{0,ads}$ reflects materials' separation ability under the condition where the interaction between adsorbate gas species is not important, which is true in the infinite diluted condition.

Besides the composition dependency, another characteristic of the adsorption selectivity is its dependency on pressure. Altintas et al.⁷⁸ computed adsorption selectivity for CH_4/H_2 separation for 4240 MOFs. They reported that the difference between pure component adsorption selectivity and mixture adsorption selectivity increases with pressure. To address this issue, the ideal adsorbed solution theory (IAST) has been applied to account for both the pressure and composition dependency of mixture adsorption. In the IAST, mixture adsorption isotherms can be predicted from single-component gas isotherms. However, IAST is incapable of accurately predicting the mixture adsorption when the mixture system deviates from the ideal condition, or the adsorbent surface is highly nonhomogeneous.^{79,80} Nevertheless, IAST remains the most used method for the estimation of mixture adsorption selectivity.

On one hand, selectivity measures the relative interaction strength difference between different adsorbate molecules and the adsorbent surface. On the other hand, we also need a metric to quantitatively measure how many molecules are adsorbed on the adsorbent surface to determine the adsorbents' capacity. For this purpose, working capacity, ΔN (mol/kg), is a good choice since it accounts for the difference between loadings at the adsorption pressure and the desorption pressure:

$$\Delta N = q_{ads} - q_{des} \tag{1.6}$$

For an economic adsorption separation, higher working capacity means better efficiency. Because it roughly matches with the swing capacity in cyclic adsorption processes such as pressure/vacuum swing adsorption, and temperature swing adsorption. Under the cyclic operation production condition, regenerability R can be applied to describe the MOFs' resilience. It is calculated as the ratio of working capacity to the amount of strongly adsorbed gas component:

$$R\% = \left(\frac{\Delta N}{q_{ads}} \times 100\right)\% \tag{1.7}$$

Unfortunately, there is generally a trade-off between adsorption selectivity and working capacity. Therefore, compound selection metrics which combine both adsorption selectivity and working capacity in various ways have been proposed. Chung et al.⁸¹ proposed adsorption performance score (APS) to evaluate adsorbents in precombustion CO₂ capture.

$$APS = \Delta N_i \times S_{ads} \tag{1.8}$$

Based on the observation that some materials have high selectivities several magnitudes larger than their capacities, Zhou et al.² introduced modified evaluation metrics known as separation performance index (SPI) by adjusting a logarithmic operator on the selectivity to avoid biased rankings.

$$SPI = q_i \times \log(S_{ads}) \tag{1.9}$$

Adsorbent performance indicator⁸² (API) is another metric which includes the adsorption enthalpy $\Delta H_{ads,i}$ of the strongly adsorbed species:

$$API = \frac{\Delta N_i}{\left| \Delta H_{ads,i} \right|} \times (S_{ads} - 1)$$
(1.10)

Recently, Leperi et al.⁸³ developed a general evaluation metric (GEM) to rank adsorbents based on overall CO₂ capture costs. According to them, the following combination of metrics has the strongest correlation to the capture costs:

$$GEM = \frac{\Delta N_{CO2}}{\Delta N_{N2}^{1.32} \times S_{des}^{0.25} \times \left| \Delta H_{ads,N2} \right|^{0.97}}$$
(1.11)

Other selection metrics focusing on specific applications have emerged over the past decade. For example, parasitic energy $E_{\text{parasitic}}^{84}$ has been proposed for the estimation of plant-wide power consumptions in carbon capture and storage,

$$E_{parasitic} = (0.75 \times Q_{thermal} \times \eta_{carnot}) + W_{comp}$$
(1.12)

where Q_{thermal} is the total energy required for adsorbent regeneration, η_{carnot} is the Carnot efficiency and W_{comp} is the compression energy required for gas transportation. For membrane based adsorptive separations, researchers have designed many selection criteria, about which we will not give a complete discussion here since this thesis focuses mainly on pressure swing adsorption processes. Interested readers are recommended to refer to this comprehensive review.⁸⁵

The choice of the different selection metrics in high-throughput screenings influences the final ranking of promising materials. Different selection criteria are adopted in different gas separations systems (e.g. $H_2/CH_4^{86,87}$, C_2H_2/CH_4^{88} , C_2H_2/CO_2^{89} , CO_2/H_2^{90} , $C_3H_8/C_3H_6^{91}$, hexane and heptane isomers⁹², and xylene isomers⁹³). For example, in the case of CH₄ storage, Wilmer et al.⁶⁹ screened the hMOF database of 137953 hypothetical MOFs at 35 bar and 298 K. They discovered a linear relationship between volumetric

methane adsorption loadings and volumetric surface areas but not between gravimetric surface areas. And they predicted that maximizing gravimetric surface area over the range of 2500-3000 m²/g would only worsen the methane storage capability. In the majority of the high-throughput screening studies of post-combustion CO₂ capture which involves the separation of CO₂/N₂, adsorption selectivity has been chosen as the primary indicator. Haldoupis et al.94 conducted GCMC simulations to predict Henry's constants of CO2 and N_2 for 489 MOFs. In total 11 highly selective MOFs (S > 190) were identified according to the infinite dilution selectivity of CO_2/N_2 at 303 K. Later on, Qiao et al.⁹⁵ further included working capacity and regenerability and they identified 15 promising MOFs for CO₂ capture. They discovered that 25% of the top MOFs contained lanthanide metal in the nodes. Recently, Leperi et al.⁸³ utilized a compound metric GEM to screen the CoRE MOF database, they estimated that for the most promising MOFs, the capture costs per tonne of CO₂ ranged from \$30 to \$40. It can be seen from the case studies of the post-combustion CO₂ capture adsorbent screening that selection metric evolved from the simplest ratio of Henery constants to the more sophisticated GEM. The difference between the metrics is that the former is computational cheap, while the latter integrates more closely with the adsorption processes. However, one should take notice that this does not mean the GEM is superior and can be universally applied in any cases. On the contrary, the more integration of the metrics to a specific adsorption process, the more generality it loses. GEM should be used with caution since a slight change in process modellings such as solvent price or utility cost may yield completely different results. Instead, selectivity remains the most useful criteria because it captures adsorption thermodynamics at the phase level.

1.3.4. State-of-the-art high-throughput screening

The current state-of-the-art high-throughput MOF screening for the separation/purification of C_2 hydrocarbons are based on properties. For example, Wu et al. performed a

comparative studied of the adsorptive C₂H₄/C₂H₆ separation in ZIF-3, ZIF-6, ZIF-8 and ZIF-10.96 With computational simulations of single component isotherms and IAST theory they computed binary mixture selectivity of C₂H₆/C₂H₄. It was found that ZIF-3 had the highest ethane selectivity of 4.79 at 1 kPa due to its strongest affinity with ethane. While ZIF-10 possessed the highest ethane selectivity of 1.75 at 8000 kPa because of the largest pore volume. They concluded that ZIF topology was likely the key factor for high C_2H_6 selectivity. Zhou et al.¹ investigated the separation of C_2H_2/C_2H_4 for the 4764 CoRE MOFs and identified 10 promising MOFs based on the mixture adsorption selectivity (Sads). Separation performance index (SPI) was proposed to eliminate the biased weights between selectivity and working capacity. Altintas and Keskin conducted a high-throughput screening of 278 MOFs for C₂H₄/C₂H₆ separation based on mixture adsorption selectivity (S_{ads}) , working capacity of ethane (ΔN_{C2H6}), and membrane permeability and found a significant number of candidates predicted with higher selectivities and working capacities compared to zeolites.⁹⁷ Liu et al. performed a high-throughput screening of 916 Cupaddlewheel-based MOFs containing open metal sites for C₂H₂/C₂H₄ separation.⁹⁸ Binary mixture selectivity (S_{ads,C2H2/C2H4}), adsorbent performance score (APS), and gas separation potential were calculated and applied to rank the adsorbent materials. They also developed new force fields established from ab initio computation. Their study revealed that the optimal range of the largest cavity diameter was from 5 to 10 Å and the pore volume fell in between 0.3 and 1.0 cm³/g. Recently, a high-throughput screening of MOFs for direct ternary mixture C₂H₂/C₂H₄/C₂H₆ separation was performed by Zhou et al.² Separation performance index (SPI) was utilized to rank MOFs in this purification scenario. Through the structure-property relationship study, it was discovered that Sads, C2H2/C2H4 decreased with increasing LCD, and Sads, C2H6/C2H4 increased with increasing LCD and the capacities of all C₂ components exhibited the trend where they increased first with pore volume until reaching the peak and after that slowly converged.

1.4. From properties to process performance-based high-throughput screening

High-throughput screening helps investigate C₂ separation MOF adsorbents by cutting down the search space for materials design and provides insightful and valuable information about the molecular or phase level properties of the adsorbent materials. But as a process engineer aiming to commercialize the technology, the question of whether the candidate MOFs can achieve process applicability (e.g. in pressure swing adsorption (PSA) processes) must be answered. Unfortunately, the state-of-the-art high-throughput screening, which has a property-centric architecture, lacks the capability in predicting such process performance.

The inability of high-throughput screening can be explained by two reasons. Firstly, process level metrics such as process productivity, overall energy consumption, and product purity generally do not directly correlate well with the intrinsic phase level properties of adsorbent materials. And most of the high-throughput material screening studies are simply property-based metrics oriented, relying on equilibrium adsorption data derived from molecular simulations. Secondly, materials selection is a multiscale problem in essence and the process scale plays a critical role. Such cross-scale influence results in complex interactions between process operating parameters (e.g. operating pressures, adsorption time duration, etc.) and adsorbent materials. To address these issues, we need a more comprehensive evaluation of not only materials' molecular or phase level properties but more importantly an inspection of their process applicability as well.

Consequently, the research paradigm has been gradually shifting to the processperformance based materials screening.^{1,89,97,99-111} The main idea of process-performance based screening is to add another layer of evaluation of process performance into the highthroughput screening framework. As a result, the process-performance based screening has a higher degree of integration than the property-based high-throughput materials screening. And it enables a coherent cross-scale materials performance evaluation from the very basic molecular scale to the industrial applicable process scale. In the process-performance based screenings, importance has been given to not only materials property evaluations but also process modelling and design. Compared to the high-throughput materials screening which only relates the molecular scale information (i.e. atomic positions) and the phase scale information (i.e. selectivity, working capacity, etc.), process-performance based materials screening instead focuses on a holistic assessment of adsorbent materials using process level metrics. (i.e. purity, productivity, energy consumption, etc.) Its workflow consists of various computational modules working together to perform different purposes. For example, GCMC simulations evaluate adsorption thermodynamics at the phase level, while adsorption process modellings predict flows of product streams.

1.4.1. Process performance-based high-throughput screening

The representation of materials is one of the important aspects in the process performancebased high-throughput screening. A well-chosen representation must ensure that relevant material properties and characteristics are captured accurately and balance both predictive ability and computational efficiency. For example, the representation of materials by the coordinates of every single atom in the framework is very detailed, and it has very high degrees of freedom in predicting materials molecular properties. However, such representation is too detailed to be useful when one wishes to carry out the process modelling, as it cannot be modelled in simple mathematics and incorporated into the system of equations. To facilitate the adsorption process modelling, the isotherm representation would be more suitable. In the isotherm representation, atomic information about MOF frameworks such as partial charges and pore structures is greatly simplified to only a few isotherm parameters depending on the type of isotherms. Such representation is advantageous not only because adsorption isotherms contain the most important adsorption-desorption information, but more importantly they have concise expression forms which can be processed efficiently from the mathematical perspective.

The modelling of P/VSA processes is the other key component in the process-performance based screening. With the aid of process modelling, it is possible to investigate the interaction between materials selection and processes design. The most detailed and complete P/VSA models involve balances in the column bed, macropores and micropores. However, solving this complete set of model equations is very challenging due to the large number of equations and the complex interrelationships. Fortunately, in most cases it is not necessary to model the complete system equations and it is often reasonable to apply simplifications to greatly reduce computational costs. Generally speaking, a complete modelling of pressure/vacuum swing adsorption processes involves mass, energy, momentum balances alongside with mass transfer rate models and gas-solid phase equilibrium relations. Depending on the adoption of the exact mass transfer rate model, the PSA models can be classified into three kinds, i.e. the local equilibrium model, the linear driving force approximation and the pore diffusion model. In terms of the complexity of the mass transfer rate models, the local equilibrium model has the least complexity, the pore diffusion model has the highest complexity, and the linear driving force approximation is in-between.

In the local equilibrium model, an instantaneous mass transfer is assumed, so that the bulk phase and inner particle concentrations of all species are always at equilibrium, displaying a zero concentration gradient. Despite its simplicity, the local equilibrium model neglects any kinetic influences in adsorption processes. Therefore its application is only limited to those processes where thermodynamics plays the dominant role.

