

High-Throughput Computational Screening of MOFs for Ethane and Methane Purification

by

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Koç University

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*To my dear parents Yüksel and Embiya and my dear sister Nihan,
and to Dory, Marlin, and Nemo.*

ABSTRACT

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Ethane purification and natural gas purification are two energy-intensive processes which can advantage from better separation techniques. Metal organic frameworks (MOFs) are a recent group of nanoporous materials which can be obtained through the combination of metal nodes and organic linkers on different topologies. Considering the large number of available MOFs, it is not possible to fabricate and test the gas separation performance of every single MOF adsorbents and membranes using purely experimental manners. Therefore, the C_2H_6/C_2H_4 , C_2H_6/CH_4 , and CO_2/CH_4 separation performances of MOFs were investigated using high-throughput computational screening methods in this thesis.

In the first part, molecular simulations were used to assess membrane-based C_2H_6/C_2H_4 and C_2H_6/CH_4 separation performances of 175 different MOF structures. Results showed that a significant number of MOF membranes is C_2H_6 selective for C_2H_6/C_2H_4 separation in contrast to the traditional nanoporous materials. Several MOFs were identified to exceed the upper bound established for polymeric membranes and many MOF membranes exhibited higher gas permeabilities than zeolites and carbon molecular sieves.

In the second part, a multi-level high-throughput computational screening methodology was used to examine the most recent MOF database for membrane-based CO_2/CH_4 separation. 8 promising MOF membranes offering the best combination of CO_2 permeability ($>10^6$ Barrer) and CO_2/CH_4 selectivity (>80) were identified by combining grand canonical Monte Carlo (GCMC) and equilibrium molecular dynamics (EMD) simulations. Permeabilities and selectivities of the mixed matrix membranes (MMM) in which the best MOF candidates were incorporated as filler particles were also investigated. Many MOF membranes could outperform polymeric membranes for CO_2/CH_4 separation and MOF-based MMMs can have significantly higher CO_2 permeabilities and moderately higher selectivities than pure polymers.

Computational identification of the promising MOF candidates for CO_2 separation depends on the accurate description of electrostatic interactions between CO_2 molecules and MOFs. In the last part, role of partial charge assignment methods in high-throughput computational screening of MOFs for CO_2/CH_4 separation was examined. A quantum based, density-derived electrostatic and chemical charge method (DDEC) and an approximate charge equilibration method (Qeq) were used to compute the adsorption of CO_2/CH_4 mixture in 1500 MOFs at two different operating conditions. Results showed that the identity of the best performing MOF candidates, which were selected based on the regenerability and adsorbent performance score of MOFs, can change based on the type of the charge assignment method used in simulations.

Overall, results showed that high-throughput screening approaches introduced in this thesis can be used to predict gas separation performance of MOF adsorbents and membranes and MOFs can perform better than commercially used materials. The results of this thesis will be useful to guide the experiments to the most promising MOF candidates and to accelerate the development of new MOFs with high performances.

ÖZETÇE

Etan ve Metan Saflaştırma Süreçlerinde Kullanılmak Üzere Metal-Organik Gözenekli Yapıların Gaz Ayırma Performansının Kapsamlı Hesaplamalı Taraması

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Etanın ve doğal gazın saflaştırılması fazla miktarda enerji harcamayı gerektiren iki farklı gaz ayırma sürecidir ve bu işlemler için daha az enerjiyle daha yüksek saflık verecek ayırma yöntemlerinin bulunması avantaj sağlayacaktır. Metal-organik gözenekli yapılar (MOF) yakın zamanda keşfedilen ve metal içeren atom kümelerinin organik bağlayıcılarla farklı bağlantı şekillerinde birleştirilebilmesiyle elde edilen bir gözenekli malzeme grubudur. MOF'ların çok fazla çeşit ve sayıda bulunabildiği göz önüne alındığında yalnızca deneysel teknikler kullanarak her bir MOF'un sentezlenmesinin ve adsorbent ya da membran olarak gaz ayırma performanslarının belirlenmesinin mümkün olmayacağı anlaşılmıştır. Bu yüzden, bu tezde çok sayıda MOF'un etan/etilen (C_2H_6/C_2H_4), etan/metan (C_2H_6/CH_4) ve karbon dioksit/metan (CO_2/CH_4) ayırma performansları hesaplamalı yöntemler kullanılarak taranmıştır.

Tezin ilk kısmında, moleküler modelleme teknikleri kullanılarak 175 farklı MOF membranının C_2H_6/C_2H_4 ve C_2H_6/CH_4 karışımlarını ayırma performansı incelenmiştir. Sonuçlar MOF membranların çoğu gözenekli malzemeye kıyasla C_2H_6/C_2H_4 ayırımında C_2H_6 seçici davrandığını göstermiştir. MOF'ların bir kısmı polimer membranlar için belirlenen üst limiti aşabilmiş, birçok MOF membran da zeolit ve karbon moleküler eleklerden daha yüksek gaz geçirgenliği göstermiştir.

İkinci kısımda, seviyeli tarama metodu kullanılarak en son MOF veritabanındaki MOF'ların CO_2/CH_4 ayırımı için membrane performansları hesaplamalı yöntemlerle elde edilmiştir. Grand Kanonik Monte Karlo (GCMC) ve Denge Halindeki Molekül Dinamikleri (EMD) metodları birleştirilerek taramanın ilk seviyesinde en yüksek CO_2 geçirgenliği ve CO_2/CH_4 seçiciliği kombinasyonunu sağlayan 8 MOF membran belirlenmiştir. Daha sonra bu 8 MOF membranının dolgu polimer membranlarda (MMM) dolgu malzemesi olarak kullanılması ile elde edilecek CO_2 geçirgenliği ve seçiciliği de incelenmiştir. Bu çalışmanın sonunda da CO_2/CH_4 ayırımı için MOF membranların çoğu polimerik membrandan daha iyi performans göstereceği ve MOF-dolgu polimer membranların saf polimer membranlara göre daha yüksek geçirgenlikler verebileceği görülmüştür.

CO_2 ayırımında yüksek performans gösterecek MOF adaylarının belirlenmesi MOF ve CO_2 molekülleri arasındaki elektrostatik etkileşimlerin doğru tanımlanmasına bağlıdır. Son kısımda, atomik yük atamak için kullanılabilecek iki farklı yöntemin yüksek sayıda MOF'un hesaplamalı taramasındaki rolü incelenmiştir. Kuantum prensibi üzerine kurulu, elektron yoğunluğuna bağlı elektrostatik ve kimyasal yük (DDEC) yöntemi ve yakınsama prensibi üzerine kurulu yük dengeleme (Qeq) yöntemi 1500 farklı MOF'un CO_2/CH_4 karışımı tutma performansını iki farklı çalışma koşulunda incelemek için kullanılmıştır. Bu çalışma sonucunda farklı yük atama yöntemiyle yük atanmış MOF'lar kullanıldığında yenilenebilme ve adsorbent performans skoru beraber dikkate alınarak belirlenen en yüksek performanslı MOF'ların aynı olmadığı görülmüştür.

Bu tezdeki çalışmalar MOF'ların adsorbent ve membran olarak gaz tutma ve ayırma performanslarının hesaplamalı tarama yöntemleri ile tahmin edilebildiğini ve MOF'ların ticari malzemelerden daha yüksek performans verebildiğini gösterebilmiştir. Bu sonuçlar MOF'ların kullanımı, dizaynı ve geliştirilmesine katkı sağlayacaktır.

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ABBREVIATIONS

Å	Angstrom
APS (mol/kg)	Adsorbent Performance Score
ASA	Accessible Surface Area
Barrer	gas permeability unit
C ₂ H ₄	Ethylene
C ₂ H ₆	Ethane
CH ₄	Methane
ChelpG	charges from electrostatic potentials using a grid-based method
cif	crystal information file
CO ₂	Carbon dioxide
CoRE	Computation-Ready Experimental
CSD	Cambridge Structure Database
DDEC	Density Derived Electrostatic and Chemical
DFT	Density Functional Theory
D_i^0 (cm ² /s)	diffusivity at infinite dilution
$D_{\text{self},i}$ (cm ² /s)	self-diffusivity
E	energy
EMD	Equilibrium Molecular Dynamics
EQeq	Extended charge equilibration
GCMC	Grand Canonical Monte Carlo
FC-Qeq	formal charge Qeq
k	Boltzmann constant
K	Kelvin
K_i^0 (mol/kg.Pa)	Henry's constant for species i

LCD (Å)	Largest Cavity Diameter
MEPO	MOF-electrostatic potential optimized
MMM	Mixed Matrix Membrane
MOF	Metal Organic Framework
N_i	gas uptake for species i
NVT	canonical ensemble
NMR	nuclear magnetic resonance
OPLS	Optimized Potentials for Liquid Simulations
P (bar)	Pressure
P_i (Barrer)	permeability of gas species i
P_{MOF}	gas permeability in MOF
P_p	gas permeability in polymer
PDMS	polydimethylsiloxane
PFG	pulsed field gradient
PLD (Å)	Pore Limiting Diameter
PPM	polypentanamer
PQeq	Periodic charge equilibration
q (e ⁻)	partial charge of an atom
Qeq	Charge equilibration
r	distance between two atoms
R%	Percent regenerability
REPEAT	repeating electrostatic potential extracted atomic
S_{ads}	Adsorption selectivity
S_{diff}	Diffusion selectivity
S_{mem}	Membrane selectivity
SQE	split-charge equilibration

T (K)	Temperature
TraPPE	Transferable Potentials for Phase Equilibria
U_{LJ}	Lennard-Jones potential
U_{elec}	Electrostatic potential
V	Volume
ZIF	zeolitic imidazolate framework
ΔN (mol/kg)	working capacity
ε (K)	energy parameter of an atom
ε_0	dielectric constant
λ_{fp}	ratio of $P_{MOF}/P_{polymer}$
μ	chemical potential
π	number pi
σ (Å)	size parameter of an atom
Φ	porosity

Chapter 1

INTRODUCTION

This thesis was prepared in a time when children felt the need to be environmental activists to alarm the communities about the results of climate change. Witnessing continental fires and unexpectedly heavy weather conditions are forcing people to change their priorities and habits. Although it does not seem as urgent as finding a cure for an epidemic disease of a newly transformed virus, it is actually urgent to find better solutions of using energy efficiently and capturing greenhouse gases, to avoid other disasters that might catch us unprepared due to our deliberate waste of resources. In 2016, a comment in *Nature* (Sholl and Lively, 2016) listed seven separations that can change the world which included the separation of alkanes from alkenes and separation of greenhouse gases like CO_2 and CH_4 from dilute emissions. The common problem of these separations, which are mostly based on distillation and/or absorption, is that they mostly require a phase change, consume lots of energy, and emit large amounts of CO_2 to the atmosphere. Therefore, highlighting better materials that can replace these technologies with alternative separation processes can be a good aim to help to change the current course of events.

Separation of gas mixtures is not favored by thermodynamics and an external driving force is required to achieve it. (Yang, 2013) Alternative gas separation methods to distillation and absorption include adsorption-based and membrane-based gas separation. In adsorption, gas molecules interact with the surface atoms of a solid which are under unsaturated forces. (Langmuir, 1918) Especially for a mixture of components with similar relative volatilities and overlapping boiling points, adsorption can provide a more efficient means of separation. (Ruthven, 1984; Yang, 2013) Based on the molecular sieving, diffusion rate, and/or equilibrium adsorption mechanisms, components of a mixture can be separated with adsorption and structural properties as well as the chemical characteristics of the adsorbent can determine the extent of separation. Although any porous solid can be utilized as an adsorbent, well-controlled high micro-porosity and feasibility of production at large scales are required for commercial adsorbents, and so

activated carbon, zeolite, silica gel, activated alumina and carbon molecular sieve are examples to industrial adsorbents. (Yang, 2013)

In adsorption-based gas separation, only the difference in the adsorption tendency of molecules is utilized at a given temperature and pressure. In membrane-based gas separation, however, the difference in the transport of different types of gas molecules through a specific area of material per unit time upon a pressure or concentration gradient can be utilized. (Yampolskii and Freeman, 2010) Therefore, it contains both an equilibrium and also a dynamic component while utilizing both the solubility and mobility of gas molecules. Organic and inorganic materials can be utilized for membrane-based gas separation processes while organic membrane materials are mostly polymeric membranes. However, these materials can experience permeability-selectivity trade-offs, plasticization problems which reduce their selectivity, or stability issues in the long-term.

Metal organic frameworks (MOFs) are considered as a recent class of nanoporous materials that can be used as adsorbents and membranes in various gas separations. They are composed of metal complexes combined by organic linkers to form highly porous frameworks. (Eddaoudi, Li, and Yaghi, 2000) One of the most important features of MOFs is their structural tunabilities that can be obtained by altering the combination of metals and linkers used during synthesis. (Simon et al., 2015) The ability of tuning the MOF structures offers a wider variety of pore sizes and functionalities than other nanoporous materials. Therefore, MOFs have appeared as a promising group of porous materials that offer huge potential both as adsorbents and membranes. (Adatoz, Avci, and Keskin, 2015; Venna and Carreon, 2015; Denny et al., 2016; Liu et al., 2017; Müller et al., 2019; Danaci et al., 2020) The number of MOFs which are experimentally synthesized and deposited into the Cambridge Structural Database (CSD) has already exceeded 100000. Due to this large material space, experimental testing of every single MOF material is impractical. Therefore, in this thesis, the performance of MOF adsorbents and membranes were investigated with high-throughput computational screening for their ethane and natural gas purification performances.

This thesis is divided into seven chapters. Chapter 1 is the Introduction, Chapter 2 is the literature review for the three topics, ethane/ethene separation, natural gas purification from CO₂ and role of partial charge assignment methods used in molecular simulations on the performance prediction of MOFs for natural gas purification. In Chapter 3, details of the molecular simulation techniques and performance prediction

approaches can be found. Specific computational details for each work (ethane/ethene separation, natural gas purification and role of partial charge assignment methods), results and discussions are presented in Chapters 4, 5, and 6. Conclusions for each work are also provided inside the specific chapter. Chapter 7 presents the outlook for future studies.



Chapter 2

LITERATURE REVIEW

2.1 Ethane/Ethene Separation

Separation of different members of the C_2 hydrocarbon family has industrial importance because these molecules are primary feedstock for various chemicals.(Banerjee, Liu, and Thallapally, 2014) Ethane/ethylene (C_2H_6/C_2H_4) separation is generally carried out using distillation. This is one of the most energy intensive single distillations practiced commercially. Separation of C_2H_6 from methane (CH_4) similarly requires energy intensive distillation operations. The energy and equipment costs associated with these gas separations could be significantly reduced by the development of alternative separation methods.(Shi et al., 2010) Adsorption-based and membrane-based gas separations provide very large reductions in energy consumption and costs of these processes. However, the greatest limitation in the applications of adsorption and membrane-based gas separation technologies is the low selectivity of materials. Therefore, research on identification of new materials that can achieve C_2H_6 separations with high selectivity has gained significant attention in the last decade.

Most of the studies related to the gas separation with MOFs in the literature focused on the CO_2 capture whereas research on C_2H_6 separation using MOFs has recently started. Several experimental studies measured single-component adsorption isotherms of CH_4 , C_2H_4 , and C_2H_6 in various MOFs and these initial studies showed that MOFs can be promising materials for C_2H_6 separations.(Gucuyener et al., 2010; Bao et al., 2011; Bux et al., 2011; Bloch et al., 2012; He, Krishna, and Chen, 2012; He et al., 2012; Böhme et al., 2013; Wilmer et al., 2013; Hartmann et al., 2015; Liao et al., 2015; Zhang et al., 2015) Considering the large number of available MOFs, it is not practical to identify the most promising adsorbent materials using purely experimental manners. Most of the works used molecular simulations to study MOFs for adsorption-based C_2H_6 separations. Guo et al.(Guo et al., 2014) used molecular simulations to study C_2H_6/CH_4 separation in IRMOF-1 (isorecticular metal organic framework) and four different zeolitic imidazolate

frameworks, ZIFs (ZIF-8, ZIF-71, ZIF-80, ZIF-90). They showed that ZIFs exhibit better C_2H_6/CH_4 separation performance compared to MOR zeolite and IRMOF-1. Wu et al. (Wu et al., 2015) studied four different ZIFs using molecular simulations and reported their C_2H_6/C_2H_4 selectivities. Pillai et al. (Pillai et al., 2015) carried out molecular simulations to explore C_2H_6/C_2H_4 separation in interpenetrated and non-interpenetrated IRMOF-8 and reported C_2H_6 selectivities. We performed the first large-scale molecular simulation study for C_2H_6/C_2H_4 and C_2H_6/CH_4 separations using MOFs and reported adsorption selectivity of 278 different MOFs. (Altintas and Keskin, 2016) Our results showed that there is a large number of MOFs that exhibit significantly higher adsorption selectivity than zeolites for separation of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures. All these studies suggest that MOFs have strong potential to be used in adsorption based C_2H_6/C_2H_4 and C_2H_6/CH_4 separations.

Membrane-based C_2H_6 separation is an alternative to the adsorption-based separation. Conventional polymeric membranes cannot achieve the desired performance, combination of high selectivity and high permeability, required for C_2H_6 separation. (Tanaka et al., 1996; Staudt-Bickel and Koros, 2000; Chan et al., 2002; Chan et al., 2003) Polymers with high selectivity exhibit low permeability and polymers that have high gas permeability suffer from low selectivity. Due to this trade-off, recent studies have been directed towards developing more advanced membrane materials for C_2H_6 separations. Identification of MOF membranes that can achieve both high selectivity and high permeability will be very useful to replace polymeric membranes with MOFs. However, we have very limited information about the membrane based C_2H_6 separation performance of MOFs and the number of studies focusing on C_2H_6/C_2H_4 and C_2H_6/CH_4 separations with MOF membranes is scarce in the literature. Only two different types of MOFs were used as membranes for C_2H_6/C_2H_4 separation. Bux et al. (Bux et al., 2011) predicted membrane selectivity of ZIF-8 as the product of adsorption and diffusion selectivities for an equimolar C_2H_6/C_2H_4 mixture. They reported that C_2H_6 adsorbs stronger than C_2H_4 but C_2H_4 diffuses faster and overcompensates the adsorption preference for C_2H_6 , resulting in a MOF membrane that is weakly selective for C_2H_4 . Pan and Lai reported single-component permeances of CH_4 , C_2H_4 and C_2H_6 through ZIF-8 membranes. (Pan and Lai, 2011) Caro's group reported single-component permeances of CH_4 and C_2H_6 for ZIF-90 membranes. (Huang et al., 2012) MOFs were recently also used as filler particles in polymers to fabricate mixed matrix membranes (MMMs) in order to

improve C_2H_6 and C_2H_4 permeabilities of polymers.(Ploegmakers, Japip, and Nijmeijer, 2013; Japip et al., 2014; Bachman et al., 2016; Mueller et al., 2016)

Predicting separation performances of MOF membranes requires diffusion coefficients of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures through the pores of MOFs. Stallmach et al.(Stallmach et al., 2006) reported intra-crystalline self-diffusion of CH_4 and C_2H_6 in MOF-5 (also known as IRMOF-1) using pulsed field gradient (PFG) nuclear magnetic resonance (NMR) technique. Ford et al.(Ford et al., 2012) reported self-diffusivity of CH_4 and C_2H_6 in MOF-5 using experiments and molecular simulations. Chmelik et al.(Chmelik et al., 2012) studied diffusion of C_2H_6/C_2H_4 mixtures in ZIF-8 using different NMR techniques and showed that C_2H_4 diffusion is 5 times faster than C_2H_6 diffusion. Molecular simulations were used to compute self-diffusivity of CH_4 in MOF-5.(Sarkisov, Duren, and Snurr, 2004; Skoulidas and Sholl, 2005; Babarao and Jiang, 2008) Borah et al.(Borah, Zhang, and Snurr, 2015) recently conducted molecular dynamics simulations to predict diffusion behavior of pure CH_4 and C_2H_6 in 6 different MOFs. Self-diffusivities of C_2H_6 , (Chokbunpiam et al., 2013) C_2H_4 , (Krokidas et al., 2015) and transport diffusivities of CH_4 , C_2H_4 , and C_2H_6 (Verploegh, Nair, and Sholl, 2015) in ZIF-8 were computed by molecular dynamics simulations. All these simulations were generally carried out for single-component gases since calculating diffusivities of gas mixtures is computationally demanding. We reported diffusion coefficients of C_2H_6/C_2H_4 and C_2H_6/CH_4 binary mixtures in 5 different MOFs and using this diffusion data we predicted membrane selectivities and gas permeabilities of the 5 MOFs for C_2H_6 separations.(Altintas and Keskin, 2016) Our results on a small number of MOFs demonstrated that MOFs are promising membranes for preferential separation of C_2H_6 from C_2H_4 due to their higher selectivities and higher gas permeabilities compared to zeolites and polymers.

2.2 Natural Gas Purification from CO_2

There is a rapidly increasing demand for the development of efficient CO_2 separation technologies due to the climate change problems and separation of CO_2 from natural gas is a global challenge with energetic and environmental importance. CO_2 does not only reduce the energy content of the natural gas, which is mainly composed of CH_4 , but also causes pipeline corrosion. Membrane-based separation of CO_2 from CH_4 has emerged as a more advantageous alternative to the current energy-intensive technologies

such as cryogenic distillation and chemical absorption as it does not require a phase change.(Guo et al., 2018) Polymeric membranes such as polyimide and polyamide have been widely utilized for CO₂/CH₄ separation due to their relatively low manufacturing costs, good processing abilities into different configurations and existence of well-documented research studies.(Zhang et al., 2013) However, due to the trade-off between permeability and selectivity of polymeric membranes, better materials with high permeability and high selectivity are desired to achieve efficient and economic membrane-based gas separation. A selective membrane provides high purity thus requires less complex units while a membrane with high gas permeability requires less surface area and smaller capital cost. Another challenge in using polymeric membranes for commercial CO₂/CH₄ separation is the plasticization problem in which CO₂ permeability increases with pressure while the CO₂/CH₄ selectivity decreases.(Venna and Carreon, 2015) In order to eliminate these problems, zeolites have been considered as alternatives to polymeric membranes for membrane-based CO₂/CH₄ separation. Zeolite membranes offer significantly higher CO₂/CH₄ selectivities than the polymeric membranes but their low CO₂ permeabilities, high costs and difficulties in reproducibility are the main problems.(Venna and Carreon, 2015) A zeolite membrane, SAPO-34, was reported to exceed the Robeson's upper bound by displaying both high selectivity and high permeance for CO₂/CH₄ mixtures.(Poshusta et al., 2000; Li, Falconer, and Noble, 2006; Carreon et al., 2008; Falconer et al., 2012) Techno-economic analysis also showed that SAPO-34 membranes can surpass the benchmark technology distillation for natural gas treatment.(Li et al., 2015)

High surface areas, large porosities, uniform pores, reasonable mechanical and thermal stabilities make MOFs ideal candidates for membrane-based CO₂ separations. Several excellent reviews have addressed a variety of novel methods to fabricate continuous, defect-free MOF membranes for CO₂ separation.(Venna and Carreon, 2015; Denny et al., 2016; Trickett et al., 2017; Zhao et al., 2018) Many thin-film MOF membranes exhibit high CO₂ permeabilities and low to moderate CO₂/CH₄ selectivities.(Adatoz, Avci, and Keskin, 2015) Most of these membranes were fabricated using the prototype MOFs, such as MOF-5 (IRMOF-1)(Liu et al., 2009; Yoo, Lai, and Jeong, 2009; Zhao et al., 2011; Zhao et al., 2013; Kasik and Lin, 2014) and CuBTC (HKUST-1).(Guerrero et al., 2010; Nan et al., 2011; Mao et al., 2013) Zeolitic imidazolate frameworks (ZIFs) including ZIF-8, ZIF-69, ZIF-78, ZIF-90 have been

widely used to make membranes.(Pan, Wang, and Lai, 2012; Shah et al., 2013; Liu et al., 2014) For example, Venna and Carreon(Venna and Carreon, 2010) fabricated reproducible, thin ZIF-8 membrane and reported that its CO₂/CH₄ selectivity ranges from ~6.5 to 10, comparable with SAPO-34 membranes. Caro's group tested ZIF-90 membranes for separation of equimolar CO₂/CH₄ mixture at 1 bar, 498 K and reported high CO₂ permeance, 1.26×10^{-8} mol/(m²×s×Pa) (corresponds to 753 Barrer) and CO₂/CH₄ selectivity of 4.7, which was reported to be among the MOF membranes having high separation performance.(Huang et al., 2014) In addition to pure ZIF-8 membranes, several mixed matrix membranes (MMMs) in which ZIF-8 is used as filler particles in various types of polymers have been fabricated to improve permeability and selectivity of polymer membranes. A recent review addressed the CO₂ capture, CO₂/CH₄, CO₂/H₂, and CO₂/N₂ separations using ZIF-8-based MMMs by summarizing the fabrication techniques and special features of each membrane.(Gong, Wang, and Kuang, 2017) MOF-based MMMs are highly promising since they combine the two advantages of polymers and MOFs, easy processability and high gas permeability.

The number of MOFs is increasing rapidly, and this large material space offers a great potential to be used as novel membranes for CO₂/CH₄ separation. Many MOFs might exhibit high CO₂/CH₄ separation potential, but they have not been identified and tested yet. Experimental fabrication and testing of even a single MOF membrane require a long time, extensive efforts and resources. Similarly, choosing the best MOF filler to make MMMs is challenging because many MOFs and polymers are available resulting in infinite number of MOF/polymer combinations. Therefore, only a small fraction of MOFs has been experimentally examined as membranes and/or as fillers in MMMs to date and molecular simulations that screen many MOFs to identify the best materials have a vital role in directing experimental efforts.(Erucar and Keskin, 2018) Computational screening studies generally focus on adsorption-based H₂/CH₄, CO₂/N₂, and CO₂/CH₄ separations and grand canonical Monte Carlo (GCMC) simulations are used to compute gas adsorption in MOFs.(Haldoupis, Nair, and Sholl, 2012; Wu et al., 2012; Qiao, Zhang, and Jiang, 2016; Altintas, Erucar, and Keskin, 2018) The number of studies on screening MOF membranes is very limited since assessing selectivity and permeability of a MOF membrane requires calculation of gas diffusivities in the MOFs' pores using equilibrium molecular dynamics (EMD) simulations, which is computationally very demanding compared to the GCMC simulations. Watanabe and Sholl(Watanabe and Sholl, 2012)

used molecular simulations to compute CO₂/N₂ separation performances of 179 MOFs and reported ideal selectivities in the range of 2-26300 and CO₂ permeabilities in the range of 2-6×10⁷ Barrer. Daglar and Keskin(Daglar and Keskin, 2018) examined 3806 MOF membranes for CO₂/N₂ separations and identified the best MOF membranes having CO₂/N₂ selectivity>350 and CO₂ permeability>10⁶ Barrer. Qiao et al.(Qiao et al., 2016) used molecular simulations to screen a large number of hypothetical MOFs, which are computer-generated materials, for membrane-based separation of CO₂/N₂/CH₄ mixture. The top 24 hypothetical MOFs were identified and their CO₂ selectivities were reported to be in the range of 260-10500 at 10 bar and 298 K. The same group also carried out molecular simulations for separation of ternary CO₂/N₂/CH₄ mixture using real MOFs at 10 bar, 298 K and reported CO₂ selectivities of MOFs in the range of 700-8100 and CO₂ permeabilities>1000 Barrer for the 7 best MOF materials.(Qiao, Xu, and Jiang, 2018) Our group used high-throughput screening methods to examine >3500 MOF membranes for H₂/CH₄ separation(Altintas et al., 2018a) and H₂/CO₂ separation.(Avci, Velioglu, and Keskin, 2018) Results showed that many MOF membranes outperform polymer and zeolite membranes in terms of H₂ selectivity and H₂ permeability. An important point to note is that previous computational works were performed using the rigid framework assumption where the crystallographic positions of MOF atoms were fixed. Significant computational time is saved due to this assumption, however flexibility of MOFs might affect gas diffusion and eventually change the predicted performances of MOF membranes.(Fairen-Jimenez et al., 2012; Haldoupis et al., 2012) Therefore, the effect of flexibility on CO₂/CH₄ separation performance of at least some of the most promising MOF membranes deserves to be examined.

2.3 Role of Partial Charge Method on MOF Performance Predictions

The number of studies on high-throughput computational screening of MOFs for CO₂ capture is increasing rapidly.(Demir, Cramer, and Siepmann, 2019; Jiang, 2019; Sturluson et al., 2019) These studies are based on molecular simulations of very large number of MOFs to compute CO₂ adsorption and in some rare cases CO₂ diffusion in the materials' pores. Due to the quadrupole moment of CO₂, electrostatic interactions between the MOF atoms and CO₂ molecules are important in determining gas adsorption and transport.(Erucar, Manz, and Keskin, 2014) Partial atomic charges are needed for the framework atoms to calculate these electrostatic interactions. Many different charge assignment approaches based on quantum mechanics are available in the literature such

as charges from electrostatic potentials using a grid-based method (ChelpG),(Breneman and Wiberg, 1990) repeating electrostatic potential extracted atomic charge method (REPEAT),(Campana, Mussard, and Woo, 2009) and density-derived electrostatic and chemical charge method (DDEC).(Manz and Sholl, 2010) Although density functional theory (DFT)-based approaches are highly accurate, they are very costly especially when very large numbers of MOFs are simulated in high-throughput screening studies. Alternatively, an approximate charge assignment method, named as charge equilibration (Qeq)(Rappe and Goddard, 1991) has been introduced. Modifications on Qeq method to better approximate the DFT-based charges led to different versions such as periodic Qeq (PQeq),(Haldoupis, Nair, and Sholl, 2012) extended Qeq (EQeq),(Wilmer, Kim, and Snurr, 2012) MOF-electrostatic potential optimized Qeq (MEPO-Qeq),(Kadantsev et al., 2013) formal charge Qeq (FC-Qeq) and ionizing Qeq (IQeq)(Wells, De Bruin-Dickason, and Chaffee, 2014) methods, which were discussed and compared in detail in a recent review.(Ongari et al., 2019) Approximate charge assignment methods have been established based on a restricted set of MOFs and it is not possible to experimentally validate the partial charges. Therefore, Qeq methods have been generally compared with the DFT-based methods to understand how well they represent CO₂ adsorption properties of MOFs.

Comparison of CO₂ adsorption data of 14 MOFs calculated using ChelpG charges with those obtained using Qeq charges showed that both methods give the same predictions for the best and worst performing MOFs.(Wilmer and Snurr, 2011) Wilmer et al.(Wilmer, Kim, and Snurr, 2012) then compared experimental CO₂ adsorption data of 12 MOFs with the simulated adsorption results obtained using Qeq, EQeq, ChelpG, and REPEAT charges. Simulations using ChelpG charges showed the best agreement with the experimental results whereas results obtained with EQeq-charges were comparable to them. PQeq and DDEC charges were compared for evaluating CO₂/N₂ separation performances of 489 MOFs.(Haldoupis, Nair, and Sholl, 2012) It was shown that using PQeq charges gives sufficiently close results to the ones obtained with quantum chemistry-based charge methods for the initial screening of MOFs based on the Henry's constants but results under real mixture conditions were found to differ significantly. Kadantsev and coworkers established MEPO-Qeq with a training set of 543 MOFs and applied it to 693 MOFs to predict CO₂ adsorption. (Kadantsev et al., 2013) Good agreements were observed for the CO₂ uptakes and heats of adsorption values of MOFs

obtained using MEPO-Qeq and DFT-derived charges.

Nazarian et al. (Nazarian, Camp, and Sholl, 2016) established DDEC-charged computation ready experimental MOF (CoRE MOF) database consisting of 2932 experimentally synthesized MOFs and calculated the selectivity of tert-butyl mercaptan over CH₄ based on the Henry's constants using DDEC and EQeq charges. Their work showed that adsorption selectivities of MOFs can differ significantly when calculated with EQeq and DDEC charges. 1627 MOFs were screened based on the Henry's constants for CO₂/N₂/H₂O separation using DDEC and EQeq charges and 8 out of top 15 MOFs with the highest CO₂/H₂O selectivity were found to be common among the results obtained with either charge method. (Li et al., 2017) Collins et al. (Collins and Woo, 2017) used split-charge equilibration (SQE)-MEPO method to better reproduce the quantum mechanical electrostatic potential inside the pores of 559 hypothetical MOFs and 45 hypothetical porous polymer networks. Compared to MEPO method, results obtained using SQE-MEPO method showed a better agreement with those obtained using REPEAT method for CO₂ uptakes and heat of adsorption values.

DDEC-charged CoRE MOF is currently the only database that provides computation-ready structures with partial charges for 2932 MOFs and offers a great potential for high-throughput computational screening of MOFs for CO₂ adsorption. The approximate charge assignment method, Qeq, on the other hand, has been already implemented in several simulation packages and it can be used to quickly assign partial charges to very large numbers of MOFs but with less accuracy compared to DDEC method. As we reviewed above, most of the works comparing Qeq- and DFT-based methods either focused on the Henry's constants of gases or single-component gas uptakes. Therefore, the impact of using different charge assignment methods on the simulated CO₂ separation performances of MOFs in high-throughput screening studies is still unknown.

Chapter 3

METHODOLOGY

3.1 Assumptions

It is very important to discuss the assumptions made in computational studies in order to evaluate the potential of new materials in real applications. The generic force fields, Universal Force Field (UFF)(Rappe et al., 1992) and Dreiding,(Mayo, Olafson, and Goddard, 1990) were used to define the potential parameters of MOF atoms. These force fields were developed a long time ago and have the advantage of being adaptable to many chemical environments. However, it may not be suitable for certain materials such as MOFs having open metal sites. For example, Dzubak et al.(Dzubak et al., 2012) reported that common force fields typically underestimate CO₂ adsorption in Mg-MOF-74 which have open metal sites and presented a novel methodology that gives accurate force fields for CO₂ adsorption in this MOF from high-level quantum chemical calculations. There have been more recently parameterized force fields which have been shown to be more appropriate for MOFs.(Bristow, Tiana, and Walsh, 2014; Boyd et al., 2017) For example, Bristow et al.(Bristow, Tiana, and Walsh, 2014) developed a transferable potential form suitable to describe majority of ligand and metal combinations for MOFs. In contrast to generic force fields, in which general parameters were not fitted for MOFs and fixed generic charges were employed, their force field was fitted explicitly to the periodic frameworks and it was shown to accurately reproduce structural parameters of several MOFs. We used generic force fields in our molecular simulations for two reasons: (a)We previously showed the good agreements between simulations employing UFF or Dreiding and experiments for adsorption and diffusion of CO₂ and CH₄ in various MOFs, validating the appropriateness of these force fields for MOFs. (b)We preferred a generic force field that is applicable to all types of MOFs in our high-throughput molecular simulations rather than developing a specific force field for every single material. It is not possible to perform high-level quantum chemical calculations for each MOF having open metal sites in large scale material screening studies. Therefore, molecular simulations using the generic force fields may be underestimating CO₂

adsorption and CO₂ separation performances of MOFs having open metal sites.

All our molecular simulations were performed on defect free, perfect, single-crystals of MOFs. In practical applications, MOF membranes may have defects which may significantly affect their separation performances. Therefore, gas permeabilities and selectivities we predicted in this thesis should be considered as the most optimistic performances that can be expected from an ideal MOF membrane. Also, our mixed matrix membrane calculations using the Maxwell model did not account for the interactions between the polymer and MOF particles, size distribution and orientation of the MOF fillers in the polymer matrices and simply predicted the separation performances of ideal MOF-based mixed-matrix membranes. However, particle size of the MOF fillers may lead to different concentrations of the non-selective pathways due to the interaction with the polymer and this may have an important effect on the overall separation performance.

