Application of MOFs-membrane in post-combustion carbon capture for electricity and thermal energy plants

Kuangdi Zhu*

Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, Canada

* Corresponding Author Email: zkd123@student.ubc.ca

Abstract. Greenhouse gas emission typically carbon dioxide which result to global warming is becoming a very acute issue to human society. In order to achieve a sustainable development and society, various approaches to reduce carbon emission have been investigated and applied to industry where the majority of carbon emission happens in recent decays. Carbon capture is one of the key ways to address the emission and widely applied to coal-fired power plants. However, typically carbon capture process requires high energy input during the absorption and desorption process with lead to a low net carbon captured rate and high cost of operation. Materials with low energy penalty and high carbon affinity is desired to address this problem. In this research, a more advanced material, metal-organic frameworks (MOFs), for carbon capture under post combustion condition is introduced and evaluated from single material and cooperating with mixed-matrix-membranes to achieve membrane separation. Furthermore, MOFs are usually lack of stability and CO_2/H_2O selectivity. CALF-20 as the solution to these problems will be introduced later.

Keywords: Carbon capture, MOFs, Mixed-matrix-membrane.

1. Introduction

Global warming is an extremely pressing issue to human society in 21th century. According to International Energy Agency (IEA) report data [1], global CO_2 emissions keeps rising after 2019 pandemic reaching over 36.8 Gt annual emission in 2022, while this value was 2 Gt in 1900. Coal and natural gas show major contribution to the global energy-related greenhouse gas emissions with amount of 15.5 and 7.3 $GtCO_2$ eq in 2022 [1]. So far, coal-fired and natural gas power plants are still dominant to majority power supply in developing countries and industrial counties [1]. According to China Electricity Council (CEC), coal-fired power plants contribute to 58.4% overall electricity generation in 2022 [2] while in America, coal-fired power plant and natural gas power plants occupies 21.8% and 38.3% of total electricity generation in 2021 [3]. A significant number of countries rely on fossil fuels for power generation and heat generation even in some counties with high clean energy composition such as Canada, most of them using coal and natural gas as predominant heat source. In Canada, although the electricity generated by coal and natural gas only stands for about 17% [4], fossil fuels provide the majority amount of heat for public facilities and individual places heating and hot water supply, donating about 13% of the greenhouse gas emission in 2021 [5].

Therefore, approaches to allocate the carbon emissions from power plant by carbon capture, utilization, and storage (CCUS) technique is prior to sustainability and carbon neutralization [6]. Without utilization of CCUS technique, the only way to carbon neutral is get rid of fossil fuel usages which is a huge trade off for human society and difficulty for energy requirements [6]. The approaches of carbon capture are categorized into pre-combustion capture, oxy-fuel capture (in-combustion) and post combustion capture [7]. Post-combustion capture, as the most important technique for power plant carbon capture process [7], dealing with flue gas emitted from the power plant with pressure of approximately 1 atm, temperature of 40-60 ℃ and CO_2 concentration of 3-20% [8]. Several carbon capture processes have been investigated including membrane separation processes, chemical absorption process, cryogenic separation, electrochemical separation and physisorption processes [9]. Chemical absorption process carried out with aqueous monoethanolamine (MEA) is widely applied to existed CCUS-equipped power plant [10] capturing a significant amount of carbon emissions in

2020s [6]. However, with significant amount of energy penalty and high cost of operation (70 $/t CO_2) [10], new materials are desired for industrial application.

Metal-organic frameworks (MOFs) are crystalline nanomaterials with organic and ligand linkage. The microporosity and surface functionality make MOFs materials suitable for carbon capture processes under low temperature and pressure with relative low energy penalty. They are also good candidates for carbon storage at high pressure [9]. Based on the porosity and high tunability of MOFs materials, it's possible to tune them for a specific application condition. In recent studies, Calgary framework-20 (CALF-20) is investigated with high opportunity for industrial carbon capture application [11]. MOFs materials can be applied in various type of structure and composites including mixed-matrix-membranes, ionic liquid composites, pure MOFs materials in pellet or bed form, mixed-matrix-membrane (MMM)/MOFs/ionic liquid composites [9, 12-13]. In this research, application of single MOFs materials and MOFs/MMM will be discussed and evaluated.