To allow for a wider range of applications, the linear driving force (LDF) approximation has been proposed. In this model, the mass transfer rate is expressed as a linear function of equilibrium concentration difference (the driving force) and all the resistance is lumped into a single effective parameter called the linear driving force coefficient (k_{LDF}).

$$\frac{\partial q_i}{\partial t} = k_{LDF}(q_i - q_i^*) \tag{1.13}$$

where q_i is the local adsorption loading of component *i*, and q^* is the equilibrium loading at the bulk phase concentration. The linear driving force approximation, widely adopted by process systems engineers, has proven the ability to provide reasonably accurate depictions of adsorption processes in various separation systems. The LDF model succeeds because the estimation of the separation performance of an adsorptive process requires several sets of averaging of kinetic properties at the particle, the column, and the overall cyclic steady state levels.¹¹²

Lastly, in the most detailed pore diffusion model, the mass transfer rate is described as a function of diffusional radial gradient which has the form of Fick's Law. For the description of multicomponent diffusion fluxes, the Maxwell-Stefan diffusion model can be applied to replace the Fick's diffusion model.¹¹³

$$\frac{\partial q_i}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(D_i r^2 \frac{\partial q_i}{\partial r} \right) \tag{1.14}$$

where D_i is the diffusion coefficient and r is the radial length of a spherical particle.

1.4.2. State-of-the-art process-performance based adsorbent

evaluations

Some studies on the modelling of PSA processes have been reported. For example, Nikolaidis et al. presented a mathematical modelling framework for the simulation and optimization of P/VSA processes for post-combustion CO₂ capture in 13X-based adsorbents.¹¹⁴ They developed a modeling framework for efficient simulation and optimization strategies of PSA/VSA processes employing adsorption and transport models of varying complexity. The core of the modeling framework encompassed a detailed adsorption column model relying on a macropore controlled LDF transport model. Using

the modeling framework, they optimized feed pressure, feed flow rate, blowdown pressure and evacuation pressure for minimal energy consumption under specified minimum requirements of CO_2 purity and in CO_2 recovery. The modeling equations were implemented and solved in the gPROMSTM modeling environment. They revealed complex relationships between optimal process performance indicators and operating conditions for different adsorbents.

In addition, Leperi et al. investigated post-combustion CO₂ capture in the presence of water for four adsorbents 13X, 5A, HKUST-1 and Ni-MOF-74. The detailed P/VSA modelling was also a macropore controlled LDF model, similar to the one used by Nikolaidis et al., but in this paper they included an additional process economics calculation, with which they managed to optimize overall capture costs (capital and operating costs) for each material.¹¹⁵ The resulting PDAE system was coded and solved in MATLABTM. They emphasized that the level of water removed before a P/VSA cycle for CO₂ capture is an important process design variable for adsorbent materials to operate with minimum dehydration of the flue gas. Their results also suggested the importance of process level thinking when it came to materials selection.

Another macropore controlled LDF modelling was conducted by Ferreira et al.¹¹⁰ They studied oxygen concentration from air in the two stage VPSA processes packed with a carbon molecular sieve and AgLiLSX. They investigated the influences of five process variables (adsorption pressure of the KPSA stage, adsorption time of the KPSA stage, adsorption time of the VPSA stage, pressurization time of the VPSA stage, and raffinate flow rate of the KPSA stage) on the product purity and recovery using ASPEN adsorption simulator. They demonstrated that with proper process configurations a maximum oxygen product purity of 99.6% can be achieved.

Moreover, Burns et al. integrated a pore diffusion model into the VSA model which was validated at the pilot scale, and they screened 1632 MOFs for post-combustion CO₂ capture. The model accounted for the dynamics of heat transfer within the column and

across the column walls, mass transfer including diffusion of gas into the macro pores of sorbent particles, frictional pressure drops, and the concentration and temperature changes due to adsorption/desorption. Parasitic energy (PE) was calculated using well established efficiencies for vacuum pumps, blowers, and compressors. They underscored the importance of process simulations in estimating accurate PE and productivity.¹⁰⁴

The above-mentioned works demonstrate that successful simulations of PSA processes depend very much on the coupled simplifications, especially the choice of mass transfer rate models. The wide application of LDF in PSA modelling serves a perfect illustration. That is the importance of balancing the tradeoff between computational time costs and simulation details when modelling the PSA processes. An extensive review of more examples of PSA process modelling is available in the literature.¹¹⁶

2. High-throughput computational screening of metalorganic frameworks for ethylene purification from ethane/ethylene/acetylene mixture

In this Chapter, a computational high-throughput screening of metal-organic frameworks (MOFs) for the purification of ethylene from the ternary ethane/ethylene/acetylene mixture under thermodynamic equilibrium conditions is conducted. In section 2.1 we reiterate the motivation of the high-throughput screening and give a detailed summary of the history of the experimental discovery of MOF materials for C₂ separations. Next, in section 2.2 we discuss the choice of CoRE MOF database and the detailed molecular simulation setups. In section 2.3 the GCMC simulations results are first verified against experimentally reported values. Then a modified evaluation metrics (*SPI*) is proposed for an efficient description of the performance of MOFs for the ternary mixture separation. Two different separation schemes are proposed, and potential MOF adsorbents are identified accordingly. The quantitative structural property relationships (QSPR) between the characteristics of MOFs and their adsorption performances are discussed. The QSPR studies reveal general adsorption characteristics among the MOFs candidates and valuable information about the optimal MOFs. In section 2.4, a brief summary of the chapter is given with a conclusion of the major findings.

2.1. Motivation

Ethylene (C₂H₄) is one of the major chemicals in the petroleum industry, which can be produced by thermal cracking from various sources; for instance, natural gas, naphtha and gasoline.¹¹⁷ In C₂H₄ production, the separations of acetylene (C₂H₂) and ethane (C₂H₆) from C₂H₄ are achieved through catalytic partial hydrogenation and cryogenic distillation, respectively.¹¹⁸ However, they are very energy consuming processes due to extreme

operating conditions. Over decades, adsorptive separation under mild conditions on a novel class of nano-porous materials, known as metal-organic frameworks (MOF), has been suggested as a substitute.¹¹⁹ Due to their structural diversities, MOFs feature many outstanding properties such as tunable pore sizes and high surface areas,¹²⁰ making them ideal for many applications, such as membranes based purification,¹²¹ removal of environmental pharmaceutical contaminants,^{122,123} gas storage and in particular gas separation.

A number of MOFs have been reported as promising materials for the separation of C_2H_2/C_2H_4 based on different mechanisms. Some utilize a size-selective sieving effect. For example, Xiang et al. discovered that M'MOF-3a could separate C_2H_2 and C_2H_4 with a high selectivity of 25.53 at 195 K and 5.23 at 295 K based on the different sizes of the solutes.³⁸ Hu et al. (2015) revealed that the suitable pores and opening windows of UTSA-100a could lead to a high C_2H_2 uptake of 4.27 mmol/g and a C_2H_2/C_2H_4 selectivity of 10.72 at 296 K and 1.0 bar. Besides, MOFs featuring open metal sites (OMS) have been found effective for the C_2H_2/C_2H_4 separation due to large affinity. However, the OMS bind strongly with both C_2H_2 and C_2H_4 , resulting in a relatively low selectivity. For instance, Bloch et al. demonstrated that Fe₂(dobdc) had a high C_2H_2 uptake of 6.8 mmol/g, but a low C_2H_2/C_2H_4 selectivity of 2.08 at 318 K and 1.0 bar.¹⁹ In addition to that, Yang et al. showed that NOTT-300 could separate the mixture through weak supramolecular interactions aligned within the host.²⁰ Finally, MOFs containing anions (such as SIFSIX) have been also found to be promising for the C_2H_2/C_2H_4 separation.²⁵

For the separation of C_2H_4/C_2H_6 , there have been many MOFs reported to be C_2H_4 selective, such as $Fe_2(dobdc)^{19}$, PAF-1-SO₃Ag⁵¹, NOTT-300²⁰ and etc. However, only limited MOFs with reverse selectivities towards C_2H_6 have been reported. Gücüyener et al. first demonstrated the C_2H_6 selectivity of ZIF-7 and concluded that its selectivity was induced by a gate-opening mechanism.⁶⁷ Liao et al. found that MAF-49 had a C_2H_6

selectivity of 2.7 and a capacity of 1.73 mmol/g at 298 K.⁵⁷ Later, Lin et al. studied Cu(Qc)₂ and found that its capacity towards C_2H_6 was 1.85 mmol/g and the C_2H_6/C_2H_4 selectivity was 3.4 at 298 K and 100 kPa.⁵⁸ Chen et al. reported an iron-based MOF PCN-250 as another C_2H_6 selective adsorbent. Its adsorption capacity towards C_2H_6 and C_2H_4 was 5.21 mmol/g and 4.22 mmol/g at 298 K and 100 kPa, respectively, and the C_2H_6/C_2H_4 selectivity was in the range of 1.9-4.0.³⁷

Unlike the widely investigated binary separations, a direct purification of C_2H_4 from the ternary mixture $C_2H_2/C_2H_4/C_2H_6$ has been much less studied. The direct purification of C_2H_2 from the ternary C_2 mixture is appealing because of it is an intensified process with less capital investment in units and potential reduced operation costs. There are basically two different strategies. Hao et al. synthesized a one-step C_2 separation MOF TJT-100 that can simultaneously trap C_2H_2 and C_2H_6 with strong binding affinities. TJT-100 was reported having high selectivities for C_2H_2/C_2H_4 of 8.5 and C_2H_6/C_2H_4 of 5.75.²⁶ Chen et al.³⁵ introduced the concept of synergistic sorbent separation technology (SSST) to enable one-step high-purity ethylene production from the ternary mixture. In the SSST, three benchmark sorbents (SIFSIX-3-Ni, TIFSIX-2-Cu-i, and Zn-atz-ipa) were selected for CO₂, C_2H_2 , and C_2H_6 removal, respectively. They successfully demonstrated that for the purification of the (1:1:1:1 CO₂/C₂H₂/C₂H₄/C₂H₆) mixture, this technology yielded 99.9% of ethylene purity and a working capacity of 0.14 mmol/g.

To identify candidates with great potential in the direct purification of the ternary C_2 mixture is a challenging task. Fortunately, a high-throughput computational screening using the grand canonical Monte Carlo (GCMC) simulation can predict adsorption equilibria of many MOFs fast and efficient.

2.2. Computational details of high-throughput screening

2.2.1. MOF database

The computation-ready, experimental metal-organic framework (CoRE MOF) database⁷² containing totally 4764 MOF candidates was chosen as the screen basis due to the following reasons. First, this database consists of a variety of MOF structures, which provide a rich search space for finding promising adsorbents; second, the structures in the database are immediately suitable for molecular simulations without any further modifications; third, each MOF has already been experimentally reported and recorded with a unique Cambridge Structural Database (CSD) code¹²⁴ so that the screened materials can be synthesized with confidence for further experimental validations.

2.2.2. Molecular simulation

Molecular simulation enables multifaceted investigations of intermolecular and intramolecular phenomena on the microscopic scale by advanced computational algorithms. GCMC simulation, with constant chemical potential, volume and temperature, but variable number of molecules, has been widely used for studying adsorption equilibrium.¹²⁵ Here, we implement GCMC simulations using the software RASPA⁷⁴ to estimate the adsorption equilibria of the ternary mixture $C_2H_2/C_2H_4/C_2H_6$ over the 4764 MOFs.

For the GCMC simulation, various parameters need to be specified properly. First, general parameters such as Monte Carlo moving probabilities, cut-off radius, cell size, and number of cycles are defined. Here, four types of Monte Carlo moves (i.e., translation, rotation, reinsertion, and swap) are considered. The probabilities of the occurrences of these moves are set equal. In addition, a cut-off radius of 12.0 Å is used. The simulation cell size is

expanded to at least 24.0 Å along all the three spatial dimensions and the corresponding periodic boundary conditions are applied. Each simulation is carried out with first 30,000 cycles for equilibration and subsequent 20,000 cycles for production. Additionally, the Peng–Robinson equation of state is used to estimate the gas phase fugacities of species.

Next, to calculate the energy state of the whole system the following force field equation is used.¹²⁶

$$U = \sum_{i,j,i\neq j} 4 \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i,j,i\neq j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$
(2.1)

where ε_{ij} is well depth, σ_{ij} is collision diameter, r_{ij} is the distance between atoms *i* and *j*, q_i is the atomic charge of atom *i*, and ε_0 is 8.8542×10⁻¹² (C²N⁻¹m⁻²). The first term describing Van der Waals interactions is the Lennard-Jones (LJ) potential and the second term representing electrostatic interactions is the columbic potential.