3.2 MOFs

As stated in the beginning, MOFs consist of metal nodes connected with organic ligands and are considered as a new class of nanoporous materials that can be used as adsorbents and membranes in various gas separations due to their well-defined pore structures, large surface areas (500-6500 m²/g), and high porosities. (Eddaoudi, Li, and Yaghi, 2000; Getman et al., 2012; Keskin, 2012; Xiang et al., 2012) They can be synthesized using various techniques like solvothermal, hydrothermal, ionothermal and microwave assisted techniques. (Stock and Biswas, 2012; Lee, Kim, and Ahn, 2013; Evans et al., 2019) Depending on the technique used, residual solvent molecules (bound and unbound solvents) can be found in the MOF pores at the end of MOF synthesis. These solvent and guest molecules should be carefully removed from the pores before molecular simulations to imitate the experimental activation process of the MOF. To accomplish this, the structural information of the MOF is required. Structural information of a MOF (atomic coordinates of MOF atoms, symmetry and unit cell information) is usually derived via X-ray Diffraction (XRD) and deposited into the Cambridge Structural Database (CSD) of Cambridge Crystallographic Data Centre (CCDC) in the format of crystallographic information file (cif). This “cif” file can then be visualized, edited, and used for further computational studies. A geometry optimization process is suggested especially after bound and unbound solvent removal to determine the final structure of MOFs before further computational investigations. (Nazarian et al., 2017)

The number of experimentally synthesized MOFs in CSD have quickly reached

~100000 in less than 30 years. It is desired to highlight the best performing MOFs for a specific gas storage or separation application in a fast manner but examining the performance of each MOF experimentally is not possible. This necessitated the screening of MOFs with computational tools before detailed experimental work. However, there can be problems about MOF structures such as the presence of disordered atoms, residual solvent molecules, missing hydrogen atoms and/or extra framework ions.(Altintas et al., 2019) Due to that, experimentally obtained structures need to be further processed to completely computation-ready structures to be used in molecular simulations. At that point, several computation-ready experimental MOF structure databases containing a large number of MOFs made it possible to conduct high-throughput simulations. The first publicly available computation-ready experimental MOF database was CoRE MOF 2014 and consisted of 5109 MOFs which are 3-dimensional with pore sizes larger than 2.4 Å.(Chung et al., 2014) CoRE MOF 2014 database was updated to CoRE MOF 2019 database of 14142 all-solvents-removed MOFs, which included the updated MOFs in the CSD, reconstructed versions of some disordered MOFs, and some MOFs provided only with their synthesis papers and not deposited into the CSD.(Chung et al., 2019) In 2017, a CSD-integrated non-disordered MOF subset was created using 7 different MOF identification criteria and provided together with a solvent removal script. (Moghadam et al., 2017) The advantage of this database is it is updated in accordance with the CSD (includes newly synthesized MOFs) and it enables computational researchers to create a database which can include MOFs with specific nodes or specific linkers. All computation ready experimental MOF databases utilize a MOF definition criteria and an algorithm to detect and clean the solvents from MOF's pores. Unfortunately, it is noted that automation of MOF identification and solvent removal might sometimes lead to wrong structures via removal of the essential parts of the framework by the solvent removal or misunderstanding of the MOF structure by the MOF identification algorithms. Our group examined the simulation results for CH₄/H₂ separation obtained with CoRE MOF 2014 and non-disordered CSD MOF subset databases to compare the results obtained for each MOF. That work identified the common MOFs in the two databases reported with the same reference codes but with different structural properties.(Altintas et al., 2019) These investigations showed that since the performance of some MOFs significantly depend on structural properties, every promising MOF identified at the end of a screening process needs to be carefully checked.

3.3 Molecular Simulations

3.3.1 Determination of Structural Properties of MOFs

MOFs can have a wide range of physical and chemical properties. We first calculated structural properties of MOFs such as limiting and largest pore diameters (PLD and LCD, respectively, as shown in Figure 3.1), pore volume, and accessible surface area using computational tools, such as Zeo++, (Willems et al., 2012) prior to molecular simulations to identify the materials with appropriate pore sizes and accessible surface areas.

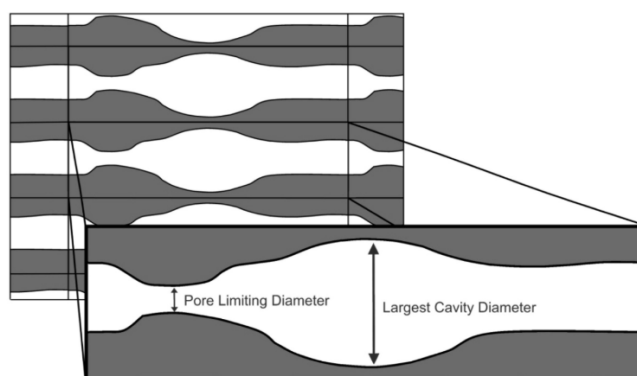


Figure 3.1. Pore limiting diameter and largest cavity diameter of a pore. Reprinted (adapted) with permission from Haldoupis et al. (Haldoupis, Nair, and Sholl, 2010). Copyright (2010) American Chemical Society.

Calculation of structural properties also enables researchers establish structure-performance relationships which can guide the design and synthesis of new MOFs with high gas capture and separation performance. (Barrett, Joyner, and Halenda, 1951; Gelb and Gubbins, 1999; Düren et al., 2007; Sarkisov and Harrison, 2011; Willems et al., 2012; Ongari et al., 2017) In Zeo++, a probe molecule with a pre-determined diameter is rolled inside the MOF to sample the available space which do not overlap with the MOF atoms. A nitrogen probe with a probe radius of 1.86 Å is used for nitrogen-accessible surface area calculations. Pore limiting diameter (PLD) and largest cavity diameter (LCD) are determined using van der Waals diameters of framework atoms. Geometric pore volume is calculated using a 0 Å probe radius while Helium pore volume is calculated with a Helium probe of 1.32 Å radius. In a recent work, it was reported that experimental pore volume is better represented with probe occupiable pore volume than pore accessible pore volume. (Ongari et al., 2017)

3.3.2 Grand Canonical Monte Carlo (GCMC) Simulations

In very general words, atomistic simulations can be divided into two categories: (i)

simulations based on interatomic potentials and nuclear coordinates (ii) simulations based on quantum mechanics and Schrodinger equation.(Catlow, Smit, and van Santen, 2004) In this thesis, we utilized classical molecular simulations which utilizes the energy of a system with functions of interatomic potentials depending on atomic coordinates.

To define the behavior of fluids (interacting individual molecules) in the computational environment, a configuration space (collection of all possible configurations, e.g. states of a system) is required. Metropolis et al.(Metropolis et al., 1953) proposed a Monte Carlo sampling technique to create this configurational space. Classical Monte Carlo approach makes direct random sampling whereas Metropolis Monte Carlo approach considers random configurations of a number of particles weighed according to their probabilities. To do this, Metropolis method calculates the energy of each configuration (E) of a system and determines the probability (p) of every configuration using ($e^{-E/kT}$) where k is the Boltzmann constant and T is temperature. If the energy of a new configuration is lower than the energy of the previous one (if the system moved towards lower energy), the new configuration is accepted. Otherwise, it is decided to move or not the system to the new configuration with comparing probability $p(e^{-E/kT})$ with a random number between 0 and 1, therefore the configurations are chosen with $p(e^{-E/kT})$. In this random sampling algorithm, it is important to make enough number of moves to reach everywhere in the configurational space.

Thermodynamic state of a system, defined by its macroscopic properties such as number of particles, temperature and pressure, is a result of a collection of many independent systems with various microscopic properties. For example, many particles can apply the same pressure even though they are arranged at different set of positions.(Tuckerman, 2010) Therefore, macroscopic properties can be seen as time averaged microscopic properties of systems taken over a long time interval according to statistical mechanics. The set of macroscopic properties that each microscopic system satisfies defines an ensemble. For example, in micro canonical ensemble (NVE ensemble), each independent, non-interacting, microscopic system evolves to the same number of molecules N , volume V , and energy E over an indefinitely long time. In canonical ensemble (NVT ensemble), each system satisfies the criteria of same number of molecules N , volume V , and temperature T . Another ensemble, called Grand Canonical ensemble (μVT ensemble), is a collection of microsystems resulting with the same chemical potential μ , volume V , and temperature T . Therefore, if a system was defined

as a collection of many particles, we can define ensemble as a collection of many systems evolving to the same set of macroscopic properties at long times. Grand Canonical Monte Carlo (GCMC) is a Monte Carlo sampling technique using the Grand Canonical ensemble. Therefore, GCMC simulations are conducted in a μVT ensemble in which μ , V (volume of the MOF) and T are kept constant and number of molecules, N , is allowed to fluctuate, until the μ of the adsorbent and the adsorbate is at equilibrium. (Frenkel and Smit, 2002)

GCMC simulations are generally utilized to calculate gas adsorption in MOFs. It calculates system's energy as a function of various chemical configurations of gas molecules in the host. Gas uptakes are obtained from the average number of adsorbed molecules in the system together with the isosteric heat of adsorption values at the end of a GCMC simulation. Isosteric heat of adsorption represents the amount of energy released upon the adsorption of gas molecules. To imitate the moves of real gas molecules, a series of moves are identified in GCMC simulations. Insertion, deletion, translation, rotation and regrow are the move types that were utilized for the gas molecules studied in this thesis to create random configurations of gas molecules inside the framework. These moves are accepted or rejected according to the Boltzmann probability of different configurations (Pardakhti et al., 2019; Sturluson et al., 2019) while Boltzmann probability distribution gives the probability of a system to be found in a state as a function of system's energy at a specified temperature. As a result, configuration integrals containing potential energy functions over all positions and orientations of gas molecules inside the MOF are obtained. By solving the configuration integrals, GCMC simulation makes it possible to obtain the probability density of gas molecules at different adsorption sites in a structure considering the energy minimization of gas molecules at thermodynamic equilibrium. In order to computationally predict gas adsorption in MOFs, GCMC simulations implemented in several software packages such as Multipurpose Simulation Code (MUSIC) (Gupta et al., 2003), RASPA (Dubbeldam et al., 2016), Materials Studio (Akkermans, Spenley, and Robertson, 2013) can be used.

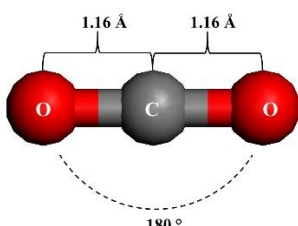
For a GCMC simulation, crystal structure of the MOF, gas model, gas-MOF interaction parameters (force field parameters), temperature (T), pressure (P), and composition of the gas feed are required. Crystal structure of the MOF contains the crystallographic information about the unit cell parameters, including cell lengths and angles, symmetry information, and fractional coordinates for all MOF atoms which can

be acquired from the cif file as mentioned above and used for the GCMC simulations.

Once the crystal structure of a MOF is ready, the potential energy of pairwise interactions can be calculated to determine the Boltzmann distribution of particles.(Frenkel and Smit, 2002) The potential energy function includes both the non-bonded and bonded terms and it is used to calculate the interaction energy between gas molecules and the framework. In order to compute gas-MOF interactions, a gas model is required. Gas model provides the physical properties and interaction parameters for a specific gas molecule. For example, due to the quadrupole moment of CO₂, its potential energy function includes both the van der Waals and electrostatic interactions between MOF atoms and CO₂ molecules. Therefore, CO₂ is modelled with van der Waals parameters in addition to partial charges assigned to constituting atoms. Quadrupole moment of CO₂ is due to the uneven distribution of charges on molecules lined along the z direction, as oxygen atoms are more electronegative than the carbon atom.(Buckingham, Disch, and Dunmur, 1968) EPM2 is one of the preliminary force fields defining the potential energy of CO₂ which is developed based on the pure-component vapor-liquid coexistence curve of CO₂ molecule.(Harris and Yung, 1995) Transferable Potentials for Phase Equilibria (TraPPE) is another mostly preferred force field for CO₂ since it better estimates the binary mixture vapor-liquid equilibria properties of CO₂ molecule.(Potoff and Siepmann, 2001) According to these force fields, CO₂ molecule is a 3-site molecule consisting of 2 oxygen and 1 C atoms with a C-O bond length of ~ 1.16 Å and O-C-O bond angle of 180°. Representation of CO₂ molecule defined by both force fields is given in Table 3.1 with its interaction parameters.

Table 3.1 Representation of CO₂ molecule by EPM2 and TraPPE force fields where ϵ is the energy parameter, σ is size parameter and k_B is the Boltzmann constant.

CO₂ model



	EPM2			TraPPE		
	ϵ/k_B (K)	σ (Å)	q (e ⁻)	ϵ/k_B (K)	σ (Å)	q (e ⁻)
C-C	28.129	2.757	0.6512	27.0	2.80	0.70
O-O	80.507	3.033	-0.3256	79.0	3.05	-0.35

The models for other gas molecules can be seen in Table A1 in Appendix A. After

defining the gas model to compute MOF-gas interactions, interatomic potential parameters for MOF atoms can be acquired from the quantum chemistry calculations or from the classical force fields. The non-bonded, intermolecular interactions between two particles are commonly known as van der Waals forces and long-range Coulombic interactions. Lennard-Jones (LJ) 12-6 potential is generally used to compute the van der Waals interactions in GCMC simulations.(Allen and Tildesley, 2017)

$$U_{LJ}=4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3.1)$$

In Eqn. 3.1, U_{LJ} is the intermolecular potential energy between two particles (i and j), r is the distance of separation from the center of one particle to the center of the other particle, ϵ_{ij} is the energy well depth and σ_{ij} is the molecular length scale based on the particle diameter. The parameters, σ , and ϵ , in the LJ potential can be taken from a force field. It is important to note that quantum chemistry-based calculations can provide very accurate description of material properties at the expense of high computational resources. Classical force fields are mostly preferred due to the ease of applicability and transferability to different systems. Classical force fields which consider intermolecular interactions between large groups of molecules can be developed based on fitting to experimental gas adsorption isotherms, vapor-liquid equilibrium curves, thermal expansion or elasticity properties.(Dubbeldam et al., 2019; Sturluson et al., 2019) Dreiding, Universal Force Field (UFF), Optimized Potentials for Liquid Simulations (OPLS), UFF4MOF, MOF-FF, and QuickFF are the force fields utilized for simulations of MOFs. Dreiding(Mayo, Olafson, and Goddard, 1990) and UFF(Rappe et al., 1992) are the two mostly used classical force fields. Dreiding force field considers general force constants and geometry parameters based on simple hybridization.(Mayo, Olafson, and Goddard, 1990) These force field parameters were mostly available for non-metal elements and a few metals (e.g. Na, Ca, Zn, Fe). UFF parameters are derived based on the element, its hybridization, connectivity and UFF can describe all the elements in the periodic table. More details about force fields were given in a recent review.(Dubbeldam et al., 2019) Lorentz-Berthelot mixing rules which are the arithmetic average of size parameters, $(\sigma_{ij}=(\sigma_i+\sigma_j)/2)$ and geometric average of energy parameters, $(\epsilon_{ij}=\sqrt{\epsilon_i \times \epsilon_j})$ are commonly used to determine the pair interaction parameters between atoms.

Electrostatic potential energy (U_{elec}) is commonly computed by using the Coulomb

potential as shown in Eqn. 3.2 where ϵ_0 , q_i and q_j show the dielectric constant, partial atomic charges of i and j , respectively. (Allen and Tildesley, 2017)

$$U_{\text{elec}} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (3.2)$$

Partial atomic charges for each atom of a MOF should be calculated to compute the electrostatic interactions. While partial charges for gas molecules can be obtained from the gas model, partial charges of MOF atoms are mostly calculated using partial charge assignment methods. Density functional theory (DFT)-based partial charge assignment methods can be utilized for assigning high accuracy partial charges to MOF atoms while approximate charge equilibration (Qeq) methods can be used in a faster manner for obtaining partial charges with a reasonable consistency. The ongoing modifications on Qeq methods to better estimate the electrostatic potential of MOFs have been recently addressed. (Ongari et al., 2019) The only MOF database provided with the high accuracy partial charges consists of 2932 Density Derived Electrostatic and Chemical (DDEC)-charged CoRE MOFs. (Nazarian, Camp, and Sholl, 2016) The DDEC method is a DFT-based method calculating the net atomic charges that can reproduce the electrostatic potential of a structure. (Manz and Sholl, 2010) Furthermore, DFT-optimized DDEC-charged CoRE MOF containing 879 MOFs provides geometry optimized and charged MOFs based on DFT calculations. (Nazarian et al., 2017)

So far, we reviewed the non-bonded intermolecular interactions which are considered when the rigid framework assumption is applied for MOFs. However, it is known that there are “stimuli-responsive” MOFs which have bonds that can behave flexible upon different stimuli including temperature, pressure, and guest adsorption. (Bahr et al., 2007; Li, Henke, and Cheetham, 2014; Chang et al., 2015; Coudert, 2015; Moghadam et al., 2019) Modeling flexible MOFs requires a flexible force-field which considers the intramolecular interactions including bond stretching, bending, torsional potential terms besides the intermolecular interactions. (Dubbeldam et al., 2019) Due to the transferability problem of the currently available flexible force fields among various MOFs and computational expense of flexible simulations, high-throughput computational screening studies are generally conducted using the rigid framework assumption.

Simulation box is extended to an infinite lattice by its replicas to avoid atoms at the surfaces of the simulation box experience a different force than the atoms in the bulk, which is called as periodic boundary conditions. (Allen and Tildesley, 2017) So that, there

are no surface atoms, because as one molecule leaves the simulation box, its image enters through the other face of the simulation box. At this point, it is important to note that the pairwise interactions between all particles and their replicas cannot be calculated and interactions between particles at very long distances can be discarded. Minimum image convention helps to accomplish this by setting a cut-off radius.(Allen and Tildesley, 2017) With the cut-off radius, a sphere is determined and only the interactions between atoms in this sphere is calculated. Cut-off radius is arranged such that it is not greater than the half of the any simulation box side length L .

Conditions of GCMC simulations such as pressure (P), temperature (T) and composition of the feed gas can be determined based on the real process conditions. Pressure of the bulk gas is converted to chemical potential (μ) using a gas equation of state like Peng Robinson in GCMC simulations.(Dubbeldam et al., 2016) A thermostat algorithm is used to keep the temperature constant. Different thermostat algorithms such as Nosé-Hoover(Evans and Holian, 1985) and Andersen(Andersen, 1980) can be used as a heat bath coupled with the MOF-adsorbent system.

At the end of a GCMC simulation, Henry's constants (K^0), gas uptakes from single-component or mixture gas feed (N_i or N_i^{mix} , respectively) and heat of adsorption (Q_{st}) values indicating the strength of gas adsorption, can be obtained which can be further used to determine the adsorbent performance evaluation metrics of MOFs as we will discuss below. The K^0 represents the affinity of the gas molecule towards the MOF adsorbent and can be calculated with GCMC simulations that are conducted at very low pressure to imitate infinite dilution conditions (one gas molecule interacting with the MOF adsorbent) or via using the Widom's particle insertion method. In Widom's method, a ghost molecule is inserted into the framework and its energy is calculated at random points.(Widom, 1963) Since the molecule is at infinite dilution conditions, it does not interact with other gas molecules.

3.3.3 Equilibrium Molecular Dynamics (EMD) Simulations

Computing membrane properties of MOFs requires diffusivities of gas molecules in the pores of materials. According to the pore diameter and collision of the molecules, diffusivity of gas molecules inside the framework can follow different trends such as molecular diffusion (dominated by the collisions between gas molecules) and Knudsen diffusion (dominated by the collisions with the pore walls).(Yang, 2013) In order to obtain self-diffusivities of gas molecules in MOFs, we performed Equilibrium Molecular

Dynamics (EMD) simulations. The mean squared displacement (MSD) data, which is the time integral of the velocity, of gas molecules calculated using modified order-N algorithm at long times (Dubbeldam et al., 2016) was used to calculate the diffusivity of each gas component from the slope of the MSD data in accordance with the Einstein's relation. (Einstein, 1956) The initial states of EMD simulations with the appropriate gas loadings were obtained from the GCMC simulations for mixture gas diffusivities while for gas diffusivities at infinite dilution the adsorbate-adsorbate interactions were switched-off and 30 gas molecules were inserted into each MOF to imitate infinite dilution.

3.4 Predicting Separation Performances of MOFs

3.4.1 Adsorption-Based Separation Performances of MOFs

Adsorbent performance evaluation metrics of MOFs were investigated only for CO₂/CH₄ separation in this thesis. Therefore, the metrics explained in this section will be based on the strongly adsorbed component of this system, which is CO₂. After computing the adsorbed CO₂ amounts for a MOF from a GCMC simulation, this data is then processed to evaluate CO₂ separation performances of MOFs. Several adsorbent performance evaluation metrics are used to accurately assess the CO₂ separation performance of MOFs under real process conditions. For example, CO₂ working capacity (ΔN_{CO_2} (mol/kg)) shows the amount of CO₂ that can be released when the pressure is decreased after adsorption. It is simply the difference between the CO₂ uptakes at adsorption ($N_{\text{CO}_2,\text{ads}}$) and desorption ($N_{\text{CO}_2,\text{des}}$) pressures.

$$\Delta N_{\text{CO}_2} = N_{\text{CO}_2,\text{ads}} - N_{\text{CO}_2,\text{des}} \quad (3.3)$$

It is a better practice to calculate working capacity with uptakes from gas mixture adsorption ($N_{\text{CO}_2}^{\text{mix}}$) although this metric can be also computed using the single-component data. (Rege and Yang, 2001; Bae and Snurr, 2011) The gas uptakes at desorption conditions is usually obtained using feed composition of the gas mixture, as was done in this thesis. It can also be taken as single-component CO₂ uptake due to the assumption that at the end of the depressurization step the adsorption column will contain almost pure CO₂. (Chung et al., 2016)

Vacuum swing adsorption (VSA), pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are cyclic adsorption processes in which CO₂

capture is followed by the CO₂ release where desorption conditions are set to release the vast majority of adsorbed CO₂ for further processing and to regenerate the MOF for re-use.(Trickett et al., 2017) Per cent regenerability (R%) is a metric to evaluate the practicality of a MOF for repeated usage in cyclic gas adsorption processes. It can be calculated as follows:

$$R\% = (\Delta N_{CO_2} / N_{CO_2,ads}) \times 100\% \quad (3.4)$$

A good MOF adsorbent for CO₂ capture should have high R% values in addition to high $N_{CO_2,ads}$ and high ΔN_{CO_2} , so that it can capture a significant amount of CO₂ between specified pressures for several times without a frequent need to replace the adsorbent.

Adsorption selectivity (S_{ads}) is another important metric which is the ratio of the uptake of more strongly adsorbed gas component (CO₂) to other gas species (j) at adsorption pressure. It helps to determine to what extent the MOF adsorbent can separate the gas species from other impurities. Ideal selectivity can be defined as the ratio of Henry's constants for different gas species ($K_{CO_2}^0$ and K_j^0) or the ratio of single-component gas uptakes obtained from GCMC simulations as follows where N_{CO_2} is the adsorbed amount of CO₂ and N_j is the adsorbed amount of less strongly adsorbed gas species j.

$$S_{ads, ideal} = K_{CO_2}^0 / K_j^0 \text{ or } S_{ads, ideal} = N_{CO_2} / N_j \quad (3.5)$$

Computational determination of ideal selectivity is rather simple and requires less time compared to mixture selectivity. Therefore, it is frequently used as an initial screening criterion to identify the most promising MOF adsorbents based on their selectivities. However, under real operating conditions, in the presence of other gas components and impurities in the gas feed, collaborative and competitive gas adsorption can be observed.(Cui, Bustin, and Dipple, 2004; Garcia et al., 2017) For example, electrostatic interactions or pore topology can strongly favor adsorption of CO₂ molecules, and the other molecules need to compete with CO₂ for the available adsorption sites. Collaborative effects such as CO₂-CO₂ interactions can attract more CO₂ molecules into the framework. In order to take these effects into account, mixture selectivity should be considered. It can be calculated using the ratio of adsorbed gas amounts obtained from mixture GCMC simulation normalized with bulk composition of the gas mixture as shown in Eqn. 3.6 (x_{CO_2} represents the mole fraction of adsorbed CO₂, x_j represents the

mole fraction of less-strongly adsorbed gas j , y_{CO_2} represents bulk feed composition of gas species CO_2 and y_j represents bulk feed composition of gas species j).

$$S_{\text{ads},(\text{CO}_2,j)} = \frac{x_{\text{CO}_2}/x_j}{y_{\text{CO}_2}/y_j} \quad (3.6)$$

Experimental investigation of mixture gas adsorption for various compositions of a gas mixture is challenging due to the lack of proper instrumentation and expertise to determine the gas mixture adsorption isotherms and also lack of time, human and financial resources.(Walton, 2019) Determination of the adsorption loadings for each gas species through weight changes or pressure changes is also difficult. This requires using theoretical models that can predict mixture gas adsorption from single-component gas adsorption data. Ideal Adsorbed Solution Theory (IAST) predicts mixture adsorption isotherms from the single-component gas uptakes based on an adsorption model such as Langmuir model. It is based on the assumptions that all gas molecules have equal accessibility to the whole surface area of a homogeneous adsorbent, gases interact with the adsorbent similarly in strength and there are no interactions between adsorbed gas molecules mimicking an ideal solution.(Myers and Prausnitz, 1965) IAST method is shown to accurately work for gas adsorption in MOFs unless the MOF has an energetically heterogeneous surface.(Walton and Sholl, 2015)

A good adsorbent is expected to provide a combination of high ΔN_{CO_2} and $S_{\text{ads},(\text{CO}_2,j)}$. However, there is generally a trade-off between these two metrics.(Garcia et al., 2014) Porous materials with large pore sizes generally exhibit high gas working capacities but due to the large pores both gas molecules can be adsorbed within the adsorbent leading to a decrease in adsorption selectivity. Therefore, other metrics combining working capacity and selectivity are developed to provide a better estimation of MOFs' performances. Adsorbent performance score (APS)(Chung et al., 2016) and PSA sorbent selection parameter (SSP)(Rege and Yang, 2001) can be defined as follows:

$$\text{APS (mol/kg)} = \Delta N_{\text{CO}_2} \times S_{\text{ads}} \quad (3.7)$$

$$\text{SSP} = \frac{\Delta N_{\text{CO}_2}}{\Delta N_j} \times S_{\text{ads}} \quad (3.8)$$

A recent work by Sholl's group(Park et al., 2020) compared the predictions of adsorbent evaluation metrics (working capacity, adsorption selectivity, sorbent selection parameter, adsorbent performance score, regenerability) with the results of detailed process models (purity, recovery, productivity, energy) for dry CO_2/N_2 separation at sub-ambient

temperatures at PSA conditions for 143 MOFs. Their results showed that ΔN_{CO_2} and APS are the two parameters that can best predict the process level rankings of MOFs for dry flue gas separation.

3.4.2 Membrane-Based Separation Performances of MOFs

Gas permeabilities of MOFs at infinite dilution (P_i^0) and ideal selectivities of MOF membranes were calculated using Eqn. 3.9 and 3.10.

$$P_i^0 = K_i^0 \times D_i^0 \quad (3.9)$$

$$S_{mem}^0 = P_i^0 / P_j^0 \quad (3.10)$$

Mixture permeabilities through MOF membranes were computed using Eqn. 3.11 where c_i , D_i and f_i correspond to adsorbed gas loading, self-diffusivity and feed side partial pressure of the gas, respectively. Permeate side of the membrane was assumed to be vacuum. (Keskin and Sholl, 2009a)

$$P_i^{mix} = c_i^{mix} \times D_i^{mix} / f_i \quad (3.11)$$

We also computed gas permeabilities through MOFs using the following expression, (Krishna and Paschek, 2002)

$$P_i = \frac{\phi \times D_{i,self} \times c_i}{f_i} \quad (3.12)$$

where P_i , ϕ , $D_{i,self}$, c_i and f_i represent the permeability of the component i (mol/m/s/Pa), the porosity of MOFs, the self-diffusivity of the component i in the mixture (m^2/s), the concentration of component i at the upstream face of the membrane (mol/m^3) and the bulk phase fugacity of the component i (Pa), respectively. Mixture selectivities for MOF membranes were computed as the ratio of gas permeabilities as given in Eqn. 3.13.

$$S_{mem}^{mix} = P_i^{mix} / P_j^{mix} \quad (3.13)$$

Finally, we examined the potential of MOF-based MMMs by estimating their gas permeabilities and selectivities. Numerous permeation models such as Maxwell, Bruggeman, Lewis-Nielson, Pal were previously studied in our group by comparing permeabilities obtained from these models with the available experimental data for CO_2 and CH_4 permeabilities of many MOF-based MMMs and it was concluded that Maxwell is the most appropriate model among the ones using the ideal morphology concept to estimate separation performances of MOF/polymer MMMs. (Erucar and Keskin, 2011) Therefore, we used the Maxwell model (Maxwell, 1954; Bouma et al., 1997) to predict

gas permeabilities of the MOF-based MMMs (P_{MMM}) using the following expression,

$$P_{MMM} = P_p \times \frac{n \times P_{MOF} + (1-n) \times P_p - (1-n) \times \phi \times (P_p - P_{MOF})}{n \times P_{MOF} + (1-n) \times P_p + n \times \phi \times (P_p - P_{MOF})} \quad (3.14)$$

where n is the geometry shape factor taken as 0.3 assuming sphere-like MOF particles, (Bouma et al., 1997) ϕ is the volume fraction of the MOF particles in the polymer matrix, P_{MOF} is the gas permeability of MOF, P_p is the gas permeability of polymer collected from the literature, and P_{MMM} is the gas permeability of the MOF-based MMM. This equation reduces to Eqn. 3.15 for sphere-like MOF particles ($n=0.3$):

$$P = P_p \left[\frac{2(1-\phi) + (1+2\phi)\lambda_{fp}}{(2+\phi) + (1-\phi)\lambda_{fp}} \right] \quad \text{where } \lambda_{fp} = \frac{P_{MOF}}{P_p} \quad (3.15)$$

In Maxwell model for MMM performance prediction, the permeability of a gas (flux of gas/negative pressure gradient) through a continuous membrane is calculated like calculating the permittivity of the electric field (dielectric constant=electric displacement/negative electric field gradient) between two continuous phases, in an analogy with dielectrics. (Bouma et al., 1997)

Chapter 4

ETHANE/ETHENE SEPARATION

Current studies on MOF membranes for C_2H_6 separations examine only a few types of structures. Considering the large variety and number of available MOFs, there may be many existing MOFs with better separation performances, high membrane selectivities and high gas permeabilities for C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures. In order to identify membrane-based C_2H_6 separation performances of a large number of MOFs, we used molecular simulations and computed adsorption equilibria and self-diffusivities of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures in 175 different MOFs. Using this data, we predicted adsorption selectivity, diffusion selectivity, membrane selectivity and gas permeability of 175 MOFs both for C_2H_6/C_2H_4 and C_2H_6/CH_4 separations. Results were compared with well-known membrane materials, polymers, zeolites and carbon molecular sieves to evaluate the potential of MOFs. Relations between adsorption selectivity, diffusion selectivity and membrane selectivity of MOFs were discussed to understand the individual effects of adsorption and diffusion on the membranes' performances. We finally examined the relations between easily computable structural properties such as pore size, surface area and porosity of MOFs and their selectivities to provide structure-performance relationships that can serve as a map for experimental synthesis of new MOFs with better gas separation performances.

4.1 Methodology

Grand Canonical Monte Carlo (GCMC)(Frenkel and Smit, 2002) simulations were used to compute binary adsorption isotherms of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures in MOFs. Dreiding force field(Mayo, Olafson, and Goddard, 1990) was used for the MOFs. In cases where the potential parameters of atoms were not available from the Dreiding force field, these parameters were taken from the Universal Force Field (UFF).(Rappe et al., 1992) These force fields were selected based on the results of our initial simulation studies that give a good agreement with the available experimental uptake data of C_2H_6 , C_2H_4 and CH_4 in various MOFs.(Altintas and Keskin, 2016) Single-site spherical Lennard-Jones (LJ) 12–6 potential was used to model CH_4 (Martin and Siepmann, 1998)

whereas two-site spherical LJ potentials were used for C_2H_6 and C_2H_4 molecules following the literature (given in Table A1 in the Appendix). (Wu et al., 2015) C_2H_6 and C_2H_4 molecules were described as uncharged united-atom models with one pseudo-atom representing $-CH_3$ group and $-CH_2$ group that was located at the position of carbon atom similar to the TraPPE united atom force field. (Martin and Siepmann, 1998) Since the adsorbate molecules did not contain any dipole, the long-range electrostatic contribution was omitted following the previous studies in the literature. (Wu et al., 2015) The cut-off distance for truncation of the intermolecular interactions was set to 12 Å for GCMC simulations. A simulation box of $2 \times 2 \times 2$ crystallographic unit cells was used. Periodic boundary conditions were applied in all simulations. During the simulations, 1.5×10^7 steps were performed to guarantee the equilibration and 1.5×10^7 steps were performed to sample the desired properties.

In order to obtain self-diffusivities of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures in MOFs, we performed EMD simulations. The initial states of EMD simulations with the appropriate gas loadings were obtained from the GCMC simulations and each system was equilibrated for 20 ps prior to taking data. The Nosé-Hoover thermostat was applied to run EMD simulations at NVT (constant number of molecules, volume and temperature) ensemble. (Frenkel and Smit, 2002) At least 10 independent EMD simulations with a length of 16 ns were performed to compute self-diffusivities of gases at the given loadings. The estimated uncertainties of the self-diffusivities were at least one order of magnitude smaller than the reported diffusion coefficients.

Molecular simulations should be performed for multiple materials on time scales shorter than the same materials can be assessed experimentally. Since we considered a large number of MOF membranes, we used rigid framework assumption. Almost all molecular simulations for MOF membranes in the literature used this assumption because it saves a significant amount of computational time. Recent studies showed that including lattice flexibility does not make any significant change in the gas adsorption results of MOFs that have pore sizes larger than the size of guest molecules. (Greathouse and Allendorf, 2008; Perez-Pellitero et al., 2010; Haldoupis et al., 2012) Chmelik et al. (Chmelik et al., 2012) could not find any evidence for gate-opening effect or another structural transitions of ZIF-8 upon adsorption of C_2H_6/C_2H_4 mixture. On the other hand, lattice flexibility can be important for the diffusion of large gas molecules in the MOFs having narrow windows. (Chokbunpiam et al., 2013; Verploegh, Nair, and Sholl, 2015)

Erucar and Keskin(Erucar and Keskin, 2016) carried out flexible EMD simulations to examine the effect of MOF's flexibility on the predicted membrane performance. Considering flexibility of the framework made a negligible effect on the gas permeability and selectivity of the MOFs having large pores whereas more pronounced changes were seen in gas permeabilities of the materials having narrow pores. Another recent study on Xe separations showed that flexibility should be considered in shape selective screening studies for the highest degree of accuracy and to achieve the best ranking of high-performance materials.(Witman et al., 2017) Since MOFs considered in this part of the thesis were specifically chosen to have larger pore diameters than the kinetic diameters of the three gas molecules C_2H_6 , C_2H_4 and CH_4 , flexibility effects were expected to be small and they were not taken into account for computational efficiency. The idea of our calculations is that once the potential value of a membrane material has been demonstrated by molecular simulations, further detailed studies such as flexible simulations can be performed to increase the precision of the initial assessment.

Adsorption selectivities (S_{ads}) of MOFs for C_2H_6/C_2H_4 and C_2H_6/CH_4 separations were calculated using the results of mixture GCMC simulations at 10 bar, 298 K for equimolar C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures. The ratio of self-diffusivities of gases obtained from the EMD simulations was used to define the diffusion selectivity of MOFs (S_{diff}). Once the adsorption and diffusion selectivities of MOFs were computed for a given gas mixture, membrane selectivity (S_{mem}), also known as permeation selectivity, was calculated as the multiplication of adsorption selectivity and diffusion selectivity at a membrane feed pressure of 10 bar as described in the literature.(Keskin and Sholl, 2009b) The validity of this model was shown by comparing its predictions with the experimentally measured selectivity and permeability data of MOF membranes for various gas separations in previous studies.(Keskin and Sholl, 2009b) Not only high selectivity but also high gas permeability is required for an efficient and economic membrane process. Therefore, gas permeability of MOFs were calculated using Eqn. 3.12. The bulk gas compositions of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures were assumed to be equimolar in all molecular simulations because Guo et al.(Guo et al., 2014) recently showed that composition does not strongly affect the C_2H_6 selectivity of a MOF material.

4.2 Results and Discussion

We validated the accuracy of our GCMC simulations to predict the adsorption of C_2H_6 , C_2H_4 , and CH_4 in various MOFs such as CuBTC, PCN-16, Co-MOF-74 and Mg-

MOF-74 by comparing results of our molecular simulations with the available experimental data of different research groups.(Altintas and Keskin, 2016) These comparisons are given Figure A1-3, in Appendix A. The accuracy of our computational approach to predict the membrane performances of MOFs for various gas mixtures using the GCMC and EMD data as explained above was shown in several of our previous studies by comparing the results of simulations with the experiments.(Adatoz and Keskin, 2015; Basdogan, Sezginel, and Keskin, 2015) We reported remarkably well agreement between our simulations and experimental measurements both for single-component and mixture CH_4 permeability through different MOF membranes including MOF-5, ZIF-78, ZIF-95.(Erucar and Keskin, 2016) In this work, we aimed to validate the accuracy of our EMD simulations for the diffusivity of C_2H_6 and CH_4 in the MOFs' pores. There is limited information about the diffusivity of these gases in MOFs due to the difficulty of measurement of self-diffusivity using purely experimental techniques and high computational demands of molecular simulations. Table 4.1 compares C_2H_6 and CH_4 diffusivities calculated from our molecular simulations with the available experimental and computational data taken from the literature. Our simulated data for C_2H_6 and CH_4 diffusivities in MOFs agreed well with the previous simulation studies of different research groups. C_2H_6 diffusivities in MOF-5 predicted by our molecular simulations agreed well with the experimental measurements of Stallmach et al.(Stallmach et al., 2006) and Ford et al.(Ford et al., 2012) whereas simulations predicted an order of magnitude slower CH_4 diffusivity in MOF-5 compared to the experiments. This discrepancy was attributed to the imperfections in the micropore structure which influenced the experimental studies but which were not taken into account in the EMD simulations.(Stallmach et al., 2006; Ford et al., 2012) Overall, the good agreement between our simulations and reported values in the literature for diffusion of C_2H_6 and CH_4 in MOFs suggests that simulated diffusion coefficients can be used to model gas transport through the MOF membranes.