2. Application of MOFs

MOFs are chemicals with usually high crystallinity consist of central metal cluster with coordinated organic ligands. The MOFs with high variety and tunability make them suitable for different types of applications including carbon capture which is an issue catching more and more public attentions recently. CO_2 is considered to have a greater quadrupole moment than nitrogen which means a polar functional group especially base amine functional groups can result in a high carbon dioxide affinity [14]. The selectivity also related to the charge of central metal and the basicity of the functional groups. Generally, MOFs have a relatively high CO_2/N_2 selectivity which can be modified by different strategies, including surface functionalization by polar functional groups especially amine bases with high basicity [14], exposed metal cation which can be further enhanced by using metal cations with larger coordinate charges [14], molecular sieving effect which is caused by the microporosity of the MOFs materials and based on the larger molecular size of CO_2 compared with H_2O and N_2 in flue gas composition [14], target modifications of linker unit and metal unit and confident solvent and MOFs composites. There also exist some special effects including small pole effect [15] which will be discussed later, and increased accessibility of alkylamine chains led by larger pore size and surface area essentially presented in metal dobpdcs (M2 dobpdc) [16]. Bunch of studies on different families of MOFs have been carried out and shows that MOFs have extraordinary performance of carbon capture under low pressure and temperature. However, they are usually lack of thermal and mechanical stability together with the high cost of synthesis restricting the industrial application of MOFs. In order to address these problem, mixed-matrix-membranes incorporated with MOFs and other materials has been used and this will be discussed later.

2.1. MOFs with high resistance to water

Aside of thermal and mechanical stability, the resistance to water is getting more attentions recently, since water molecules are highly polarized and the high humidity of flue gas led to a competitive adsorption between water and CO_2 [15, 16]. Water can result in a huge drop in the CO_2 adsorption capacity, because the strong polarity of water molecules makes it able to occupied the available sites for CO_2 adsorptions [16]. In some MOFs, water can lead to hydrolysis of the organic linkage and cause the defect in MOFs structure [14]. Therefore, for most adsorption processes applying MOFs as adsorbent, water must be removed before adsorption happens which requires huge amount of heat and cost of operation [17]. Therefore, investigating MOFs with high resistance to water and CO_2/H_2O selectivity is prior to industrial application. Several kinds of Mg2 dobpdcs with different alkylamine functional groups are examined and screened. And the researchers analyze the binding strength and water effects quantitatively [16]. The results show that the presence of water makes the induced ammonium carbamate chains which is responsible for CO_2 chemisorption in ndmpn-Mg2 (dobpdc), more stable by hydrogen bonding interaction [16], giving a CO_2 capacity of 1.57 mmol/g at 60 ℃ adsorption and 145 ℃ desorption. The capacity is relatively low compared with

other MOFs, but this result reveals a new way of tuning MOFs especially metal dobpdcs which are family of interest among MOFs.