In addition to the force filed equation, force field parameters are provided. First, for adsorbate molecules (C_2H_2 , C_2H_4 , and C_2H_6), the Lennard-Jones (LJ) potential parameters (σ and ε), partial charge (q), and bond length (l) are specified. Table 2-1 lists all the molecular parameters of the gas components where those of C_2H_2 are taken from the reference¹²⁷ and those of C_2H_4 and C_2H_6 are adopted from the reference¹²⁸. Next, for host frameworks, the LJ potential parameters are adopted from the DREIDING force field¹²⁹ and those of the missing atoms taken from the UFF force field¹³⁰. EQeq method¹³¹ are used to estimate the charges on the MOF framework. In the simulations, MOFs are considered as rigid and thus the interactions between MOF atoms are ignored. The cross LJ parameters are computed using the Lorentz-Berthelot combining rule¹³⁰ except those between Cu of MOF and C of C₂H₂ that are modified according to the reference¹²⁷.

	Atoms	σ (Å)	<i>ε</i> (К)	<i>q</i> (e)	Bond length <i>l</i> (Å)
C_2H_2	C in C_2H_2	3.800	57.875	-0.278	1.211 (C≡C)
	H in C ₂ H ₂	0	0	0.278	1.071 (C—H)
C_2H_4	CH_2 (sp ²)	3.685	93.0	0	1.330 (C=C)
C_2H_6	$CH_3(sp^3)$	3.750	98.0	0	1.540 (C-C)

Table 2-1: Molecular parameters for modelling of C₂H₂, C₂H₄, and C₂H₆

2.3. Results and discussions

2.3.1. GCMC validation

The reliability of GCMC simulations was validated by experimental data. In the literature, the amount of C_2H_2 and C_2H_4 adsorbed on different MOFs (i.e., MOF-5, ZIF-8, and UTSA-20) has been measured at 298 K and 10⁵ Pa.^{19,36,132} In addition, the adsorption uptakes of C_2H_6 on Fe-MOF-74, MOF-505, and UTSA-20 have also been measured at 318 K and 10⁵ Pa.³⁶ Under the same experimental conditions, the pure component uptakes of C_2H_6 were simulated and those of C_2H_2 and C_2H_4 were directly taken from our previous work.¹

The comparison of the GCMC results and experimental data is presented in Figure 2-1. Clearly, the majority of the data lies close to the parity line, indicating an overall good agreement between experimental and simulated uptakes. However, some MOFs such as Mg-MOF-74 and Fe-MOF-74 lie far away from the parity line. This is mainly due to the fact that the M-MOF-74 (where M = Mg, Fe, et al.) family contains open metal sites (OMS) which can strongly bind with the adsorbates.¹³³ In this case, the standard force field parameters are unable to appropriately capture these interactions. For better illustration, we calculated the zero coverage isosteric heat of adsorption Q_{st}^0 for the two outliers. Note that the absolute value of Q_{st}^0 indicates the strength of the MOF-adsorbate interactions. As

shown in Table 2-2, the two Q_{st}^0 derived from molecular simulation are significantly lower than the corresponding experimental values, which demonstrates the lack of accurate force field parameters for the description of coordination interactions between OMS and adsorbates. Some methods such as quantum mechanics (QM) calculations^{134,135} have been developed to improve the accuracy of force field parameters. However, the identification of MOFs containing OMS is very laborious and the re-adjustment of force field parameters through rigorous QM calculations is computationally expensive. Therefore, to facilitate the large-scale MOF screening, we adopted the general force field parameters to keep a compromise between simulation precisions and computational cost.



Figure 2-1: Comparison between the experimental and GCMC simulated purecomponent adsorption uptakes

	Simulated Q ⁰ st (kJ/mol)	Experimental Q ⁰ st (kJ/mol)
C ₂ H ₆ in Fe-MOF-74 at 318 K	-20.1	-28.2
C ₂ H ₄ in Mg-MOF-74 at 298 K	-22.8	-43.0

Table 2-2: Isosteric heat of adsorption at zero coverage Q^{0}_{st}

2.3.2. Capacity and selectivity

For the evaluation of separation performance of adsorbent, the capacity and selectivity are two important indicators. The adsorption capacity q_i ($i = C_2H_2$, C_2H_4 and C_2H_6) is usually defined as the amount of gas adsorbed in the solid adsorbent. Additionally, the selectivity is typically defined for a binary system (component = i, j):

$$S_{i,j} = \frac{K_i}{K_j} = \frac{x_i}{y_i} / \frac{x_j}{y_j}$$
 (2.2)

where K_i is the equilibrium constant. y_i and x_i are the molar fractions of species *i* in the gas and solid phases, respectively. In a ternary system, selectivity can be defined likewise. For instance, in order to obtain a purified C₂H₄ product C₂H₄ needs to be separated from C₂H₂ and C₂H₆ impurities in the ternary mixture. Obviously, MOFs with high C₂H₂ and C₂H₆ uptakes and low C₂H₄ uptake are desired. Thus, two selectivity indicators ($S_{C2H2/C2H4}$ and $S_{C2H6/C2H4}$) can be defined for MOF screening where the first is the selectivity of C₂H₂ over C₂H₄ and the second is the selectivity of C₂H₆ over C₂H₄ in the ternary mixture.

We conducted GCMC simulations for all the 4764 MOFs in the CoRE MOF database. The concentrations of the three components $C_2H_2/C_2H_4/C_2H_6$ were set to 5.0/90/5.0 (mol/mol/mol) and the adsorption simulation was conducted at ambient conditions (i.e., 298 K and 1.0 bar). Note that only 4462 of the 4764 MOFs show valid non-zero uptakes. The obtained equilibrium adsorption loadings of the 4462 MOFs are plotted in Figure 2-2

with each point representing a single MOF. From this figure, we found that the adsorption uptakes of the three components are roughly in the order of $q_{C2H2} > q_{C2H4} > q_{C2H6}$. This can be explained by the differences in the molecular model parameters. As indicated in Table 2-1, for both C₂H₆ and C₂H₄ we used two-site models with three parameters. In contrast, C₂H₂ was modeled as a four-site molecule with additional point charge parameters. The introduction of point charges on the C and H atoms provides additional electrostatic interactions between C₂H₂ and the MOF atoms, which leads to the highest adsorption uptake of C₂H₂. Furthermore, a strong correlation between the uptakes of C₂H₄ and C₂H₆ can be observed from Figure 2-2. This is primarily due to their similar molecular models and parameters (see Table 2-1).



Figure 2-2: Equilibrium adsorption uptakes of C_2H_2 , C_2H_4 and C_2H_6 in the ternary mixture at 298 K and 1 bar

In addition to the adsorption capacity, we calculated the separation selectivity of C_2H_6/C_2H_4 and C_2H_2/C_2H_4 for each MOF candidate. The results are shown in Figure 2-3.

It can be found that the selectivity of C_2H_2/C_2H_4 spans a wide range. By contrast, the distribution of C_2H_6/C_2H_4 selectivity is much narrower. Moreover, most of the C_2H_6/C_2H_4 selectivity is lower than 2.0 (red dash line), which reveals the relative difficulty for the separation of C_2H_6 from C_2H_4 .



Figure 2-3: Adsorption selectivity of C_2H_2/C_2H_4 and C_2H_6/C_2H_4 in the ternary mixture at 298 K and 1 bar

2.3.3. Selection of potential MOFs

The product of selectivity and capacity has been widely used as a criterion for the selection of MOFs for binary gas separations.^{89,136} However, this simple performance indicator needs some modifications before it can be used to rank MOF candidates for ternary separation systems. First, unlike binary systems where a unique pair of selectivity and capacity is involved, for ternary mixtures selectivity and capacity must be carefully defined to give an appropriate description of the separation performance. Second, the selectivity and capacity often differ in several orders of magnitude. Thus, the direct product of selectivity and capacity can be dominated by one single factor. Such a biased metrics is not useful for the screening of best adsorbents. Based on these considerations, we propose a new selection performance indicator (*SPI*) for the evaluation of the performance of MOFs for the separation of the ternary $C_2H_2/C_2H_4/C_2H_6$ mixture.

$$SPI = \log(S_{C2H2/C2H4}) \times q_{C2H2} \times \log(S_{C2H6/C2H4}) \times q_{C2H6}$$
(2.3)

$$SPI_{C2H2} = \log(S_{C2H2/C2H4}) \times q_{C2H2}$$
 (2.4)

$$SPI_{C2H6} = \log(S_{C2H6/C2H4}) \times q_{C2H6}$$
 (2.5)

To provide a deeper insight of the selection metrics, we divide the SPI into two parts. The product of the first two terms denoted as SPI_{C2H2} represents the performance of MOF for C₂H₂ separation. Similarly, the product of the last two terms denoted as SPI_{C2H6} measures MOF's performance for C₂H₆ separation. Figure 2-4 plots the SPI_{C2H2} and SPI_{C2H6} for all the MOF candidates. It can be observed that SPI_{C2H6} is generally much smaller than SPI_{C2H2} . This confirms that the separation of C₂H₆ from C₂H₄ is more difficult than the separation of C₂H₂ from C₂H₄. Moreover, the distribution of

 SPI_{C2H2} and SPI_{C2H6} forms a Pareto-like front, which indicates a competitive relation between the separation of C_2H_2 and C_2H_6 .



Figure 2-4: C_2H_2/C_2H_4 separation performance *versus* C_2H_6/C_2H_4 separation performance (red dash line: *SPI* = 50)

Two different separation schemes are proposed for the ternary mixture: i.e., single-step separation using only one single MOF as the adsorbent and multi-step separation using multiple MOFs packed in sequence as the adsorbent. As illustrated in Figure 2-5(a), in the single-step separation process, C_2H_2 and C_2H_6 are adsorbed simultaneously in a single sorption cycle and a pure C_2H_4 product stream can be obtained directly. This separation process uses only one adsorbent material, which significantly reduces the process complexity. Accordingly, the MOF selection criterion is the maximization of SPI that compromises the material performance for both C_2H_2 and C_2H_6 separations. Table 2-3 lists the best 10 MOFs for the single-step separation as well as their corresponding structural properties, selectivity, capacity, and SPI values. As depicted,

Rank	CSD Code	Metal	LCD (Å)	Pore Volume (cm ³ /g)	S _{C2H2/C2H4}	<i>q</i> С2H2 (сm ³ /g)	S _{С2H6/С2H4}	<i>q</i> С2H6 (ст ³ /g)	SPI (cm ⁶ /g ²)
1	CUNXIS	Al	4.73	0.22	22.2	22.2	18.7	18.6	705.8
2	CUNXIS10	Al	4.73	0.22	16.6	20.4	13.3	16.3	455.0
3	GIHBII	Ga	4.58	0.17	17.5	18.3	6.56	6.85	127.4
4	NEXXEV	Li	10.14	0.92	36.7	128.8	1.18	4.15	60.8
5	JAVTAC	Al	5.08	0.21	147.4	51.5	2.97	1.04	54.7
6	BEKSAM	Ga	4.04	0.13	30.8	27.1	2.99	2.63	50.4
7	XEDPON	Zn	7.48	0.56	48.0	114.6	1.17	2.80	37.6
8	LEVNOQ01	Mg	5.91	0.58	16.4	56.1	1.32	4.52	37.0
9	XEKCAT01	Mg	5.92	0.67	11.5	61.1	1.22	6.50	36.4
10	EYACOX	Eu	8.14	0.72	15.3	64.5	1.23	5.17	34.9

Table 2-3: Structural properties, selectivity, capacity and SPI of the top 10 MOF candidates for the single-step separation of C₂H₂/C₂H₄/C₂H₆



Figure 2-5: Schematic diagram of two adsorption process configurations for the separation of the $C_2H_2/C_2H_4/C_2H_6$ mixture (a) single-step separation (b) multi-step separation

Although the single-step process is easy to operate, it may be difficult to find an adsorbent that shows excellent separation performance for both C_2H_2 and C_2H_6 . Additionally, the regeneration of MOF produces an C_2H_6/C_2H_2 mixture, which need to be further separated and recycled back to the cracking reactor for maximizing the C_2H_4 yield. Considering these factors, another multi-step separation process shown in Figure 2-5(b) is introduced. Unlike the single-step separation, the multi-step process separates each impurity on an individual adsorbent sequentially. For purifying C_2H_4 from $C_2H_2/C_2H_4/C_2H_6$, two different strategies can be employed. Specifically, one can first select a C_2H_2 -selective MOF to separate C_2H_2 and then employ another C_2H_6 -selective MOF to adsorb C_2H_6 . Alternatively, the opposite separation sequence can be also applied. The top five C_2H_2 -selective MOFs and C_2H_6 -selective MOFs are listed in Table 2-4 according to their individual SPI values. The numerous combinations of one

adsorbent from each group provide a great chance for the successful implementation of the multi-step separation process. For example, out of all the 25 combinations, ORAQUU and CUNXIS can be selected due to their highest *SPI*_{C2H2} and *SPI*_{C2H6} values.