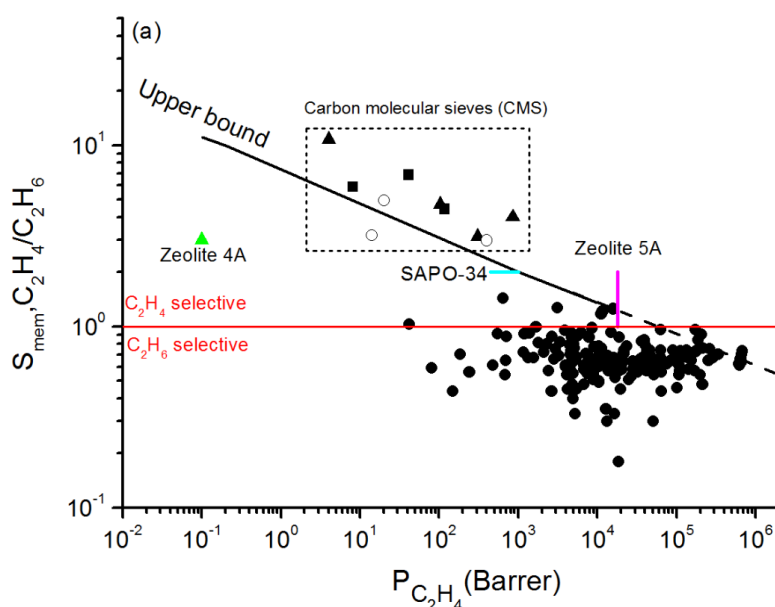
Table 4.1. Comparison of simulated self-diffusivities of gases in MOFs with the literature

		This work		Other simulations		Ref.	Experiments		Ref.
MOF		D_{CH_4} (cm ² /s)	$D_{\text{C}_2\text{H}_6}$ (cm ² /s)	D_{CH_4} (cm ² /s)	$D_{\text{C}_2\text{H}_6}$ (cm ² /s)		D_{CH_4} (cm ² /s)	$D_{\text{C}_2\text{H}_6}$ (cm ² /s)	
NU-125	Single	3.89×10^{-4}	7.87×10^{-5}	$2-3 \times 10^{-4}$	$1-1.7 \times 10^{-4}$	(Borah, Zhang, and Snurr, 2015)			
	Binary	3.39×10^{-4}	1.47×10^{-4}	1.2×10^{-4}	1.2×10^{-4}	(Borah, Zhang, and Snurr, 2015)			
PCN-14	Single	2.10×10^{-4}	7.62×10^{-5}	$1-1.5 \times 10^{-4}$	$0.3-1 \times 10^{-4}$	(Borah, Zhang, and Snurr, 2015)			
	Binary	1.92×10^{-4}	8.02×10^{-5}	1×10^{-4}	6×10^{-5}	(Borah, Zhang, and Snurr, 2015)			
COF-10	Single	9.88×10^{-4}		7.7×10^{-4}		(Garberoglio and Vallauri, 2008)			
MOF-5	Single	3.37×10^{-4}	1.51×10^{-4}	3×10^{-4}	1.5×10^{-4}	(Ford et al., 2012)	2×10^{-3}	1.8×10^{-4}	(Ford et al., 2012)
	Single			3.1×10^{-4}		(Skoulidas and Sholl, 2005)	1.7×10^{-3}	2.1×10^{-4}	(Stallmach et al., 2006)
	Single			3.08×10^{-4}		(Sarkisov, Duren, and Snurr, 2004)			
	Single			3.5×10^{-4}		(Babarao and Jiang, 2008)			

Combining adsorption data obtained from the GCMC simulations and diffusion data obtained from the EMD simulations, we computed selectivity and permeability of MOF membranes for C_2H_6/C_2H_4 and C_2H_6/CH_4 mixture separations as shown in Figure 4.1. In order to compare MOFs with traditional membrane materials, we collected selectivity and permeability data of zeolites, carbon molecular sieves (CMSs) and polymers for C_2H_6/C_2H_4 separations. At that point it is important to reiterate that membrane materials that preferentially select C_2H_6 over C_2H_4 are very scarce. Zeolites, CMSs and polymers are generally C_2H_4 selective. In order to be consistent with the literature data, we showed C_2H_4/C_2H_6 selectivity and C_2H_4 permeability of MOF membranes in Figure 4.1(a). Traditional polymeric membranes, such as Matrimid, 4,4'-(hexafluoroisopropylidene) dipthalicanhydride-2,4,6-trimethyl-1,3-phenylene diamine (6FDA-DAM), 4,4'-(hexafluoroisopropylidene) dipthalicanhydride: 3,3',4,4'-biphenyltetracarboxylic dianhydride -2,4,6-trimethyl-1,3-phenylene diamine (6FDA:BPDA-DAM) selectively separate C_2H_4 from C_2H_6 , generally due their sorption selectivities. (Rungta et al., 2013) The black solid line in Figure 4.1(a) represents the experimental C_2H_4/C_2H_6 upper bound for polymers which was established by Rungta et al. (Rungta et al., 2013) based on the pure gas permeability data, similar to the Robeson's upper bound. (Robeson, 2008) Polymeric membranes are mostly located below this bound and it is highly desired to identify new membrane materials that can exceed this bound by exhibiting higher selectivity and/or higher permeability than polymers.

Since MOFs are highly porous materials compared to polymers, C_2H_4 permeabilities of MOF membranes are significantly higher than those of polymers. According to the upper bound, the C_2H_4 permeabilities of polymeric membranes are in the range of $0.1-10^4$ Barrer whereas MOF membranes we considered in this part exhibit C_2H_4 permeabilities in the range of $42-6.75 \times 10^5$ Barrer. Therefore, we extrapolated the Robeson's upper bound with a dashed line in Figure 4.1(a) to show the high C_2H_4 permeabilities of MOFs. In fact, 4 MOFs, YUTYOC, IDIWOH, OWITAQ and OWITUQ were found to exceed the upper bound due to their high C_2H_4 permeabilities. The red solid line shows the selectivity preference of the membranes in Figure 4.1(a). MOFs located above (below) this line are C_2H_4 (C_2H_6) selective. A significant number of MOF membranes was identified to show C_2H_6 selectivity over C_2H_4 and these MOFs were located below the red line. Well-known zeolites such as zeolite 4A, zeolite 5A, SAPO-34 and CMSs are C_2H_4 selective membranes in C_2H_6/C_2H_4 separations. (Rungta et al., 2013)

For example, zeolite 4A membrane has C_2H_4 selectivity of 3 and C_2H_4 permeability of 0.1 Barrer whereas the MOFs we considered in this part are mostly C_2H_6 selective with significantly higher C_2H_4 permeabilities. (Rungta et al., 2013) The maximum C_2H_4 selectivity of CMS membranes was reported to be around 10 and their maximum C_2H_4 permeabilities were around 1000 Barrer. (Hayashi et al., 1996; Centeno and Fuertes, 1999; Fuertes and Menendez, 2002) A recent study reported that a ZIF-8-filled 6FDA-DAM MMM exhibit C_2H_4 selectivity of 3.2 and permeability of 72.9 Barrer depending on the ZIF loading in the polymer. (Zhang et al., 2012) All these comparisons show that C_2H_4 permeability of MOF membranes are significantly higher than that of zeolite 4A, zeolite 5A, SAPO-34, and ZIF-8-filled MMM.



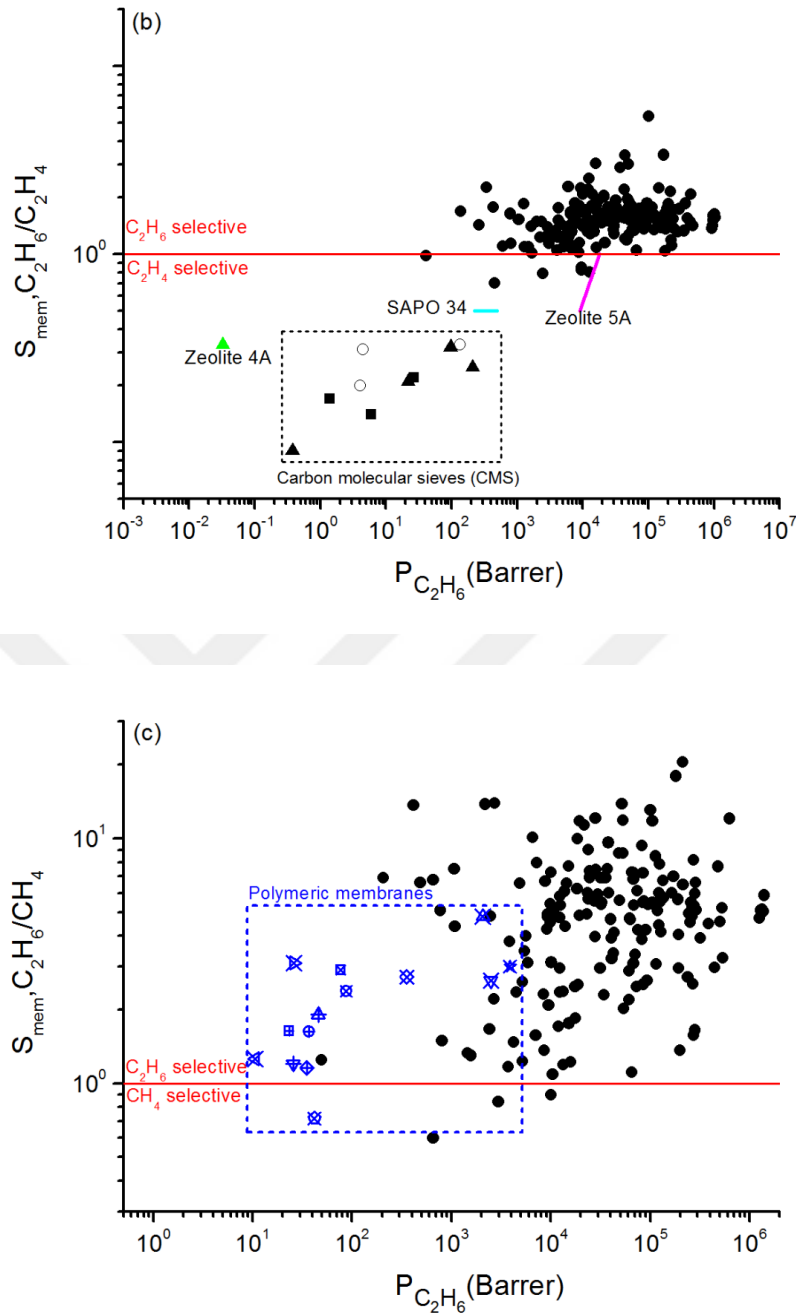


Figure 4.1. Selectivity and permeability of MOFs for (a) C_2H_4/C_2H_6 , (b) C_2H_6/C_2H_4 , (c) C_2H_6/CH_4 separations. In (a),(b) data for CMSs shown with filled circles are taken from Centeno&Fuertes(Centeno and Fuertes, 1999), triangles are taken from Fuertes&Menendez(Fuertes and Menendez, 2002), squares are taken from Hayashi et al.(Hayashi et al., 1996) and data for zeolites are taken from the literature. (Ruthven and Reyes, 2007; Romero-Perez and Aguilar-Armenta, 2010; Dai et al., 2012) Similarly, data for polymeric membranes shown with blue symbols in (c) were taken from the literature. (Robb, 1968; Alentiev et al., 2004; Pinnau and He, 2004; Starannikova et al., 2006; Khosravi and Sadeghi, 2013; Japip et al., 2014; Tirouni, Sadeghi, and Pakizeh, 2015)

Since majority of the MOFs we examined in this part are C_2H_6 selective, we additionally showed the C_2H_6 selectivity and C_2H_6 permeability of MOFs in Figure 4.1(b). This figure shows that MOF membranes can selectively separate C_2H_6 from C_2H_4 with high selectivity. 169 out of 175 MOFs are C_2H_6 selective with selectivities in the range of 1.0-5.4. Among these MOFs, EYOPUE has the highest C_2H_6/C_2H_4 selectivity (5.4) and OWITIY has the highest C_2H_6 permeability (1.04×10^6 Barrer). Selectivity of 11 MOFs was found to be slightly different than unity which means they do not have a strong preference for C_2H_6 or C_2H_4 and therefore they cannot be used as selective membranes for C_2H_6/C_2H_4 separations. A small number of MOF membranes (6 out of 175) was identified to show low/mediocre C_2H_4 selectivity over C_2H_6 and located below the red line.

Figure 4.1(c) represents C_2H_6/CH_4 selectivity and C_2H_6 permeability of MOF membranes. Although an upper bound is not established yet, several polymeric membranes were tested for C_2H_6/CH_4 separation and we collected this data from the literature to compare MOF membranes with polymers.^{34, 71-76} Most of the polymeric membranes exhibit C_2H_6 permeabilities between 10-100 Barrer and C_2H_6/CH_4 selectivities between 0.7 and 3. Only polydimethylsiloxane (PDMS) and polypentanamer (PPM) membranes show higher C_2H_6 permeabilities reaching to 2070 Barrer (Starannikova et al., 2006) and 3900 Barrer, (Pinnau and He, 2004) respectively. Most of the MOFs studied in this part exhibit higher C_2H_6 permeabilities and higher C_2H_6/CH_4 selectivities than these polymers. Among 175 MOFs, all the MOFs except 3 of them (XENZUN, GITVAH and YARYEV) were identified to be C_2H_6 selective over CH_4 and their C_2H_6 permeabilities were computed to be in the range of 49.5- 1.39×10^6 Barrer. The most selective MOF for C_2H_6/CH_4 separation was identified as NEXXIZ, with a selectivity of 20.5 and C_2H_6 permeability of 2.12×10^5 Barrer. OWITAQ was identified as the most permeable MOF with C_2H_6 permeability of 1.39×10^6 Barrer and C_2H_6/CH_4 selectivity of 6. All these results indicate that MOFs are promising membrane materials for preferential separation of C_2H_6 from CH_4 .

Combination of adsorption and diffusion selectivity determines the membrane selectivity of a MOF. In order to evaluate the individual effects of gas adsorption and diffusion on the membrane performance of MOFs, we examined the relation between adsorption, diffusion, and membrane selectivity in Figure 4.2. All selectivities were computed for equimolar gas mixtures. The colored dots in Figure 4.2(a) show the

distribution of the diffusion selectivities of MOFs for C₂H₆/C₂H₄ mixture. The LJ energy parameter was higher for C₂H₆ ($\epsilon_{\text{C}_2\text{H}_6}/k_B = 108 \text{ K}$) than C₂H₄ ($\epsilon_{\text{C}_2\text{H}_4}/k_B = 92.8 \text{ K}$), reflecting stronger dispersion interactions. Since C₂H₆ is energetically preferred over C₂H₄, C₂H₆(C₂H₄) is the strongly (weakly) adsorbed component in all MOFs. Therefore, adsorption selectivities favor C₂H₆ over C₂H₄ (C₂H₆/C₂H₄ selectivity > 1) for all MOFs. Diffusion selectivities favor C₂H₄ (C₂H₆/C₂H₄ selectivity < 1) in most of the MOFs since C₂H₄ molecules diffuse faster than C₂H₆ molecules. C₂H₄ molecules are lighter, smaller and weakly adsorbed into the pores of MOFs which leads to faster diffusion of C₂H₄ than C₂H₆. For 50 MOFs shown by red color, the diffusion selectivity for C₂H₆ over C₂H₄ is ranged from 0.45 to 0.83. Since the membrane selectivity was estimated as the multiplication of the adsorption and diffusion selectivities, the predicted membrane selectivities of these MOFs for C₂H₆ are lower than their adsorption selectivities as shown in Figure 4.2(a). In other words, these MOFs are more useful in adsorption-based C₂H₆/C₂H₄ separations than in membrane-based separations in terms of C₂H₆ selectivity. 113 MOFs shown by green color have diffusion selectivities around unity (0.83-1.10), which means diffusion does not strongly favor one gas species over other in the mixture. Since diffusion selectivities are close to one, membrane selectivities of these MOFs are only slightly lower than their adsorption selectivities. On the other hand, 12 of the MOFs shown by blue color exhibit diffusion selectivities higher than unity (1.11-1.82). That means self-diffusion coefficient of C₂H₆ is slightly higher than C₂H₄. In this case, both adsorption and diffusion favors the same component, C₂H₆ over C₂H₄ in the mixture. As a result, membrane selectivities of these MOFs are higher than their adsorption-based selectivities. In fact, it is highly desired to find materials in which both adsorption and diffusion favor the same gas component and lead to high membrane selectivities. Table 4.2 summarizes top ten C₂H₆ selective MOF membranes together with their adsorption, diffusion, membrane selectivities in addition to the self-diffusivities of each gas species in these materials. Both adsorption and diffusion selectivities of the MOFs listed in Table 4.2 are higher than 1, which means C₂H₆ is favored over C₂H₄ by both mechanisms. For example, EYOPUE has both high adsorption selectivity and high diffusion selectivity for C₂H₆ over C₂H₄. As a result, it was identified as the most selective MOF membrane. Therefore, it is more useful to utilize the MOFs listed in Table 4.2 as membranes rather than as adsorbents for selective separation of C₂H₆ from C₂H₄.

Table 4.2. Top ten MOF membranes for C₂H₆/C₂H₄ separation.

MOF	$S_{\text{ads, C}_2\text{H}_6/\text{C}_2\text{H}_4}$	$D_{\text{C}_2\text{H}_6}$ (cm ² /s)	$D_{\text{C}_2\text{H}_4}$ (cm ² /s)	$S_{\text{diff, C}_2\text{H}_6/\text{C}_2\text{H}_4}$	$S_{\text{mem, C}_2\text{H}_6/\text{C}_2\text{H}_4}$	$P_{\text{C}_2\text{H}_6}$ (Barrer)	$P_{\text{C}_2\text{H}_4}$ (Barrer)
EYOPUE	2.98	1.45×10^{-4}	7.97×10^{-5}	1.82	5.41	1.01×10^5	1.86×10^4
EYOPOY	3.18	1.62×10^{-4}	1.53×10^{-4}	1.06	3.37	1.73×10^5	5.12×10^4
AMAFUQ	2.61	8.09×10^{-5}	6.27×10^{-5}	1.29	3.36	4.42×10^4	1.32×10^4
YUVSUE	2.87	1.56×10^{-5}	1.47×10^{-5}	1.06	3.04	1.60×10^4	5.25×10^3
CAYDOX	2.94	1.28×10^{-4}	1.25×10^{-4}	1.02	3.01	4.95×10^4	1.64×10^4
CAYGIU	2.79	9.65×10^{-5}	9.34×10^{-5}	1.03	2.88	3.71×10^4	1.29×10^4
BUSNAF	2.14	2.84×10^{-5}	2.41×10^{-5}	1.18	2.53	1.24×10^4	4.92×10^3
TUSGUJ	1.92	3.80×10^{-6}	3.19×10^{-6}	1.19	2.28	6.05×10^3	2.65×10^3
UHAXUW	2.22	6.58×10^{-7}	6.45×10^{-7}	1.02	2.26	3.40×10^2	1.50×10^2
NEXXIZ	2.18	1.27×10^{-4}	1.23×10^{-4}	1.03	2.25	1.45×10^5	6.44×10^4

Table 4.3. Top MOF membranes for C₂H₄/C₂H₆ separation.

MOF	$S_{\text{ads, C}_2\text{H}_4/\text{C}_2\text{H}_6}$	$D_{\text{C}_2\text{H}_4}$ (cm ² /s)	$D_{\text{C}_2\text{H}_6}$ (cm ² /s)	$S_{\text{diff, C}_2\text{H}_4/\text{C}_2\text{H}_6}$	$S_{\text{mem, C}_2\text{H}_4/\text{C}_2\text{H}_6}$	$P_{\text{C}_2\text{H}_4}$ (Barrer)	$P_{\text{C}_2\text{H}_6}$ (Barrer)
XENZUN	0.74	7.62×10^{-7}	3.94×10^{-7}	1.93	1.43	6.47×10^2	4.53×10^2
AVEROJ	0.57	5.47×10^{-6}	2.44×10^{-6}	2.24	1.27	3.12×10^3	2.45×10^3
TUDJOS	0.62	2.22×10^{-5}	1.10×10^{-5}	2.01	1.25	1.59×10^4	1.28×10^4
YARYEV	0.70	2.19×10^{-5}	1.26×10^{-5}	1.74	1.21	1.17×10^4	9.65×10^3
KEXFAU	0.80	2.15×10^{-5}	1.46×10^{-5}	1.47	1.17	1.12×10^4	9.60×10^3

It is interesting to discuss the MOFs for which diffusion selectivity for C_2H_4 overcompensates adsorption selectivity for C_2H_6 and makes the membrane C_2H_4 selective. We listed adsorption, diffusion, membrane selectivities and gas permeabilities of the C_2H_4 selective MOFs in Table 4.3. All these five MOFs are weakly selective for C_2H_4 . For example, XENZUN was predicted to show the highest membrane selectivity. Adsorption weakly favors C_2H_6 over C_2H_4 in this MOF whereas diffusion favors C_2H_4 over C_2H_6 and dominates the adsorption selectivity. AVEROJ has a low C_2H_4/C_2H_6 adsorption selectivity but the diffusion selectivity strongly favors C_2H_4 over C_2H_6 and makes the membrane C_2H_4 selective. KEXFAU has the highest adsorption selectivity for C_2H_4/C_2H_6 separation as can be seen from Table 4.3, but its diffusion selectivity is close to unity making the membrane weakly selective for C_2H_4 . These examples signify the importance of diffusion selectivity in governing membrane's separation performance. If the adsorption selectivity does not strongly favor one component in the mixture, then diffusion selectivity determines the membrane's gas separation performance.

Similar selectivity analysis was done for C_2H_6/CH_4 separation in Figure 4.2(b). Adsorption strongly favors C_2H_6 and strongly adsorbed C_2H_6 molecules move slower than weakly adsorbed, lighter CH_4 molecules. As a result, diffusion selectivity favors CH_4 over C_2H_6 and becomes less than 1 for almost all MOFs as shown by red and green points in Figure 4.2(b). Since adsorption strongly favors C_2H_6 and diffusion weakly favors CH_4 , membrane-based C_2H_6 selectivities of MOFs are less than their adsorption-based selectivities. There are 11 MOFs shown by blue color in Figure 4.2(b) in which diffusivity of C_2H_6 is slightly higher than the diffusivity of CH_4 . Our EMD simulations showed that gas molecules generally diffuse only in one direction in these MOFs and the high number of slowly diffusing C_2H_6 molecules hinders the fast diffusion of CH_4 molecules in the pores. As a result, diffusion selectivities are around 1.1-1.3 and these MOFs are promising membrane materials since both adsorption and diffusion favors the same component C_2H_6 over CH_4 . Performances of the top ten promising MOF membranes for selective separation of C_2H_6 from CH_4 were summarized in Table 4.4. For example, adsorption and diffusion favor C_2H_6 over CH_4 in NEXXIZ, TIRQOB, ZUQPOQ, UHAXUW whereas high adsorption selectivity towards C_2H_6 dominates the diffusion selectivity towards CH_4 in other MOFs as shown in Table 4.4.

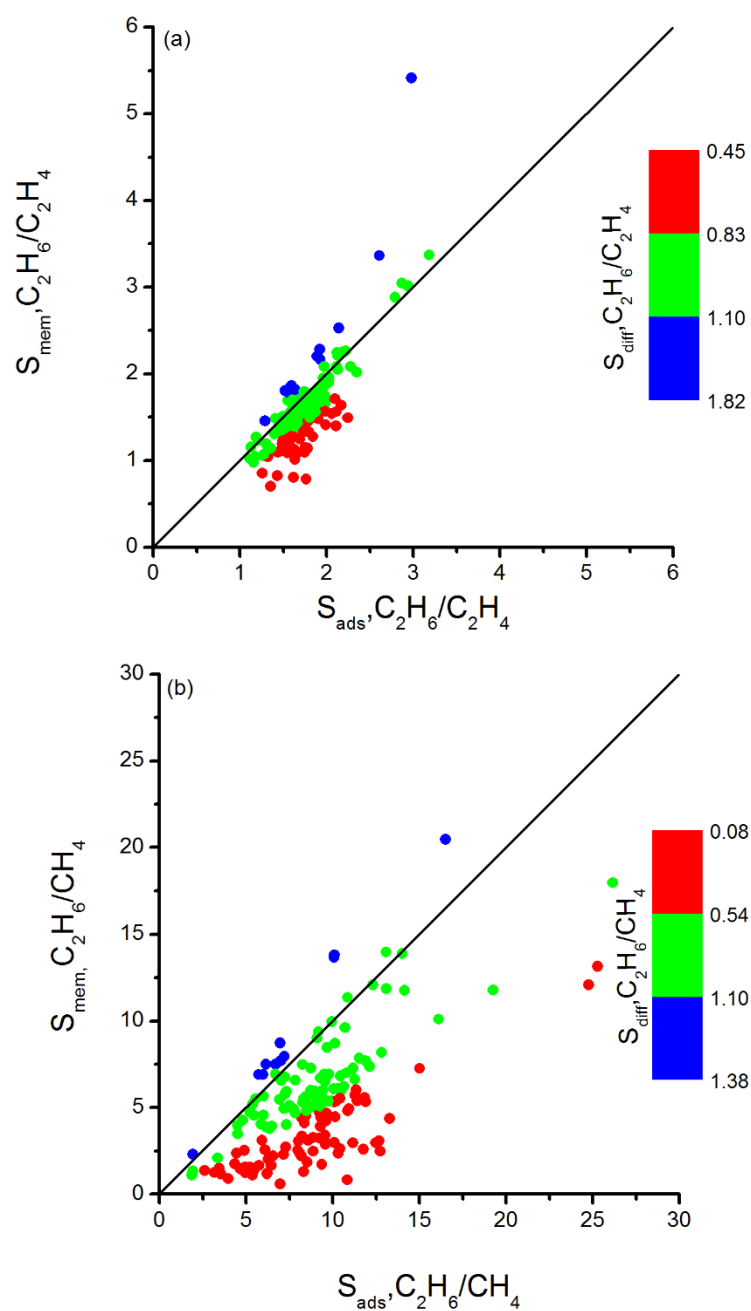


Figure 4.2. Adsorption, diffusion and membrane selectivities of MOFs for (a) $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ and (b) $\text{C}_2\text{H}_6/\text{CH}_4$ separations.

Table 4.4. Top ten MOF membranes for C₂H₆/CH₄ separation.

MOF	S _{ads} , C ₂ H ₆ /CH ₄	D _{C₂H₆} (cm ² /s)	D _{CH₄} (cm ² /s)	S _{diff} , C ₂ H ₆ /CH ₄	S _{mem} , C ₂ H ₆ /CH ₄	P _{C₂H₆} (Barrer)	P _{CH₄} (Barrer)
NEXXIZ	16.49	1.41 × 10 ⁻⁴	1.14 × 10 ⁻⁴	1.24	20.46	2.12 × 10 ⁵	1.04 × 10 ⁴
EYOPOY	26.16	1.36 × 10 ⁻⁴	1.98 × 10 ⁻⁴	0.69	17.97	1.81 × 10 ⁵	1.01 × 10 ⁴
TIRQOB	13.07	1.81 × 10 ⁻⁶	1.70 × 10 ⁻⁶	1.07	13.98	2.72 × 10 ³	1.95 × 10 ²
CAYDOX	14.01	1.10 × 10 ⁻⁴	1.11 × 10 ⁻⁴	0.99	13.88	5.20 × 10 ⁴	3.74 × 10 ³
ZUQPOQ	10.10	3.71 × 10 ⁻⁶	2.72 × 10 ⁻⁶	1.37	13.81	2.18 × 10 ³	1.58 × 10 ²
UHAXUW	10.08	6.34 × 10 ⁻⁷	4.68 × 10 ⁻⁷	1.35	13.65	4.15 × 10 ²	3.04 × 10 ¹
EYOPUE	25.29	1.14 × 10 ⁻⁴	2.20 × 10 ⁻⁴	0.52	13.10	1.01 × 10 ⁵	7.68 × 10 ³
LUMDIG	24.77	2.01 × 10 ⁻⁵	4.12 × 10 ⁻⁵	0.49	12.08	2.81 × 10 ⁴	2.33 × 10 ³
SUTBIT	12.32	2.13 × 10 ⁻⁴	2.17 × 10 ⁻⁴	0.98	12.07	6.31 × 10 ⁵	5.23 × 10 ⁴
CAYGIU	13.09	1.12 × 10 ⁻⁴	1.23 × 10 ⁻⁴	0.91	11.86	5.31 × 10 ⁴	4.48 × 10 ³

As we discussed above, some MOFs are promising for adsorption-based gas separations whereas some others are good candidates for membrane-based gas separations. We aimed to identify the MOFs that can be used both as effective adsorbents and membranes for the preferential separation of C₂H₆ from C₂H₄ and CH₄. Selectivity is generally considered as the most critical factor to assess equilibrium and kinetic-based separation performances of materials. High adsorption selectivity is desired for adsorbents whereas both high selectivity and permeability are required for membranes. Therefore, we considered these three performance metrics, adsorption selectivity, membrane selectivity and permeability of the desired gas in order to identify the most promising MOFs that can be used both as adsorbents and membranes. For C₂H₆/C₂H₄ separation, adsorption and membrane selectivities of MOFs were computed to be 1.1-3.2 and 0.7-5.4, respectively and C₂H₆ permeabilities of MOFs were predicted to be 41-1.04 × 10⁶ Barrer. For C₂H₆/CH₄ separation, adsorption and membrane selectivities were calculated to be 1.9-26.2 and 0.60-20.5, respectively with C₂H₆ permeabilities of 49.5-1.39 × 10⁶ Barrer. We set the minimum adsorption and membrane selectivity to 2 and showed the top ten MOFs with the highest C₂H₆ permeabilities for C₂H₆/C₂H₄ separation in Figure 4.3(a). Similarly, for C₂H₆/CH₄ separation, we considered the MOFs that have adsorption and membrane selectivities larger than 10. After these two constraints we identified the MOFs with the highest C₂H₆ permeabilities in Figure 4.3(b). Results show that MOFs EYOPOY, NEXXIZ, EYOPUE, CAYDOX, WEMGAY, CAYGIU, LUMDIG and YUVSUE are common in the top ten promising material list of C₂H₆/C₂H₄ and C₂H₆/CH₄ separations. For example, EYOPOY has high adsorption-based selectivity both for C₂H₆/C₂H₄ (3.2) and C₂H₆/CH₄ (26.2) in addition to high membrane-based selectivity both for C₂H₆/C₂H₄ (3.4) and C₂H₆/CH₄ (18). This result suggests that these 8

MOFs can be used as effective adsorbents and membranes for the selective separation of C_2H_6 from C_2H_4 and CH_4 .

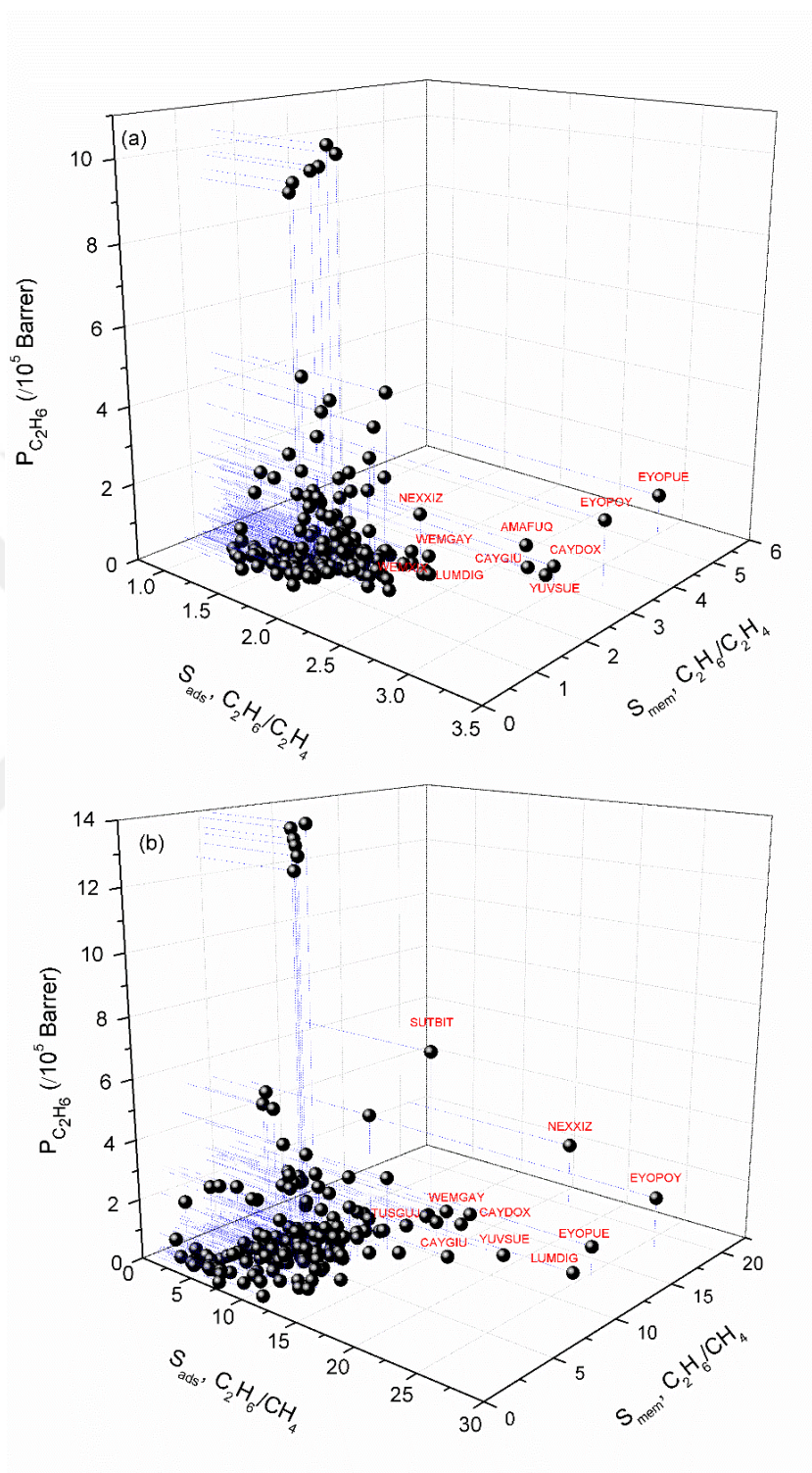


Figure 4.3. Adsorption selectivity, membrane selectivity and C_2H_6 permeability of MOFs for (a) C_2H_6/C_2H_4 and (b) C_2H_6/CH_4 separations. Top ten MOFs for (a) C_2H_6/C_2H_4 and (b) C_2H_6/CH_4 separations are labelled with red labels. Blue dashes are to guide the eye.

3.2 Structure-performance relations for MOFs:

We so far focused on the gas separation performance of MOFs as adsorbents and membranes. Establishing relation between structures and separation performances of MOFs would be very useful to save computational time and to guide the experimental studies for the synthesis of materials with the desired topology. However, clear identification of this type of relations is challenging because separation performance of a material is determined by the interplay of various factors such as chemical topology, porosity, pore size and shape and it cannot be simply correlated to only a single or two structural properties. (Ozturk and Keskin, 2014) In order to simply make a structure-performance analysis, we examined the relation between selectivity and easily computable structural properties of MOFs such as pore size, porosity, and surface area. Figure 4.4 shows that there is a correlation between adsorption selectivity and LCD as well as porosity of MOFs. MOFs with LCDs around 4.5-6 Å generally exhibit higher C_2H_6/C_2H_4 and C_2H_6/CH_4 selectivities (>2 and >10 , respectively) than MOFs with larger pore sizes. As the LCD increases, selectivity generally decreases. MOFs that have large LCDs (>6 Å) have lower C_2H_6/C_2H_4 and C_2H_6/CH_4 selectivities (<2 and <10 , respectively) since both gas molecules can easily pass through the pores. Figure 4.4 also shows that increasing porosity decreases the adsorption selectivity and this is the common outcome for both gas separations. The porosity of MOFs we considered in this part ranges from 0.22 to 0.83. Although the color labeling is not distinct in Figure 4.4, it is clear that MOFs with porosity lower than 0.50 exhibit higher selectivity.

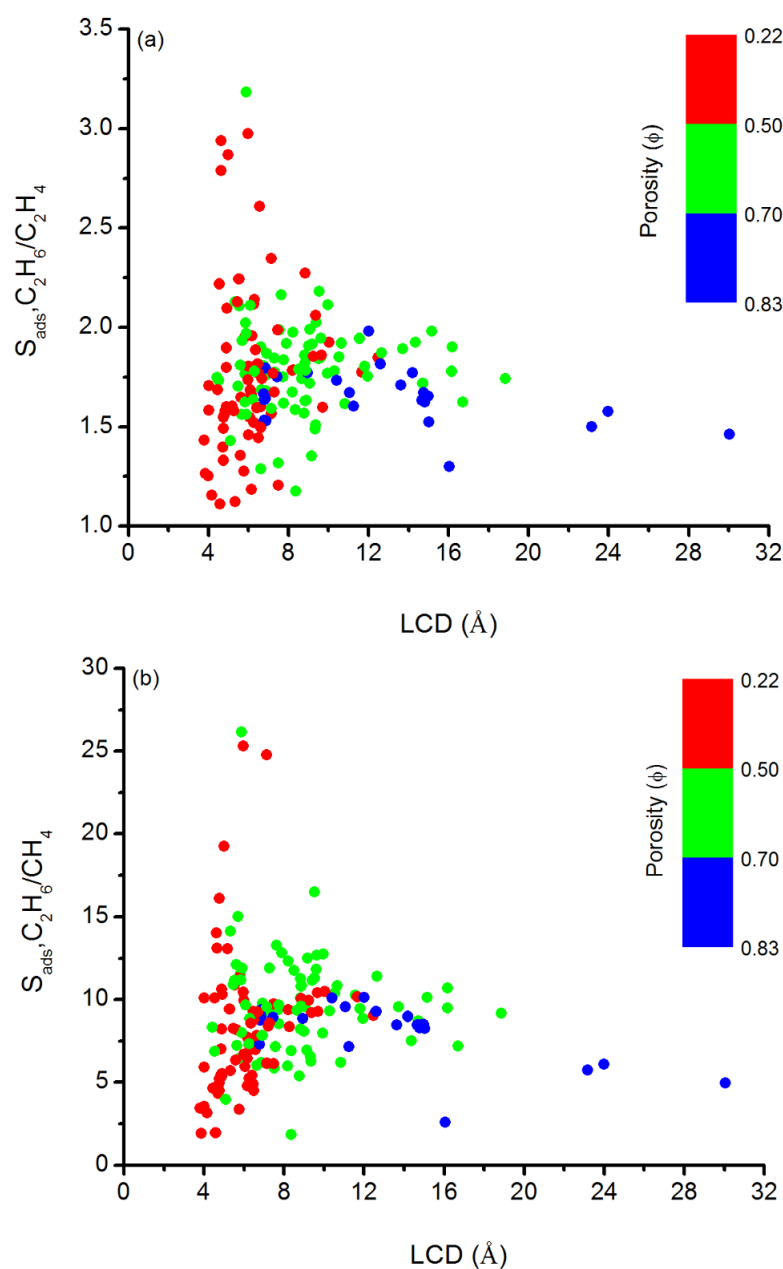


Figure 4.4. Relation between adsorption selectivities and LCDs of MOFs as a function of porosities for (a) C_2H_6/C_2H_4 and (b) C_2H_6/CH_4 separations.