2.2. Carbon capture

Recently, some MOFs with super hydrophobic properties have been investigated including CALF-20 (2020) [11, 18] and ZJU-620 (Al) (2023) [19]. Among these MOFs, CALF-20 is one of the most applicable MOF with high H_2O/CO_2 selectivity up to 40% relative humidity (RH). The high H_2O/CO_2 selectivity is induced by the small pore effect [15] where the quadruple moment is reinforced by the summation of van der Waals interactions within the pores. The resulted interaction is stronger than hydrogen bonding which is responsible for the water adsorption in CALF-20. By this, there exists no functional groups for water to bond at a low RH. The zero-loading heat of CO_2 and H_2O which refers to the heat of negligible amount of gas is adsorbed onto a surface, is -33.5 kJ/mol and -17.5 kJ/mol respectively [11]. This confirms that CALF-20 indeed has a high CO_2 affinity compared to H_2O. Under the real-world simulation conditions which includes impurities under temperature of 20 ℃ and pressure of 1 bar, the CO_2 loading capacity is shown to be about 3.8 mmol/g [11]. The CALF-20 experience a transformation of structure after exposed to an increasing RH gas, about 11-23% RH at room temperature [18] where the central five coordinated zinc metal changes into a four coordinated metal due to the presence of bidentate oxalate anions instead of bis-bidentate oxalate anions in original structure. The new structure is called beta structure while the original one is called alpha structure. This transformation is probably resulted by the hydrogen bonding between oxalate and water. The study turns out that there exists a slightly increase in the affinity of CO_2 in beta structure and the increasing adsorbed amount of CO_2 will not affect the affinity significantly. Thus, the adsorbed CO_2 is considered to be neutral towards to the free CO_2 and will not affect the adsorption mechanism in CALF-20. On the other hand, the notable increase in the CO_2 affinity suggests that the smaller pore volume in beta structure will further enhance the summation effect mentioned before. Through this study, CALF-20 is considered to be a flexible structure rather than a ridged crystal which provides a key information for further simulation and modelling to process. Besides these theoretical advantages, CALF-20 is extremely durable and highly scalable. Due to the high solid content rate and high yield over 90%, CALF-20 is able to be produced at 550 kg/m^2 space-time yield for precipitation step where this value for zeolites is about 50-150 kg/m^2. For durability consideration, CALF-20 only experience a loss of 1.3% of the overall capacity after application of real fuel gas composition stream for 6 days of operation [11]. The extraordinary performance of CALF-20 makes it the most considerable material to be applied on industrial scale.

2.3. Typical MOFs adsorption processes

Typically, the adsorption conducted by MOFs undergoes temperature swing adsorption (TSA) or vacuum swing adsorption (VSA) process. The basic theory supporting TSA and VSA is applying the difference in adsorption capacity of target component at different temperature and pressure to regenerate the adsorbent [17]. Limited to existed materials usually sensitive to moister composition, the fuel gas has to undergoes a dry out process before adsorption happens which typically includes high energy consumption. According to previous study, at a recovery level of 90%, over 70% of the energy supply is consumed by heater in TSA process and vacuum remover in VSA process [17]. Thereby, simulating more energy favourable process is key to reduce the cost of operation for physisorption processes. In the following section, an alternative way of carbon capture process carried out by MOFs/MMM is discussed to meet the purpose of reducing energy penalty during the regeneration process, since a typical membrane usually do not require to be regenerated during the operation.

3. Appliaciton of MMM

MMM belongs to heterogeneous systems with polymer membranes filled up by dispersed nanoparticles [12], in this case MOFs disperse into the polymer membranes to enhance the CO_2/N_2 separation performance by increasing the selectivity and permeability. The advantages of MMMs separation with regards to MOFs physisorption is considered as lower cost, higher efficiency and advanced thermal favourability, since membrane separation is a relatively mature technology and under high temperature and pressure situations such as pre-combustion capture or chemical plants (CaO production), the gas permeability is driven by the thermal condition and almost no energy penalty or extra process is required to restore the capture materials theoretically [12]. As shown in Fig. 1, the separation of CO_2 includes a synchronized adsorption on the flue gas rich side and desorption at CO_2 rich side which differs from the typical VSA or TSA process mentioned before [13]. Without the external energy demand, the process is highly energy favorable with extremely low cost of operation which could be 50 \$/CO_2 removed compared to 64 \$/CO_2 removed by PIM-1 membrane and 70 \$/CO_2 removed by MEA mentioned before. And membrane separation technology shows higher cost-efficiency at a small scale of operation, but a lower cost-efficiency at larger scale of operation compared to traditional absorption process [17]. This is caused by the compression processes for adsorption and vacuum process for desorption [17]. Cost of compression and vacuum process occupies over 80% of the annual operation cost which donates over half of the annual cost. Therefore, investigating materials with high selectivity and permeability at low pressure condition is key to reduce the cost of operation for membrane separation process where permeability is a measure of ability of gas to transfer through the membrane materials and selectivity is a measure of the ratio of CO_2/N_2 separated by the capture material in this case.