Table 2-4: Structural properties, selectivity, capacity and SPI of the top five MOFs for C_2H_2 separation (ranked according to SPI_{C2H2}) as well as the top five MOFs for C_2H_6 separation (ranked according to SPI_{C2H6}) for the multi-step separation of

			02112/	02114/02110			
Rank	CSD Code	Metal	LCD (Å)	Pore Volume (cm ³ /g)	Sc2H2/C2H4	<i>q</i> C2H2 (cm ³ /g)	<i>SPI</i> _{C2H2} (cm ³ /g)
1	ORAQUU	Bi, Zn	8.39	0.68	5216.4	354.7	1318.5
2	FENVOL	Zn	6.69	0.44	39528.8	281.4	1293.7
3	ZUQVIQ	Mn	5.78	0.66	5033.4	232.8	861.6
4	OHOFEW	Co	7.31	0.68	5735.7	202.6	761.5
5	VEHNED	Na, Ni	3.81	0.22	454736.8	115.0	650.5
Rank	CSD Code	Metal	LCD (Å)	Pore Volume (cm ³ /g)	S _{C2H6/C2H4}	<i>q</i> _{С2H6} (ст ³ /g)	<i>SPI</i> _{C2H6} (cm ³ /g)
1	CUNXIS	Al	4.73	0.22	18.7	18.6	23.6
2	CUNXIS10	Al	4.73	0.22	13.3	16.3	18.3
3	GIHBII	Ga	4.58	0.17	6.56	6.85	5.6
4	UFATEA01	Ni	5.37	0.42	2.02	7.41	2.3
5	CEYPUT	Co	5.37	0.42	1.82	6.71	1.7

 $C_2H_2/C_2H_4/C_2H_6$

2.3.4. Structure-property relationships study

Some valuable insights about the relation between MOF materials and their adsorption abilities can be extracted from the high-throughput screening by conducting the structure-property relationship study. These insights provide useful information for the experimental design of novel high-performing adsorbents. First, to quantify the influence of structural parameters on the adsorption selectivity, the relationship between the largest cavity diameter (LCD) and the selectivity of C_2H_2/C_2H_4 and C_2H_6/C_2H_4 is shown in Figure 2-6. As depicted Figure 2-6(a), the majority of the C_2H_2/C_2H_4 selectivity are higher than 1.0 and the highest selectivities are generally achieved at small LCDs (below 4.0 Å). It can be observed from the data, the C_2H_2/C_2H_4 selectivity generally decreases as the LCD increases when it is above 1. Similar trends in relations between LCD and selectivity were reported in the literature.^{95,137} In Figure 2-6(b), however, one can see that the selectivity of C_2H_6/C_2H_4 increases with LCD and reaches its highest value at around 4.7 Å. As the LCD increases further, both selectivities tend to converge to 1.0. This indicates that MOFs with very large LCDs are neither C_2H_2 selective nor C_2H_6 -selective. This is not surprising because when the LCD is small, where three components have to compete for limited adsorption space, molecules with smaller size will be bound more easily. When LCD increases more adsorption sites become available, hence all the components eventually will have equal chances to be adsorbed in the large pores of the frameworks till saturation.





Figure 2-6: Adsorption selectivity of MOF with respect to (a) C_2H_2/C_2H_4 and (b) C_2H_6/C_2H_4 versus LCD

Figure 2-7 shows the dependency of adsorption capacity on pore volume of MOF. As indicated in Figure 2-7(a), the adsorption capacity of C_2H_2 increases with the pore volume until it achieves a maximal value of 354.7 cm³/g at pore volume of 0.68 cm³/g. As the pore volume increases further, the capacity of C_2H_2 starts to decline and finally converges to 2.5 cm³/g. Figure 2-7(b) and Figure 2-7(c) share a similar trend. Generally, the adsorption capacities of both C_2H_4 and C_2H_6 increase with pore volume until reaching the peak. Further increasing the pore volume, the adsorption capacities of C_2H_4 and C_2H_6 gradually decline to a limit value of 25.0 cm³/g and 1.5 cm³/g, respectively. It is observed that high capacities are achieved at moderate pore volumes between 0.5-1 cm³/g. This might be explained by the fact that the pore volume is inversely proportional to framework density as demonstrated by Kong et al.¹³⁸ Thus, adsorption capacities are always subjected to a balance between pore volume and MOF

density. Comparing Figure 2-7(a-c), although increasing the pore volume until 0.68 cm³/g leads to a larger adsorption capacity of impurities C_2H_2 and C_2H_6 , it also causes a higher loss of product C_2H_4 . Besides, due to the very analogous dependency of adsorption capacities of C_2H_4 and C_2H_6 on pore volume, the amount of removed C_2H_6 is always proportional to the amount of lost C_2H_4 .







Figure 2-7: Adsorption capacity of MOF for (a) C₂H₂, (b) C₂H₄ and (c) C₂H₆ in dependence on pore volumes

2.4. Chapter summary and outlook

In summary, we studied the separation of C₂H₄ from the C₂H₂/C₂H₄/C₂H₆ mixture and screened the MOF adsorbents from the CoRE MOF database by GCMC simulation. We first validated its accuracy and showed that the force field in general yielded satisfactory results for adsorption equilibrium prediction expect for a few MOFs with the OMS effect. In the property based high-throughput screening, a quick and efficient identification and ranking of MOF candidates has been realized. Based on evaluation metrics *SPI*, two separation strategies for C₂ ternary mixtures have been proposed. In the single-step (one adsorbent) separation strategy, among all CUNXIS with the highest *SPI* value at 705.8 (cm⁶/g²) was identified as the best. In the multi-step (two adsorbents) separation strategy, ORAQUU and CUNXIS with the highest *SPI* being 1318.5 (cm³/g) and 23.6 (cm³/g) respectively formed the best combination. In addition, quantitative

relationships between MOFs' physical structures and adsorption abilities have been unveiled. We discovered that $S_{C2H2/C2H4}$ generally decreases with increasing LCD, while $S_{C2H6/C2H4}$ displays an opposite trend where it increases with increasing LCD. However, for all three components, capacities share a similar pattern where they all increased first with pore volume until reaching the peak (peak pore volume range between 0.5-1 cm³/g) and after that slowly converged. Despite the identification of a few promising adsorbents, the selection criteria SPI derived from the phase level properties may not guarantee a success in practical processes because of the interactions between materials and processes. For this reason, in the next chapter we will present a study of the influence of adsorbents on adsorption processes with the aid of detailed process modellings for improvement.
3. Multiscale screening of metal-organic frameworks for one-step ethylene purification in pressure swing adsorption processes

In this Chapter, a model-based hierarchical process performance-based high-throughput screening framework is proposed to select MOF adsorbents and design the adsorption processes simultaneously. By combining property-based (selectivity and regenerability) material screening, breakthrough simulation, and P/VSA process optimization, we demonstrate not only the suitability of MOFs for one-step C₂H₄ purification but also their practical applicability in P/VSA processes. In Chapter 0, we first define the ethylene purification problem and introduce the P/VSA model in detail. Then, Chapter 3.3 starts with a simulation case study of the P/VSA process using TJT-100 as the benchmark adsorbent and put forward a P/VSA process optimization problem. We then proceed to identify promising MOF candidates from the CoRE MOF database by a revision of previously used selection metrics and optimize the corresponding P/VSA processes to maximize the C₂H₄ purity and recovery. Finally, we examine the energy consumption and productivity of the feasible MOFs meeting the purity and recovery requirements. Moreover, we estimate the unit costs of the best two P/VSA processes and evaluate their operating robustness in response to the feed composition fluctuation. Finally, in Chapter 3.4 we end this chapter with major findings and a discussion of potential improvements for our study.

3.1. Motivation

Ethylene production plays a critical role in the petrochemical industry with a global annual consumption of over 150 million tonnes.¹¹⁷ At present, steam cracking of naphtha or ethane remains the primary method for ethylene production in spite of being energy intensive. It has been estimated that in a typical steam cracking process, 35-50% of the total energy is consumed during the fractionation, compression, and separation of C₂ light hydrocarbons steps.³ Fortunately, in the last two decades, adsorptive separation on metal-organic frameworks has emerged as an energy-efficient alternative technology with great potential to address the challenge of C₂ separations.^{139,140}

MOFs, comprised of metal node clusters linked by organic linker ligands forming 2D or 3D porous networks, exhibit a large variety of pore chemistries. They can be finetuned to meet specific needs, leading to wide applications including gas storage, separation, and purification.¹⁴¹ Many MOFs have been reported with high ethylene selectivity in binary systems (C₂H₄/C₂H₂ or C₂H₄/C₂H₆), such as Cu-BTC¹⁴², ZIF-8¹⁸, $Fe_2(dobdc)^{19}$, NOTT-300¹⁴³, M₂(*m*-dobdc) (M = Mn, Fe, Co, Ni; *m*-dobdc⁴⁻ = 4,6dioxido-1,3-benzenedicarboxylate)²¹, etc. In comparison, the design of C_2H_4 purification adsorbents for ternary mixtures (C₂H₂/C₂H₄/C₂H₆) was much less explored, due to the separation difficulty stemming from the complex multicomponent adsorption environment.²²⁻²⁵ To address this challenge, a number of one-step C₂H₄ purification MOFs with customized binding sites have been synthesized, for instance, $TJT-100^{26}$, Azole-Th-1²⁷, UiO-67-(NH₂)2²⁸, PCP-FDCA²⁹, MOF [Zn-(BDC)(H₂BPZ)]·4H₂O³⁰, UPC-612 and UPC-613³¹. Apart from the modifications of host-adsorbate interactions, researchers also developed MOFs with tailor-made pore structures to capture target molecules, for example, NPU- $1/2/3^{34}$ and CuTiF₆-TPPY²². In addition to the efforts in designing one-step C₂H₄ purification MOFs, Chen et al.³⁵ introduced the concept of synergistic sorbent separation technology (SSST). The idea was to split the adsorption

column into multiple sections to accommodate different MOFs so that impurities can be removed sequentially. In their work, TIFSIX-2-Cu-i was packed in the first section to remove C_2H_2 , followed by a second section where Zn-atz-ipa was packed to adsorb C_2H_6 . Using this approach, the authors managed to produce polymer-grade ethylene (purity > 99.9%) from an equimolar ternary C_2 mixture.

Experimental discovery of C₂ purification MOFs is time-consuming. Fortunately, highthroughput computational material screening, with the ability to identify promising materials from thousands of candidates in a short time, can accelerate the discovery of novel materials.^{94,144} Wu et al.⁹⁶ presented a comparative study on the adsorptive separation of C₂H₄/C₂H₆ in ZIF-3, ZIF-6, ZIF-8, and ZIF-10 by coupling singlecomponent isotherm simulations with ideal adsorbed solution theory (IAST)-based selectivity calculations. Altintas and Keskin were the first to conduct a high-throughput screening of 278 MOFs for C₂H₄/C₂H₆ separation. By evaluating adsorption selectivity, diffusion selectivity, working capacity and gas permeability, they proposed five MOFs outperforming traditional membrane materials.⁹⁷ Similarly, Liu et al. performed a screening of 916 Cu-paddlewheel-based MOFs containing open metal sites for C₂H₂/C₂H₄ separation, and rationally designed three MOFs with fluorine functional groups.⁹⁸ Recently, a direct screening of 4764 MOFs for ternary C₂H₂/C₂H₄/C₂H₆ separation was performed and ten most promising one-step C₂ purification MOFs were identified.²

All the previous high-throughput studies used property-based metrics (mainly selectivity and capacity) to screen adsorbents. The exclusion of process influence prevented a satisfactory prediction on the practical applicability of the materials in real adsorption processes. As a consequence, the research paradigm has been gradually shifting to the process performance-based materials screening,^{1,89,97,99-111} where process performances (e.g., purity and recovery) instead of property-based metrics are targeted.

Nikolaidis et al.¹¹⁴ presented a mathematical modelling framework for the optimization of energy consumption in P/VSA processes using 13X-based adsorbents for postcombustion CO₂ capture. Leperi et al.¹¹⁵ further investigated post-combustion CO₂ capture in the presence of water using four adsorbents, i.e., 13X, 5A, HKUST-1, and Ni-MOF-74. By comparing the capture cost of each material, they concluded that 13X was the best adsorbent with a capture cost of \$32.1/tonne under the dry flue gas condition while 13X and 5A performed equally well (\$34.1/tonne) under the humid flue gas condition. In addition to CO₂ capture, Ferreira et al.¹¹⁰ studied oxygen concentration from air in a two-stage P/VSA processes packed with a carbon molecular sieve and a zeolite. They investigated the influence of process operating variables on the purity and recovery of oxygen product using ASPEN adsorption simulator and achieved a maximal oxygen purity of 99.6%.