Similarly, Figure 4.5 shows that MOFs having lower surface areas exhibit higher adsorption selectivity. For example, MOFs with surface areas in the range of 500-1000 m^2/g and 750-1000 m^2/g tend to show adsorption selectivities higher than 2 and 10 for C_2H_6/C_2H_4 and C_2H_6/CH_4 separations, respectively. Overall, results of our structure-performance analysis suggest that MOFs with LCDs around 4.5-6 Å, porosities less than 0.50, and surface areas in the range of 500-1000 m^2/g can be potentially promising adsorbents for efficient C_2H_6 separations.

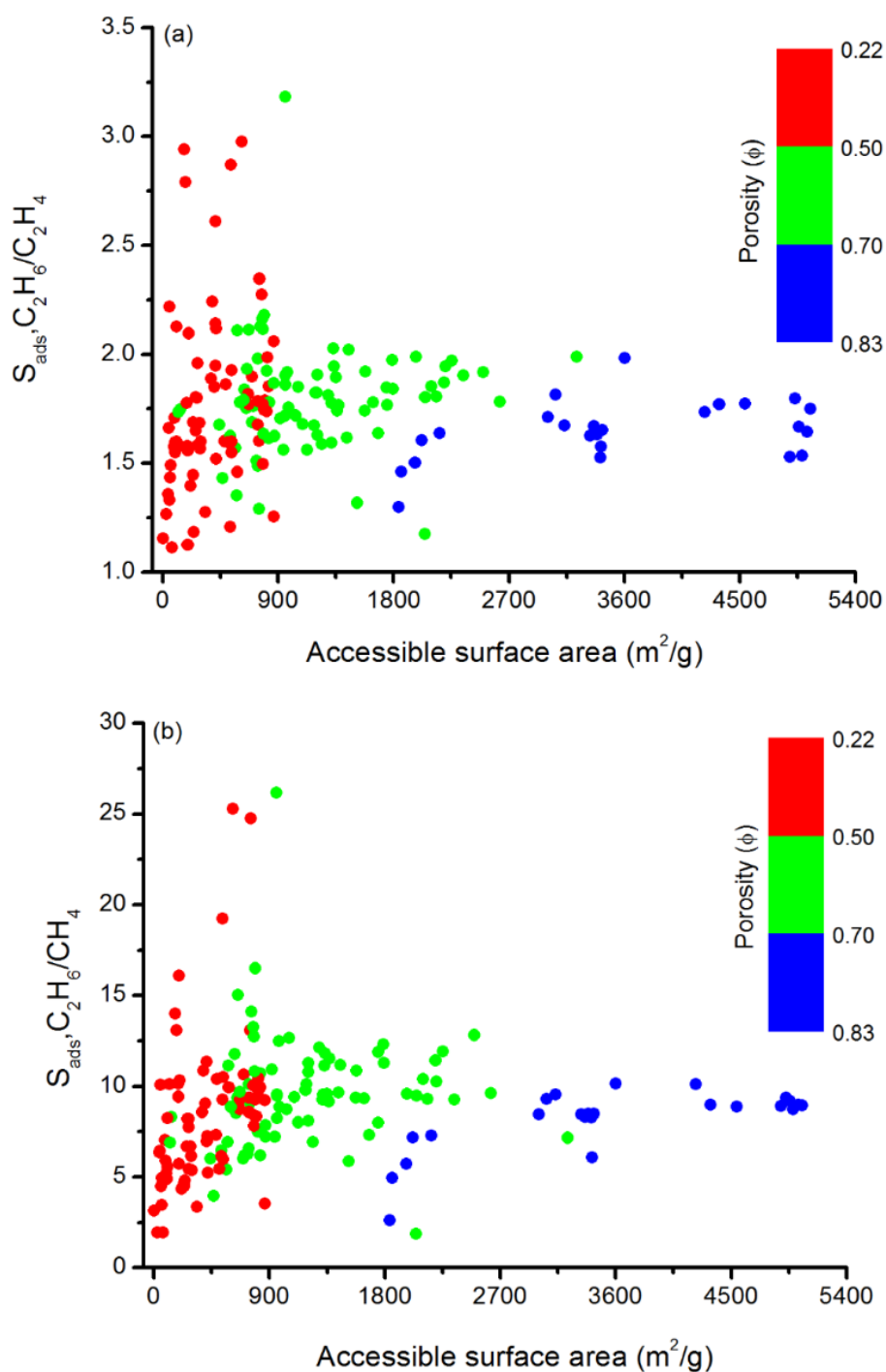


Figure 4.5. Relation between adsorption selectivities and surface areas of MOFs as a function of porosities for (a) C₂H₆/C₂H₄ and (b) C₂H₆/CH₄ separations.

Similar structure-performance analysis was carried out to unlock the relation between membrane selectivity of MOFs, pore sizes, porosities and surface areas. Figure 4.6 shows that membranes with LCDs in the range of 6-7 Å and 6-9 Å are more selective for separation of C₂H₆ from C₂H₄ and CH₄, respectively. It is also observed that among

the two MOFs with close LCDs but different porosities, the MOF with lower porosity generally have higher membrane selectivity. For example, EYOPUE and SUBDOI have close LCDs (5.97 Å and 6.29 Å) but different porosities (0.46 and 0.56). The one with the lower porosity exhibits high membrane selectivity (5.41) whereas the other one has low membrane selectivity (1.14). This example underlines the importance of the material's porosity on the membrane selectivity. Similar to the adsorption selectivity, as the surface area and porosity decrease, membrane selectivity increases as shown in Figure 4.7. For C_2H_6/C_2H_4 and C_2H_6/CH_4 separation, we obtained the highest membrane selectivities (5.4 and 20.5, respectively) when the surface areas of the MOFs are between 500-1000 m^2/g and 750-1000 m^2/g , respectively.

We finally investigated the effect of pore size on the gas permeabilities of MOFs in Figure 4.8. Vertical solid lines in this figure represent the kinetic diameter of the gas molecules present in the mixture. We specifically focused on the PLD, the smallest pore diameter in the structure, rather than LCD since we refined our MOF database to have the LCDs greater than the kinetic diameters of the gas molecules as we discussed before. It can be seen that once the PLD is slightly larger than the kinetic diameter of a gas molecule, permeability of that gas increases. In Figure 4.8(a), C_2H_6 (C_2H_4) permeability increases from 10^5 to 10^6 (10^4 to 10^5) Barrer when PLD is larger than 3.76 (3.68) Å, which is the kinetic diameter of C_2H_6 (C_2H_4) molecule. In Figure 4.8(b), C_2H_6 and CH_4 permeabilities increase from 10^5 to 10^6 Barrer and from 10^4 to 10^5 Barrer for the MOFs that have PLD values slightly larger than 3.76 Å and 3.73 Å, the kinetic diameters of C_2H_6 and CH_4 , respectively. These increases can be attributed to the easier diffusion of gas molecules in the larger pores of MOFs. These results suggest that it is reasonable to choose MOFs with PLD values slightly larger than the kinetic diameters of the gas molecules that are desired to be separated in order to obtain high gas permeabilities.

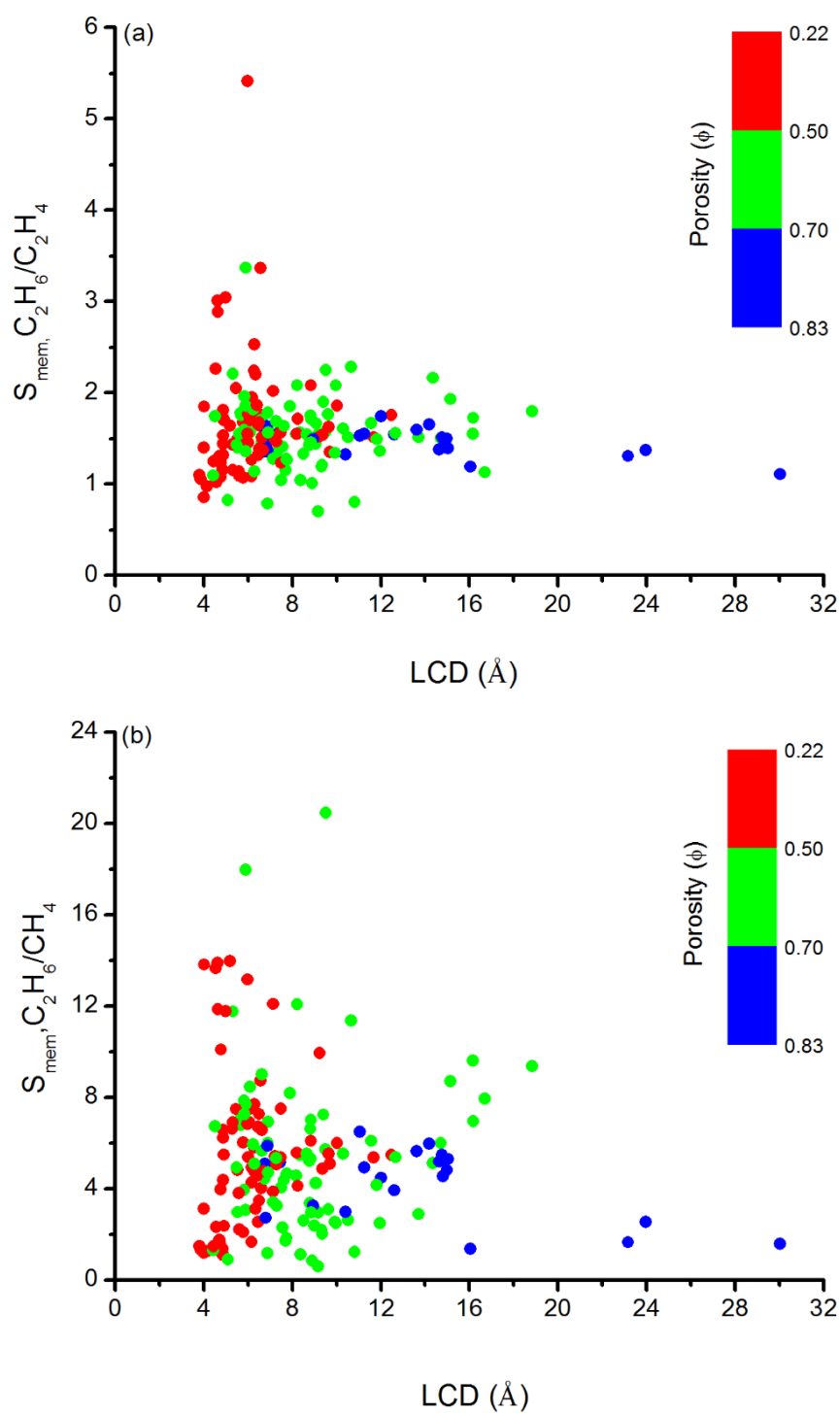


Figure 4.6. Relation between membrane selectivities and LCDs of MOFs as a function of porosities for (a) $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ and (b) $\text{C}_2\text{H}_6/\text{CH}_4$ separations.

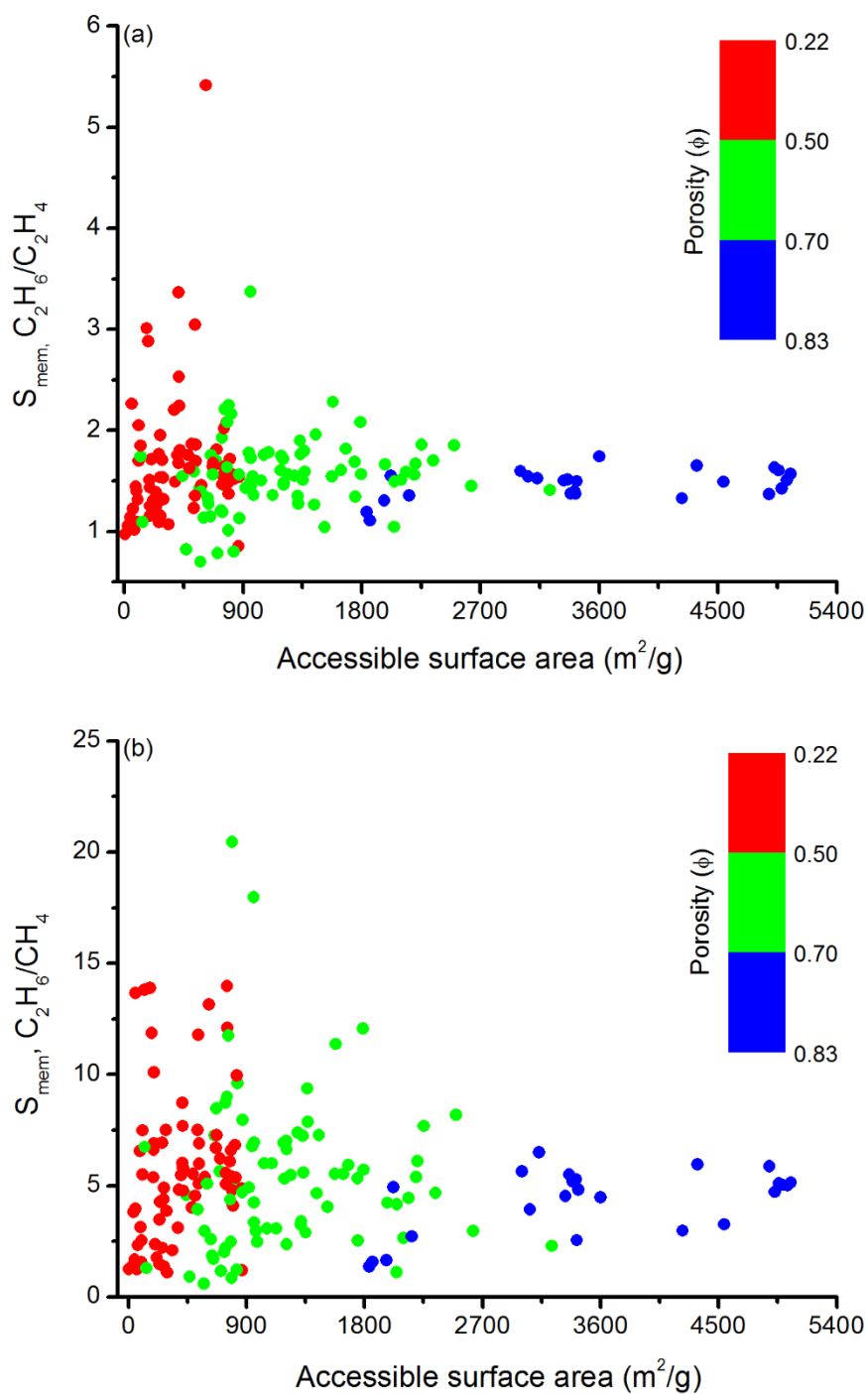


Figure 4.7. Relation between membrane selectivities and accessible surface areas of MOFs as a function of porosities for (a) $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ and (b) $\text{C}_2\text{H}_6/\text{CH}_4$ separations.

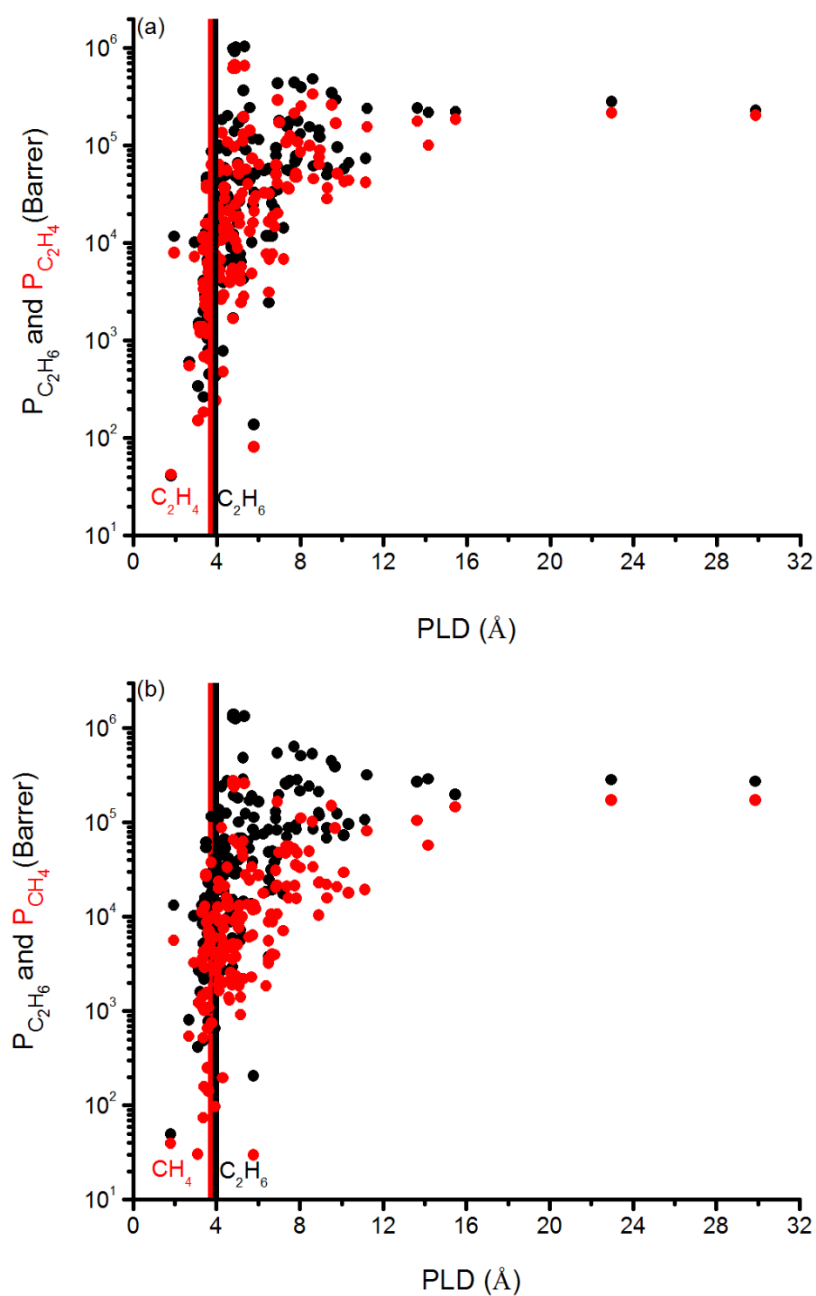


Figure 4.8. Relation between gas permeabilities and PLDs of MOFs for (a) C_2H_6/C_2H_4 and (b) C_2H_6/CH_4 separations. Black symbols represent the C_2H_6 permeabilities, red symbols represent permeabilities of C_2H_4 in (a) and CH_4 in (b).

4.3 Conclusion

In this study, we computed adsorption and diffusion data of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures in 175 different MOFs. Using this data, membrane performances of MOFs were assessed for these two important gas separations. Majority of the MOFs we considered was identified as C_2H_6 selective membranes and a small number of MOFs was identified as C_2H_4 selective. This result is important since membranes that are selective for C_2H_6 over C_2H_4 are scarce in the literature and almost all traditional membrane materials such as polymers, zeolites and CMSs are C_2H_4 selective. MOF membranes that we considered in this part were found to exhibit higher gas permeabilities than these well-known membrane materials due to their highly porous structures. Examining the structure-performance relations of MOF membranes revealed that MOFs with porosities lower than 0.50, LCD values between 6-9 Å, and surface areas between 500-1000 m²/g have the highest selectivities for C_2H_6/C_2H_4 and C_2H_6/CH_4 separations.

Our idea was to identify promising MOF membranes for C_2H_6 separations using molecular simulations in order to direct experimental efforts, time and resources to those promising materials for experimental fabrication and testing of membranes under real operating conditions. Once the potential value of a membrane material has been demonstrated by molecular simulations, further experimental studies can be used to increase the precision of initial assessment. Our molecular simulations do not provide any information about the stability of MOFs, which is very important for real applications. An efficient membrane material must keep its structural stability under industrial operation conditions. This issue is more likely to be addressed experimentally. We searched for the stability information of the two MOFs, EYOPUE and NEXXIZ, which were identified as the top promising membrane material for selective separation of C_2H_6 from C_2H_4 and CH_4 , respectively. Experiments reported that they can retain their crystalline integrity at ambient conditions.(Cui et al., 2011; Kim et al., 2013b) The value of our computational work is that it can provide a motivation to perform detailed experimental studies for the thermal and structural stability of promising membrane materials. We believe that results provided in this part will guide experimental studies for the design and synthesis of new MOFs with better separation performances for C_2H_6 separations.

*The content of this chapter is directly obtained from our published work(Altintas and Keskin, 2017) and adapted for thesis.

Chapter 5

NATURAL GAS PURIFICATION FROM CO₂

We applied a multi-level, high-throughput computational screening methodology showing increasing computational expense and complexity at each level to study the most recent MOF database reported in the literature (Moghadam et al., 2017) for CO₂/CH₄ separation. In the first-level of screening, we calculated CO₂ permeabilities and CO₂/CH₄ selectivities of MOF membranes using single-component gas adsorption and diffusion data obtained from the GCMC and EMD simulations performed at infinite dilution. Predicted separation performances of MOF membranes were compared with polymeric and zeolite membranes. The top 8 MOF membranes exhibiting CO₂ permeabilities > 10⁶ Barrer and CO₂/CH₄ selectivities > 80 were identified. In the second-level of calculations, we carried out GCMC and EMD simulations for the top MOF membranes considering equimolar CO₂/CH₄ mixtures. Impacts of adsorption and diffusion on the separation performance of the top membranes were investigated in detail. In the third level of calculations, framework flexibility was considered and its impact on the membrane properties of MOFs was studied by comparing the results of rigid and flexible EMD simulations. Relations between structures and performances of MOFs were also investigated to provide atomic-level insights into the design of novel MOFs which will be useful for CO₂/CH₄ separation processes. Finally, the potential of using top MOFs as filler particles in polymer membranes was examined by computing gas permeability and selectivity of MOF/polymer MMMs for separation of CO₂/CH₄ mixture. The results presented in this study will be beneficial in guiding the selection of the best MOF membranes and MOF-based MMMs for natural gas purification process.

5.1 Methodology

The most recent MOF database(Moghadam et al., 2017) reported in the literature was used in this work. Solvent molecules were removed from the structures as described in the literature(Moghadam et al., 2017) and Zeo++ software(Willems et al., 2012) (version 0.2) was utilized to calculate pore limiting diameters (PLDs), the largest cavity diameters (LCDs), porosities, and, surface areas of MOFs. This MOF database was refined to only include materials with non-zero accessible surface areas and PLDs>3.75 Å to let the permeation of both CO₂ (3.3 Å) and CH₄ (3.73 Å) molecules through the membranes. We also excluded the MOFs for which molecular simulations resulted in gas diffusivities <10⁻⁸ cm²/s, which is the limit of EMD to accurately characterize molecular diffusion. As a result, we ended up with 3794 MOFs having various structural properties.

Molecular simulations were initially performed to calculate the Henry's constants (K^0) and self-diffusivities (D^0) of CO₂ and CH₄ at infinite dilution using the RASPA simulation code.(Dubbeldam et al., 2016) The adsorbate-adsorbate interactions were switched-off and 30 gas molecules were inserted into each MOF to imitate infinite dilution. The Widom particle insertion method was used to calculate K^0 of each gas at 298 K.(Frenkel and Smit, 2002) For the Monte Carlo simulations, the number of initialization and production cycles was set to 5000 and 10000, respectively. The MSD of gas molecules was computed and its slope with respect to time obtained from the EMD simulations was used to calculate D^0 of each gas component. EMD simulations were performed in the NVT ensemble using the Nosé-Hoover thermostat(Frenkel and Smit, 2002) for 10⁶ cycles with a time step of 1 fs. Lennard-Jones (LJ) potential was used to define intermolecular interactions between the gas molecules and MOFs atoms. CO₂ molecule was modeled as a three-site rigid molecule and its partial point charges were positioned at the center of each site following the TraPPE model.(Potoff and Siepmann, 2001) CH₄ was modeled as a single-sphere.(Martin and Siepmann, 1998) The Universal Force Field (UFF)(Rappe et al., 1992) was used to define the potential parameters of MOF atoms. Charge equilibration method (QEq)(Rappe and Goddard, 1991; Wilmer and Snurr, 2011) existing in RASPA was employed to assign partial point charges to MOF atoms and electrostatic interactions between MOFs and CO₂ were calculated using the Ewald summation.(Ewald, 1921) The good agreement between simulations and experiments for adsorption and diffusion properties of CO₂ and CH₄ in various MOFs was shown in our earlier studies(Ozturk and Keskin, 2014; Sumer and Keskin, 2016; Altintas, Erucar, and

Keskin, 2018) and validated the appropriateness of the selected force fields for MOFs and gas molecules.

Gas permeabilities of MOFs at infinite dilution (P_i^0) were calculated using Eqn. 3.9. Ideal CO₂/CH₄ selectivities of MOF membranes were calculated as the ratio of gas permeabilities, as shown in Eqn. 3.10. Top 8 MOFs having high membrane selectivities, $S_{\text{mem,CO}_2/\text{CH}_4}^0 > 80$ and high CO₂ permeabilities, $P_{\text{CO}_2}^0 > 10^6$ Barrer were identified at the end of first-level of calculations. In the second-level of calculations, we computed adsorption of binary CO₂/CH₄:50/50 mixtures in top 8 MOFs. Binary mixture simulations were performed at two different pressures, 1 bar and 10 bar, at 298 K. In contrast to the first-level of calculations, both gas-gas and gas-MOF interactions were taken into account in the mixture simulations. Intermolecular interactions were truncated at a cut-off distance of 13 Å. A total of 15000 cycles was used where 5000 cycles were used for initialization and 10000 cycles were used to obtain the ensemble averages. GCMC simulations of equimolar CO₂/CH₄ mixtures performed at 1 and 10 bar, at 298 K were used to define the initial states of mixture EMD simulations. After 10000 initialization and 10000 equilibration cycles, 10^7 cycles were used to obtain mean square displacement of gases in the NVT ensemble using a time step of 1 fs. Gas diffusivities were computed using at least two trajectories. Mixture permeabilities through MOF membranes were computed using Eqn. 3.11. Permeate side of the membrane was assumed to be vacuum. (Keskin and Sholl, 2009a) Mixture selectivities were computed as the ratio of gas permeabilities using Eqn. 3.13. It is important to note that we previously validated the accuracy of this computational methodology by showing the good agreement between our predictions and experimentally measured permeances/permeabilities of single-component CO₂ and CH₄ gases through MIL-53-Al, (Adatoz and Keskin, 2015) Ni-MOF-74, (Adatoz and Keskin, 2015; Altintas et al., 2018a; Avci, Velioglu, and Keskin, 2018; Daglar and Keskin, 2018) IRMOF-1, (Adatoz and Keskin, 2015; Altintas et al., 2018a; Daglar and Keskin, 2018) ZIF-69, (Adatoz and Keskin, 2015) ZIF-78, (Adatoz and Keskin, 2015) ZIF-90, (Adatoz and Keskin, 2015; Altintas et al., 2018a; Daglar and Keskin, 2018) ZIF-95 (Altintas et al., 2018a; Daglar and Keskin, 2018) membranes and even for the equimolar mixture permeability of CO₂ and CH₄ through ZIF-69 membranes. (Adatoz and Keskin, 2015)

In the third-level of calculations, flexible EMD simulations were performed using the Forcite module of Materials Studio 17.2 (Altintas and Keskin, 2019) to study the influence of flexibility on the predicted membrane performances of MOFs. Due to the

computational expense of the flexible EMD simulations, only 2 of the top 8 MOFs were simulated and these MOFs were selected based on their pore sizes to represent a narrow-pored MOF (LOYMET, PLD: 3.98 Å) and a large-pored MOF (KIPJUQ, PLD: 7.29 Å). Before starting the flexible EMD simulations, the number of gas molecules that was computed using mixture GCMC simulations were loaded into the MOFs by the Fixed Loading task of the Sorption module in Materials Studio. The force fields used in RASPA were employed in Materials Studio. Both the equilibration and production steps were set as 5×10^6 steps. Van der Waals interactions were summed with atom-based interaction method with cubic spline truncation, cut-off distance of 13 Å and spline width of 1 Å were used in the Fixed Loading simulations. Partial charges for the framework atoms were assigned using QEq(Rappe and Goddard, 1991) charge method as implemented in Materials Studio. Electrostatic interactions were summed with the Ewald summation method with an Ewald accuracy of 10^{-3} kcal/mol. The frame with the lowest energy obtained at the end of the fixed loading simulation was used for the flexible EMD simulations. EMD simulations were performed using NVT ensemble with a step size of 1 fs up to a total of 10 ns by removing the fixed constraints on each coordinate of the MOF atoms. Initial velocities of gas molecules were randomly assigned. Similar to the rigid simulations, UFF and Nosé-Hoover thermostat were used in the flexible EMD simulations. We validated the generic FF parameters used in flexible EMD simulations of MOFs by comparing the experimental and simulated gas permeabilities in our previous work.(Erucar and Keskin, 2015) A recent work(Garberoglio and Taioli, 2012) also showed that results obtained with the UFF description of MOF flexibility is quantitatively comparable with the Density-Functional Tight-Binding predictions. To evaluate the differences between the results of rigid and flexible EMD simulations, the changes in pore sizes of the MOFs were investigated. Crystal structures of MOFs were recorded at different time points during the flexible EMD simulations using Materials Studio and pore sizes of materials were computed using Zeo++.

Finally, we examined the potential of MOF-based MMMs by estimating their gas permeabilities and selectivities. The top 8 MOFs were used as filler particles in 8 different types of polymers including the widely used ones such as cellulose acetate,(Houde et al., 1996) Matrimid,(Khan, Li, and Vankelecom, 2011b) polysulfone,(Guo et al., 2015) SPEEK-3 (sulfonated aromatic poly(ether ether ketone)),(Khan, Li, and Vankelecom, 2011a) Pebax (poly(ether-b-amide-6),(Khosravi et al., 2017) 6FDA-DAM (6FDA: 2,2-

bis (3,4-carboxyphenyl) hexafluoropropane dianhydride and DAM: diaminomesitylene),(Bae et al., 2010) PIM-1 (polymer of intrinsic microporosity)(Swaidan et al., 2014) and PIM-6FDA-OH (6FDA: hexafluoroisopropylidene bisphthalic dianhydride).(Swaidan et al., 2013) These polymers were selected considering availability of the experimental permeability data for CO₂/CH₄ mixture. We used Maxwell model(Maxwell, 1954) to predict gas permeabilities of MOF-based MMMs (P_{MMM}) using Eqn. 3.14. Since the Maxwell model was reported to be valid at low filler loadings,(Bouma et al., 1997) we used ϕ as 0.2 in this work. If the permeability of polymer was measured at a feed pressure lower than 5 bar (Pebax and 6FDA-DAM), permeability of MOF computed at 1 bar was used for the Maxwell model, for all other polymers, permeability of MOF calculated at 10 bar was used.

5.2 Results and Discussion

We first computed K^0 and D^0 values of CO₂ and CH₄ in 3794 MOFs as shown in Figure 5.1(a). K^0 can be considered as a representative of gas affinity of materials. As it gets higher, interaction of gas molecules with the adsorption sites of MOFs increases leading to stronger adsorption. K^0 vary between 10^{-7} and 10^{-1} mol/kg/Pa for CO₂ and between 10^{-7} and 10^{-4} mol/kg/Pa for CH₄. Higher K^0 values of CO₂ can be explained with the existence of three interaction sites of CO₂ molecule compared to the single-sphere representation of CH₄, in addition to the quadrupolar moment of CO₂ which causes electrostatic interactions with the MOFs that are absent in the case of nonpolar CH₄ molecules. The value of D^0 varies between 10^{-8} and 10^{-4} cm²/s for CO₂ and between 10^{-8} and 10^{-3} cm²/s for CH₄. Since CH₄ molecules are weakly adsorbed in MOFs and lighter compared to CO₂ molecules, they are able to move quicker. Strongly adsorbing gas molecules need to overcome a larger interaction energy barrier to move through the pores whereas diffusion of the weakly adsorbed gas molecules is easier.(Kim et al., 2013a) Therefore, there is an inverse relationship between K^0 and D^0 of gases as shown in Figure 5.1(a). This relationship is less linear for CH₄ molecules because in some MOFs, PLDs are very close to the kinetic diameter of CH₄ which leads to very slow diffusion of CH₄ even though K^0 is low. It is important to note that MOFs for which gas diffusivities were calculated to be less than 10^{-8} cm²/s (the limit of EMD simulations to accurately access gas diffusivity on the nanosecond scale) were eliminated in our work. The MOFs having high diffusion selectivities due to the presence of very slow diffusing gas molecules might

be highly selective membranes, but we eliminated them to remove the uncertainties resulting from the time scale limitation of EMD simulations.

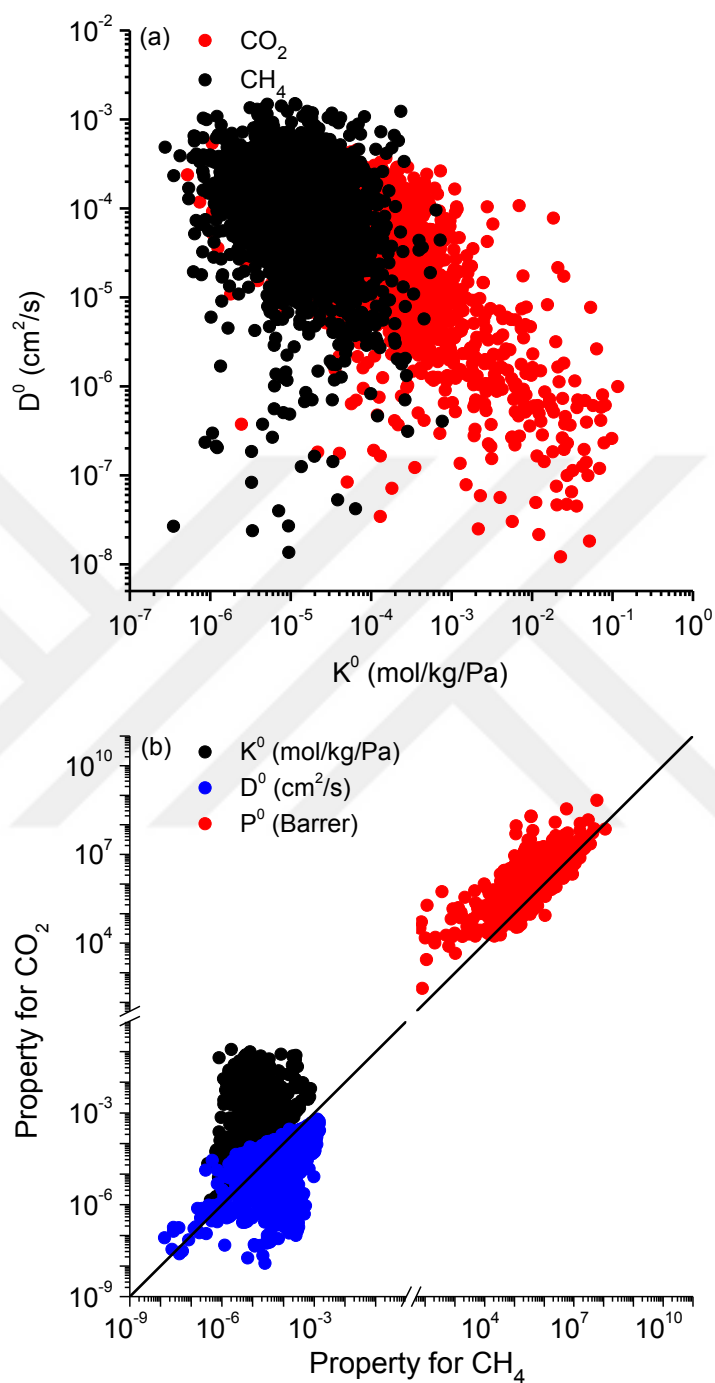


Figure 5.1. (a) Self diffusivity of gases (D^0) as a function of Henry's constants (K^0) calculated at infinite dilution. (b) Comparison of K^0 , D^0 and P^0 values of gases.

