POROUS MATERIALS FOR CO_2 CAPTURE IN GEOTHERMAL SYSTEMS

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Keywords: *CO2 capture, MOFs, COFs*

ABSTRACT

The manifestation of the effects of climate change has underlined the need to curb down the levels of carbon dioxide (CO_2) emitted in the atmosphere. The shift towards renewable energy (RE) sources has significantly decreased global CO_2 emissions. While a zero carbon emission for the energy sector is unrealistic considering a full life cycle assessment; geothermal energy, which remains a reliable RE, has the highest CO_2 emission equivalent per kilowatt-hour (kWh) during operations, compared to the other RE sources. Thus, there is a continuing movement within the geothermal industry for decarbonization. Present carbon capture and storage (CCS) methods include injecting CO_2 into a porous reservoir below an impermeable caprock whether as a supercritical fluid or dissolved in either freshwater or geothermal brine. While these technologies effectively decrease CO_2 emissions, they are energy intensive, require additional infrastructure and specific geological conditions. Thus, there is a need to look for alternative methods to help the decarbonization of the energy sector. Porous materials are being studied as alternatives to selectively capture CO_2 from flue gas emitted from traditional thermal energy power plants. Metal organic frameworks (MOFs) and covalent organic frameworks (COFs) belong to this class of materials that use their high porosity and surface area to capture CO_2 either by chemisorption or physisorption. MOFs and COFs can also be designed not only to store CO_2 but convert it into other useful compounds. It is therefore proposed to explore the use of MOFs and COFs to capture CO_2 in geothermal systems.

1. BACKGROUND

1.1 Greenhouse Gas (GHG) emissions in geothermal power plants

Recent extreme weather conditions such as super typhoons that cause excessive flooding or very high temperatures that lead to droughts or forest fires have reinforced the harsh reality of climate change all over the world. There have been a lot of significant efforts from different nations to meet the required levels of carbon emissions by 2030 just to keep the average global temperature rise at 1.5°C (Masson-Delmontte et al., 2018). Part of these massive changes has been the shift in the energy sector from traditional thermal energy powerplants to renewable sources of energy (RE) – such as geothermal, wind, solar and hydrothermal – even with some countries promising to be coal-free by 2030.

Geothermal energy, which is the most reliable renewable energy source, is increasingly being noticed as having the highest GHG (CO_2 only) emission compared to the other sources of renewable energy. On a worldwide average, the GHG emission from geothermal systems at 128 g CO_2/kWh are much lower than that of traditional thermal power plants which range from 1,030 gCO_2/kWh (subcritical circulating fluidized bed coal-fueled power plant) to 580 gCO_2/kWh (open cycle gas-fueled power plant) (Fridriksson et al., 2016). However, a few outliers were reported to reach GHG emissions of 900-1300 gCO_2/kWh which were observed to occur in rare high temperature carbonate-rich geothermal reservoir (Fridriksson et al., 2016). Within New Zealand, the average GHG emission (CO_2 and CH_4) is 76 gCO_2e/kWh, but with high levels reaching 340 gCO_2e/kWh for Ohaaki and 304 gCO_2e/kWh for Ngawha (McLean & Richardson, 2019). Figure 1 shows a comparison of the GHG emissions from different energy sources worldwide and within New Zealand; the values for the worldwide estimates may be slightly higher considering that the CH_4 equivalent in CO_2 was not included. The estimated values show that while geothermal energy has significantly lower GHG emissions compared to coal-fired or gas-fueled powerplants; however, when these powerplants will eventually be phased out, geothermal energy has significantly higher GHG emissions than the other renewable energy sources which has zero GHG emissions during operations.

Proceedings 43rd New Zealand Geothermal Workshop
23-25 November 2021
Wellington, New Zealand
ISSN 2703-4275

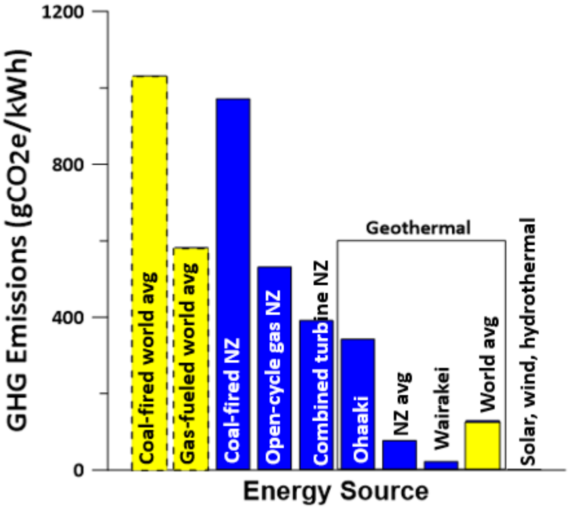

Figure 1. Comparison of GHG Emissions from different energy sources: worldwide averages (2016) and within New Zealand (2018). Solid bars include CO_2 and CH_4 emissions, while dashed lines only count CO_2 emissions so values may be slightly higher. (Fridriksson et al., 2016; McLean & Richardson, 2019)