Despite the progress, a process performance-based high-throughput screening of onestep C_2H_4 purification MOFs has not been systematically undertaken yet. Here, we present a multiscale hierarchical framework, which combines property-based highthroughput material screening and model-based process optimization, to identify promising one-step C_2H_4 purification MOFs for the four-step P/VSA process.

3.2. Problem formulation

3.2.1. Four-step P/VSA process

The feed composition for the ethylene purification process depends on the type of cracking reactor and its feedstock. In this work, the mixture composition was set to 5 mol% C_2H_2 , 90 mol% C_2H_4 , and 5 mol% C_2H_6 , which simulated the outlet composition of the liquid furnace in a typical industrial thermal naphtha cracking process.¹⁴⁵ For the removal of the impurities, namely C_2H_2 and C_2H_6 , a four-step P/VSA process was

applied. An illustration of the four-step cyclic P/VSA process is shown in Figure 3-1. It consists of the following steps: (I) pressurization; (II) adsorption; (III) blowdown; and (IV) evacuation. In step I, the pressure level at the inlet of the adsorption column is initially low at $P_{\rm L}$ and gradually increases to $P_{\rm H}$. After the column is fully pressurized to $P_{\rm H}$, the outlet valve is opened. Then the adsorption step (II) starts where the feedstock continuously flows in from the bottom of the column. As a result of adsorption, a purified ethylene stream leaves from the top of the column and is collected as the product. When the adsorption is complete, the bottom end of the column is closed and the blowdown step (III) begins. In this step, the pressure is decreased to an intermediate level P₁ to allow for partial desorption. Finally, the bottom end of the column is opened and the top is closed to initiate the evacuation step (IV). During this step, the heavy component is gathered from the bottom as the pressure further drops from $P_{\rm I}$ to $P_{\rm L}$. At the end of step IV, a clean bed is regenerated for reuse in the next cycle. By repeating these four steps (I-IV), the P/VSA process swings cyclically between different pressure levels, so that the pressure-dependent binding affinities between gas molecules and adsorbents can be harnessed for the purpose of separation or purification.



Figure 3-1: Illustration of the four-step P/VSA process

3.2.2. Mathematical modelling

To model the 4-step P/VSA process, the following assumptions are incorporated.

- 1) one-dimensional axial plug flow
- 2) all gases obey the ideal gas law
- 3) mass transfer rate can be described with the linear driving force (LDF) model
- 4) pressure drop can be described by the Darcy's law

- 5) the process can be considered isothermal
- mixture's adsorption equilibrium can be predicted by the extended Langmuir-Freundlich isotherm model

Based on the above assumptions, a mathematical model for the P/VSA process can be established. The model consists of component mass balances, total mass balance, mass transfer rate correlation, momentum balance accounting for pressure drops, adsorption isotherm, and relevant boundary conditions of the four P/VSA steps. All of the equations are nondimensionalized by defining the following variables according to the work of Haghpanah et al.¹⁴⁶ The meaning of every symbol is listed in the List of Symbols:

$$\bar{P} = \frac{P}{P_0}; \ \bar{T} = \frac{T}{T_0}; \ x_i = \frac{q_i}{q_{s,0}}; \ \bar{\nu} = \frac{\nu}{\nu_0}; \ Z = \frac{z}{L};$$
$$\tau = t \frac{\nu_0}{L}; \ \alpha_i = \frac{k_i L}{\nu_0}; \ Pe = \frac{\nu_0 L}{D_L}; \ \psi = \frac{RT_0 q_{s,0}}{P_H} \left(\frac{1-\varepsilon}{\varepsilon}\right)$$
(3.1)

component mass balances:

$$\frac{\partial y_i}{\partial \tau} = \frac{\bar{T}}{Pe \,\bar{P}} \frac{\partial}{\partial Z} \left(\frac{\bar{P}}{\bar{T}} \frac{\partial y_i}{\partial Z} \right) - \frac{\bar{T}}{\bar{P}} \frac{\partial}{\partial Z} \left(\frac{y_i \bar{P}}{\bar{T}} \bar{\nu} \right) - \psi \frac{\bar{T}}{\bar{P}} \frac{\partial x_i}{\partial \tau} - \frac{y_i}{\bar{P}} \frac{\partial \bar{P}}{\partial \tau}$$
(3.2)

total mass balance:

$$\frac{\partial \bar{P}}{\partial \tau} = -\bar{T} \frac{\partial}{\partial Z} \left(\frac{\bar{P}}{\bar{T}} \bar{v} \right) - \psi \bar{T} \sum_{i=1}^{n} \frac{\partial x_i}{\partial \tau}$$
(3.3)

mass transfer rate:

$$\frac{\partial x_i}{\partial \tau} = \alpha_i (x_i^* - x_i) \tag{3.4}$$

pressure drop:

$$-\frac{\partial \bar{P}}{\partial Z} = \frac{150}{4} \frac{1}{r_p^2} \left(\frac{1-\varepsilon}{\varepsilon}\right)^2 \frac{\nu_0 L}{P_0} \mu \bar{\nu}$$
(3.5)

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adsorption isotherm:

$$q_i^* = \frac{q_{m,i}b_i(Py_i)^{n_i}}{1 + \sum_{j=1}^n b_j(Py_j)^{n_j}}$$
(3.6)

boundary condition (pressurization):

$$\frac{\partial y_i}{\partial Z}\Big|_{Z=0} = -\bar{v}_{Z=0}Pe(y_{i,feed} - y_i|_{Z=0}); \frac{\partial y_i}{\partial Z}\Big|_{Z=1} = 0; \frac{\partial \bar{P}}{\partial Z}\Big|_{Z=1} = 0$$
(3.7)

boundary condition (adsorption):

$$\frac{\partial y_i}{\partial Z}\Big|_{Z=0} = -\bar{v}_{Z=0} Pe(y_{i,feed} - y_i|_{Z=0}); \left.\frac{\partial y_i}{\partial Z}\right|_{Z=1} = 0; \ \bar{P}|_{Z=1} = 1$$
(3.8)

boundary condition (blowdown):

$$\frac{\partial y_i}{\partial Z}\Big|_{Z=0} = 0; \frac{\partial y_i}{\partial Z}\Big|_{Z=1} = 0; \frac{\partial \overline{P}}{\partial Z}\Big|_{Z=0} = 0$$
(3.9)

boundary condition (evacuation):

$$\frac{\partial y_i}{\partial Z}\Big|_{Z=0} = 0; \frac{\partial y_i}{\partial Z}\Big|_{Z=1} = 0; \frac{\partial \bar{P}}{\partial Z}\Big|_{Z=1} = 0$$
(3.10)

The dynamic process converges eventually to a steady state called the cyclic steady state (CSS). Once the CSS is reached, the changes of all state variables between two consecutive cycles are zero. In practice, the CSS condition is deemed satisfied when the changes are smaller than a relative tolerance, which in this work is set to 5%.

In order to solve the above partial differential and algebraic equation (PDAE)-based system to CSS, all the partial differential equations are spatially discretized to 10 cells using the finite volume method. The upwind difference scheme is applied to approximate wall values on the boundaries of the finite volume cells. Consequently, the problem reduces to a system of ordinary differential and algebraic equations (ODAE), which can be solved by the ODE solver in scipy¹⁴⁷ with initial values set to a clean bed.

The separation process performance is measured for each MOF candidate using the time averaged product purity and recovery defined as follows:

$$Purity = \frac{mole_{out,C2H4}|_{C2H4,rich}}{\sum_{i}^{n} mole_{out,i}|_{C2H4,rich}}$$
(3.11)

$$\operatorname{Recovery} = \frac{mole_{out,C2H4}|_{C2H4,rich}}{mole_{in,C2H4}|_{pre} + mole_{in,C2H4}|_{ads}}$$
(3.12)

$$mole_{in,C2H4} = \frac{P_0 v_0}{RT_0} \varepsilon A \int_0^{\tau_{step}} \left. \bar{v} \frac{y_{C2H4} \bar{P}}{\bar{T}} \right|_{Z=0} d\tau \qquad (3.13)$$

$$mole_{out,i} = \frac{P_0 v_0}{RT_0} \varepsilon A \int_0^{\tau_{step}} \bar{v} \frac{y_i \bar{P}}{\bar{T}} \Big|_{Z=1} d\tau$$
(3.14)

The subscript C_2H_4 ,rich refers to the step where C_2H_4 is obtained as a rich product. The determination of the exact step depends on the C_2H_4 binding affinities with MOFs. Different MOFs have different adsorption and desorption affinities with C_2H_4 . For example, if C_2H_4 is the lightest, heaviest, or intermediate component compared to the other two, the enriched product C_2H_4 must be collected at the adsorption step, the evacuation step, or the blowdown step, respectively (see Figure 3-1).

Furthermore, for the processes meeting the purity and recovery requirements, it is essential to know how much energy is required for production. Therefore, energy consumption and productivity need to be computed as well. In this work, it is assumed that the C₂ mixture feed stream coming from the cracking furnace is at the atmospheric condition ($P_f = 1$ bar) and all vacuum pumps discharge also at $P_{atm} = 1$ bar. During the pressurization step, if $P_H > P_f$ compression energy is required to elevate P_f up to P_H . During the adsorption step, compression energy is needed to overcome frictional pressure drops in the column. During the blowdown step, if $P_I > P_{atm}$, no energy is needed. Otherwise, evacuation energy is required to take the pressure from P_{atm} to P_I . Likewise, in the evacuation step, if $P_I > P_{atm}$, evacuation energy is required to take the pressure from P_{atm} to P_L , if $P_I < P_{atm}$, then evacuation energy is required to take the pressure from P_I to P_L . The equations for the computation of energy consumption in each step are listed as follows:

$$E_{pre} = \frac{1}{\eta} \varepsilon \pi r_{in}^2 v_0 P_0 \frac{\gamma}{\gamma - 1} \int_0^{t_{pre}} \bar{v} \bar{P}|_{Z=0} \left[\left(\frac{P_0 \bar{P}|_{Z=0}}{P_f} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] dt, if P|_{Z=0} > P_f$$

$$E_{pre} = 0, \quad if P|_{Z=0} \le P_f \qquad (3.15)$$

$$E_{ads} = \frac{1}{\eta} \varepsilon \pi r_{in}^2 v_0 P_0 \frac{\gamma}{\gamma - 1} \int_0^{t_{ads}} \bar{v} \,\bar{P}|_{Z=0} \left[\left(\frac{P_0 \bar{P}|_{Z=0}}{P_f} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] dt$$
(3.16)

$$E_{blw} = \frac{1}{\eta} \varepsilon \pi r_{in}^2 v_0 P_0 \frac{\gamma}{\gamma - 1} \int_0^{t_{blw}} \bar{v} \, \bar{P}|_{Z=1} \left[\left(\frac{P_{atm}}{P_0 \bar{P}|_{Z=0}} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] dt, if \, P|_{Z=L} < P_{atm}$$

$$E_{blw} = 0, \quad if \, P|_{Z=L} > P_{atm}$$
(3.17)

$$E_{eva} = \frac{1}{\eta} \varepsilon \pi r_{in}^2 v_0 P_0 \frac{\gamma}{\gamma - 1} \int_0^{t_{eva}} \bar{v} \, \bar{P}|_{Z=0} \left[\left(\frac{P_{atm}}{P_0 \bar{P}|_{Z=0}} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] dt$$
(3.18)

where $\eta = 0.72$ is the compression efficiency and $\gamma = 1.4$ is the adiabatic constant. The total energy consumption (kWh/tonne C₂H₄) is calculated by:

$$E_{total} = \frac{E_{pre} + E_{ads} + E_{blw} + E_{eva}}{\text{mass of ethylene in product stream per cycle}}$$
(3.19)

and productivity $(mol/m^3/s)$ is calculated as:

$$Pr = \frac{mole_{out,C2H4}|_{C2H4,rich}}{\text{adsorbent volume} \times \text{cycle time}}$$
(3.20)

3.3. Results and discussions

3.3.1. Benchmark process with TJT-100

TJT-100²⁶ was chosen as the benchmark adsorbent because it was the first experimentally reported MOF for one-step ethylene purification and has been extensively studied. Moreover, its adsorption behavior aligns with our model assumptions and adsorbent screening conditions. Its extended Langmuir-Freundlich adsorption isotherm parameters were acquired from literature.²⁶ The process simulation parameters were set according to Table 3-1 (supplementary material). Other process design variables were first fixed as follows: $P_{\rm H} = 1$ bar, $P_{\rm I} = 0.5$ bar, $P_{\rm L} = 0.25$ bar, $t_{\rm pre} = 15$ s, $t_{\rm ads} = 30$ s, $t_{\rm eva} = 30$ s, L = 1 m, and $v_{\rm feed} = 0.5$ m/s. Exponential functions were chosen for the description of temporal pressure changes in the pressurization, blowdown, and evacuation steps (see Figure 3-1).