The relationship between K^0 and D^0 determines gas permeabilities ($P_i^0 = K_i^0 \times D_i^0$) as shown in Figure 5.1(b) and drives the membrane-based separation performances of MOFs. K^0 always favors CO₂ molecules whereas D^0 mostly favors CH₄ molecules. As a result, gas permeabilities of MOFs are generally close to each other but mostly higher for CO₂ than CH₄ as shown in Figure 5.1(b). Kim et al. (Kim et al., 2013a) investigated the performance of zeolite membranes and discussed that membranes should have well-balanced adsorption-diffusion properties for the effective CO₂/CH₄ separation: If the zeolites had very small $K_{CO_2}^0$, CO₂ permeability and selectivity was too low and if structures had very large $K_{CO_2}^0$, they had strong adsorption sites that significantly hinder gas diffusion. They showed that optimal zeolite membranes with the highest CO₂ permeabilities ($>10^5$ Barrer) had $10^{-5} < K_{CO_2}^0 < 10^{-4}$ mol/kg/Pa. We showed the combined effects of K^0 and D^0 on gas permeabilities of MOF membranes in Figure 5.2. Analyzing MOFs exhibiting high CO₂ permeabilities ($>10^6$ Barrer) showed that 1787 highly permeable MOFs have $10^{-6} < K_{CO_2}^0 < 10^{-1}$ mol/kg/Pa whereas 702 of them have $10^{-5} < K_{CO_2}^0 < 10^{-4}$ mol/kg/Pa. This comparison shows that MOFs we examined in this part have a wider range of $K_{CO_2}^0$ values than the zeolites. The highest CO₂ permeability, 6.72×10^8 Barrer, belongs to the MOF having $K_{CO_2}^0$ of 1.85×10^{-2} mol/kg/Pa, indicating the strong affinity of MOF towards CO₂.

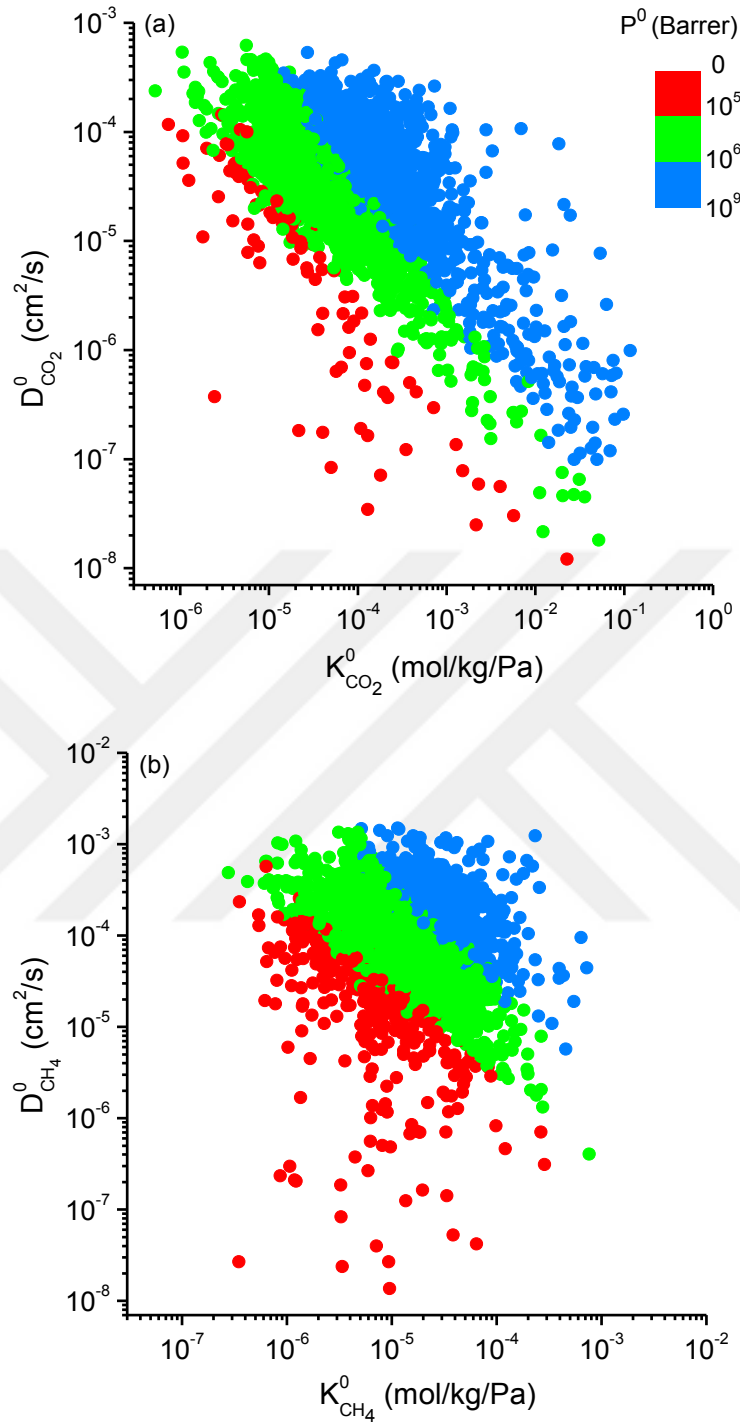


Figure 5.2. Combined effect of K^0 and D^0 on P^0 of CO₂ and CH₄ in MOFs.

We examined adsorption selectivity ($S_{ads}^0 = K_{CO_2}^0 / K_{CH_4}^0$), diffusion selectivity ($S_{diff}^0 = D_{CO_2}^0 / D_{CH_4}^0$) and membrane selectivity (also known as perm-selectivity) calculated at infinite dilution ($S_{mem}^0 = P_{CO_2}^0 / P_{CH_4}^0 = (K_{CO_2}^0 \times D_{CO_2}^0) / (K_{CH_4}^0 \times D_{CH_4}^0)$) in Figure 5.3. S_{ads}^0 is always higher than 1 which means all the MOFs selectively adsorb CO₂ over CH₄.

While S_{ads}^0 ranges from 1.2 to 7.82×10^4 , S_{diff}^0 tends to favor CH₄. MOFs shown in Figure 5.3 are color-scaled according to their S_{diff}^0 values, ranging from 3.86×10^{-4} to 58. Red, green and blue points show MOFs having strong, moderate and low S_{diff}^0 values for CH₄ over CO₂, respectively. Small numbers of MOFs shown with purple points (395 MOFs) have S_{diff}^0 values equal to or higher than unity, indicating that diffusivity favors CO₂ over CH₄ in these materials. When both adsorption and diffusion favor the same gas molecule, CO₂, membrane selectivity becomes higher than the adsorption selectivity. In fact, those are the highly desired membrane materials for selective separation of CO₂ from CH₄. For the other 3399 MOFs, CH₄ has higher diffusivity through the MOFs' pores, therefore S_{diff}^0 values are less than unity as shown with red, green and blue points in Figure 5.3. In this case, S_{mem}^0 could not reach as high values as S_{ads}^0 because diffusion selectivity favoring CH₄ compensates adsorption selectivity favoring CO₂. 429 MOFs have S_{mem}^0 lower than 1. For these MOFs, it can be concluded that CO₂ adsorption is not strong enough to dominate the fast CH₄ diffusivity. These MOFs are shown below the red dashed line in Figure 5.3 as CH₄ selective MOF membranes and CO₂ can be obtained in the retentate stream rather than the permeate when this type of membrane is used.

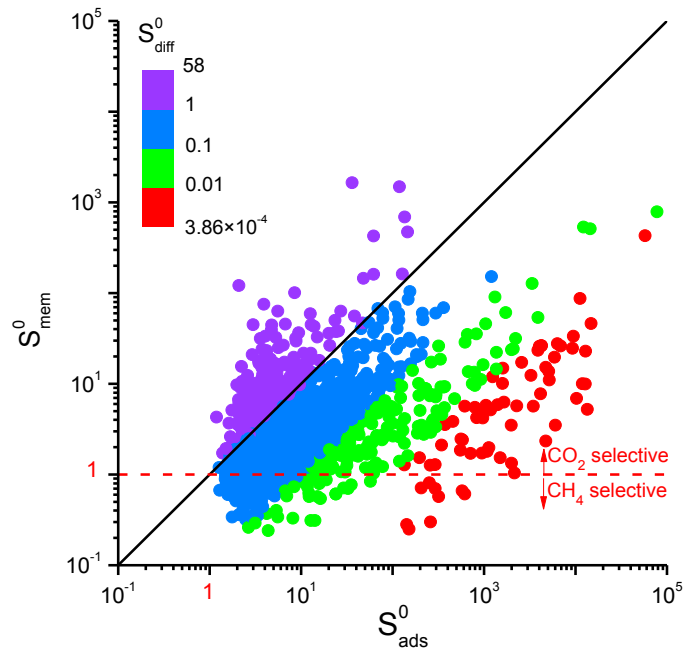


Figure 5.3. Adsorption, diffusion and membrane selectivities of MOFs calculated for CO₂ over CH₄ separation at infinite dilution. The diagonal line is given to guide the eye, the dashed line shows the gas preference of the membrane.

Maximum CH₄ selectivity of these membranes was calculated to be 12.5 indicating that they are at most moderately CH₄ selective. 11 MOFs were predicted to have S_{mem}^0 of exactly 1 which means these membranes are not useful for selective separation of CO₂ from CH₄. A large number of MOFs (3354) was computed to have S_{mem}^0 larger than 1 and these CO₂ selective MOF membranes are shown above the red dashed line in Figure 5.3. As we discussed in Figure 5.1(b), some MOFs have similar CO₂ and CH₄ permeabilities, therefore their CO₂ selectivities are low. For example, 1598 MOFs have S_{mem}^0 between 1 and 2 indicating that they do not have a very strong preference for CO₂. These are the MOFs for which adsorption selectivity for CO₂ is almost the same with diffusion selectivity that prefers CH₄ and as a result the membrane is almost non-selective. The remaining 1756 MOFs have S_{mem}^0 between 2 and 1643 and these are the potential membrane candidates.

For an efficient membrane-based gas separation process, not only the purity (selectivity) but also the amount of gas transported through the membrane (permeability) is critical because the required surface area of membrane is the dominant factor determining the cost of the separation process. Figure 5.4 represents the membrane selectivity (S_{mem}^0) as a function of CO₂ permeability ($P_{\text{CO}_2}^0$) of MOFs.

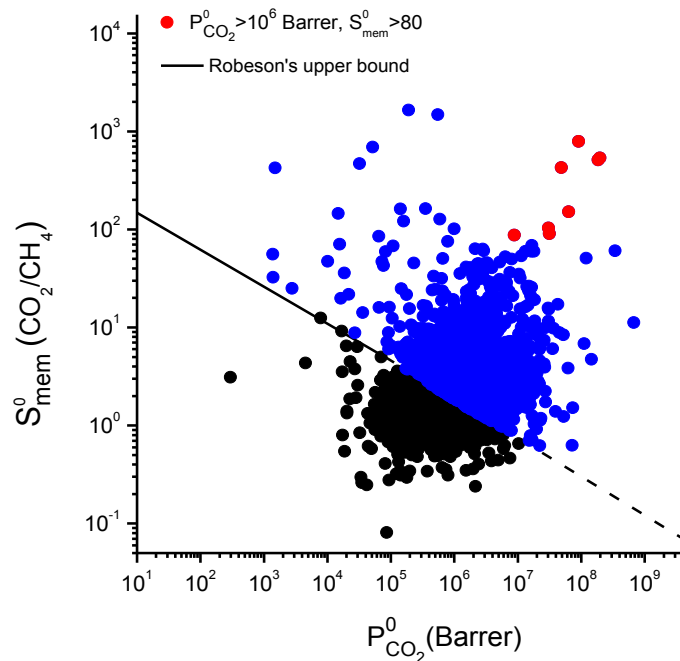


Figure 5.4. Selectivity and permeability of MOF membranes computed at infinite dilution.

Performance of MOF membranes is shown together with the famous Robeson's upper bound which is established based on the single-component CO₂ permeability and ideal CO₂/CH₄ selectivity of polymeric membranes.(Robeson, 2008) In contrast to the well-known trade-off of polymeric membranes between the gas permeability and selectivity, permeability of MOF membranes usually increases as the selectivity increases. Predicted CO₂ permeability of MOFs varies between 10² and 10⁸ Barrer, significantly higher than the corresponding permeabilities of polymeric membranes. Therefore, the upper bound was extended with a dashed line in Figure 5.4. There are 1995 MOFs which can exceed Robeson's upper bound due to their high permeabilities, or their high selectivities or both and these are shown with blue points. The most promising MOF membranes that will be further examined in the second-level of screening were selected as the materials that offer $P_{CO_2}^0 > 10^6$ Barrer and $S_{mem}^0 > 80$. 1483 MOFs which are over the upper bound have $P_{CO_2}^0$ higher than 10⁶ Barrer while 8 of these MOFs have S_{mem}^0 higher than 80. These 8 MOFs, shown as red points in Figure 5.4, are identified as the top membrane candidates. We would like to note that all the MOFs we considered in this thesis are real, synthesized MOFs, they are not hypothetical materials. However, none of the top MOFs has been tested as membranes.

In the second-level of screening, we computed adsorption and diffusion of equimolar CO₂/CH₄ mixtures for the top 8 MOFs and predicted mixture permeabilities and selectivities of these top MOF materials. Figure 5.5(a) compares permeability and selectivity predictions obtained at the first-level of screening (using single-component gas data at infinite dilution) and predictions obtained at the second-level (using equimolar mixture data at 1 and 10 bar). As shown in Figure 5.5(a), both CO₂ permeabilities and CO₂/CH₄ selectivities obtained from the mixture simulations performed at practical operating pressures are lower than the ones obtained from the single-component gas simulations performed at infinite dilution. This difference can be attributed to the competitive adsorption and collaborative diffusion between gas species in the mixture. At infinite dilution, a gas molecule can prefer the most favorable adsorption site since the intermolecular interactions between the gases are turned-off. However, at mixture conditions, gas-gas interactions exist, and adsorbates compete with each other for the same adsorption sites. Moreover, at infinite dilution, self-diffusivity of a gas molecule is not affected by the diffusivity of another gas molecule. On the other hand, at mixture conditions, fast diffusing gas species (CH₄) can fasten the slow diffusing molecules (CO₂)

and slow diffusing molecules can hinder the transport of other gas species. In order to better illustrate the mixture adsorption and diffusion effects, we compared all three selectivities computed at infinite dilution with the ones computed at mixture conditions in Figure 5.5(b).

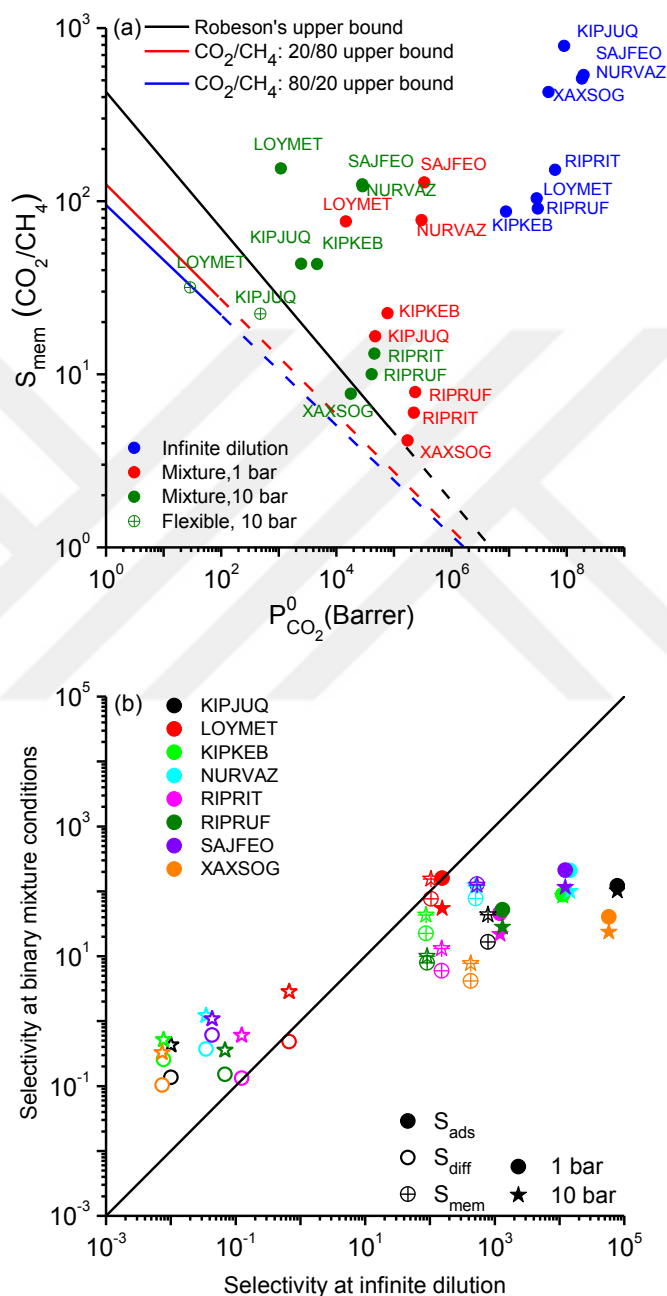


Figure 5.5. (a) Separation performances of the top 8 MOF membranes computed at infinite dilution (blue), 1 bar (red), and 10 bar (green). Results of flexible simulations for the two MOFs are also shown at 10 bar (green, crossed). (b) Comparison of adsorption (full symbols), diffusion (empty symbols) and membrane (crossed symbols) selectivities computed at infinite dilution and mixture conditions at 1 bar (circles) and 10 bar (stars).

Almost for all the MOFs, S_{ads} is higher at infinite dilution than the mixture case since there is no competitive adsorption at infinite dilution. The diffusivity of CO₂ increases due to the presence of fast CH₄ molecules and diffusivity of CH₄ decreases because of the presence of slow diffusing CO₂ molecules. As a result, S_{diff} values in mixture are higher than those in the infinite dilution as shown in Figure 5.5(b). For example, one of the best performing MOF membranes is SAJFEO at infinite dilution with $P_{\text{CO}_2}^0$ of 2×10^8 Barrer and S_{mem}^0 of 535. At mixture conditions, permeability and selectivity of this MOF membrane were computed as 3.4×10^5 Barrer and 128, respectively. These dramatic decreases in the membrane properties can be explained by the significant decrease in the adsorption selectivity and increase in the diffusion selectivity. Adsorption selectivity decreased from 12266 at the infinite dilution to 210 whereas diffusion selectivity increased from 0.04 at infinite dilution to 0.61 at 1 bar. The increase in diffusion selectivity could not compensate the decrease in adsorption selectivity. As a result, predicted separation performance of the membrane (permeability and selectivity) was lower at the mixture case compared to the infinite dilution case. Here, the important point is that mixture permeabilities and selectivities of the top 8 MOF membranes were still high enough to locate them above the Robeson's upper bound as shown in Figure 5.5(a). We also note that in this figure there are two additional upper bounds named as mixture upper bounds which have been established for separation of CO₂/CH₄ mixtures having different compositions. (Lin and Yavari, 2015) Permeabilities and selectivities obtained from the mixture calculations showed that top MOF membranes exceed the mixture upper bounds. These results suggest that initial screening of MOF membranes based on the membrane properties computed at infinite dilution is efficient to quickly identify the most promising materials and more detailed and computationally expensive mixture simulations should be performed for the top membrane candidates to unlock their actual separation performances at practical operating conditions.

Details on the separation performance of the top 8 MOF membranes at two different feed pressures, 1 bar and 10 bar, are given in Table 5.1. As pressure increases, gas uptakes increase but this increase is more pronounced for CH₄ leading to a decrease in the adsorption selectivities.

Table 5.1. Performances of the top 8 MOF membranes for separation of equimolar CO₂/CH₄ mixture at 1 bar and 10 bar.
All selectivities were calculated for CO₂ over CH₄.

MOF	LCD (Å)	PLD (Å)	Volume fraction	N _{CO₂} (mol/kg)	N _{CH₄} (mol/kg)	D _{CO₂} (cm ² /s)	D _{CH₄} (cm ² /s)	P _{CO₂} (Barrer)	P _{CH₄} (Barrer)	S _{ads}	S _{diff}	S _{mem}
1 bar												
SAJFEO	6.63	6.00	0.60	6.31	0.03	6.16×10^{-6}	1.01×10^{-5}	3.39×10^5	2.64×10^3	210.33	0.61	128.28
NURVAZ	6.58	6.00	0.60	6.29	0.03	5.52×10^{-6}	1.49×10^{-5}	3.02×10^5	3.89×10^3	209.67	0.37	77.61
LOYMET	5.37	3.98	0.37	1.43	0.01	1.10×10^{-6}	2.30×10^{-6}	1.47×10^4	1.93×10^2	158.89	0.48	76.34
KIPKEB	7.31	7.00	0.46	2.65	0.03	3.14×10^{-6}	1.23×10^{-5}	7.74×10^4	3.44×10^3	88.33	0.25	22.52
KIPJUQ	7.29	6.98	0.46	2.43	0.02	1.78×10^{-6}	1.31×10^{-5}	4.75×10^4	2.87×10^3	121.50	0.14	16.59
RIPRUF	6.48	4.09	0.59	4.17	0.08	5.86×10^{-6}	3.87×10^{-5}	2.34×10^5	2.97×10^4	52.13	0.15	7.89
RIPRIT	6.46	4.22	0.60	4.10	0.09	5.73×10^{-6}	4.36×10^{-5}	2.22×10^5	3.71×10^4	45.56	0.13	5.99
XAXSOG	7.71	5.92	0.63	4.42	0.11	4.65×10^{-6}	4.51×10^{-5}	1.73×10^5	4.17×10^4	40.18	0.10	4.14
10 bar												
LOYMET	5.37	3.98	0.37	1.63	0.03	7.21×10^{-7}	2.53×10^{-7}	1.10×10^3	7.09×10^0	54.33	2.85	154.59
SAJFEO	6.63	6.00	0.60	8.11	0.07	4.02×10^{-6}	3.73×10^{-6}	2.84×10^4	2.27×10^2	115.86	1.08	125.09
NURVAZ	6.58	6.00	0.60	8.01	0.08	4.10×10^{-6}	3.37×10^{-6}	2.86×10^4	2.35×10^2	100.13	1.21	121.63
KIPJUQ	7.29	6.98	0.46	3.04	0.03	7.33×10^{-7}	1.71×10^{-6}	2.45×10^3	5.63×10^1	101.33	0.43	43.45
KIPKEB	7.31	7.00	0.46	3.37	0.04	1.49×10^{-6}	2.89×10^{-6}	4.66×10^3	1.08×10^2	84.25	0.51	43.35
RIPRIT	6.46	4.22	0.60	6.08	0.28	7.95×10^{-6}	1.31×10^{-5}	4.57×10^4	3.47×10^3	21.71	0.61	13.17
RIPRUF	6.48	4.09	0.59	6.16	0.22	6.97×10^{-6}	1.95×10^{-5}	4.11×10^4	4.11×10^3	28.00	0.36	10.00
XAXSOG	7.71	5.92	0.63	7.53	0.32	2.83×10^{-6}	8.62×10^{-6}	1.79×10^4	2.32×10^3	23.53	0.33	7.73

For most MOFs, diffusivities of both gas molecules decrease with increased pressure as higher loadings hinder gas diffusion. CH₄ diffusivity is more affected than CO₂ diffusivity because spherical CH₄ molecules are larger and bulkier in size than the linear CO₂ molecules. As a result, higher S_{diff} values were calculated at 10 bar compared to 1 bar for all MOFs. The increase in S_{diff} dominated the decrease in S_{ads} therefore, higher S_{mem} values were observed at 10 bar compared to 1 bar.

All simulations that we discussed so far were carried out using rigid framework assumption. It is known that some MOFs may show inherent flexibility upon various stimuli including pressure, temperature or loading. This flexibility might affect the pore properties of MOFs and change their separation performances.(Caro, 2011) We previously examined the effect of flexibility on the CO₂/CH₄ separation performance of bio-MOFs and showed that flexibility has a significant impact on the permeability and selectivity of MOFs having narrow pore diameters close to the size of adsorbates.(Erucar and Keskin, 2015) Therefore, we carried out computationally demanding flexible EMD simulations in the third-level of our calculations for 2 top MOFs, one representing a narrow-pored material (LOYMET) and another representing a large-pored MOF (KIPJUQ). We note that these simulations required significant computation time and resources, therefore, we were able to perform them only for 2 representative MOFs. Since the selected 2 MOFs do not have significantly different structural features than the other top materials, similar results are expected for the remaining top MOFs. Results of flexible EMD simulations were compared with the results of rigid simulations in Table 5.2. Gas diffusivities computed using flexible simulations were less than the ones obtained from rigid simulations. Therefore, both permeabilities and selectivities of MOFs were predicted to be lower in flexible case compared to the rigid case as shown in Figure 5.5(a). The decreases in gas permeabilities and selectivities were more pronounced for LOYMET than KIPJUQ since PLD of the former is narrower. For example, membrane selectivity of LOYMET decreased from 155 to 32 while selectivity of KIPJUQ decreased from 43 to 22 when the flexibility was considered.

Table 5.2. Comparison of rigid and flexible simulations.

MOF	Rigid						Flexible					
	D _{CO₂} (cm ² /s)	D _{CH₄} (cm ² /s)	P _{CO₂} (Barrer)	P _{CH₄} (Barrer)	S _{diff}	S _{mem}	D _{CO₂} (cm ² /s)	D _{CH₄} (cm ² /s)	P _{CO₂} (Barrer)	P _{CH₄} (Barrer)	S _{diff}	S _{mem}
LOYMET	7.21×10 ⁻⁷	2.53×10 ⁻⁷	1096	7	2.85	154.59	1.91×10 ⁻⁸	3.27×10 ⁻⁸	29	0.9	0.58	31.74
KIPJUQ	7.33×10 ⁻⁷	1.71×10 ⁻⁶	2448	56	0.43	43.45	1.43×10 ⁻⁷	6.50×10 ⁻⁷	478	21	0.22	22.34

Changes in pore sizes of MOFs were examined using the snapshots taken at different time points of flexible EMD simulations by considering the frameworks with and without the adsorbate molecules and shown in Figure 5.6.

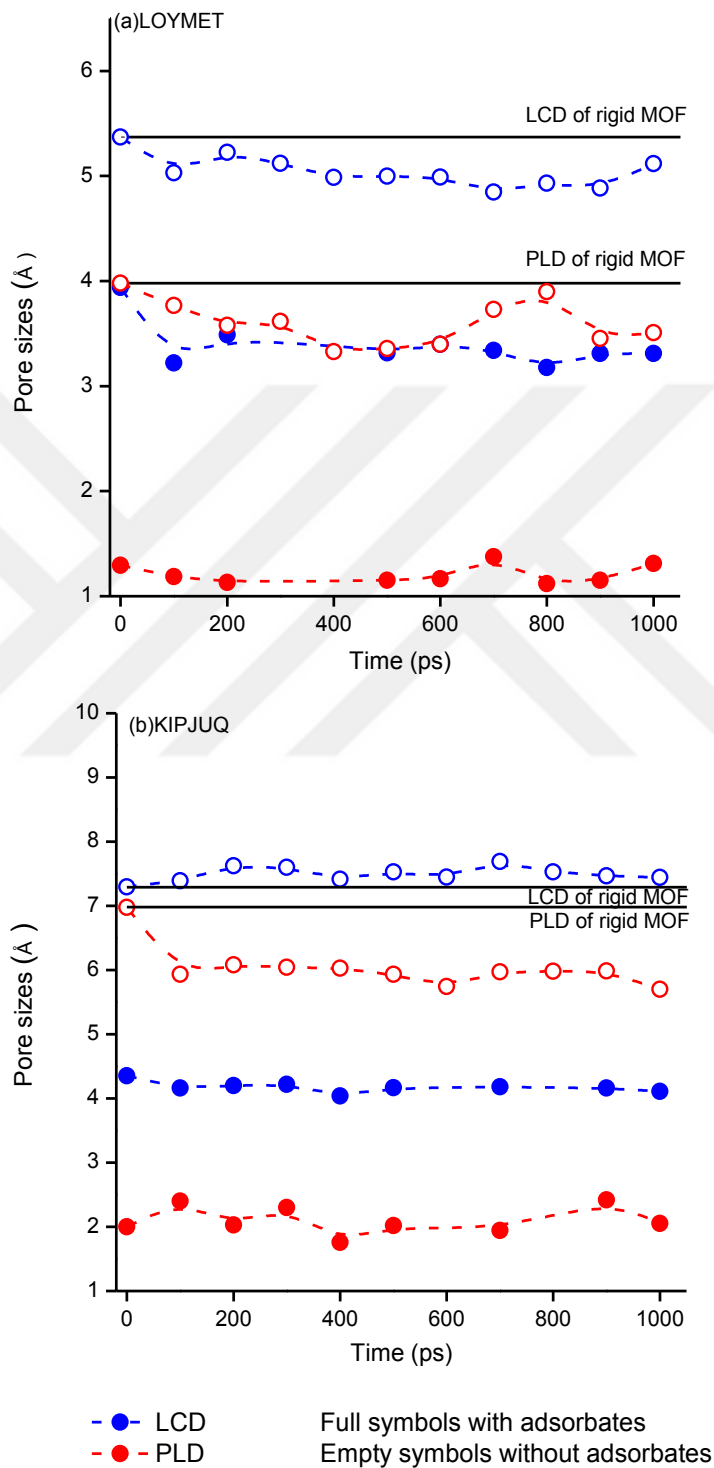


Figure 5.6. Change in the pore sizes of MOFs (LCD, PLD) during flexible simulations.

As shown in Figure 5.6(a), pore sizes of LOYMET significantly decreased and its PLD became smaller than the kinetic diameter of CH₄ molecule (~ 3.8 Å). Its LCD was also smaller than the size of CH₄ molecule when the framework was full with adsorbate molecules. As a result, diffusivities of both gas molecules were computed to be very slow, in the orders of $\sim 10^8$ cm²/s. On the other hand, pore sizes of KIPJUQ in the flexible case were still larger than the kinetic diameters of both gases as shown in Figure 5.6(b), even when the pores were filled with the adsorbates, resulting in higher CO₂ and CH₄ diffusivities compared to the ones observed in LOYMET. Although gas permeabilities and selectivities of flexible MOFs were found to be lower than the ones computed for rigid MOFs, MOF membranes were still located over the mixed gas upper bound. In other words, the overall assessment about the separation performance of the top MOF membranes did not change even if the structures were flexible.

We so far compared separation performance of MOF membranes with polymers and zeolites and concluded that MOFs can outperform traditional membranes for CO₂/CH₄ separations due to their high gas permeabilities. It is also useful to compare our results with other simulation studies where MOFs are examined. Large numbers of hypothetical MOFs, which are not experimentally synthesized but computer-generated materials, were screened for membrane-based separation of ternary CO₂/N₂/CH₄:10/70/20 mixtures using molecular simulations.(Qiao et al., 2016) The best 5 MOFs were computed to have CO₂ permeabilities and CO₂/CH₄ selectivities in the range of 1500-6780 Barrer and 460-8970, respectively at 10 bar, 298 K. We predicted CO₂ permeabilities and CO₂/CH₄ selectivities of MOFs in the range of 1090-45700 Barrer and 7.7-155, respectively for separation of equimolar CO₂/CH₄ mixture at the same pressure and temperature. The lower gas permeabilities and higher membrane selectivities of hypothetical MOFs compared to the real MOFs we considered in this part of the thesis are due to the narrow pore sizes of the hypothetical MOFs. Hypothetical MOFs were selected to have PLDs between 3 and 4 Å. Since the kinetic diameter of CH₄ is close to 4 Å, hypothetical MOFs act as molecular sieves resulting in high CO₂/CH₄ selectivities. In this thesis, we especially focused on MOFs having PLDs > 3.75 Å to guarantee the adsorption and diffusion of both CO₂ and CH₄ molecules in the pores. In another study focusing on separation of a ternary mixture of CO₂/N₂/CH₄, dominated by N₂ in contrast to our equimolar CO₂/CH₄ binary mixture, the top 7 MOFs were identified using molecular simulations at 10 bar, 298 K.(Qiao, Xu, and Jiang, 2018) The top MOFs were

again selected to have narrow pores in the range of $2.9 < \text{PLD} < 3.26$ Å and they were computed to have lower permeabilities ($1170 < P_{\text{CO}_2} < 5090$ Barrer, $0.18 < P_{\text{CH}_4} < 2.61$ Barrer) and higher selectivities ($704 < S_{\text{mem}} < 8155$) compared to the ones we calculated for separation of equimolar CO₂/CH₄ mixtures.

We also investigated the impacts of structural belongings on the separation performances of MOFs. Figure 5.7(a) shows that porosity of MOFs increases as the LCD increases as expected. We marked the location of the top 8 MOF membranes in Figure 5.7(a). These best membrane candidates have low porosities between 0.4 and 0.6 and narrow pore sizes, LCDs between 5 and 8 Å and PLDs between 4 and 7 Å. 5 of the MOFs overlapped in the figure since they have almost the same porosities, 0.6. Figure 5.7(b) shows that permeabilities of CO₂ and CH₄ significantly vary at small LCDs (< 10 Å) leading to selective membranes whereas permeabilities of gases become similar as the LCD increases (> 10 Å). As shown in Figure 5.7(a), MOFs with LCDs > 15 Å generally have porosities larger than 0.75 so that both gas molecules can easily adsorb and diffuse in the pores. This eliminates the capability of the pores to sieve the larger gas molecule and leads to lower membrane selectivities. As a result, Figure 5.7 suggests that membrane materials with small porosities and narrow pore sizes are desired for effective separation of CO₂/CH₄.

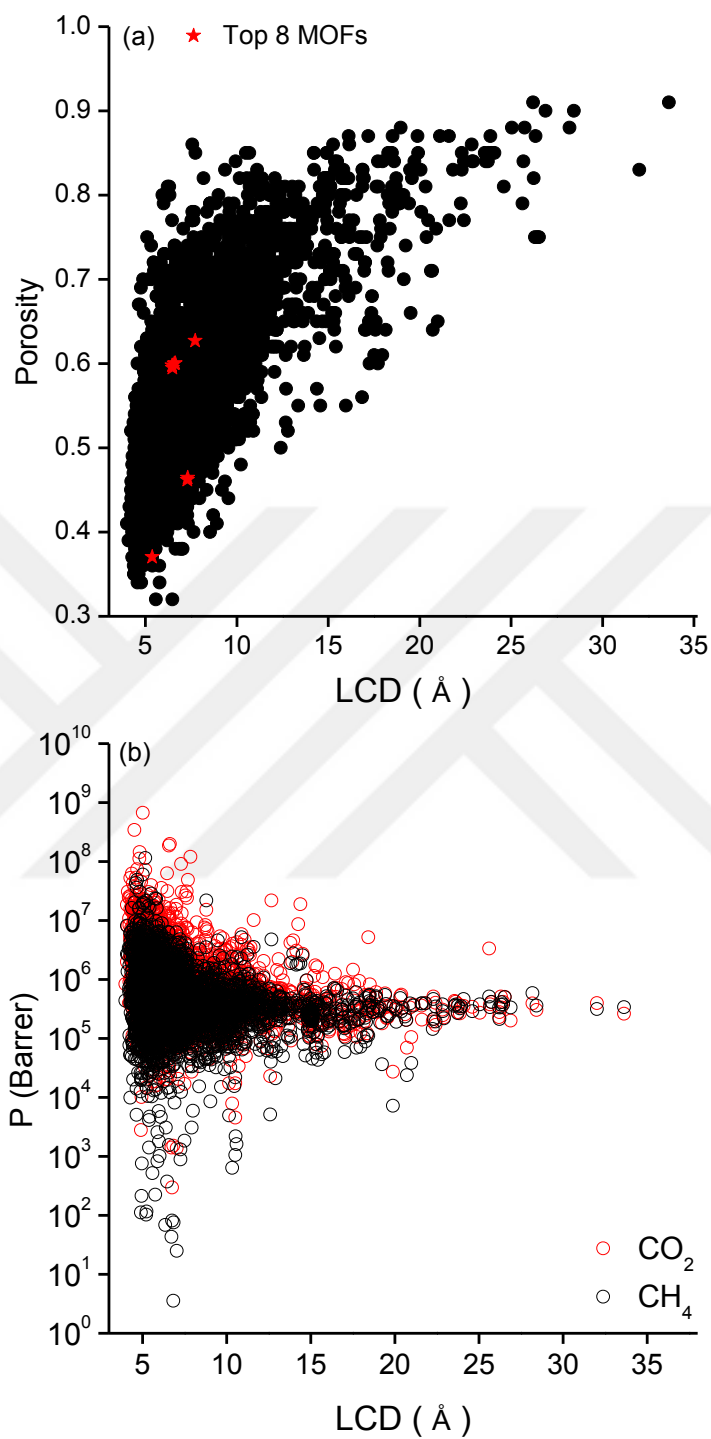


Figure 5.7. (a) Porosity and LCD of MOFs. Stars represent the top 8 MOF membranes. (b) Gas permeabilities of MOFs as a function of their LCDs.

MOFs have been widely used as fillers in MMMs to improve the CO₂ permeability and CO₂/CH₄ selectivity of polymers.(Dechnik et al., 2017) Motivated from this, we examined the impact of using the top MOFs as fillers in polymer membranes on the CO₂ permeability and CO₂/CH₄ selectivity of MOF-based MMMs. We collected available experimental CO₂/CH₄ mixture permeation data for 8 different polymeric membranes as given in Table 5.3.