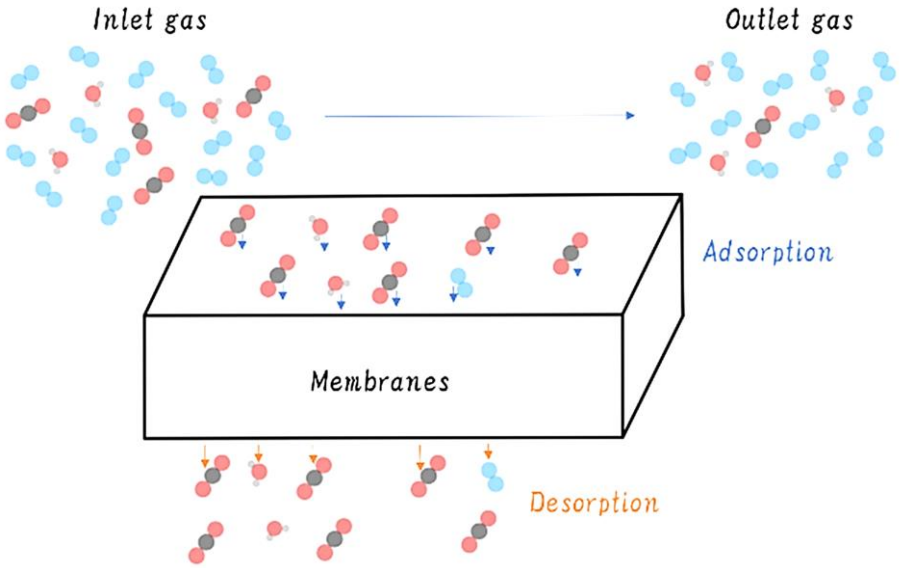

Fig. 1 The process description of MMM separation process for carbon capture in flue gas.

3.1. Advantages

MMMs as mentioned before, have higher permeability and selectivity compared to traditional membranes with the help of internal nanoparticles and a higher thermal and mechanical stability with respect to MOFs materials with the help of polymer matrix [13]. The cooperation with MOFs enables polymer membranes to be highly tunable on selectivity and other specialized functionalities, due to MOFs are highly tunable. As mentioned before, polar functional groups are favorable for high carbon affinity and surface functionalization with organic functional groups especially amine bases have a significant improvement on the CO_2/N_2 selectivity [14]. On the other hand, MMMs usually suffers from interfacial defects which is lead by the low compatibility between organic polymeric structure and inorganic fillers [13]. Moreover, the over loading of nanofiller will also lead to interfacial defects

as the overdose fillers will occupy the free spaces and attracted each other to form agglomeration. The presence of interfacial defects is able to drop the selectivity, permeability and stability of MMM. Increasing the compatibility between the filler content and polymer framework is an approach widely used to overcome this limitation which also exists in MOFs/MMM system.

PIM-1 is incorporated with amino-functionalized NUS-8 to give MOFs/MMM with high compatibility and carbon separation performance including high selectivity and permeability. The result show that with 10 wt% of MOFs filler, the CO_2 permeability gives an extremely high value of about 14000 Barrer and CO_2/N_2 selectivity of approximately 30. Those values for PIM-1 which is a typical polymer membrane material for carbon separation are 7500 Barrer and 14 respectively. The high compatibility between PIM-1 and NUS-8-NH_2 nanosheet is found to be induced by the formation of hydrogen bonds between these two materials which prove that MOFs are able to increase the compatibility between the polymer membrane structure by surface functionalization. PIM-1/NUS-8-NH_2 shows a rising CO_2 permeability from 7500 Barrer at 0 wt% loading to a maximum of about 15000 Barrer at 10.4 wt% and 13.0 wt%. As the number of NUS-8 with high porosity disperse into the MMM structure increases, an increasing free volume between polymer chains is induced. High amount of free volume enhances the gas permeability among the PIM-1 structure which has relatively high gas permeability itself. Together with the interface regulation, which is caused by the hydrogen bond between MOFs nanosheet and polymer chains [20]. However, as the MOFs loading goes above 13 wt%, the gas permeability experiences a continuously. This phenomenon is a result of the filling up of free volume among the polymer chains. As the overdose MOF nanofiller filling up the free volume at the end of polymer chains, the polymer structure will show more glassy properties which means the material is becoming more brittle and a decreasing gas permeability exists. Similar with the CO_2 permeability, the CO_2/N_2 selectivity with respect to MOFs loading undergoes same pattern. The peak value is reported at 5.6 wt% with value of about 32.5. At 10.4 wt%, as mentioned before, the permeability and selectivity are considered to be the best performance for this structure and is above the separation performance line. This experiment is conducted under temperature of 298 K and pressure of 2 bar with mixture with CO_2/N_2 ratio of 20/80 which means this material is suitable for post-combustion capture application. In some cases, MOFs nanosheet is able to create shortcut for gas to pass through in the MMM structure. Generally speaking, MOFs fillers with small pores, surface areas, and moderated porosities will generate MMMs with high CO_2/N_2 selectivity according to simulation by previous study.