Parameter	Value
column diameter $D(m)$	0.30
void fraction ε	0.37
particle radius r (m)	7.00×10^{-4}
room temperature $T_{\rm R}$ (K)	298.00
universal gas constant R (m ³ Pa mol ⁻¹ K ⁻¹)	8.314
mass transfer coefficient k_i (s ⁻¹)	0.62
adsorbent density ρ (kg m ⁻³)	1.13×10^{3}
fluid viscosity μ (kg m ⁻¹ s ⁻¹)	1.72×10^{-5}
diffusion coefficient $D_{\rm L}$ (m ² s ⁻¹)	4.90×10^{-4}

Table 3-1: Simulation parameters for the P/VSA process

The P/VSA system was accurately solved to the CSS state with an absolute error less than 0.2%. As depicted in Figure 3-2a, $P_{\rm H}$, $P_{\rm I}$, and $P_{\rm L}$ determine the shape of pressure

evolution in every adsorption-desorption cycle. In addition, the molar fraction of ethylene at the top of the column is plotted. As shown in Figure 3-2b, C₂H₄ is first concentrated to 92.5% during the adsorption step and then in the evacuation step C₂H₄ is diluted back to 90.0%. The enrichment of C₂H₄ during the adsorption step is the result of the fixation of impurities (C₂H₂ and C₂H₆) at high pressure $P_{\rm H}$. Similarly, the dilution is caused by the release of impurities at low pressure $P_{\rm L}$. Clearly, both operating pressures and step time durations are critical design variables in P/VSA processes. Under the current process configuration, the purity and recovery of ethylene reach 92.5% and 18.4%, respectively (the suboptimal solution in Figure 3-2c).



Figure 3-2: Analysis of TJT-100 in P/VSA processes (a) temporal pressure change at the top of the column for one adsorption-desorption cycle (b) temporal C₂H₄ molar fraction change at the top of the column (c) non-dominated Pareto front of C₂H₄ purity and recovery optimized by NSGA-II

Note that the C_2H_4 purity and recovery from the above simulation of TJT-100 are far from satisfactory. To tackle the problem and completely unleash the potential of TJT-100, an optimization of the P/VSA process would be indispensable. Therefore, we formulate an optimization problem as follows:

max C₂H₄ purity & C₂H₄ recovery

s.t. PDAE model (Eq. 3.1 – Eq. 3.14)

 $P_{\rm L} < P_{\rm I} < P_{\rm H}$

 $LB \leq P_H, P_I, P_L, t_{pre}, t_{ads}, t_{blw}, t_{eva}, v_{feed}, L \leq UB$

where C_2H_4 purity and recovery are the two objectives to be optimized. There are in total nine characteristic design variables selected. Each is bounded by a lower bound (LB) and upper bound (UB) (see Table 3-2). According to the simulation results, the choice of the first eight design variables (P_H , P_I , P_L , t_{pre} , t_{ads} , t_{blw} , t_{eva} , and v_{feed}) is self-evident as they directly influence the operation of P/VSA cycles. In addition, the column length is added to account for the effect of the quantity of adsorbents. Lastly, an inequality constraint which demands that P_H , P_I , and P_L maintain a descending order is enforced to ensure solution feasibility.

Design variables	Lower and upper bounds
$P_{\rm L}$ (bar)	0.001 - 1
$P_{\rm I}$ (bar)	0.001 - 10
$P_{\rm H}$ (bar)	1 - 10
$t_{\rm pre}$ (s)	10 - 50
$t_{\rm ads}$ (s)	10 - 500
$t_{\rm blw}$ (s)	10 - 500
$t_{\rm eva}$ (s)	10 - 500
$v_{\text{feed}} (\text{m/s})$	0.1 – 2
<i>L</i> (m)	1 - 20

Table 3-2: Lower and upper bounds of design variables in P/VSA optimizations

The optimization framework is depicted in Figure 3-3. It consists of a P/VSA simulator and an optimizer. In the simulator, the P/VSA process simulations are carried out with

given design variables. All the simulations are iterated until the CSS condition is satisfied. After iterations converge, process performance indicators (i.e. ethylene purity and recovery) are computed and reported to the optimizer. In the optimizer, a stochastic optimization algorithm known as non-dominated sorting genetic algorithm II (NSGA-II) is employed to optimize the purity and recovery. The algorithm has been proven a powerful tool for handling multi-objective optimization problems.¹⁴⁸ It controls the generation of design variables through the interaction with the P/VSA simulator. In the beginning, an initial generation of 380 individuals is created. Every individual has totally nine design variables which are initialized randomly. Then these individuals are sent to the PSA simulator for process evaluations. After the process performance indicators are reported back to the optimizer, genetic operations (i.e., addition, deletion, crossover, and mutation) are performed on the individuals of the current parent generation to create a new child generation. The new generation repeats the same procedure until a predefined maximum number of generations is reached.



Figure 3-3: Flow diagram of multi-scale screening of adsorbents and multi-objective optimization of P/VSA processes

Through NSGA optimization, the product purity and recovery of TJT-100 improve significantly as shown in Figure 3-2c. There are totally 15 non-dominated solutions

represented by blue dots. These 15 solutions together form a Pareto front. On the Pareto front, solutions are non-dominated to each other but are superior to the rest of solutions in the search space. For example, the former suboptimal simulation case represented by the blue star in Figure 3-2c has only a purity of 92.5% and recovery of 18.4%. It is dominated by optimum 2, which has a higher purity of 94.4% and also a higher recovery of 95.0%. Optimum 1 has even a higher purity 99.9% overstepping the threshold of polymer-grade C₂H₄ production, but at the expense of shrunk recovery of 37.8%. In contrast, optimum 3 achieves the highest product recovery 99.9% but very low purity 90.2%. Clearly, the Pareto front of TJT-100 represents a trend in which purity increases as recovery declines. A similar tradeoff relationship between purity and recovery has also been reported for other adsorbents.^{115,146,149}

3.3.2. P/VSA process performance evaluation of promising MOFs

In our previous study², we conducted a systematic screening among CoRE MOF database using phase level indicators derived from equilibrium adsorption loadings, i.e., adsorption selectivity and capacity. Several MOF candidates were identified as promising adsorbents. However, whether these candidates were effective in P/VSA processes was unclear. To answer this question, we take the following steps to assess their process performance. First, as a complementary selection criterion, regenerability is calculated. Second, isotherm parameters are fitted based on mixture adsorption loadings. Then, full P/VSA process optimizations of product purity and recovery are performed. Energy consumption and productivity of the promising MOFs are also calculated and discussed. Best MOFs and the associated optimal P/VSA processes are recommended. Finally, the robustness of adsorbents is examined by investigating the effect of the feed composition fluctuation.

3.3.3. Fitting of isotherm parameters

As shown in the case of TJT-100, adsorption isotherms are the critical factor affecting adsorbents' separation performance. Note that direct calculations of adsorption isotherms for all the MOF candidates would be ideal but extremely computational expensive. For this reason, we apply a decomposition approach where we first rank the 4764 MOF candidates in CoRE MOF database using property-based metrics according to our previous work ² and then for the top-ranking MOFs we further compute adsorption data at different pressure levels and mixture compositions, and fit the isotherms based on these data.

Clearly, the selectivity at the adsorption pressure alone cannot adequately reflect the P/VSA process performance. For this reason, we introduce regenerability for the measurement of adsorbents' adsorption-desorption abilities in the P/VSA process cycles as proposed by Bae and Snurr.¹⁵⁰ Accordingly, additional GCMC simulations were carried out for all 4764 CoRE MOF candidates at both the adsorption pressure 10 bar and the desorption pressure 0.1 bar and the mixture composition was kept the same as the feed composition (0.05/0.90/0.05). As a result, the ranking of the top candidates can be found in Table 3-3. In this ranking list, MOF candidates are biasedly ranked by their adsorption selectivity $S_{C2H6/C2H4}$ at 10 bar, as the C₂H₆/C₂H₄ separation was identified as the bottleneck of the C₂ separation from our previous study.¹ In order to save energy consumption, we also demand the candidate adsorbents to have such adsorption preference that ethylene is the least adsorbed component ($S_{C2H2/C2H4}$ and $S_{C2H6/C2H4}$ at both adsorption and desorption pressures are greater than unity).

	Sc2н2/C2н4 (0.1 bar)	Sc2н6/C2н4 (0.1 bar)	S _{C2H2/C2H4} (10 bar)	S _{C2H6/C2H4} (10 bar)	<i>Rg</i> _{C2H2} (%)	<i>Rg</i> _{С2Н6} (%)
GIHBII	20.72	3.57	15.84	18.00	-60.3	75.7
GOMREG	51.23	2.47	24.78	17.56	-73.3	88.2
JAVTAC	310.72	4.76	125.01	17.22	-35.2	85.0
CUNXIS10	19.64	5.19	15.92	15.92	-43.5	62.0
CUNXIS	15.60	2.08	8.44	14.06	-109.9	83.2
ISAYOQ	26.13	1.54	21.39	3.79	1.3	67.1
AMIWUP	38.30	2.01	28.50	3.08	-10.0	46.6
MAPFOY	9.44	2.14	10.81	2.53	13.6	16.1
YAZZAC	19.69	1.78	19.62	2.42	28.9	48.1
OFUCAV	4605.34	1.91	2631.33	2.42	0.4	55.0
TJT-100	1.77	2.86	1.77	2.86	27.0	44.0

Table 3-3: List of potential CoRE MOF candidates based on adsorption-desorption abilities for C₂ separation calculated under mixture condition $(5/90/5 C_2H_2/C_2H_4/C_2H_6)$

As shown in Table 1, the top 5 MOFs have the C_2H_6/C_2H_4 selectivity over 10 at 10 bar, while the 6th to 10th MOFs show selectivity below 3.79. It is worth noticing that C_2H_2 regenerability of the top 5 MOFs are negative. It is speculated that the negative regenerability is caused by the differences in adsorption-desorption binding strengths of the three components upon pressure changes. Specifically, at 10 bar, all three components exhibit almost equally high adsorption loadings, suggesting that their adsorption affinities are of a similar magnitude. When pressure drops to 0.1 bar, the loadings of C_2H_4 and C_2H_6 decrease while the C_2H_2 loading increases inversely. The adsorption sites formerly occupied by C_2H_4 and C_2H_6 release as pressure decreases to 0.1 bar. However, these sites are quickly saturated by the more strongly adsorbed C_2H_2 since C_2H_2 maintains a strong adsorption tendency towards the adsorbents regardless of pressure decrease. To verify these hypotheses, we also performed GCMC simulations for pure C_2H_2 adsorption between 0.1 and 10 bar. It was observed that the C_2H_2 loadings of the top 5 MOFs were invariant to the pressure change between 0.1 and 10 bar. And only at extremely low pressure 0.1 Pa can C_2H_2 molecules thoroughly desorb from the adsorbents. In summary, the strong binding affinities of MOFs towards C_2H_2 provide high $S_{C2H2/C2H4}$ even under 0.1 bar, but accompanied with a huge regeneration energy demand.

Adsorption data of the top MOF candidates for fitting isotherms have been obtained via GCMC simulations in RASPA.⁷⁴ Mixture adsorption equilibrium loadings were sampled at different pressures spanning over the entire operating range $(1 \times 10^{-3}, 1 \times 10^{2}, 1 \times 10^{4}, 2 \times 10^{4}, 5 \times 10^{4}, 8 \times 10^{4}, 1 \times 10^{5}, 2 \times 10^{5}, 5 \times 10^{5}, 1 \times 10^{6}$ Pa), a uniform adsorption temperature at 298 K, and totally 11 different mixture compositions, half of which were selected near the feed condition. Details about sampling points can be found in Table 3-4. The rest of the GCMC related parameters were given in our previous paper ². After GCMC simulations, for all the candidate MOFs, their equilibrium loadings under the mixture condition were regressed using the extended Langmuir-Freundlich adsorption isotherm model. A complete list of regressed isotherm parameters of $q_{m,i}$, b_i , and n_i can be found in Table 3-5. The average regression error RRMSE is 31% and coefficient of determination R² is 0.78, indicating a moderate fit of the isothermal data to the Extended Langmuir-Freundlich isotherm model.