Table 5.3. Experimental data for gas separation performances of polymeric membranes.

Polymer	P _{CO₂} (Barrer)	P _{CH₄} (Barrer)	S _{mem}	CO ₂ /CH ₄ composition	T (°C)	P _{feed} (bar)	Reference
Cellulose acetate	3.65	0.14	26	46.1/53.9	35	10	(Houde et al., 1996)
Matrimid	7	0.4	17	50/50	25	8	(Khan, Li, and Vankelecom, 2011b)
Polysulfone	7.3	0.27	27	50/50	30	10	(Guo et al., 2015)
Pebax	81	5.30	15	50/50	30	3	(Khosravi et al., 2017)
6FDA-DAM	390	16.25	24	50/50	25	2	(Bae et al., 2010)
PIM-6FDA-OH	557	37	15	50/50	35	20	(Swaider et al., 2013)
PIM-1	5000	500	10	50/50	35	10	(Swaider et al., 2014)
SPEEK-3	12.61	0.81	16	50/50	25	10	(Khan, Li, and Vankelecom, 2011a)

This data was then combined with the gas permeability data of the top 8 MOF membranes obtained from our molecular simulations using Eqn. 3.14. As a result, permeability and selectivity of 64 different MOF-based MMMs were predicted and shown in Figure 5.8 together with the data of polymeric membranes. The arrows represent how the performance (permeability and selectivity) of the polymeric membrane changes when the MOF filler is incorporated. Gas permeabilities of the 8 top MOFs are very high compared to the corresponding permeabilities of polymers, cellulose acetate, Matrimid, polysulfone, Pebax, SPEEK-3, and 6-FDA-DAM. For example, P_{CO₂} (P_{CH₄}) of Matrimid is 7 (0.4) Barrer while the lowest P_{CO₂} (P_{CH₄}) among the top 8 MOFs is 1095 (7) Barrer. As shown in previous works,(Bouma et al., 1997; Yilmaz and Keskin, 2014) when the permeability of filler is very high compared to that of polymer, achievable permeability of the MMM becomes limited. This is because Eqn. 3.15 reduces to $P_{MMM} = P_p \times 1.75$ at a volume fraction of 0.2 if $P_{MOF} \gg P_p$. Therefore, regardless of the identity of the MOF used in a given polymer, similar gas permeabilities and selectivities were obtained for the MMMs and a single data point was used in Figure 5.8 to represent the MMMs of each polymer except PIM-1 and PIM-6FDA-OH.

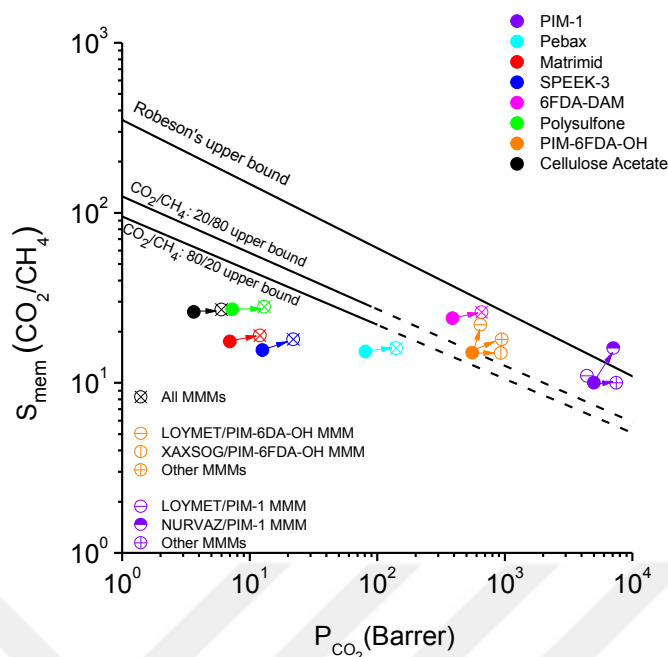


Figure 5.8. Predicted separation performances of MOF-based MMMs (open symbols) together with separation performances of polymeric membranes (closed symbols).

Incorporation of MOFs into polymers either provides a permeability improvement without significantly affecting the selectivity as in the cases of cellulose acetate, Matrimid, SPEEK-3, Pebax, 6-FDA-DAM and polysulfone or causes a change in both permeability and selectivity as in the cases of PIM-1 and PIM-6FDA-OH. For example, P_{CO_2} of Matrimid increased from 7 to 12 Barrer but its selectivity remained around 18 when MOFs are used as fillers. Since CO_2 and CH_4 permeabilities of MOFs are very high compared to the permeabilities of Matrimid, addition of MOFs increases gas permeabilities without changing the selectivity. For PIM-6FDA-OH, while 6 MOFs caused an increase both in permeability and selectivity, LOYMET significantly increased selectivity with a slight increase in permeability and XAXSOG increased only the permeability. Similarly, for PIM-1, NURVAZ and SAJFEO increased permeability and selectivity. When LOYMET was used as the filler, selectivity of PIM-1 increased at the expense of a reduced permeability due to the lower CO_2 permeability of LOYMET compared to that of PIM-1. Other 5 MOFs increased the polymer's permeability without a significant change in selectivity. It is important to highlight the importance of MOF/polymer matching for the separation performance of MOF-based MMMs: While LOYMET provided the highest increase both in permeability and selectivity of PIM-

6FDA-OH, the same MOF decreased the permeability of PIM-1. Figure 5.8 shows that MOFs can carry the polymers over the upper bound by increasing both the CO₂ permeability and selectivity if the polymer is close to the upper bound. For example, PIM-6FDA-OH is located just below the upper bound and using LOYMET as a filler significantly improved its CO₂ selectivity from 15 to 22 while increasing its CO₂ permeability from 557 to 960 Barrer. These results suggest that the top MOFs we identified in this part are not only good membrane candidates, but they are also highly promising for making MOF-based MMMs. We would like to note that performances of MOF membranes and MOF/polymer membranes were evaluated based on the Robeson's upper bound. It is important to note that this bound has not been updated since 2008. Several polymer membranes have been developed in the last decade and it is possible that the new polymer membranes may shift the upper bound.

We only focused on the separation of binary CO₂/CH₄ mixture, however natural gas may include H₂S and water vapor as impurities that need to be removed. Our molecular simulations cannot provide information about the MOF membranes' stabilities under the presence of these impurities. A recent study showed some MOFs may decompose after H₂S exposure (Liu et al., 2017) whereas another one reported that some ZIFs degrade in the presence of humid CO₂ (Bhattacharyya et al., 2017). Molecular simulation studies also showed that the presence of H₂O may decrease CO₂ adsorption and selectivity of MOFs due to the competitive adsorption between H₂O and CO₂ (Yu, Wu, and Balbuena, 2016). Similarly, compatibility and stability may be a problem for the MMMs based on the selected MOF-polymer combination. The main motivation of our calculations was to screen very high number of materials to identify a small number of promising MOFs and the issues discussed above can be examined for the top membrane candidates by further experimental efforts.

5.3 Conclusion

In this part, we combined GCMC and EMD simulations to screen 3794 MOF membranes for CO₂/CH₄ separation. In the first-level of screening, we computed gas permeabilities and selectivities of MOFs at infinite dilution to efficiently identify the promising materials. The top 8 MOFs that have CO₂ permeabilities greater than 10⁶ Barrer and CO₂/CH₄ selectivities higher than 80 were identified as the best candidates and further studied at the second-level of calculations by performing mixture simulations at two different pressures. Results showed that separation performances of MOF

membranes computed at infinite dilution are overestimated compared to the ones computed at practical operating conditions considering binary gas mixtures. We also showed that the top MOF membrane candidates identified using the simulations at infinite dilution are still located above the upper bound based on their gas permeabilities and selectivities computed using the mixture simulations, indicating the efficiency and validity of our screening approach. We finally performed computationally demanding flexible EMD simulations for the two MOFs and showed that these materials are still above the mixed gas upper bound and promising membrane candidates although lower permeabilities and selectivities were estimated compared to the rigid simulations. Materials having narrow pore sizes and low porosities were found to be potential candidates for membrane-based separation of CO₂/CH₄ mixtures. We finally investigated permeabilities and selectivities of 64 different types of MMMs composed of 8 polymers and 8 MOF fillers and showed that incorporation of MOFs significantly enhances CO₂ permeabilities of all polymers and even enhances CO₂/CH₄ selectivities of some polymers. All these results suggest that MOFs can be used as membranes and MMMs for efficient separation of CO₂/CH₄ mixtures. Results of molecular simulations showed that using highly permeable MOFs as pure membranes may be more effective than using them as fillers in polymers since permeability of the MMM is limited when the permeability of filler is very high compared to polymer. The computational screening approach that we introduced in this part of the thesis would advance the design and development of MOF membranes and MOF/polymer MMMs by identifying the best MOF candidates and contribute to the sustainable chemistry and engineering in the field of natural gas purification.

*The content of this chapter is directly obtained from our published work(Altintas and Keskin, 2019) and adapted for thesis.

Chapter 6

ROLE of PARTIAL CHARGE ASSIGNMENT METHOD on MOF PERFORMANCE PREDICTION for NATURAL GAS PURIFICATION

In this part of the thesis, we aim to uncover the role of partial charge assignment methods used in high-throughput computational screening of MOFs by studying both adsorption-based and membrane-based CO₂/CH₄ separation. We used two different charge assignment methods, a DFT-based method, DDEC, and an approximate method, Qeq, and performed molecular simulations to compute adsorption of CO₂/CH₄ mixtures in 1500 different MOF structures considering two different operating conditions and gas compositions. Results of molecular simulations were then used to calculate several adsorbent performance evaluation metrics for MOFs including adsorption selectivity, working capacity, adsorbent performance score, regenerability, in addition to membrane performance evaluation metrics including gas permeability and membrane selectivity. These performance metrics obtained from simulations using DDEC and Qeq charges were compared in detail to explore the impact of the type of the charge assignment method on the ranking and identification of the top MOF adsorbents and membranes. We also investigated structural properties of MOFs that make the predicted performance of materials more sensitive to the choice of the charge assignment method.

6.1 Methodology

We started with the MOF database consisting of 2932 MOFs for which DDEC charges were assigned.(Nazarian, Camp, and Sholl, 2016) We computed PLDs, LCDs, and accessible surface areas (ASAs) of MOFs using Zeo++ software(Willems et al., 2012) (version 0.3). The MOF database was then constrained to only cover materials with non-zero ASAs and PLDs>3.75 Å so that both CO₂ (kinetic diameter of 3.3 Å) and CH₄ (kinetic diameter of 3.73 Å) molecules can pass through the pores for the adsorption and membrane-based CO₂/CH₄ separations. QEq(Wilmer and Snurr, 2011) method as implemented in the RASPA simulation package(Dubbeldam et al., 2016) was used to assign the partial point charges to framework atoms. MOFs for which partial charge

assignment using Qeq method could not produce reasonable results were excluded. We finally ended up with 1500 different MOF structures and performed GCMC simulations to compute adsorption of CO₂/CH₄ mixtures in all MOFs. We note that DDEC-charged MOFs used here were not geometry-optimized and therefore the only difference between DDEC-charged and Qeq-charged MOFs was the partial charges of the atoms in the frameworks.

Previously used gas models were again used for CH₄ and CO₂ molecules as given in Table A1 in Appendix A.(Martin and Siepmann, 1998; Potoff and Siepmann, 2001) The potential parameters of MOF atoms were taken from the Universal Force Field (UFF)(Rappe et al., 1992) since it was shown to accurately reproduce the experimental CO₂ and CH₄ adsorption data of MOFs in our previous works.(Sezginel, Uzun, and Keskin, 2015; Sumer and Keskin, 2016; Altintas et al., 2018b) Lorentz-Berthelot mixing rules were used to calculate the interaction parameters between different atoms. Long-range electrostatic interactions were calculated by the Ewald summation.(Ewald, 1921) The cut-off distance for the truncation of intermolecular interactions was set to 13 Å. The simulation cell lengths were increased to at least 26 Å along each dimension and periodic boundary conditions were applied in all simulations. MOFs were assumed to be rigid in their reported crystallographic structures. For GCMC simulations, five different types of moves were considered including translation, rotation, reinsertion, and swap (insertion-deletion) of a molecule with equal probability. For each MOF, simulations were carried out for 10000 initialization cycles followed by 50000 production cycles for taking the ensemble averages. Peng-Robinson equation of state was used to convert pressure to the corresponding fugacity. We performed GCMC simulations at room temperature at two different conditions: (i) Vacuum swing adsorption (VSA) at P_{ads} :1 bar and P_{des} : 0.1 bar (ii) Pressure swing adsorption (PSA) at P_{ads} :5 bar and P_{des} :1 bar. Here, P_{ads} and P_{des} represent adsorption and desorption pressures. Simulations were conducted for two different bulk mixture compositions, CO₂/CH₄:10/90 and CO₂/CH₄:50/50, to represent natural gas purification and landfill gas separation, respectively.

We first used the DDEC partial charges already provided for the framework atoms in the MOF database and computed the electrostatic interactions between MOF atoms and CO₂ molecules. All GCMC simulations were then repeated using Qeq-charged MOFs to compare the effect of partial charge assignment method on the gas adsorption results. Results of GCMC simulations were used to calculate four different adsorbent

performance evaluation metrics of MOFs, S_{ads} , ΔN , APS, and R%. Mathematical definitions of these metrics can be seen in Chapter 3 and Table B1 in Appendix B.

In order to examine the effect of charge assignment method on the gas permeability (P_i) of species i and selectivity of the selected MOF membranes (S_{mem}), we also performed equilibrium molecular dynamics (EMD) simulations for CO₂/CH₄:10/90 mixture using RASPA on selected MOFs. Gas loadings (c_i) obtained from GCMC simulations that were performed at 1 bar, 298 K for a feed mixture of CO₂/CH₄:10/90 were used as the input of EMD simulations to compute self-diffusivities of gases ($D_{self,i}$) at their corresponding loadings. NVT ensemble was used for the EMD simulations with a time step of 1 fs. The temperature was kept constant using the Nosé-Hoover chain thermostat algorithm. (Tuckerman et al., 2006) After 10000 initialization and 10000 equilibration cycles, 4×10^6 cycles were used to obtain the mean squared displacement (MSD) data of gas molecules calculated using modified order-N algorithm at long times. (Dubbeldam et al., 2016) $D_{self,i}$ of gas molecules were computed from the slope of the MSD data in accordance with the Einstein's relation. (Einstein, 1956) These simulations were repeated three times to compute the average self-diffusivities of each gas component. Mathematical descriptions used to compute performance metrics of MOF membranes, mixture permeabilities of gas components (P_i) and mixture selectivities of membranes (S_{mem}) are as given in Chapter 3.

Performance evaluation metrics computed for MOF adsorbents and membranes using two different charge assignment methods were compared. In order to explore the correlation (or lack of correlation) between simulation results based on the atomic charge assignment method, the coefficient of determination ($0 \leq R^2 \leq 1$) and the Spearman's ranking correlation coefficient ($-1 \leq SRCC \leq 1$) were computed. R was calculated using the formula,

$$R = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n \sum x^2 - (\sum x)^2][n \sum y^2 - (\sum y)^2]}}$$

calculated for a MOF using Q_{eq} (DDEC) charges and n is the total number of MOFs. In order to determine the SRCC of MOFs for a given metric, we first ranked the MOFs according to the value of the metric of interest computed using either of the charge assignment method and then calculated the R value between the rankings of MOFs. Therefore, in SRCC calculation, x (y) represents the ranking of a MOF for a metric calculated using Q_{eq} (DDEC) charges and n is the total number of MOFs. The value of the SRCC ranges from -1 to 1 where positive (negative) values represent that two rankings

are highly similar (dissimilar) and SRCC becomes unity when there is a perfect correlation between the two rankings.

Before discussing the results of adsorbent and membrane performance evaluation metrics of 1500 MOFs in detail, we compared experimentally reported CO₂ uptakes of 10 different MOF structures taken from the literature (Millward and Yaghi, 2005; Arstad et al., 2008; Yazaydin et al., 2009; Aprea et al., 2010; Du et al., 2012; Wriedt et al., 2012; Xiang et al., 2012) with our simulated CO₂ uptakes using both charge methods. Figure 6.1 shows that molecular simulations using DDEC charges generally give CO₂ uptakes closer to the experimental results compared to Qeq charges. There were two MOFs (CuBTC and MIL-47) for which CO₂ uptakes obtained by Qeq method were in a better agreement with the experiments compared to those obtained by DDEC method. We also observed that simulated CO₂ uptakes obtained from two charge assignment methods can be similar to each other but might vary from the experimental CO₂ uptakes in some cases as shown in Figure 6.1.

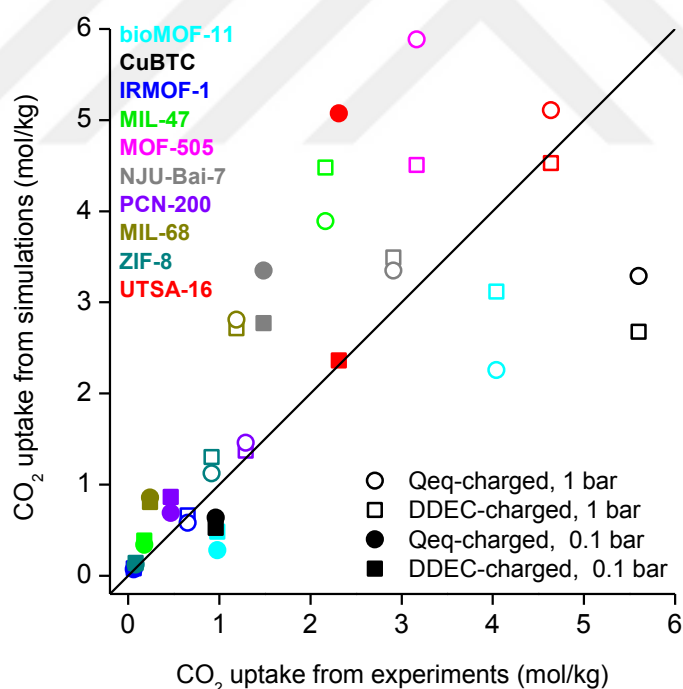


Figure 6.1. Comparison of the experimental CO₂ uptakes (Millward and Yaghi, 2005; Arstad et al., 2008; Yazaydin et al., 2009; Aprea et al., 2010; Du et al., 2012; Wriedt et al., 2012; Xiang et al., 2012) with our simulation results obtained using different charge assignment methods. Squares (circles) represent the simulation results of DDEC (Qeq)-charged MOFs while filled (empty) symbols are the results for 0.1 (1) bar.

At that point, we note that our ultimate aim is to investigate the effect of using different charge assignment methods on the predicted adsorbent and membrane performances and hence ranking of MOFs but not to discuss the accuracy of these methods which already exists in the literature.(Ongari et al., 2019)



6.2 Results and Discussion

We first examined the effect of using DDEC and Qeq charges on the adsorption of CO₂/CH₄ mixtures in 1500 MOFs. The number/type of the accessible adsorption sites and van der Waals potential parameters of the framework atoms are the same regardless of the charge assignment method used in molecular simulations. Hence, the charge assignment method directly affects the electrostatic interactions between CO₂ molecules and MOF atoms. Although CH₄ was modeled as nonpolar, CH₄ uptake also changes depending on the charge assignment method due to the competition between CO₂ and CH₄ molecules in the mixture for the same adsorption sites of MOFs. The MOFs for which negligible CH₄ uptake was observed in the molecular simulations were excluded. Figure 6.2 compares gas uptakes computed at 0.1, 1 and 5 bar for CO₂/CH₄:10/90 mixture using both charge methods. In order to facilitate the visualization of the charge effect on the simulated gas uptakes, we first identified the atom with the largest charge in a DDEC-charged MOF ($q_{\text{DDEC}}^{\text{largest}}$) and Qeq-charged MOF ($q_{\text{Qeq}}^{\text{largest}}$), and then color-coded the data points based on the difference of those charges ($q_{\text{DDEC}}^{\text{largest}} - q_{\text{Qeq}}^{\text{largest}}$). Figure 6.2(a-c) shows that the method that assigns the largest charge mostly resulted in higher simulated CO₂ uptakes compared to the other method at all pressures. However, we note that when a method assigns a larger charge to one of the atoms in the framework, this does not claim that charges of every atom in that framework would be larger than those assigned by the other method. For most MOFs, 896 among 1500, DDEC method assigned a higher largest charge than Qeq, while there are MOFs for which DDEC and Qeq assigned the largest charge to different atoms in the same framework.

Figure 6.2 shows that the discrepancy between the CO₂ uptakes obtained using DDEC- and Qeq-charged MOFs is more observable at low pressures. Gas molecules at low pressures first interact with the accessible metal centers and organic linkers of MOFs where van der Waals interaction parameters and partial charges play important roles in attracting guest molecules. (Zheng et al., 2009) Due to the electrostatic interactions, atoms with the largest charges become more attractive for CO₂ molecules, and these adsorption sites are primarily saturated at low pressures. As the pressure increases and with the saturation of the most favorable adsorption sites, adsorbate-adsorbate interactions start to dominate, and the effect of atomic partial charges diminishes. In order to quantify this, we computed R² values at each pressure as shown in Figure 6.2.

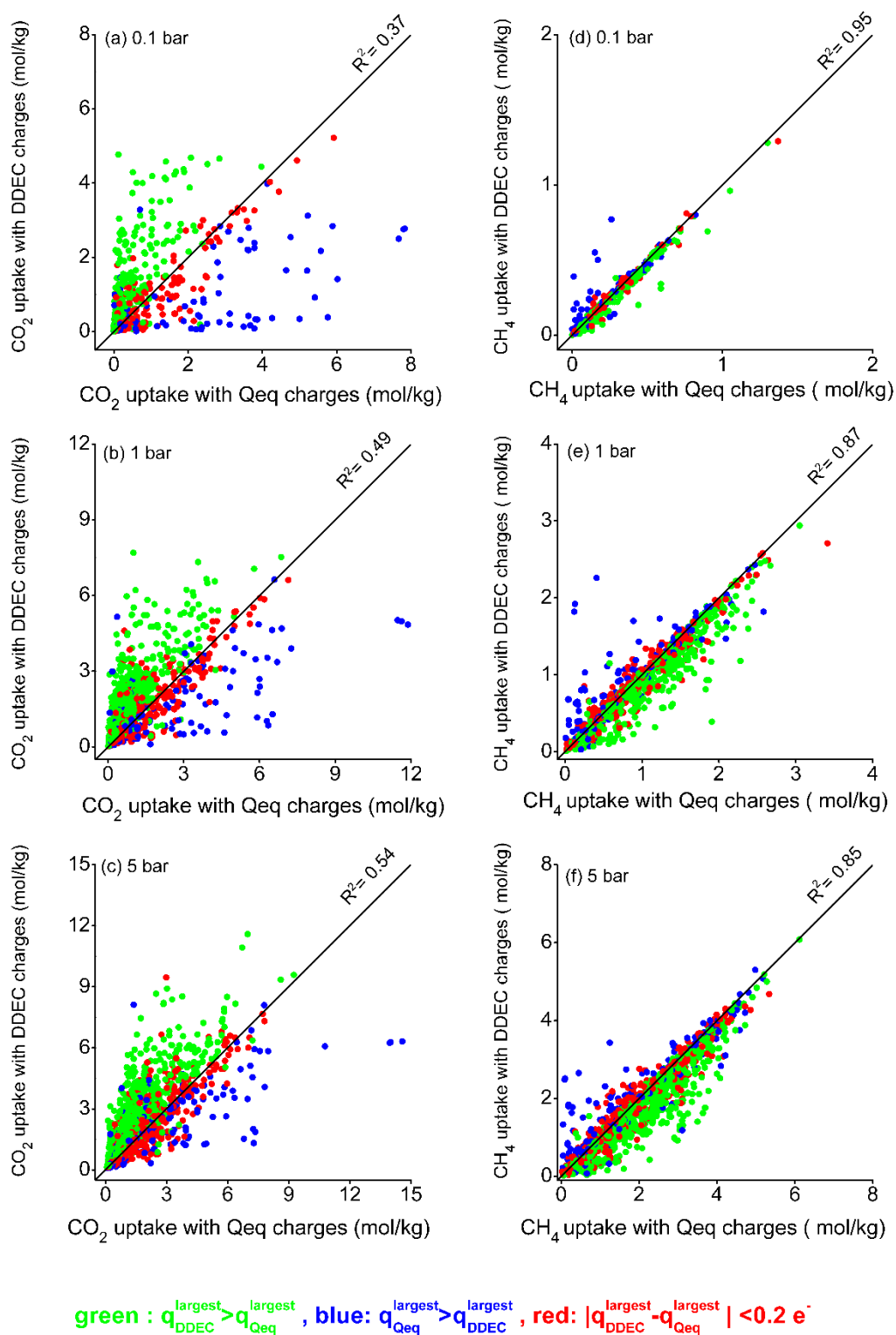


Figure 6.2. CO₂ uptakes (a-c) and CH₄ uptakes (b-f) obtained from simulations using Qeq and DDEC charges at 0.1, 1, 5 bar for CO₂/CH₄: 10/90 mixture.

At low pressure, low R^2 values were observed for CO_2 uptakes obtained from simulations using two different charge assignment methods (R^2 of 0.37 at 0.1 bar as shown in Figure 6.2(a)), showing the importance of electrostatic interactions hence the choice of charge assignment method. As the pressure increases, CO_2 uptakes obtained from different charge assignment methods become moderately similar leading to increased R^2 values of 0.49 and 0.54 at 1 bar and 5 bar, respectively, as shown in Figure 6.2(b-c). Figure 6.2 (d-f) shows that the type of charge assignment method had a less pronounced impact on the simulated CH_4 uptakes of MOFs compared to CO_2 uptakes. We finally note that although we used a simple representation of the effect of charges, the difference between the largest charges assigned by two methods to an atom in a MOF ($q_{\text{DDEC}}^{\text{largest}} - q_{\text{Qeq}}^{\text{largest}}$), there are cases when this difference was not directly reflected on the simulated CO_2 uptakes. For example, $q_{\text{DDEC}}^{\text{largest}}$ can be only slightly lower than $q_{\text{Qeq}}^{\text{largest}}$ in a MOF, but CO_2 uptake of DDEC-charged MOF can be significantly higher than Qeq-charged MOF. This occurs when the two methods assign the largest charge to different atoms which may not be equally accessible as an adsorption site for CO_2 molecules. In other words, charges of atoms in the pore surrounding walls play an important role in describing CO_2 adsorption.

Throughout this part, results for adsorption of CO_2/CH_4 :10/90 mixture will be given while the results for adsorption of equimolar CO_2/CH_4 mixture will be provided in Appendix B. Figure B1 shows that the effect of charge assignment method on CO_2 uptakes is less pronounced for CO_2/CH_4 :50/50 mixture compared to the results for CO_2/CH_4 :10/90 mixture. Higher R^2 values of 0.47, 0.62, and 0.78 were observed for CO_2 uptakes at 0.1, 1, and 5 bar, respectively, for the adsorption of equimolar mixture. This can be explained with the following: when an equimolar mixture was considered, there were enough CO_2 molecules in the feed to compete with CH_4 molecules and to dominate the adsorption sites at low pressures due to the electrostatic interactions with the frameworks.

Differences between CO_2 and CH_4 uptakes of DDEC- and Qeq-charged MOFs ultimately affect the calculated adsorbent performance evaluation metrics of MOFs. We examined how these metrics change depending on the charge method used in the molecular simulations. The effect of the charge method on adsorbent metrics was more observable for CO_2/CH_4 :10/90 mixture at VSA conditions and results were demonstrated

in Figure 6.3 whereas results for other operating condition and mixture composition can be found in Table B2 and Figure B2-S4 of Appendix B. Figure 6.3(a) shows that CO₂ working capacities (ΔN_{CO_2}) of DDEC-charged MOFs were calculated to range from 0.02 to 5.64 mol/kg and ΔN_{CO_2} values of Qeq-charged MOFs range between 0.01 and 5.51 mol/kg. Significant differences between calculated ΔN_{CO_2} values were observed for some MOFs based on the charge method. Calculated ΔN_{CO_2} of a large number of DDEC-charged MOFs (326 MOFs) were at least double of those of Qeq-charged MOFs while ΔN_{CO_2} of many Qeq-charged MOFs (69 MOFs) were at least two times higher than those of DDEC-charged MOFs. This led to a low R^2 value, 0.44, for the working capacities computed by two different methods. Similarly, we observed large differences between the adsorption selectivities (S_{ads}) of DDEC- and Qeq-charged MOFs as shown in Figure 6.3(b). S_{ads} values of DDEC-charged MOFs were calculated to range from 1.6 to 1633.8 whereas values of Qeq-charged MOFs vary from 1.2 to 2477.7. As shown in Figure 6.3(b), two orders of magnitude differences were observed in CO₂/CH₄ selectivities of some MOFs depending on the charge method, leading to a low R^2 of 0.28.

There is generally a trade-off relation between selectivity and working capacity of MOFs. APS was defined as the multiplication of those two to efficiently identify the materials offering both high selectivity and high working capacity. (Chung et al., 2016) Figure 6.3(c) represents that APS values of DDEC-charged MOFs vary between 0.03 and 2180 mol/kg whereas those computed for Qeq-charged MOFs range from 0.02 to 2716 mol/kg. Since APS combined two metrics (selectivity and working capacity) computed differently by DDEC and Qeq methods, a very weak correlation, R^2 of 0.19, was observed. Regenerability (R%) was calculated by dividing ΔN_{CO_2} of MOFs with the CO₂ uptake at the adsorption pressure. As shown in Figure 6.3(d), R% values vary depending on the charge assignment method used in molecular simulations, leading to an R^2 of 0.50. As high R% is desired for an efficient adsorption-based gas separation, we represented 85% limit with a dashed line in Figure 6.3(d). 683 MOFs were found to have R%>85% when DDEC method was used but 36 of these MOFs were identified to have R%≤85% by Qeq method. On the other hand, there were 799 MOFs with R%>85% when Qeq charges were used while 152 of them were computed to have R%≤85% with DDEC charges. 647 common MOFs were found to have R%>85% using either charge methods.

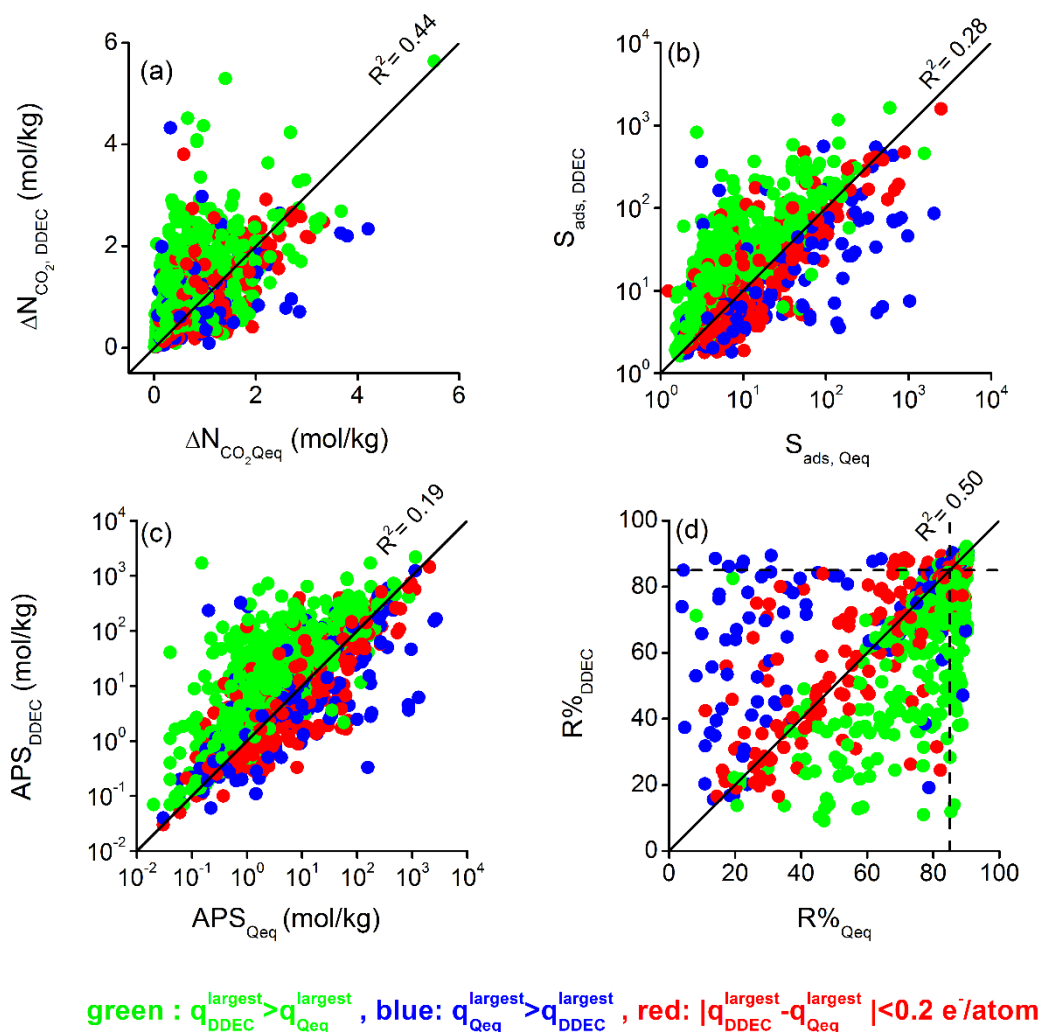


Figure 6.3. Calculated adsorbent performance evaluation metrics using Qeq and DDEC charges at VSA conditions at 298 K, for CO₂/CH₄:10/90 mixture; (a) ΔN_{CO_2} , (b) S_{ads} , (c) APS, (d) R%. Dashed lines in (d) show R% =85%.

In high-throughput computational screening of MOFs, materials are generally ranked based on the adsorbent performance evaluation metrics to identify the most promising ones among many. We separately ranked 1500 MOFs based on their calculated S_{ads} , ΔN_{CO_2} , APS, and R% metrics using the simulation results of DDEC-charged and Qeq-charged MOFs. In order to quantify how the rankings of MOFs change depending on the charge method, we computed the SRCC values and presented them in Table 6.1 for different compositions of the gas mixture and at different operating conditions.

Although R^2 values were generally low for performance metrics calculated by DDEC and Qeq methods, all SRCC values were found to be higher than 0.7. This result indicates that although calculated performance metrics quantitatively alter depending on the charge method, the rankings of MOFs based on individual metrics are not significantly affected from the charge method used in molecular simulations. Table 6.1 suggests that either charge method can be used in high-throughput screening of MOFs if the main aim of a study is to rank the materials based on one of the metrics that we considered above.

Table 6.1. Calculated R^2 and SRCC of adsorbent performance evaluation metrics between DDEC-charged and Qeq-charged MOFs at PSA and VSA conditions.

	CO ₂ /CH ₄ :10/90				CO ₂ /CH ₄ :50/50			
	R^2		SRCC		R^2		SRCC	
	VSA	PSA	VSA	PSA	VSA	PSA	VSA	PSA
S_{ads}	0.28	0.18	0.72	0.72	0.16	0.07	0.73	0.75
ΔN_{CO_2}	0.44	0.57	0.77	0.80	0.62	0.85	0.82	0.94
R%	0.50	0.74	0.86	0.88	0.61	0.77	0.85	0.88
APS	0.19	0.09	0.75	0.73	0.07	0.07	0.74	0.76

Choosing the best adsorbent material for a target gas separation process solely based on a single criterion cannot be highly accurate. For example, a MOF with a very high CO₂/CH₄ selectivity could not find place in practical gas separation applications if it has a low R% value. We, therefore, described an approach where the best material candidates having a good combination of each metric, S_{ads} , ΔN_{CO_2} , and R%, were identified by solely focusing on MOFs having R%>85% and ranking them based on their calculated APSs.(Altintas et al., 2018b; Altintas, Erucar, and Keskin, 2018) Following the same approach, we compared R% and APS values of DDEC- and Qeq-charged MOFs in Figure 6.4. Due to lower R% values obtained at PSA conditions, we set the limit to 70% at this operating condition. In Figure 6.4(a) and 6.4(b), dashed lines show R%=85 and R%=70, respectively. We also set an arbitrary limit of APS>50 mol/kg as a good performance indicator considering that MOFs having ΔN_{CO_2} >5 mol/kg and S_{ads} >10 would perform well for CO₂/CH₄ separation.(Rufford et al., 2012; Aghaji et al., 2016) One important

result from Figure 6.4(a) is that most of the MOFs having $\text{APS} > 50$ mol/kg suffer from low $R\%$ regardless of the charge assignment method. For example, majority of the Qeq-charged MOFs computed to have $R\% > 85\%$ exhibited $\text{APS} < 50$ mol/kg (green data points). Similarly, most of the DDEC-charged MOFs calculated to have $R\% > 85\%$ were predicted to exhibit $\text{APS} < 50$ mol/kg (blue data points). Figure 6.4(b) shows that almost all MOFs predicted to have $\text{APS} > 50$ mol/kg by both charge methods suffered from low $R\%$ values (red data points) whereas most MOFs computed to have $\text{APS} < 50$ mol/kg by both methods were found to exhibit $R\% \leq 70\%$ (black data points). In other words, either DDEC or Qeq charges can be used in high-throughput simulations to narrow down the material candidates by eliminating MOFs having low $R\%$ and low APS.