3.2. Limitation

However, limitations including interfacial defects, material selection, trade-off between performance criteria. As mentioned before, interfacial defects happens when the compatibility of fillers and membrane materials is low. For MOFs, this can be addressed by surface functionalization and modified the morphology to select a most compatible combo between the filler materials and MMMs. For the trade-off between performance criterion, as discussed before, the trade-off happens as the filler loading increases. Therefore, simulation of these two criteria is key to address this limitation. However, these models are not able to give a more general prediction to the MOFs/MMMs performance, a more modern way to simulate the performance is by applying machine learning [21] which is able to identify and simulate the relationship between different variables and even nonlinear interpolations by different machine learning algorithms. By applying random forest models trained by literature data on CO_2/CH_4 separation data, they report that the MOFs with pore size greater than 1 nm and surface area around 800 m^2/g gives the best separation performance [21]. Overall speaking, by applying machine learning to the prediction and simulation of MOFs/MMMs performance based on their complexity gives a better approach able to work with limited amount of data available and is very likely to be applied further even on the simulation of industrial application and design of new MOFs/MMMs for different application purpose. Furthermore, the few numbers of polymers suitable for MOFs/MMM synthesis leads to a limitation on material selection. The most promisable polymers for this application are shown to be PIM-1, PEBAX, cellulose acetate and polyether sulfone. These

polymers are not environmentally friendly which means emission occurs during the whole lifecycle [12]. The industrial production of PIM-1 undergoes precipitation polycondensation in dimethylsulfoxide and via polycondesation in N, N, N', N'-tetramethylurea making PIM a non-biodegradable polymer with high emission during the production process [22]. Therefore, developing new polymer and synthesize techniques are also important to further improve the materials to be applied in the future.

4. Conclusion

To be concluded, in this research, a comparation between single MOFs materials and MOFs composites with MMM is made. Overall speaking, MOFs materials show great adsorption performance compared with usual materials with promisable capacity and selectivity. Although most of MOFs are lack of stability and selectivity against water moister, hydrophobic MOFs such as CALF-20 are clearly crucial for industrial application. To achieve a more advanced approach of carbon capture, MOFs are cooperated with polymer membranes which is able to make the separation process more theoretically energetically favourable to minimize the cost of operation. The existed membrane separation processes are based on the MOFs with low stability and selectivity under the presence of water and leading to a significant energy penalty during the water removal process. Therefore, cooperating with more advanced MOFs including CALF-20, is a valuable way to be tested and studied further.

References

[1] IEA (2023), CO2 Emissions in 2022, IEA, Paris https://www.iea.org/reports/co2-emissions-in-2022

[2] National Bureau of Statistics. China electricity industry economic performance report for 2022, National Bureau of Statistics, 2023, Available: lwzb.stats.gov.cn/pub/lwzb/fbjd/202306/W020230605420997463323.pdf

[3] EIA. (2023 November 29th). U.S. Energy-Related Carbon Dioxide Emissions, U.S. Energy Information Administration, https://www.eia.gov/environment/emissions/carbon/

[4] Statista. Electricity generation in Canada in 2022, by energy source. Statista, 2022, Available: https://www.statista.com/statistics/248155/electricity-generation-in-canada-by-type/

[5] Government of Canada. Greenhouse gas emissions. Government of Canada, 2023, Available: https://www.canada.ca/en/environment-climate-change/services/environmental-indicators/greenhouse-gas-emissions.html

[6] IEA. The role of CCUS in low-carbon power systems, IEA, Paris, 2022, Available: https://www.iea.org/reports/the-role-of-ccus-in-low-carbon-power-systems

[7] Qingru C., Rui Z., Tiankun W., et al. A 150 000 t·a−1 Post-Combustion Carbon Capture and Storage Demonstration Project for Coal-Fired Power Plants. Engineering, 2022, 14: 22-26.