No.	<i>у</i> С2H2	<i>У</i> С2Н4	У С2Н6
1	0.01	0.90	0.09
2	0.025	0.90	0.075
3	0.05	0.90	0.05
4	0.075	0.90	0.025
5	0.09	0.90	0.01
6	0.05	0.05	0.90
7	0.90	0.05	0.05
8	0.33	0.34	0.33
9	0.50	0.25	0.25
10	0.25	0.50	0.25
11	0.25	0.25	0.50

Table 3-4: Selected gas compositions for the simulation of C2 mixture adsorptionequilibrium adsorption loadings

	q _{m,C2H2} (mmol/g)	q _{m,C2H4} (mmol/g)	q _{m,C2H6} (mmol/g)	<i>b</i> _{C2H2} (bar ⁻¹)	<i>b</i> _{C2H4} (bar ⁻¹)	<i>b</i> _{С2Н6} (bar ⁻¹)	<i>п</i> С2H2	п С2H4	п С2H6
GIHBII	2.72	2.82	1.66	2.99	1.98	4.98	0.17	0.17	0.32
GOMREG	4.45	2.81	2.12	4.60	2.35	6.16	0.21	0.21	0.60
JAVTAC	4.70	1.13	0.72	3.68	0.90	2.80	0.03	0.03	0.21
CUNXIS10	3.80	3.26	2.16	2.97	2.06	5.04	0.08	0.07	0.28
CUNXIS	3.86	3.24	2.13	2.88	1.98	5.08	0.07	0.07	0.28
ISAYOQ	1.33	1.42	1.05	9.61	1.41	2.49	0.53	0.50	0.81
AMIWUP	1.96	1.74	1.38	8.92	1.60	2.30	0.41	0.40	0.67
MAPFOY	3.53	3.54	3.19	9.96	2.77	4.28	0.60	0.56	0.77
YAZZAC	1.56	1.63	1.48	10.65	1.56	2.13	0.62	0.58	0.78
OFUCAV	4.14	2.07	1.34	8.30	0.09	0.40	0.21	0.12	0.64

 Table 3-5: Extended Langmuir-Freundlich isotherm parameters of top MOF candidates

3.3.4. Breakthrough simulations

Breakthrough experiment is commonly used to quickly verify materials' separation feasibility before full P/VSA process design. In the breakthrough simulation, both ends of the column were open. The inlet feed composition (0.05/0.90/0.05) and flow rate (1 m/s) were kept constant. The pressure at the column outlet were maintained at 10 bar. The boundary conditions were the same as the adsorption step in four-step P/VSA (Eq. 3.8) and the column was assumed to be initially empty. Figure 3-4 shows the breakthrough profiles of C₂H₂, C₂H₄, and C₂H₆ on GIHBII in the adsorption columns of length 5 m and length 10 m. C₂H₄ is the first component to break through at 20 s

with a product purity over 99.9%. At around 120 s there is a transition period where C_2H_2 elutes. Although a peak of C_2H_2 is observed between 120 and 220 s, in the effluent stream C_2H_4 remains a relatively high concentration. The completion time of the breakthrough experiment is around 300 s. For comparison, we also conducted a similar simulation with an increase of column length to 10 m. As shown in Figure 3-4b, the breakthrough order of the components remains the same. The breakthrough window for purified C_2H_4 collection extends to 180 s, almost twice of the previous case. Meanwhile, the total breakthrough time accumulates to around 600 s. On one hand, a longer column expands the operating window for C_2H_4 collection enabling higher productivity. On the other hand, a longer column also means a longer total breakthrough time and thus a higher pressurization energy. Clearly, a detailed process optimization balancing various process variables including the column length is highly necessary.



Figure 3-4: Breakthrough curves of GIHBII for different column lengths (a) 5 m and (b) 10 m (C_A: concentration at column outlet; C₀: concentration at column inlet)

3.3.5. Optimal design of P/VSA processes for promising MOFs

Following the optimization framework described in Figure 3-3, we examined the top 10 MOF candidates by maximizing C₂H₄ product purity and recovery in P/VSA processes. As expected, the nondominated optimal solutions form a purity and recovery Pareto front, indicating a similar tradeoff relation as observed in the benchmark TJT-100 case. In addition, all the MOF candidates show superior C₂H₄ purification capability than TJT-100, because their Pareto fronts dominate that of TJT-100. The domination happens mainly because of the much better overall C2H2 and C2H6 selectivities (see Table 3-3). However, as shown in Figure 3-5, seven out of the 10 MOFs are able to produce polymer-grade C₂H₄ with 99.9% purity. Although the three infeasible MOFs (CUNXIS, CUNXIS10, and GOMREG) have high selectivity, they suffer from negative C_2H_2 regenerabilities, which hinders a thorough bed cleanup at the evacuation pressure $P_{\rm L}$. A clean bed is critical in P/VSA processes as well as breakthrough experiments to gain high-purity product. Even though selectivity is a crucial indicator, it alone cannot accurately predict purity and recovery performance because of the influences of process variables on different adsorbents with different adsorption isotherms. This suggests that a good balance between selectivity and regenerability is critical for efficient ethylene purification.



Figure 3-5: Purity and recovery Pareto optimal fronts of the top 10 MOF candidates

3.3.6. Energy consumption and productivity

So far, we have successfully identified 7 adsorbents based on the purity constraint; however, two most important aspects, namely, energy consumption and productivity, have not been evaluated yet. For a comprehensive inspection of their process applicability, we gathered the optimal processes (Pareto optimal solutions in Figure 3-5) meeting the C_2H_4 99.9% purity constraint and the 50% recovery constraint for all the 7 MOF candidates and then computed their corresponding energy consumption and productivity using Eq. 3.15 – Eq. 3.20. As depicted in Figure 3-6, there are totally 126 feasible processes, with a mean energy consumption of 173 kWh/tonne C_2H_4 and productivity of 0.0247 mol C_2H_4/m^3 adsorbent/s. Out of the 7 feasible candidates, OFUCAV has a maximum productivity of 0.158 mol C_2H_4/m^3 adsorbent/s, while JAVTAC shows a minimum energy consumption of 42.76 kWh/tonne C_2H_4 .



Figure 3-6: Energy consumption and productivity of the 7 feasible MOF candidates in optimized P/VSA processes (C₂H₄ purity \geq 99.9% and recovery \geq 50.0%)

A breakdown analysis of the energy consumptions and other specifications can be found in Table 3-6. For JAVTAC, evacuation is the most energy intensive step (22.86 kWh/tonne) constituting half of the total energy requirement, which can be attributed to the long evacuation duration (134 s) and low desorption pressure (0.001 bar). On the other hand, the adsorption pressure is near atmospheric condition (1.385 bar), making the compression energy (13.53 kWh/tonne) in the adsorption step insignificant. In contrast, for OFUCAV, as adsorption dominates evacuation due to the relatively high adsorption pressure (6.312 bar), the compression energy becomes significant (90.96 kWh/tonne). Meanwhile, the evacuation duration triples to 431 s, resulting in two times increment of the evacuation energy to 62.80 kWh/tonne. Note that the blowdown energy of OFUCAV is slightly over zero due to the numerical diffusion (discretization error) of P_1 near the pressure boundary. Nevertheless, it is worth noting that both JAVTAC and OFUCAV can considerably reduce the C₂H₄ purification energy consumption, compared to the traditional cryogenic distillation process, whose energy consumption was reported to be 216.24 kWh/tonne.¹⁵¹

	JAVTAC	OFUCAV
productivity (mol/m ³ /s)	0.049	0.158
total energy consumption (kWh/ton)	42.76	174.85
C ₂ H ₄ purity (%)	99.91	99.99
C ₂ H ₄ recovery (%)	87.27	89.46
bed length (m)	2.920	1.481
adsorbent volume (m ³)	0.207	0.105
pressurization time (s)	46.58	27.73
adsorption time (s)	49.98	24.23
blowdown time (s)	142.45	12.34
evacuation time (s)	134.08	431.28
total cycle time (s)	373.09	495.59
feed velocity (m/s)	0.394	0.289
adsorption pressure P_H (bar)	1.385	6.312
intermediate pressure P_I (bar)	0.112	1.028
desorption pressure P_L (bar)	0.001	0.001
pressurization energy (kWh/ton)	0.535	18.52
adsorption energy (kWh/ton)	13.53	90.96
blowdown energy (kWh/ton)	5.827	2.579
evacuation energy (kWh/ton)	22.86	62.80

Table 3-6: Breakdown of the P/VSA energy consumptions of the top performing MOFs

3.3.7. P/VSA process economics

Despite the improvement of the P/VSA processes in terms of energy consumption, their full economic performance may not be necessarily advantageous due to the uncertainty in MOF pricing. For this reason, we performed detailed techno-economic analyses on the P/VSA and cryogenic distillation processes, encompassing not only the operating

cost but the adsorbent and equipment investments. The associated cost models are provided in the as follows:

The total annualized cost of the P/VSA process is calculated as follows.^{115,152,153}

$$TAC = ACC + AOC \tag{3.21}$$

where ACC is the annualized capital cost and AOC is the annualized operating cost.

The ACC is defined as:

$$ACC = \phi_{equip}C_{bm,equip} + \phi_{adsorbent}C_{adsorbent} + MC$$
(3.22)

where ϕ_{equip} is the annualization factor for equipment, $\phi_{adsorbent}$ is the annualization factor of adsorbent, $C_{bm,equip}$ is the total bare module cost for equipment, $C_{adsorbent}$ is the cost of adsorbent, and *MC* is the maintenance cost, which is assumed to be 5% of the annualized equipment cost.

$$\phi_{equip} = \frac{IR}{1 - (1 + IR)^{-LS_{equip}}} \tag{3.23}$$

$$\phi_{adsorbent} = \frac{IR}{1 - (1 + IR)^{-LS_{adsorbent}}}$$
(3.24)

$$MC = 5\% * \phi_{equip} C_{bm,equip} \tag{3.25}$$

where *IR* is the interest rate assumed to be 2%, LS_{equip} is the life span of equipment, $LS_{adsorbent}$ is the life span of adsorbents, both assumed to be 25 years.

The bare module cost of equipment is calculated as follows.

$$C_{bm,equip} = N_{col} \left(F_{bm,comp} C_{p,comp} + F_{bm,vac} C_{p,vac} + F_{bm,col} C_{p,col} \right)$$
(3.26)

.

where N_{col} is the number of adsorption columns (1 in this work), $F_{bm,comp}$ is the bare module factor of compressors, $F_{bm,vac}$ is the bare module factor of vacuum pumps, $F_{bm,col}$ is the bare module factor of the column shell, $C_{p,comp}$ is the purchase cost of compressor, $C_{p,vac}$ is the purchase cost of vacuum pump, $C_{p,col}$ is the purchase cost of column shell. In this estimation, $F_{bm,comp}$, $F_{bm,vac}$, and $F_{bm,col}$ are set to 2.15, 2.15, and 4.15, respectively to take into account installation and auxiliary pipeline costs.

The purchase cost of column shell is calculated by:

$$C_{p,col} = C_v + C_{pl} + C_{dr} (3.27)$$

where C_v is the cost of the vessel, C_{pl} is the cost of platforms and ladders, and C_{dr} is the cost of flow distributors. These are directly linked to the weight and length of the column and can be estimated as follows:

$$W_{col} = \pi (2r_{in} + t_{col})(L + 1.6r_{in})t_{col}\rho_{col}$$
(3.28)

$$C_{\nu} = \exp(7.0132 + 0.18255 \ln(2.2W_{col}) + 0.02297 \ln(2.2W_{col})^2) \qquad (3.29)$$

$$C_{pl} = (6.56r_{in})^{0.7396} (3.28L)^{0.70684}$$
(3.30)

$$C_{dr} = 125\pi (3.28r_{in})^2 \tag{3.31}$$

where W_{col} is the weight of the column shell, r_{in} is the inner radius of the column set to be 0.15 m, L is the height of the column. t_{col} is the thickness of the column set to be 0.015 m, ρ_{col} is the density of column materials and for carbon steel this value is 7800 kg/m³.

The purchase cost of vacuum pumps is calculated as follows:

$$C_{p,vac} = 8250 \left(0.588 \left(1 - \frac{y_{feed,C2H4} \times Recovery}{Purity} \right) F \left(\frac{t_{ads} + t_{pre}}{t_{blw} + t_{eva}} \right) \frac{RT}{P_L} \right)^{0.35}$$
(3.32)

where $y_{\text{feed},\text{C2H4}}$ is the molar fraction of C₂H₄ in the feed stream, *Recovery* is the recovery of C₂H₄, *Purity* is the purity of C₂H₄ in the product stream, *F* is the molar flow rate of the feed stream, *R* is the universal gas constant 8.314 m³ Pa mol⁻¹ K⁻¹, *T* is temperature 298 K, *P*_L is the operating pressure level in the evacuation step.

The purchase cost of compressor shared in the pressurization and adsorption steps is calculated as follows:

$$PW_{ads} = \frac{1}{\eta} RTF \frac{\gamma}{\gamma - 1} \left(\left(\frac{1.05P_H}{P_{atm}} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right)$$
(3.33)

$$C_{p,comp} = \exp\left(6.8929 + 0.79 \ln\left(\frac{PW_{ads}}{745.7}\right)\right) \ if \ P_H \le 2 \ bar$$
 (3.34)

$$C_{p,comp} = \exp\left(7.58 + 0.8 \ln\left(\frac{PW_{ads}}{745.7}\right)\right) \ if \ P_H > 2 \ bar$$
 (3.35)

where η is the compression efficiency set to 0.72, γ is the adiabatic constant set to 1.4.