The top 10 MOFs providing $R\% > 85\%$ (70%) with the highest APSs were identified using both charge methods at VSA (PSA) conditions. We marked the top 10 MOFs identified by Qeq charges with blue and those by DDEC charges with green in Figure 6.4(c-d). The main observation from Figure 6.4(c) is that 5 of the top MOF adsorbents predicted from simulations using Qeq charges (blue points) suffer from very low $R\%$ when DDEC method was used and they cannot be selected as the best candidates by DDEC method. Similarly, 3 of the top MOFs identified using DDEC charges (green points) would be eliminated due to their low $R\%$ when Qeq method was used. Figure 6.4(d) shows that all the top 10 DDEC-charged MOFs have $R\% > 70$ when Qeq charges were used. However, only 3 of the top 10 Qeq-charged MOFs could have $R\% > 70$ when DDEC charges were utilized. Similar results as shown in Figure B5 were obtained when an equimolar mixture was considered. Overall, we concluded that although the two charge methods give similar ranking of MOFs based on the individual performance metrics that we considered in this work, identity of the top adsorbent materials was found to completely alter depending on the charge method used in simulations. Hence, if the aim of the computational screening study is to identify and name the individual best materials, selection of the charge assignment method has a critical importance.

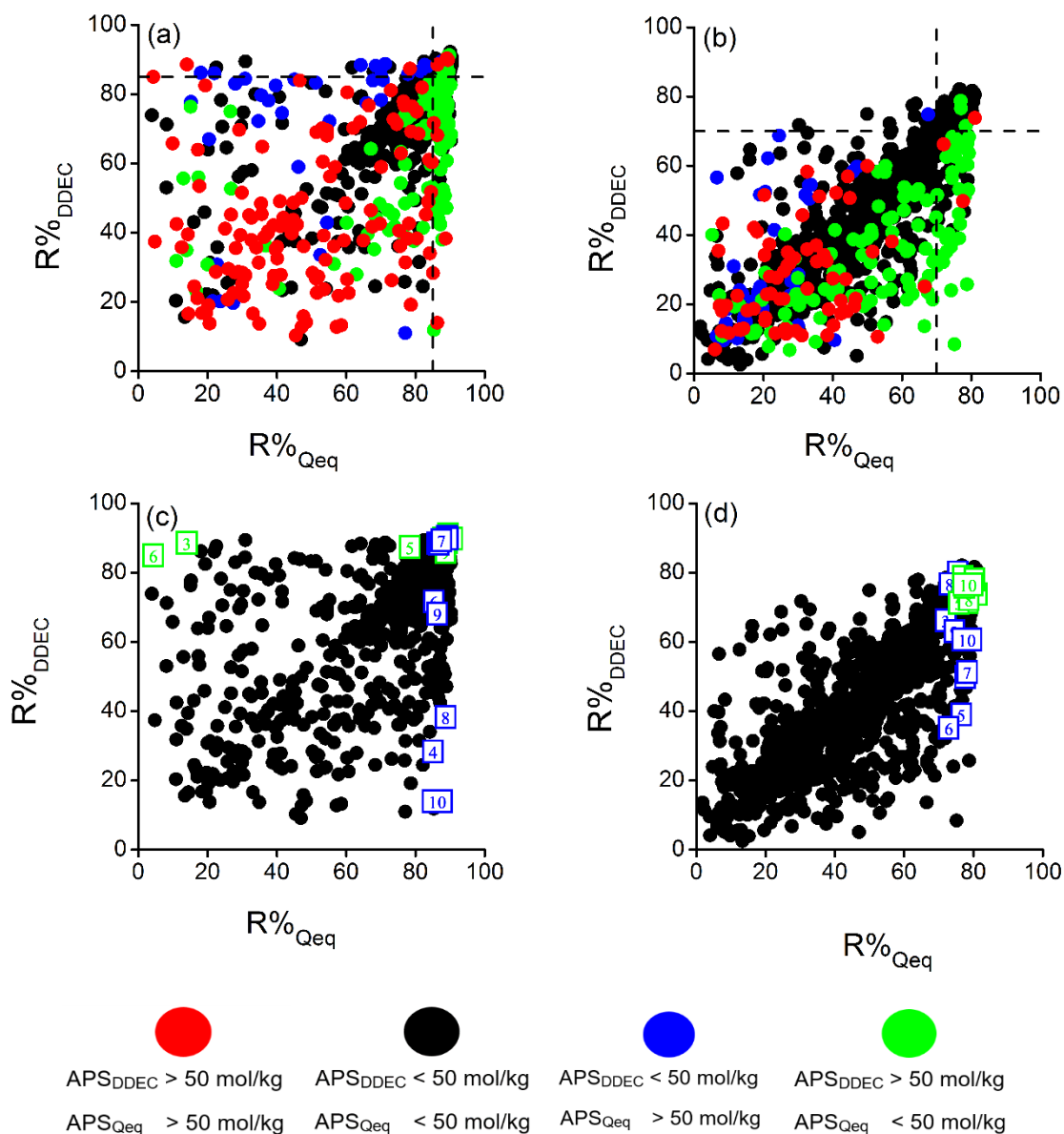


Figure 6.4. Comparison of R% of DDEC and Qeq-charged MOFs at (a, c) VSA (b, d) PSA conditions for CO₂/CH₄:10/90 mixture. Dashed lines show R%=85% in (a), R%=70% in (b). The top 10 MOFs identified by DDEC and Qeq methods are shown with green and blue, respectively, in (c) and (d).

Structural properties of MOFs are one of the intrinsic determinants that define their performances. In order to investigate structure-performance relations of MOFs based on the charge assignment method, we used the ratios of performance metrics calculated with DDEC charges to those calculated with Qeq charges, $\Delta N_{CO_2, DDEC} / \Delta N_{CO_2, Qeq}$, $S_{ads, DDEC} / S_{ads, Qeq}$, $APSD_{DDEC} / APS_{eq}$, and $R\%_{DDEC} / R\%_{Qeq}$. These ratios were shown as a function of PLDs of MOFs for CO₂/CH₄:10/90 mixture at VSA condition in Figure 6.5.

The main message of Figure 6.5 is that as the pore size increases, the effect of the charge method becomes less pronounced for all metrics (also for CO₂ uptakes as shown in Figure B6). The highest change in the ratio of calculated metrics was observed for APS. APS_{DDEC}/APS_{Qeq} varied between 10⁻³-10⁴ indicating that some of the APS values calculated with DDEC charges were orders of magnitude higher than those calculated with Qeq charges. The highest APS_{DDEC}/APS_{Qeq} values were observed for MOFs having low PLDs (<6 Å). This is due to the stronger confinement of the gas molecules in narrow pores causing a much stronger interaction with the surrounding atoms. (Zheng et al., 2009) Overall, results demonstrate that the charge assignment method does not significantly affect the predicted adsorbent performance metrics of MOFs having very large pore sizes but it has a major effect on MOFs with narrow pores.

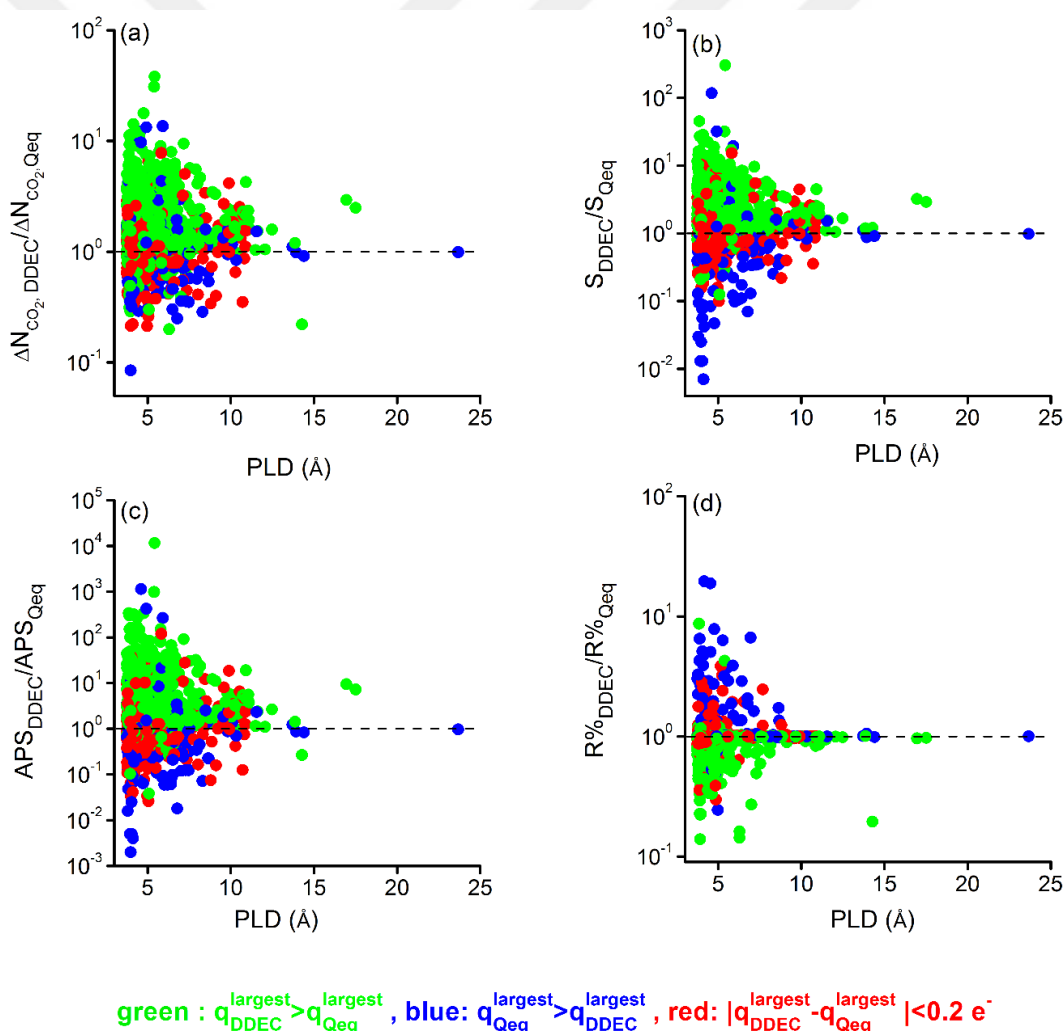


Figure 6.5. The ratio of (a) ΔN_{CO_2} , (b) S_{ads} , (c) APS, (d) R% computed by DDEC charges to the ones computed by Qeq charges as a function of PLD of MOFs.

We so far examined the impact of the selected charge assignment method on the predicted performance evaluation metrics of MOF adsorbents. Combination of GCMC and EMD simulations can be used to estimate membrane-based CO₂/CH₄ separation performances of MOFs.(Altintas and Keskin, 2019) Therefore, unlocking the effects of charge assignment method used in both GCMC and EMD simulations on the computed gas permeabilities and selectivities of MOF membranes is also important. Performing mixture EMD simulations for a large number of MOFs is computationally challenging, therefore we specifically focused on 10 selected MOFs exhibiting a large variety of adsorption selectivities and pore sizes. Differences in partial charges of MOF atoms led to different gas loadings and hence differences in calculated self-diffusivities and permeabilities of gases. Gas loadings obtained at the feed side of the membrane from the GCMC simulations, self-diffusivities of gases computed using EMD simulations, adsorption, diffusion and membrane selectivities of MOFs calculated using Qeq and DDEC charges are all given in Table 6.2. We first compared CO₂ and CH₄ permeability obtained using different charge methods at a feed pressure of 1 bar, permeate pressure of vacuum for CO₂/CH₄:10/90 mixture. CO₂ permeability predictions of DDEC-charged MOFs, 4×10^4 - 2×10^6 Barrer, were similar to those of Qeq-charged MOFs, 3×10^4 - 2×10^6 Barrer, leading to a high R² of 0.9 as shown in Figure 6.6(a). DDEC-charged MOFs were calculated to have CH₄ permeabilities of 3×10^3 - 5×10^5 Barrer while Qeq-charged MOFs were computed to have CH₄ permeabilities in the range of 3×10^2 - 1×10^6 Barrer, leading to a lower R² of 0.6. Considerably higher CH₄ permeabilities predicted by DDEC charges can be discussed with an example MOF, CAZGIT. Although the difference between the largest charges assigned by two methods was small, adsorbed CO₂ (CH₄) amount in Qeq-charged CAZGIT was higher (lower) than that in DDEC-charged MOF as shown in Table 6.2. Due to the higher amount of total gas loading in Qeq-charged MOF, self-diffusivities for both gases were computed to be an order of magnitude lower than those computed for DDEC-charged MOF, resulting in gas permeabilities lower than the ones computed by using DDEC charges.

Table 6.2. Calculated uptakes and diffusivities of CO₂ and CH₄ in DDEC-charged and Qeq-charged MOFs; adsorption, diffusion and membrane selectivities of MOFs for separation of CO₂/CH₄ mixture.

MOFs	PLD (Å)	N _{CO₂} (mol/kg)	N _{CH₄} (mol/kg)	D _{self, CO₂} (cm ² /s)	D _{self, CH₄} (cm ² /s)	S _{ads}	S _{diff}	S _{mem}
		DDEC (Qeq)	DDEC (Qeq)	DDEC (Qeq)	DDEC (Qeq)	DDEC (Qeq)	DDEC (Qeq)	DDEC (Qeq)
REFTUT	5.82	1.70 (0.21)	0.19 (0.35)	4.55×10 ⁻⁶ (3.50×10 ⁻⁵)	9.83×10 ⁻⁶ (3.74×10 ⁻⁵)	81.96 (5.34)	0.47 (0.94)	38.71 (5.03)
GIQYIP	3.91	4.69 (6.88)	0.13 (0.17)	4.17×10 ⁻⁷ (4.96×10 ⁻⁷)	5.20×10 ⁻⁶ (2.13×10 ⁻⁶)	318.39 (362.88)	0.09 (0.25)	29.74 (91.66)
LIFWEE	3.87	1.18 (1.39)	0.71 (0.69)	6.80×10 ⁻⁶ (6.17×10 ⁻⁶)	5.93×10 ⁻⁶ (3.49×10 ⁻⁶)	14.83 (18.20)	1.15 (1.82)	17.13 (33.18)
CAZGIT	3.98	0.50 (1.68)	0.85 (0.25)	2.53×10 ⁻⁶ (4.78×10 ⁻⁷)	2.08×10 ⁻⁶ (2.69×10 ⁻⁷)	5.31 (59.52)	1.27 (2.12)	6.75 (126.11)
ATAFIK	5.70	2.82 (0.32)	0.74 (0.88)	2.04×10 ⁻⁵ (1.41×10 ⁻⁴)	1.08×10 ⁻⁴ (2.98×10 ⁻⁴)	34.45 (3.26)	0.19 (0.48)	6.55 (1.55)
ACODED	3.79	1.28 (0.83)	1.70 (1.86)	6.23×10 ⁻⁶ (9.90×10 ⁻⁶)	8.31×10 ⁻⁶ (1.08×10 ⁻⁵)	6.81 (4.03)	0.76 (0.91)	5.17 (3.68)
PEPBAO	3.96	0.55 (0.31)	0.97 (1.10)	1.87×10 ⁻⁶ (2.75×10 ⁻⁶)	2.42×10 ⁻⁶ (3.35×10 ⁻⁶)	5.09 (2.57)	0.77 (0.82)	3.93 (2.12)
Co26NDP	10.60	0.48 (0.36)	1.11 (1.11)	4.51×10 ⁻⁵ (6.82×10 ⁻⁵)	1.07×10 ⁻⁴ (1.06×10 ⁻⁴)	3.87 (2.92)	0.42 (0.64)	1.64 (1.87)
LOQLIN	13.93	1.00 (1.06)	1.26 (1.18)	2.42×10 ⁻⁵ (3.06×10 ⁻⁵)	1.28×10 ⁻⁴ (1.40×10 ⁻⁴)	7.11 (8.08)	0.19 (0.22)	1.35 (1.75)
KIGCEK	10.28	0.17 (0.26)	0.59 (0.59)	4.67×10 ⁻⁵ (3.80×10 ⁻⁵)	1.16×10 ⁻⁴ (1.08×10 ⁻⁴)	2.54 (3.93)	0.40 (0.35)	1.02 (1.38)

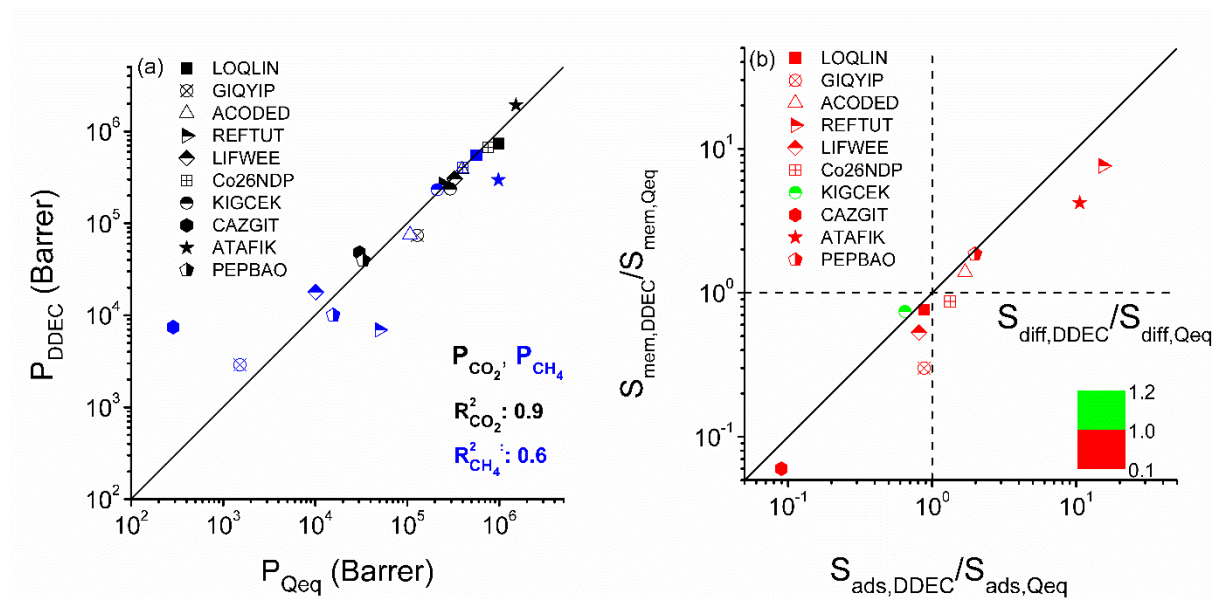


Figure 6.6. (a) Comparison of gas permeabilities of DDEC-charged MOFs with those of Qeq-charged MOFs. (b) Comparison of adsorption, diffusion and membrane selectivities of MOFs based on the charge method.

We finally investigated how adsorption, diffusion and membrane selectivities of MOFs would change based on the charge method used in molecular simulations. The ratio of adsorption selectivities ($S_{ads,DDEC}/S_{ads,Qeq}$), diffusion selectivities ($S_{diff,DDEC}/S_{diff,Qeq}$), and membrane selectivities ($S_{mem,DDEC}/S_{mem,Qeq}$) computed with DDEC charges to the ones computed with Qeq charges are presented in Figure 6.6(b). For all MOFs, $S_{mem,DDEC}/S_{mem,Qeq}$ values depend on $S_{ads,DDEC}/S_{ads,Qeq}$ values. For 7 MOFs, $S_{ads,DDEC}/S_{ads,Qeq}$ values were close to 1 (0.65-1.98) and $S_{mem,DDEC}/S_{mem,Qeq}$ values (0.30-1.86) were close to $S_{ads,DDEC}/S_{ads,Qeq}$ values. There was a MOF, GIQYIP, for which $S_{mem,DDEC}/S_{mem,Qeq}$ value was calculated to be much lower than $S_{ads,DDEC}/S_{ads,Qeq}$. GIQYIP was computed to have higher CO_2 loading when Qeq charges were used and diffusivity of CH_4 molecules were hindered due to its narrow pores, 3.91 Å. The difference between CH_4 diffusivities in DDEC- and Qeq-charged GIQYIP led to a very low $S_{diff,DDEC}/S_{diff,Qeq}$ value (0.37) and eventually low $S_{mem,DDEC}/S_{mem,Qeq}$ (0.30). LOQLIN was computed to have a similar $S_{ads,DDEC}/S_{ads,Qeq}$ value with GIQYIP, however membrane selectivity of the former did not notably change based on the charge method due to its large pores (13.93 Å). Gas loading and diffusivities were not significantly affected from the charge method for MOFs having large pores as previously discussed in Figure 6.5. For the other 3 MOFs, $S_{ads,DDEC}/S_{ads,Qeq}$ values were significantly different than 1 which directly affected their

$S_{\text{mem,DDEC}}/S_{\text{mem,Qeq}}$ values. For example, $S_{\text{ads,DDEC}}/S_{\text{ads,Qeq}}$ and $S_{\text{mem,DDEC}}/S_{\text{mem,Qeq}}$ values of REFTUT were calculated as 15.34 and 7.60, respectively, which can be explained by the difference of the partial charges assigned by DDEC and Qeq methods to Zn atoms. Overall, it can be concluded that unless a MOFs has narrow pore sizes and charges that were very differently assigned by DDEC and Qeq methods, predicted gas permeability and membrane selectivity of that MOF using these two methods would be close to each other. We note that only 10 MOF membranes were considered in this part and studying a larger set of MOFs might provide more insights.

In this work, we aimed to understand the impact of the charge assignment method used in molecular simulations on the predicted adsorbent and membrane performance metrics of MOFs. For this aim, we used a computation-ready MOF database where crystal structures of the solvent-free MOFs mimicking the experimental activation process are directly ready to be used in molecular simulation.(Nazarian, Camp, and Sholl, 2016) It is important to note that MOFs in computation ready databases might not be stable after the solvent removal and/or there might be structural problems such as missing hydrogen atoms, extra framework ions etc. as discussed in detail in our recent work.(Altintas et al., 2019) We also note that the MOFs we examined were limited with the ones for which DDEC charges were currently available in the literature. A final point to note is that we focused on a gas mixture where one component has a quadrupole moment, CO_2 , whereas the other was nonpolar, CH_4 . We believe that examining the role of charge methods used in molecular simulations for separation of a binary mixture where both components are polar, such as $\text{CO}_2/\text{H}_2\text{O}$, having electrostatic interactions with the MOF atoms will be interesting for future studies.

6.3 Conclusion

In this part, we performed a high-throughput computational screening of MOFs for CO₂/CH₄ separation using two different charge methods. The performance metrics of MOF adsorbents and membranes obtained from DDEC-charged and Qeq-charged MOFs were compared at two different operating conditions to assess the role of the charge method used in molecular simulation in predicting CO₂ separation potential of MOFs. Results showed that calculated CO₂ and CH₄ uptakes, CO₂ working capacities, CO₂/CH₄ selectivities, APSs, and R% of MOFs significantly alter depending on the charge method used in molecular simulations. We then ranked the MOFs based on each metric and examined the correlation between the DDEC-charged and Qeq-charged MOF rankings. Results showed that there is a high correlation between the rankings of MOFs but the best-performing MOF adsorbents identified by DDEC and Qeq methods are different. Effects of the charge method on gas diffusivity, gas permeability and membrane selectivity of materials were also tested on a smaller set of MOF membranes and results suggested that charge methods predicted similar separation performances unless the pore size of the MOF is very narrow. Based on these results, we concluded that an approximate partial charge assignment method such as Qeq can be used to screen large numbers of MOFs in a time-efficient manner to narrow down the number of promising materials for a target application but ultimate identification of top performing materials requires using a more accurate charge assignment method like DDEC.

*The content of this chapter is directly obtained from our published work(Altintas and Keskin, 2020) and adapted for thesis.

Chapter 7

OUTLOOK

Recent developments in algorithms and computational tools have facilitated the high-throughput computational screening of MOFs for gas separation. Our work as presented in this thesis showed that MOFs can be considered as promising materials for CO₂ capture from natural gas and for C₂H₆/C₂H₄ and C₂H₆/CH₄ separations. Several issues as given below which require further experimental and/or computational investigations can be considered as the future directions of the field:

- The top materials are identified based on solvent-free, activated, rigid MOF structures in all molecular simulations conducted for this thesis. However, MOFs may not be perfectly crystalline, and they may have defects in their structures. After the solvent removal, some MOFs can lose their crystalline structure and collapse. These structures need to be further checked and tested with more accurate and detailed simulations to determine their exact performances.
- Another important point is that a good MOF adsorbent should have a good thermal, mechanical, and chemical stability to find place in real gas adsorption and separation processes. Especially, stability of MOFs under impurities of natural gas such as H₂S and H₂O is important since these gases may change the chemical environment of the pores and stability of the MOF adsorbent. These issues, especially stability, is most likely to be examined by further experimental studies.
- Some MOFs can form into a different structure upon an external stimulus like temperature and pressure due to their flexibility and these can affect their performance under real conditions. Development of transferable flexible force fields are required for more detailed performance analysis of flexible MOFs.
- Experimental investigation of multi-component gas adsorption in MOFs is not straightforward as discussed previously. However, the presence of water and other gas-phase components such as O₂, CO, H₂S, H₂O, SO_x and NO_x in a CO₂ capture process may significantly affect the predicted CO₂ capture performances of

MOFs. Therefore, considering the real CO₂ capture process, multi-component gas adsorption in MOFs, is an important future direction for MOF simulations.

- Another direction in the field is to combine quantum-level calculations, molecular simulations, machine learning algorithms to estimate the detailed process-level performance parameters of MOFs such as purity, recovery, productivity, energy cost for CO₂ capture. Among these, energy cost is of paramount importance since the future of MOFs in industrial applications is strongly dependent on a detailed cost analysis of the process.

We hope that the results of this thesis will help the acceleration of MOF research for large-scale application of MOFs for gas separation with contributions from scientists from various backgrounds including chemistry, material science, data science and chemical/process/energy engineering.

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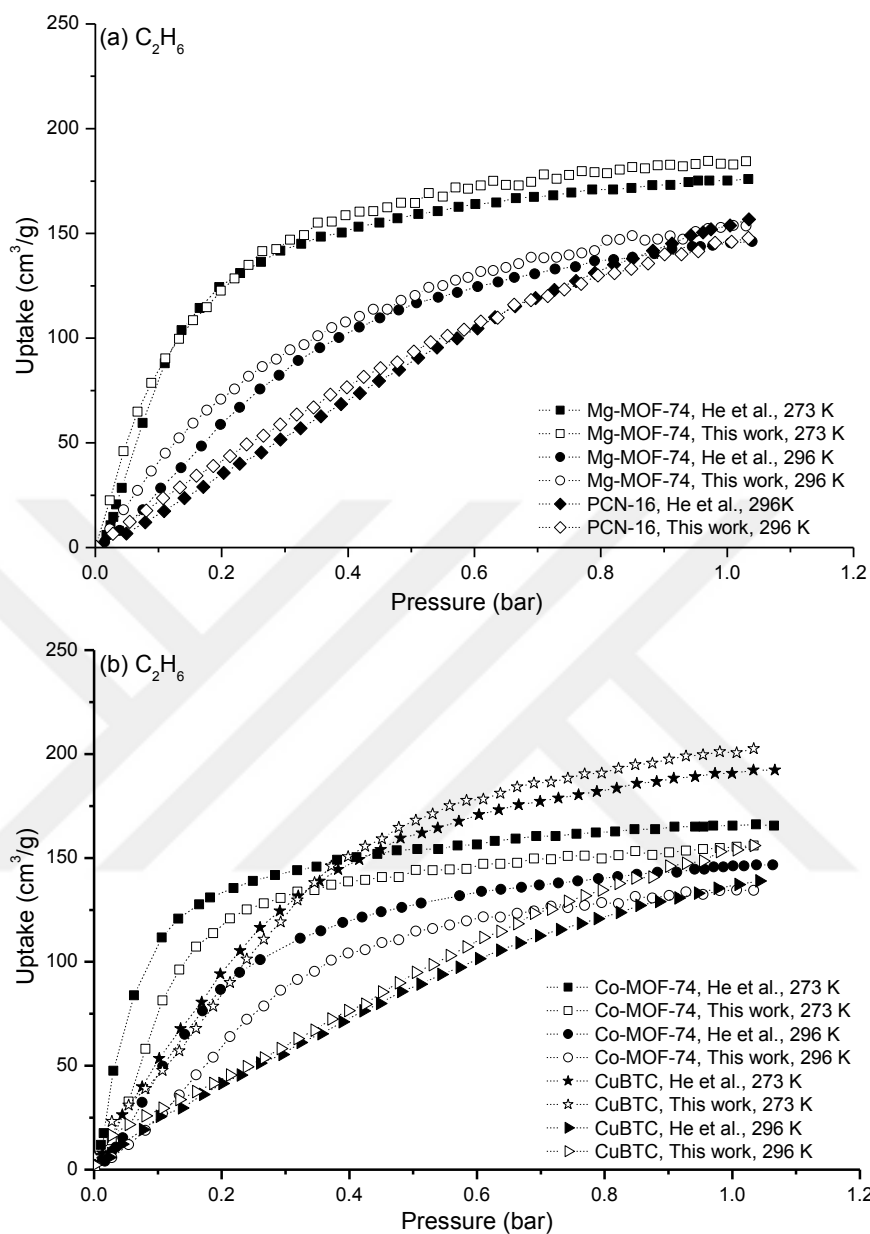
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APPENDIX A

Table A.1. Potential parameters of C₂H₆, C₂H₄, CO₂ and CH₄ molecules used in the simulations

Molecule		ϵ/k_b (K)	σ (Å)	Bond length (Å)	Partial charge (e ⁻)
C₂H₆ ^(Wu et al., 2015)	(CH ₃ -CH ₃)	108.0	3.76	1.54	-
C₂H₄	(CH ₂ =CH ₂)	92.8	3.68	1.33	-
CO₂ ^(Potoff and Siepmann, 2001)	C	27.0	2.80	1.16	0.70
	O	79.0	3.05		-0.35
CH₄		148	3.73	-	-



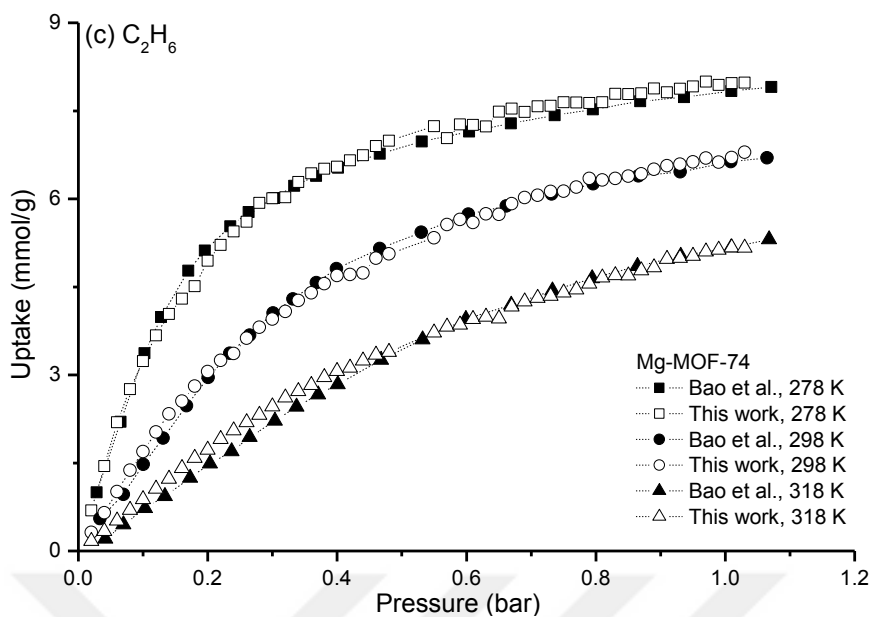
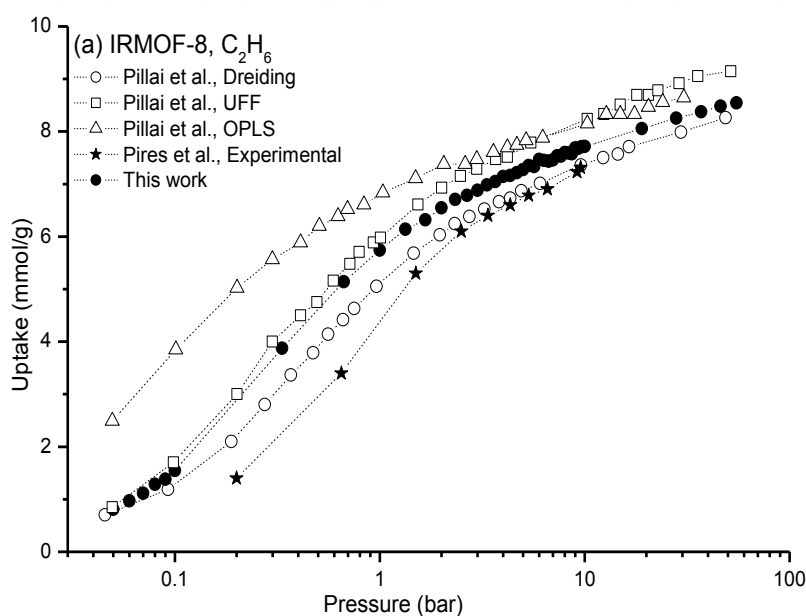


Figure A1. Comparison of our GCMC simulations for C_2H_6 adsorption in (a)MgMOF-74 and PCN-16 (b)CoMOF-74 and CuBTC with the experimental results of He and coworkers.(He, Krishna, and Chen, 2012) (c)MgMOF-74 with the experimental results of Bao and coworkers.(Bao et al., 2011)



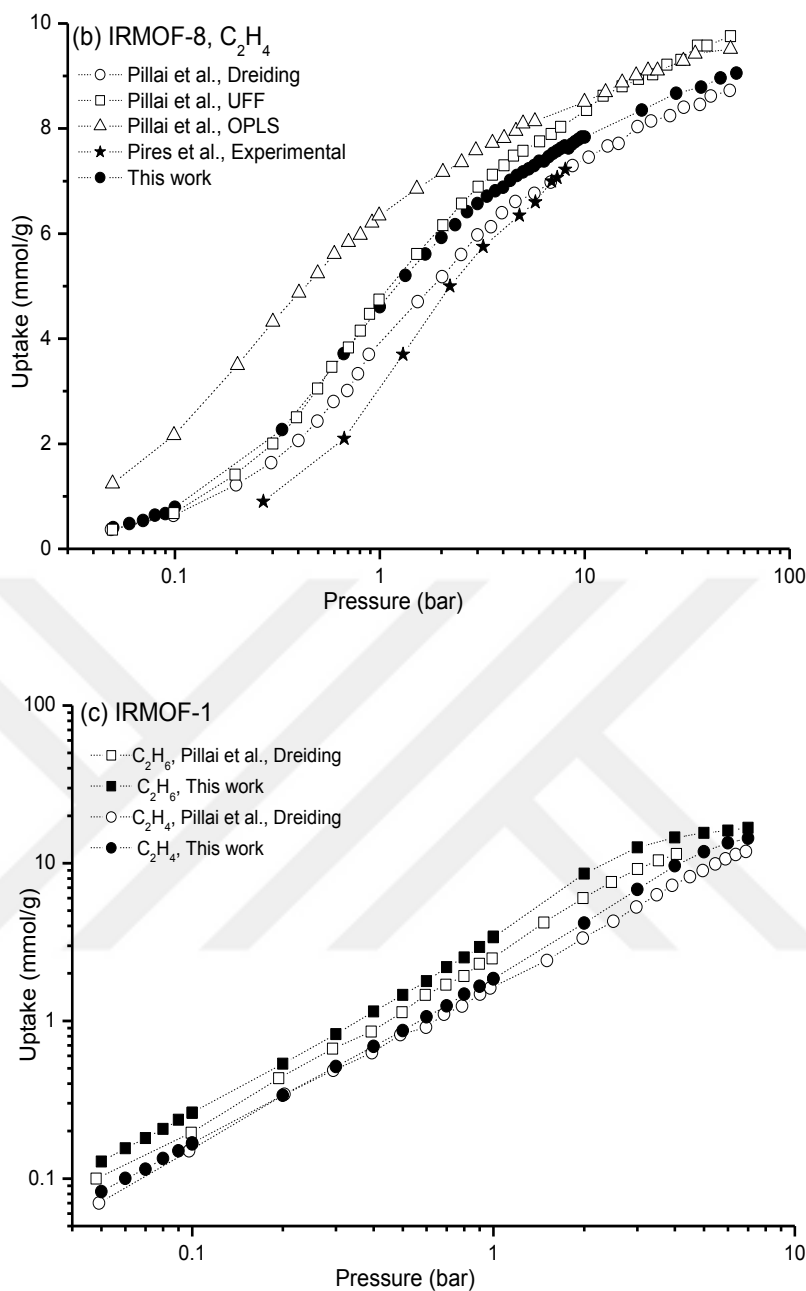
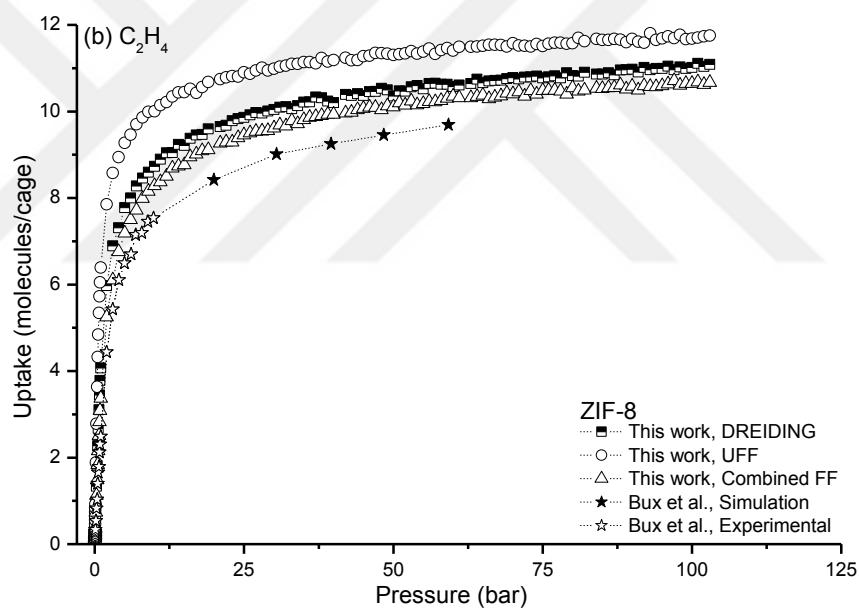
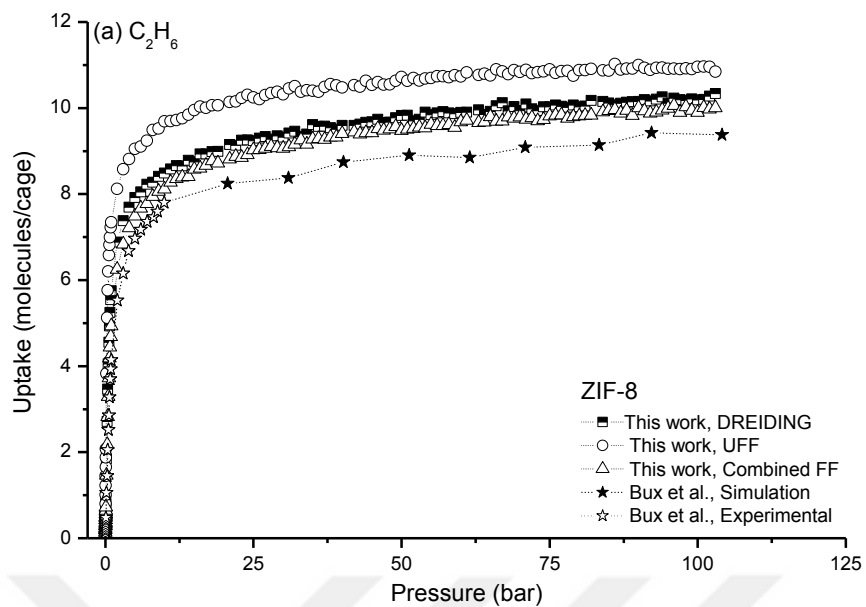


Figure A2. Comparison of our GCMC simulations for C_2H_6 and C_2H_4 adsorption in (a,b)IRMOF-8 (c)IRMOF-1 with the experimental results of Pires and coworkers (Pires, Pinto, and Saini, 2014) and simulated results of Pillai and coworkers (Pillai et al., 2015) at 298 K.