[8] Jia Yen L., Lock Hei N., Siti Salwa H. A review of CO2 adsorbents performance for different carbon capture technology processes conditions. GHG, 2021, 11(5): 1076-1117

[9] Mohammad Y., Mashallah R., Muhammad D., et al. Recent progress and remaining challenges in post-combustion CO2 capture using metal-organic frameworks (MOFs). Progress in Energy and Combustion Science, 2020, 80: 100849.

[10] Alisson A. V. J., Rafael C. A., Francois M., et al. Exergy and economic analysis of the trade-off for design of post-combustion CO2 capture plant by chemical absorption with MEA. Energy, 2023, 280: 128004.

[11] Jinbin L., Tian T. N., Ramanathan V., et al. A scalable metal-organic framework as a durable physisorbent for carbon dioxide capture. Science, 2021, 374(6574): 1464-1469.

[12] Hakan D, Gokhan O. A., Hasan C. G., Seda K. MOF Membranes for CO2 Capture: Past, Present and Future. Carbon Capture Science & Technology, 2022, 2: 100026.

[13] Aviti K., Shubham K., Sukanya K., et al. Mixed Matrix Membranes for Carbon Capture and Sequestration: Challenges and Scope. ACS Omega, 2023, 8(20): 17511-17522.

[14] Kenji S., David L. R., Jarad A. M., et al. Carbon Dioxide Capture in Metal–Organic Frameworks. Chemical Reviews, 2012, 112(2): 724-781.

[15] Arvind R., George K. H. S., Tom K. W. The Challenge of Water Competition in Physical Adsorption of CO2 by Porous Solids for Carbon Capture Applications. Advanced Materials, 2023, 4: 2301730.

[16] Stefano E. Z., Jose-Fransisco P., Antonio G., et al. Postcombustion CO2 Capture: A Comparative Techno-Economic Assessment of Three Technologies Using a Solvent, an Adsorbent, and a Membrane. ACS Engineering Au, 2021, 1(1): 50-72.

[17] Stefano E. Z., Jose-Fransisco P., Antonio G., et al. Postcombustion CO2 Capture: A Comparative Techno-Economic Assessment of Three Technologies Using a Solvent, an Adsorbent, and a Membrane. ACS Engineering Au, 2021, 1(1): 50-72.

[18] Zhihengyu C., Ching-Hwa H., Xiaoliang W., et al. Humidity-Responsive Polymorphism in CALF-20: A Resilient MOF Physisorbent for CO2 Capture. ACS materials letters, 2023, 5: 2942-2947.

[19] Laigang H., Wenhao W., Ling J., et al. Methyl-Functionalized Al-Based MOF ZJU-620(Al): A Potential Physisorbent for Carbon Dioxide Capture. Energy, Environmental, and Catalysis Applications, 2023, 15(37): 43925-43932.

[20] Jingmeng W., Mengjie N., Chao Y., et al. Interface regulation of mixed matrix membranes by ultrathin MOF nanosheet for faster CO2 transfer. Journal of Membrane Science, 2022, 642(15): 119991.

[21] Jian G., Tan H., Wei L., et al. Design and prediction of metal organic framework-based mixed matrix membranes for CO2 capture via machine learning. Cell Reports Physical Science, 2022, 3(5): 100864.

[22] Ponomarev I. I., Razorenove Y. D., Blagodatskikh V. I., et al. Polymer with Intrinsic Microporosity PIM-1: New Methods of Synthesis and Gas Transport Properties. Polymer Science, Series B., 2019, 61: 605-612.