The purchase cost of the adsorbent is calculated as follows:

$$C_{adsorbent} = C_{pk} \rho_{adsorbent} V_p \tag{3.36}$$

$$V_p = \pi r_{in}^2 L \tag{3.37}$$

where C_{pk} is the cost of adsorbent per unit mass, which is presently assumed to be \$100/kg, $\rho_{adsorbent}$ is the adsorbent density, set to 1130 kg/m³, V_p is the packing volume of the adsorbent in the column.

On the other hand, the operating cost is calculated as follows:

$$AOC = EC \times PPA \times (W_{pre} + W_{ads} + W_{blw} + W_{eva})$$
(3.38)

$$PPA = F \times y_{feed,C2H4} \times Recovery \times MW_{C2H4} \times OT \times 3600 \left(\frac{t_{pre} + t_{ads}}{t_{pre} + t_{ads} + t_{eva} + t_{blw}}\right)$$
(3.39)

where *EC* is the electricity cost, assumed to be 0.06/kWh, W_{pre} , W_{ads} , W_{blw} , and W_{eva} are energy consumptions in the four steps (unit: kWh/tonne C₂H₄). *PPA* is the total annual productivity of C₂H₄, *MW* is the molar weight, *OT* is the total annual operating hours that is assumed to be 8000 hours.

Finally, the unit cost of C₂H₄ production (\$/tonne) is calculated as:

$$UC = \frac{TAC}{PPA} \tag{3.40}$$

Based on the equations, the unit costs ($\frac{1}{0} + \frac{1}{0} = \frac{1}$

3.3.8. Effect of feed composition fluctuation

The fluctuation of the feed composition sometimes occurs in industrial practice. Therefore, investigating the performance of the adsorbents under different feedstock conditions to assess their operating robustness is important. For this purpose, additional optimizations with different feed compositions, i.e., one with mainly C_2H_2 impurity (9/90/1) and the other with predominantly C_2H_6 impurity (1/90/9), were carried out on JAVTAC, OFUCAV, and TJT-100. The robustness of adsorbents is ranked in the order of OFUCAV > JAVTAC > TJT-100, as indicated in Figure 3-7. OFUCAV displays the least fluctuation in Pareto fronts in response to the variation of the feed composition, followed by JAVTAC and then TJT-100. In particular, when the feed composition of C_2H_2 ramps up to 9%, the purity-recovery Pareto front of TJT-100 deteriorates dramatically due to its low C_2H_2 selectivity. The better stability of both screened MOFs in handling C_2H_4 purification, in comparison to TJT-100, can be mainly attributed to their high C_2H_2 selectivities.





Figure 3-7: Influence of feed compositions on the C_2H_4 purity and recovery for JAVTAC (a), OFUCAV (b), and TJT-100 (c)

3.4. Chapter summary and outlook

A systematic study of MOFs as adsorbents in P/VSA processes was conducted for onestep purification of polymer-grade C₂H₄. OFUCAV and JAVTAC were successfully identified as the most promising MOFs outperforming the benchmark adsorbent, TJT-100. OFUCAV was found to have the highest C₂H₄ productivity up to 0.158 (mol C₂H₄/m³ adsorbent/s), while JAVTAC exhibited the lowest energy consumption of 42.76 (kWh/tonne C₂H₄). The latter can potentially save 80% of the energy consumption compared to cryogenic distillation. Moreover, the resulting two P/VSA processes showed high robustness in response to composition fluctuations in the feed stream. The successful application to ethylene purification demonstrated the efficiency of our proposed design framework for the simultaneous identification of promising adsorbents and associated P/VSA processes. Notably, this design framework can be easily adopted to other separation or purification systems. Finally, we would like to point out some possible future directions. First, the material screening was conducted on the 2016 CoRE MOF database. An updated version of the database¹⁵⁴ containing over 14,000 MOFs is now available, with which we might discover even better adsorbents. Second, kinetic effects and gate opening effects have not been considered in this work. Further studies taking these aspects into account would benefit coordination chemists. Last, in P/VSA process modelling, we applied a few simplifications (e.g., uniformed pellet size and one-dimensional plug flow) to reduce the computational complexity. The implementation of more rigorous models that consider the pellet-scale effects will help increase the robustness of the results.

4. Conclusions and Outlook

This thesis presents a systematic study on the selection of suitable MOFs as adsorbent materials for the separation and purification of ethylene from the C₂ hydrocarbon mixture. From the vast number of candidates, a few promising MOF candidates have been identified. In the property based high-throughput screening, a quick and efficient identification and ranking of MOF candidates has been realized. Based on evaluation metrics SPI, two separation strategies for C2 ternary mixtures have been proposed. In the one adsorbent separation strategy, among all CUNXIS with the highest SPI value at 705.8 (cm^6/g^2) was identified as the best. In the two adsorbent separation strategy, ORAQUU and CUNXIS with SPI being 1318.5 (cm³/g) and 23.6 (cm³/g) respectively formed the best combination. In addition, quantitative relationships between MOFs' physical structures and adsorption abilities have been unveiled. We discovered that $S_{C2H2/C2H4}$ generally decreases with increasing LCD, while $S_{C2H6/C2H4}$ displays an opposite trend where it increases with increasing LCD. However, the capacities of all three components share a similar pattern where they all increase first with pore volume until reaching the peak (peak pore volume range between $0.5-1 \text{ cm}^3/\text{g}$) and after that slowly converge to stable capacities.

More importantly, we have demonstrated by the process performance-based highthroughput screening that the selected MOFs can significantly mitigate energy consumptions in the ethylene purification processes. Under the proposed multiscale framework combining property-based material screening, breakthrough simulation, and P/VSA processes optimization, OFUCAV and JAVTAC were successfully identified as the most promising MOFs, outperforming the benchmark adsorbent, TJT-100. OFUCAV was found to have the highest C₂H₄ productivity up to 0.158 (mol C₂H₄/m³ adsorbent/s), while JAVTAC showed the lowest energy consumption of 42.76 (kWh/ton C₂H₄). In addition, both OFUCAV and JAVTAC showed better robustness than TJT- 100, as evidenced by the study of feed composition fluctuation. Our study highlights the benefits of multiscale material and process design incorporating adsorbent screening and process optimization. Overall, we hope that with the MOFs we found, improved sustainability in the chemical industry can be achieved by the implementation of a more energy efficient ethylene purification process.

This thesis provides a basis for potential future computational studies. Here are some of the key directions. These directions include a complete design of separation processes for not only C_2 hydrocarbons but all other light hydrocarbons (such as C_3H_4 , C_3H_6 , C_3H_8 , etc.). The involvement of C_3 , and C_{4+} hydrocarbons would help further reduce overall separation energy consumption but might also increase the separation complexity as the choice of adsorption separation sequence (as mentioned in section 1.1) would influence the selection of suitable adsorbents. Regarding the highthroughput screening of materials in the hypothetical MOF database, such as hMOF database and ToBaCCo database, an advanced algorithm for an efficient evaluation of MOFs' structures integrity is required.

Another aspect is that we should not be confined in the screening domain and move forward into the field of materials design. Recent studies by Xiang et al. ^{106,155} illustrate the benefits of an integrated materials and process design. With the machine learning tool, they established a quantitative relationship between MOF structures and adsorption isotherms and formulated an integrated materials and process design problem. They proposed a MOF matching strategy with a subsequent generation of vast number of MOFs structures to match the best pseudo-MOF found in the solution of the integrated problem. However, the descriptors used are not chemically meaningful because they are not building blocks based. We strongly believe that a group contribution (GC) based thermodynamics modelling of MOF materials using building blocks could solve the problem and facilitate the discovery of MOF materials.
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List of Symbols

A =cross-sectional area of the column (m²)

b = extended Langmuir-Freundlich isotherm parameter (bar⁻¹)

 D_L = axial dispersion (m² s⁻¹)

E = energy consumption (kWh)

- E_{total} = total energy consumption (kWh tonne⁻¹)
- $k = mass transfer coefficient (s^{-1})$
- L = column length (m)

mole = cumulative mole number (mol)

- n = extended Langmuir-Freundlich isotherm parameter
- P =pressure (Pa)
- \overline{P} = dimensionless pressure

Pe = Peclet number

- $Pr = Productivity (mol m^{-3} s^{-1})$
- q = concentration in the solid phase (mmol g⁻¹)
- q_m = extended Langmuir-Freundlich isotherm parameter (mmol g⁻¹)
- $q_{s,0}$ = reference concentration in the solid phase (mmol g⁻¹)

 r_{in} = column inner radius (m)

 r_p = particle radius (m)

- R = universal gas constant (Pa m³ mol⁻¹ K⁻¹)
- Rg = regenerability
- S = selectivity
- t = time (s)
- T = temperature (K)
- \overline{T} = dimensionless temperature
- v = interstitial velocity (m s⁻¹)
- \overline{v} = dimensionless interstitial velocity
- x = dimensionless solid phase concentration
- x^* = dimensionless equilibrium concentration in solid phase
- y = composition in the gas phase

- z = bed coordinate (m)
- Z = dimensionless axial coordinate

Greek Symbols

- α = dimensionless mass transfer coefficient
- $\varepsilon = bed voidage$
- $\eta =$ compression efficiency
- γ = adiabatic constant
- μ = fluid viscosity (kg m⁻¹ s⁻¹)
- τ = dimensionless time
- ψ = dimensionless group in component and total mass balance equations

Subscripts

- 0 = reference value
- ads = adsorption step
- atm = atmospheric
- blw = blowdown step
- $C_2H_2 = acetylene$
- $C_2H_4 = ethylene$
- $C_2H_6 = ethane$
- eva = evacuation step
- f = cracking gas
- feed = feed stream
- H = high
- i = index of component
- in = inlet
- I = intermediate
- j = alias of i
- L=low
- out = outlet
- pre = pressurization step
- rich = rich stream step
- step = four PSA steps pre, ads, blw, eva

Postface

The thesis had been written and completed in July 2024. On 10. October 2024, a new paper^{S1} discussing MOFs' structure fidelity was published. The authors developed a new tool called MOSAEC (Metal Oxidation State Automated Error Check) to detect problematic structures. According to them, 28% of the structures in the CoRE MOF 2014 database were in question (95% confidence). Part of the erroneous structures arises from the incorrect metal oxidation states (MOS).

To ensure the general structure validity of the MOFs candidates that we proposed in this thesis, we supplement a manual post-examination of the structures which have been presented in Chapter 2 (including the top 10 best MOFs for the single step scheme and the top 10 best MOFs for the multi-step scheme) and Chapter 3 (including the top 10 best MOFs for processes). Out of the 24 different MOFs (6 duplicates), only CUNXIS, CUNXIS10, and GIHBII are spotted with a few framework atoms overlapping with each other, while the other 21 MOFs have chemically correct structures. The influence on their adsorption uptakes and selectivity is unknown and requires further investigation. Fortunately, the best two MOFs for processes in Chapter 3 are not affected. Readers should be careful with the experimental validation of the three questionable MOFs. Nevertheless, we have provided a sufficient number of promising candidates in case these three MOFs are not applicable for experimental validation.

Reference

S1. White A, Gibaldi M, Burner J, Mayo RA, Woo T. Alarming structural error rates in MOF databases used in data driven workflows identified via a novel metal oxidation state-based method. *ChemRxiv*. 2024;doi:10.26434/chemrxiv-2024-ftsv3

Declaration of Honor

I hereby declare that I produced this thesis without prohibited external assistance and that none other than the listed references and tools have been used. In the case of coauthorship, the own contribution is correctly and completely stated. I did not make use of any commercial consultant concerning graduation.

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List of Publications

Journal articles:

1. <u>Y. Zhou</u>, X. Zhang, T. Zhou, K. Sundmacher, Computational screening of metalorganic frameworks for ethylene purification from ethane/ethylene/acetylene mixture, *Nanomaterials*, 12 (2022):869.

Contribution: conceptualization of the study; preparation of software; data analysis, visualization of the data; writing and editing of the draft.

2. <u>Y. Zhou</u>, X. Cao, J. Shang, K. Sundmacher, T. Zhou, Multiscale screening of metalorganic frameworks for one-step ethylene purification in pressure swing adsorption processes, *AIChE J.*, 70 (2024):e18544.

Contribution: conceptualization of the study; preparation of software; data analysis, visualization of the data; writing and editing of the draft.

Proceeding chapters:

3. <u>Y. Zhou</u>, T. Zhou, K. Sundmacher, In silico screening of metal-organic frameworks for acetylene/ethylene separation, in: S. Pierucci, F. Manenti, G.L. Bozzano, D. Manca (Eds.) *Comput. Aided Chem. Eng.*, Elsevier, 48 (2020):895-900.

Contribution: conceptualization of the study; preparation of software; data analysis, visualization of the data; writing and editing of the draft.