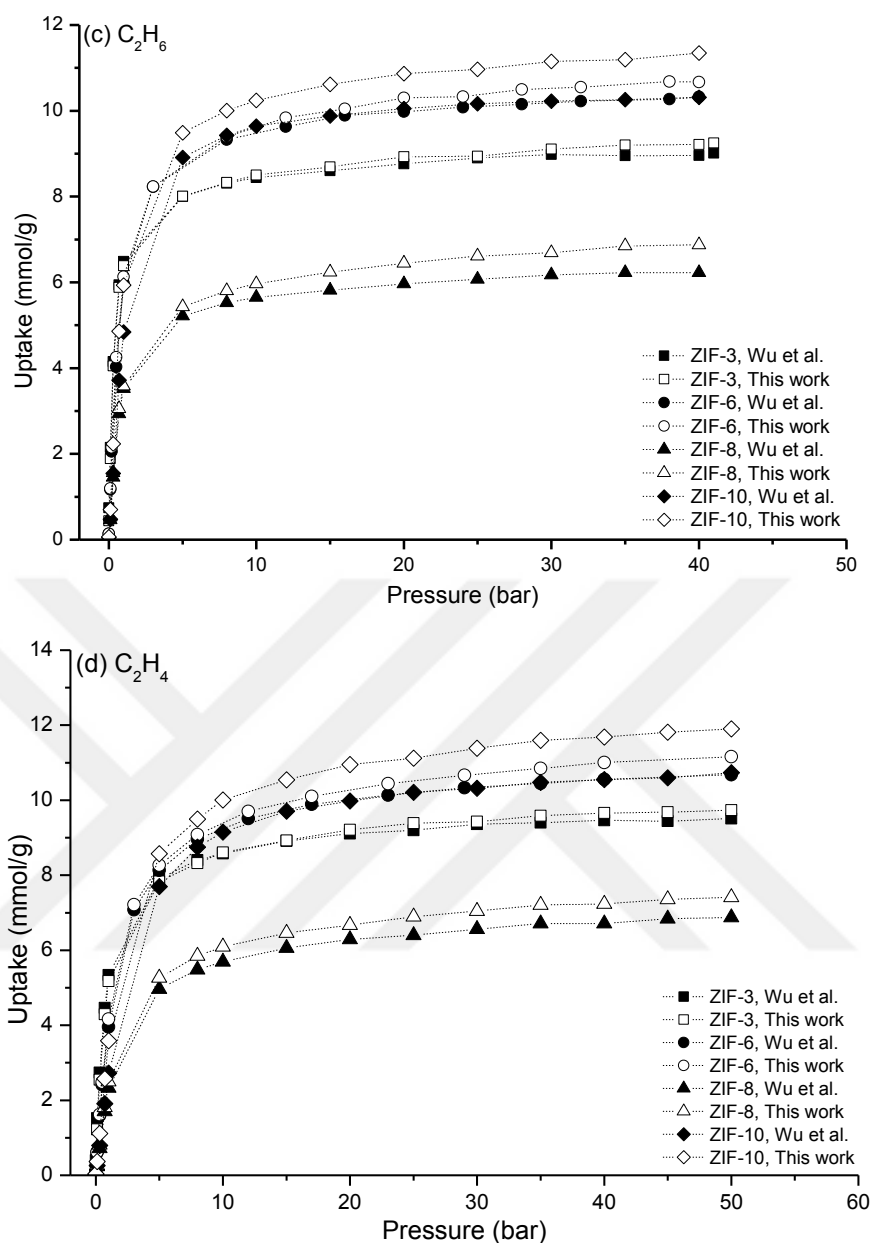


Figure A3. Comparison of our GCMC simulations for (a) C_2H_6 and (b) C_2H_4 adsorption in ZIF-8 with the experimental and simulated results of Bux and coworkers. (Bux et al., 2011) Comparison of our GCMC simulations for (c) C_2H_6 and (d) C_2H_4 adsorption in ZIF-3, ZIF-6, ZIF-8, ZIF-10 with the simulated results of Wu and coworkers. (Wu et al., 2015)

APPENDIX B

Table B.1. Adsorbent and membrane performance evaluation metrics.*

Metric	Formula
Adsorption selectivity	$S_{\text{ads}} = \frac{x_{\text{CO}_2}/x_{\text{CH}_4}}{y_{\text{CO}_2}/y_{\text{CH}_4}}$
CO ₂ working capacity	$\Delta N_{\text{CO}_2} = N_{\text{CO}_2,\text{ads}} - N_{\text{CO}_2,\text{des}}$
Adsorbent performance score	$\text{APS} = S_{\text{ads}} \times \Delta N_{\text{CO}_2}$
Per cent regenerability	$R\% = \frac{\Delta N_{\text{CO}_2}}{N_{\text{CO}_2,\text{ads}}} \times 100\%$
Gas permeability	$P_i = \frac{(c_i \times D_{\text{self}, i})}{f_i} \quad i: \text{CO}_2, \text{ or } \text{CH}_4$
Diffusion selectivity	$S_{\text{diff}} = \frac{D_{\text{self}, \text{CO}_2}}{D_{\text{self}, \text{CH}_4}}$
Membrane selectivity	$S_{\text{mem}} = S_{\text{ads}} \times S_{\text{diff}}$

* x: adsorbed phase gas composition; y: bulk phase gas composition; N_{CO_2} : CO₂ uptake (mol/kg); i: gas species;
 P_i : gas permeability (Barrer), c_i : gas loadings used in EMD simulation (mol/kg), $D_{\text{self}, i}$: self-diffusivity of gas species (cm²/s); f_i : fugacity of gas species i (Pa).

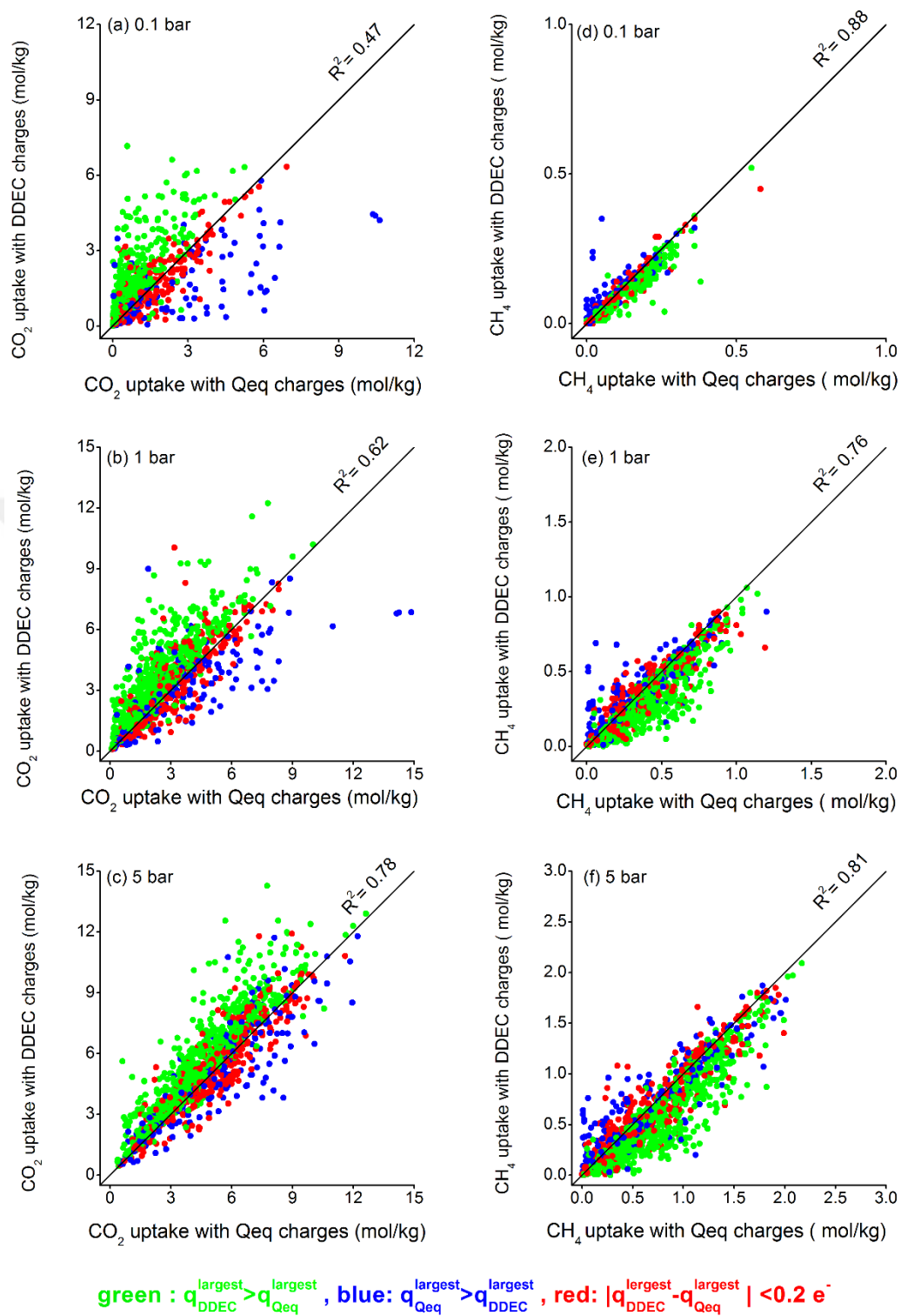


Figure B1. CO₂ uptakes (a-c) and CH₄ uptakes (b-f) obtained from simulations using Qeq and DDEC charges at 0.1, 1, 5 bar for CO₂/CH₄: 50/50 mixture.

Table B.2. Range of calculated adsorbent evaluation metrics.

Composition	Adsorbent metric	Range _{DDEC} (Range _{Qeq})	Range _{DDEC} (Range _{Qeq})
		P _{ads} :1 bar, P _{des} : 0.1 bar	P _{ads} :5 bar, P _{des} :1 bar
CO ₂ /CH ₄ : 10/90	ΔN_{CO_2} (mol/kg)	0.02-5.64 (0.01-5.51)	0.02-8.07 (0.02-5.43)
	S _{ads}	1.62-1633.80 (1.23-2477.74)	1.54-1068.04 (1.14-1329.03)
	APS (mol/kg)	0.03-2179.55 (0.02-2715.96)	0.03-846.23 (0.04-1910.94)
	R%	9.14-92.22 (3.93- 90.58)	2.52-82.07 (1.77-81.05)
CO ₂ /CH ₄ : 50/50	ΔN_{CO_2} (mol/kg)	0.09-10.17 (0.06-6.97)	0.03-8.30 (0.10-10.26)
	S _{ads}	1.66-1068.28 (1.02-1215.28)	1.54-883.75 (0.97-1009.64)
	APS (mol/kg)	0.17-1282.70 (0.11-3026)	0.20-706.53 (0.13-1315.55)
	R%	4.49-93.31 (3.65-91.02)	1.43-85.19 (2.42-83.74)

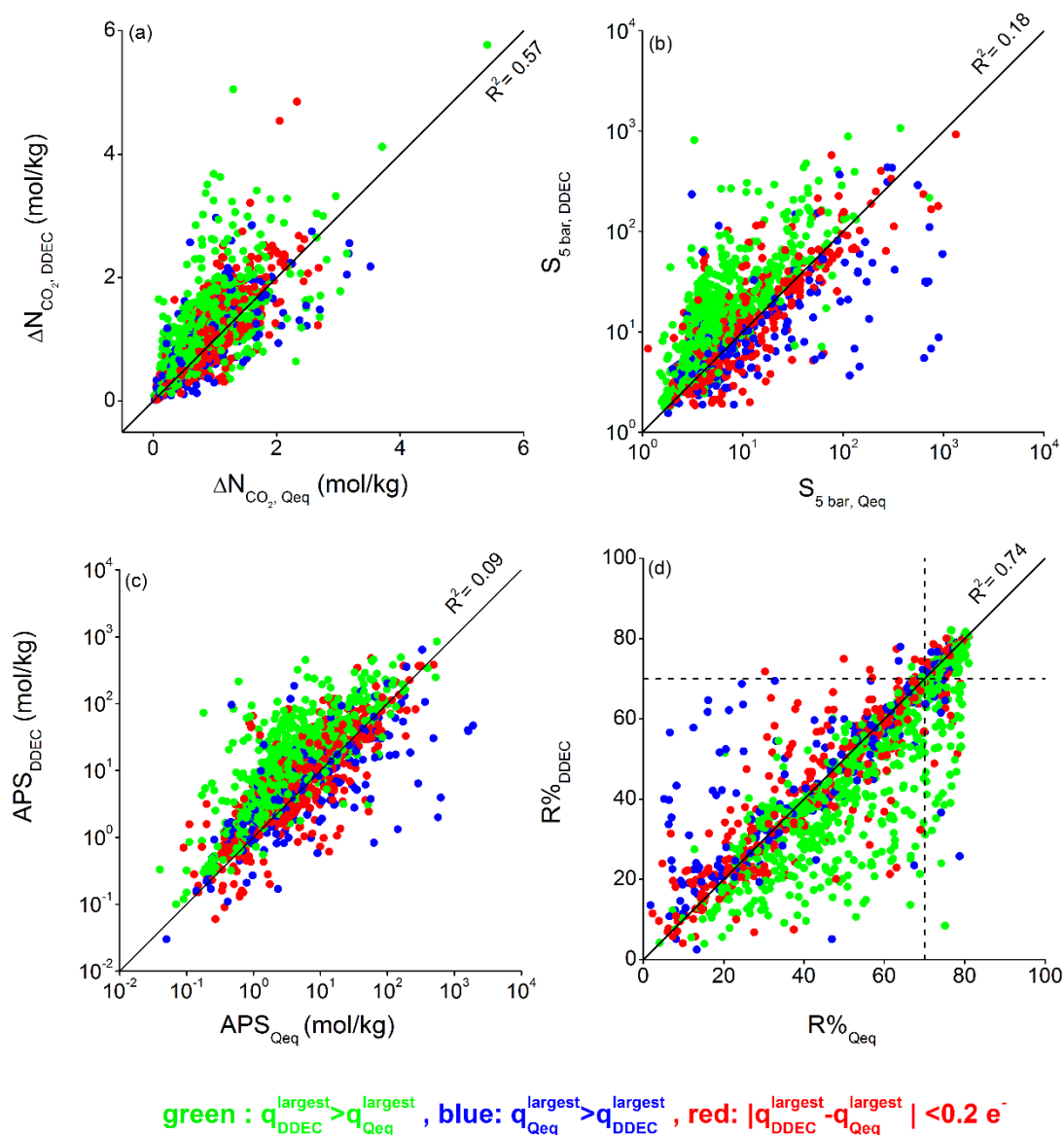


Figure B2. Calculated adsorbent performance evaluation metrics using Qeq and DDEC charges at PSA condition, 298 K for CO₂/CH₄:10/90 mixture; (a) ΔN_{CO_2} , (b) S_{ads} , (c) APS, (d) R%. Dashed lines in (d) show $R\% = 70\%$.

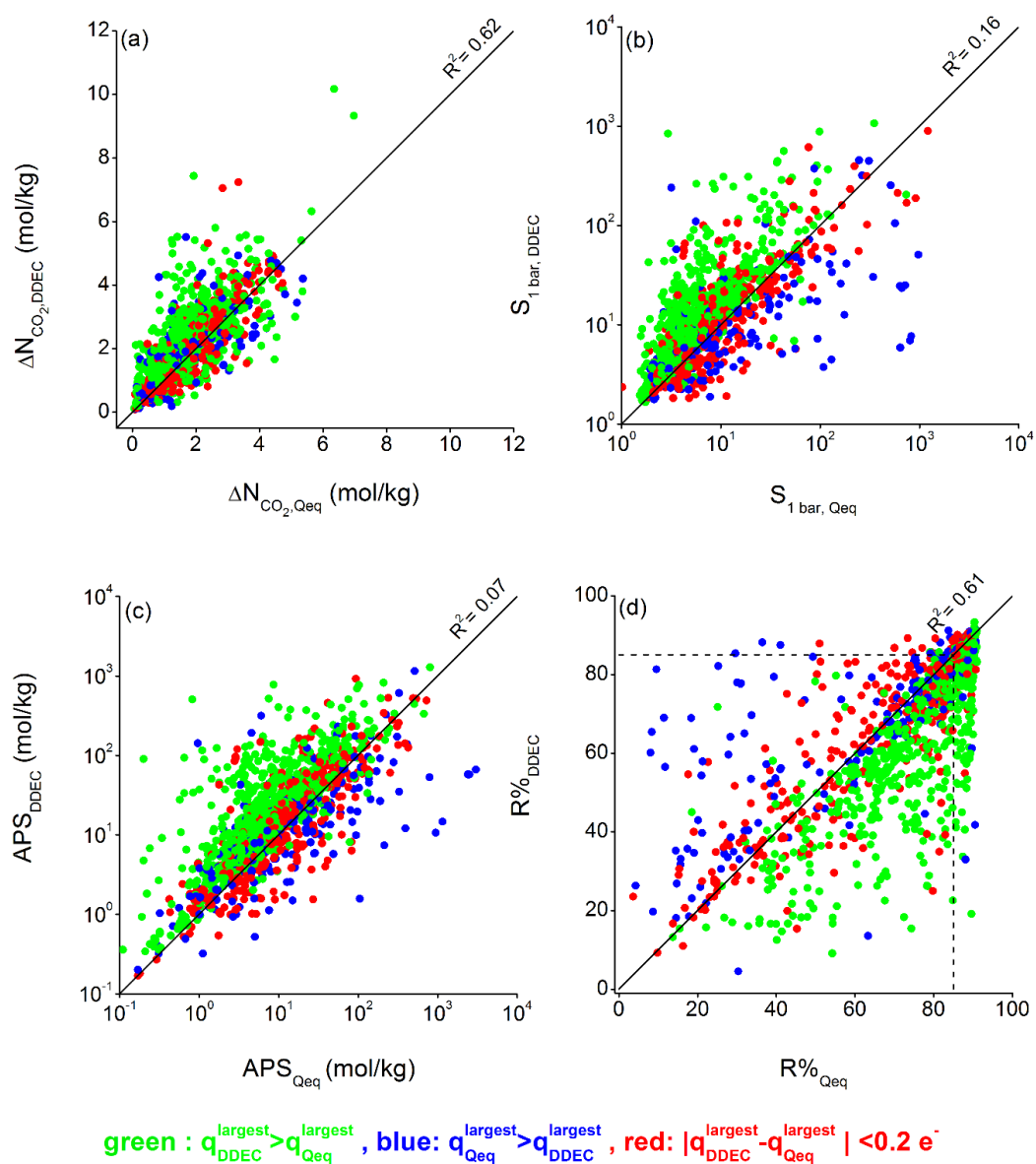


Figure B3. Calculated adsorbent performance evaluation metrics using Qeq and DDEC charges at VSA condition, 298 K for CO₂/CH₄:50/50 mixture; (a) ΔN_{CO_2} , (b) S_{ads} , (c) APS, (d) R%. Dashed lines in (d) show R% =85%.

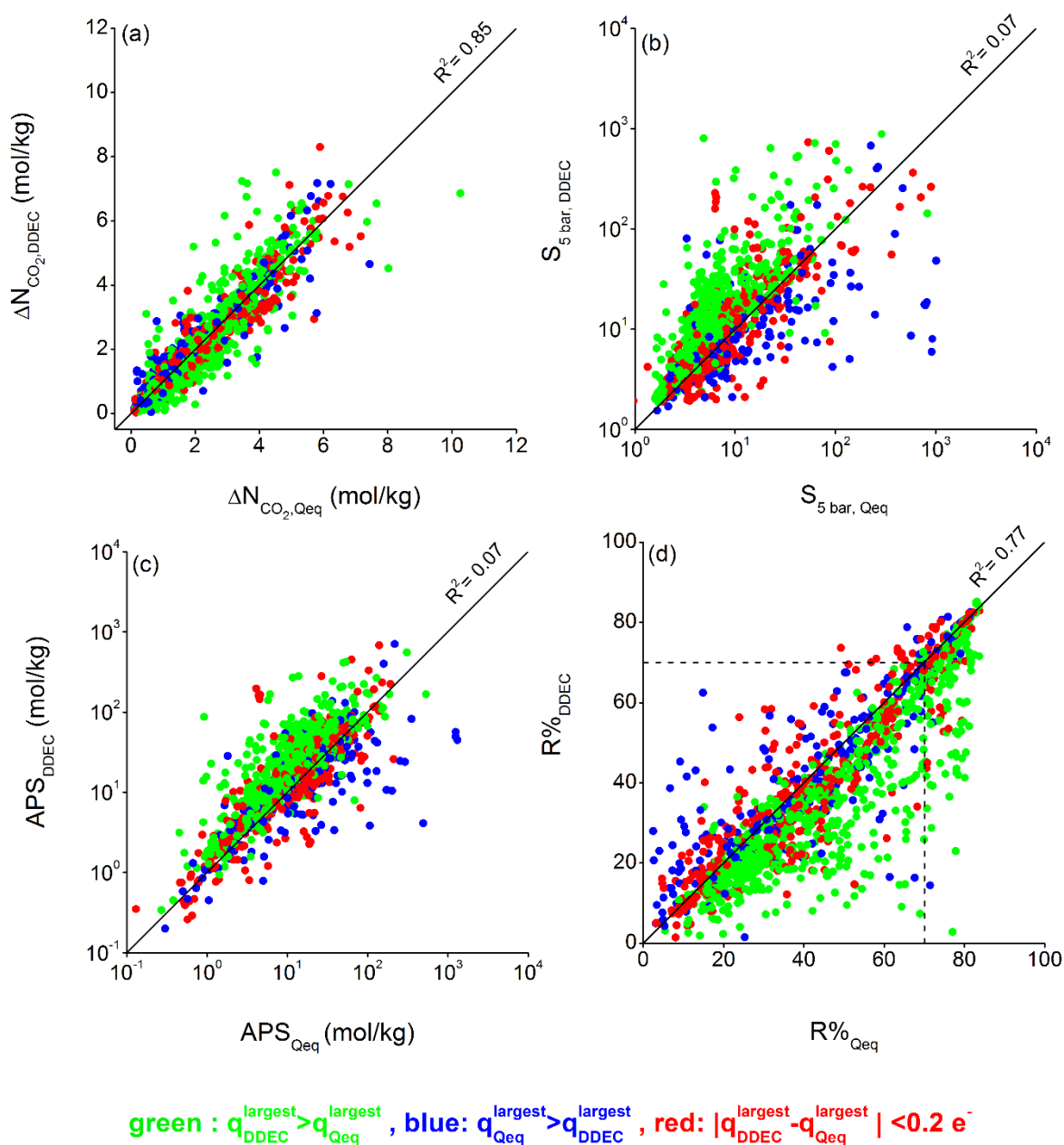


Figure B4. Calculated adsorbent performance evaluation metrics using Qeq and DDEC charges at PSA condition, 298 K for CO₂/CH₄:50/50 mixture; (a) ΔN_{CO_2} , (b) S_{ads} , (c) APS, (d) R%. Dashed lines in (d) show $R\% = 70\%$.

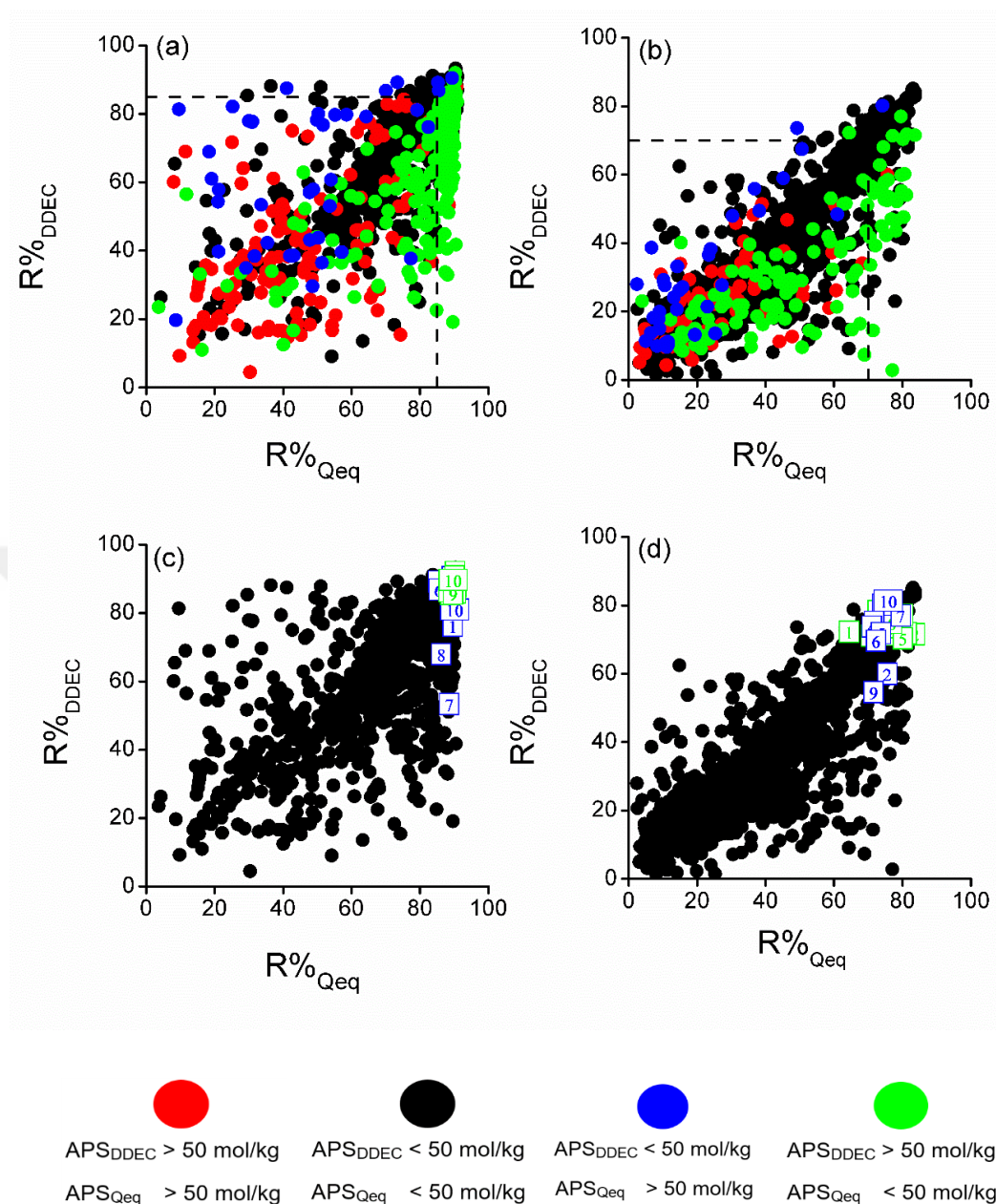


Figure B5. Comparison of R% of DDEC and Qeq-charged MOFs at (a, c) VSA (b, d) PSA conditions for CO_2/CH_4 : 50/50 mixture. Dashed lines show $R\%=85\%$ in (a), $R\%=70\%$ in (b). The top 10 MOFs identified by DDEC and Qeq methods are shown with green and blue, respectively.

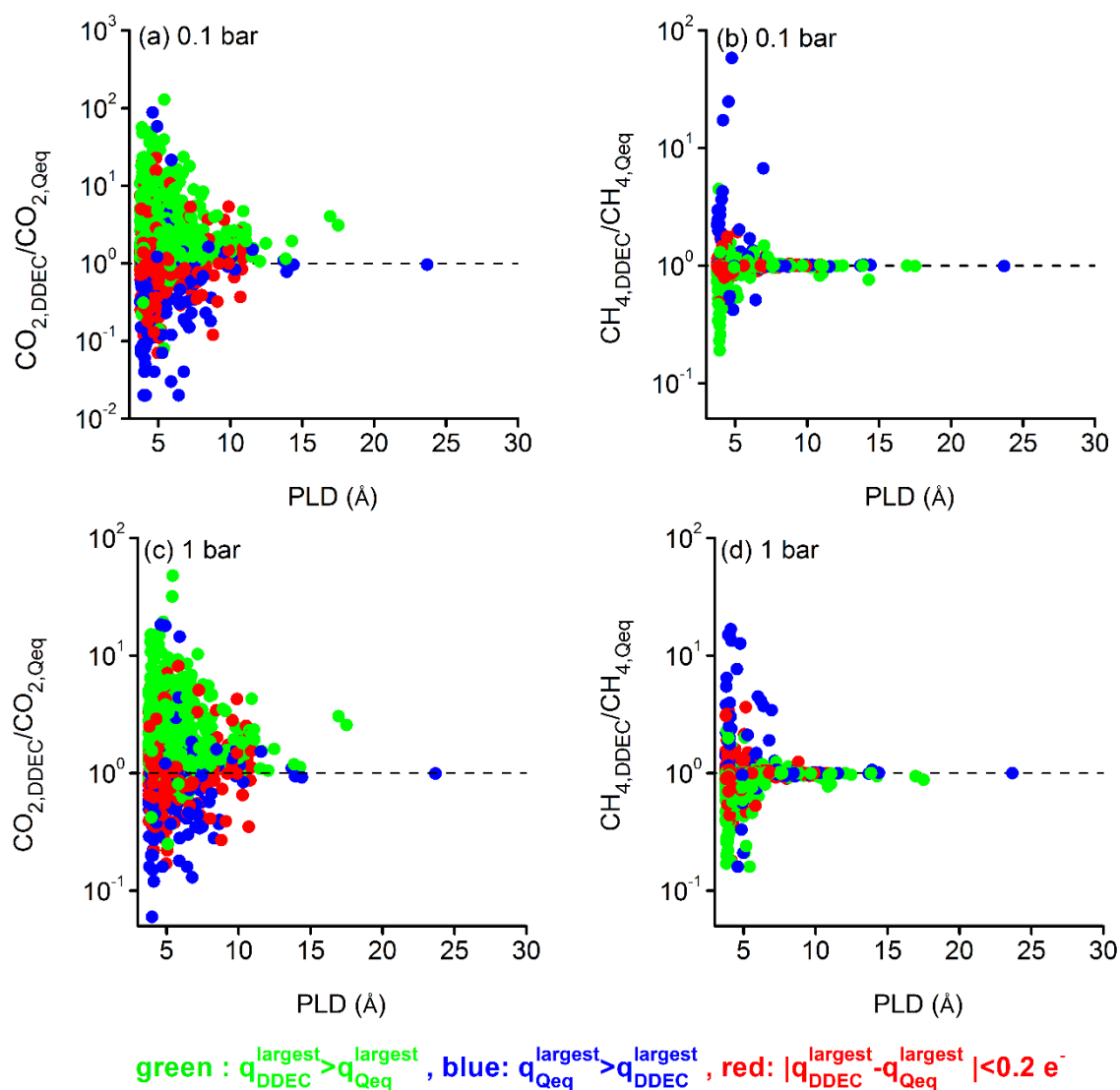


Figure B6. The ratio of (a, c) CO_2 uptakes (b, d) CH_4 uptakes computed by DDEC-charged to the ones computed by Qeq-charged MOFs as a function of PLD.

LIST OF PUBLICATIONS

Publications included in this thesis:

1. Altintas, C. and Keskin, S. "Role of Partial Charge Assignment Methods in High-Throughput Screening of MOF Adsorbents and Membranes for CO₂/CH₄ Separations" *Molecular Systems Design & Engineering* 5, 532-543 (2020).
2. Altintas, C. and Keskin, S. "Molecular Simulations of MOF Membranes and Performance Predictions of MOF/Polymer Mixed Matrix Membranes for CO₂/CH₄ Separations" *ACS Sustainable Chemistry & Engineering* 7, 2739-2750 (2019).
3. Altintas, C. and Keskin, S. "Molecular Simulations of MOF Membranes for Separation of Ethane/Ethene and Ethane/Methane Mixtures" *RSC Advances* 7, 52283-52295 (2017).
4. Altintas, C., Erucar, I. and Keskin, S. "Computational Screening of MOFs for CO₂ Capture" for the book "Metal-Organic Frameworks in Biomedical and Environmental Field" by Springer Nature. Under revision. (Only the "Methodology" part is adapted for thesis.)

Publications not included in this thesis:

1. Altintas, C., Avci, G., Daglar, H., Azar, A. N. V. , Erucar, I, Velioglu, S, and Keskin, S., "An Extensive Comparative Analysis of Two MOF Databases " *Journal of Materials Chemistry A* 7, 9593-9608 (2019).
2. Altintas, C., Avci, G., Daglar, H., Azar, A., Velioglu, S., Erucar, I. and Keskin, S. "Database for CO₂ Separation Performances of MOFs Based on Computational Materials Screening" *ACS Applied Materials & Interfaces* 10, 17257-17268 (2018).
3. Altintas, C., Avci, G., Daglar, H., Gulcay, E., Erucar, I. and Keskin, S. "Computer Simulations of 4,240 MOF Membranes for H₂/CH₄ Separations: Insights into Structure-Performance Relations" *Journal of Materials Chemistry A* 6, 5836-5847 (2018).
4. Altintas, C., Erucar, I. and Keskin, S. "High-throughput Computational Screening of the MOF Database for CH₄/H₂ Separations" *ACS Applied Materials & Interfaces* 10, 3668-3679 (2018).
5. Koyuturk, B., Altintas C., Kinik, F.P., Keskin, S., Uzun, A. "Improving Gas Separation Performance of ZIF-8 by [BMIM][BF₄] Incorporation: Interactions and Their Consequences on Performance" *Journal of Physical Chemistry C* 121, 10370-10381 (2017).
6. Kinik, F.P., Altintas, C., Balci, V., Koyuturk, B., Uzun, A. and Keskin S. "[BMIM][PF₆] Incorporation Doubles CO₂ Selectivity of ZIF-8: Elucidation of Interactions and Their Consequences on Performance" *ACS Applied Materials & Interfaces* 8, 30992-31005 (2016).
7. Altintas, C. and Keskin, S. "Computational Screening of MOFs for C₂H₆/C₂H₄ and C₂H₆/CH₄ Separations" *Chemical Engineering Science* 139, 49-60 (2016).
8. Altintas, C. and Keskin, S. "Molecular Simulations of Porous Coordination Network-based Mixed Matrix Membranes for CO₂/N₂ Separations" *Molecular Simulation* 41, 1396-1408 (2015).