A zero carbon emission for the energy sector is unrealistic considering a full life cycle assessment (LCA) of powerplants that takes into account all the associated emissions from the building, operating, and decommissioning the powerplants, regardless of the energy source (Mclean et al., 2020). Thus, when the median values of a full LCA of powerplants are considered, the four main RE sources continue to have significantly lower GHG emissions compared to coal; and geothermal energy now has comparable LCA emissions as solar energy from photovoltaic cells (Figure 2) (Mclean et al., 2020). In both operational and full LCA, geothermal still has a high GHG emission compared to wind and hydrothermal. Thus, there is a conscious ongoing movement within the geothermal industry to further lower or eliminate the GHG emissions during operations.

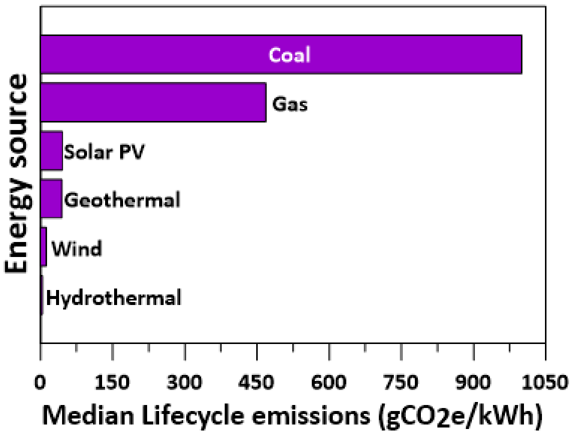

Figure 2. Median lifecycle emissions from different energy sources in New Zealand (Mclean et al., 2020)**.**

It is important to note that the GHG emissions in geothermal fields vary over time. Most medium to high temperature geothermal systems start out as liquid-dominated systems. After years of operations, the massive amount of fluids taken out from the reservoir do not get fully replenished even with the practice of reinjection and can thus lead to pressure drawdown within the reservoir. The pressure decline results in the lowering of the boiling temperature of the geothermal fluids and thus increasing the volume of vapor within the reservoir resulting in a steam cap (Fridriksson et al., 2016). Boiling due to pressure drawdown is usually characterized with an observed increase in CO_2 concentrations in the vapor phase of the extracted geothermal fluid. While the effects of the steam cap formation to GHG emissions varies and is dependent on the mode of operations; in general, vapor-dominated geothermal systems have higher GHG emissions compared to liquid-dominated ones (Fridriksson et al., 2016). However, it has also been observed in Iceland and Italy that the concentration of gases within steam caps also decreases over time and thus gradually lowering GHG emissions (Fridriksson et al., 2016). On the other hand, it had been observed in New Zealand that the degassing of the geothermal reservoir due to operations and emissions from thermal areas led to the decrease in GHG emissions (McLean & Richardson, 2019).

1.2 Carbon capture and sequestration in geothermal systems

The initial carbon capture and storage (CCS) method was to inject supercritical CO_2 into a porous reservoir below an impermeable caprock which is rather costly at a large scale, especially when it requires additional transport to the injection site (Kervévan et al., 2014; Randolph & Saar, 2011). Alternative CCS technologies were developed within the geothermal industry – Iceland's CarbFix and France’s CO2-DISSOLVE – which dissolve CO_2 in either freshwater or geothermal brine before it is reinjected into the same reservoir (Kervévan et al., 2014; Strandmann et al., 2019). France’s CO2-DISSOLVE project which stands for CO_2 Dependable Injection and Storage System Optimized for Local Vaporization of the geothermal Energy Delivered involves the use of a closed-loop low-enthalpy geothermal doublet system: starting with a production well extracting two-phase fluids, the fluids go through a heat exchanger and then using Pi-Innovation’s patented aqueous post-combustion capture system (Pi-CO_2) to dissolve back the CO_2 into the brine; after which the CO_2-saturated brine will be reinjected back into the reservoir (Kervévan et al., 2014). On the other hand, Iceland’s CarbFix starts with the separation (abatement) of H_2S from CO_2, the CO_2 gas is then diverted towards a reinjection well that at the same time has water pumped into it separately at a rate of 27 L/s for every 1kg/s of CO_2 at 25°C (Ragnheidardottir et al., 2011). CO_2 and water remain to be separately injected up to 350m depth wherein the CO_2 becomes dissolved in water and then at 500m depth the saturated CO_2-water reaches the aquifer (Ragnheidardottir et al., 2011). Subsequent water-to-rock interactions with the basaltic crust will eventually lead to formation of carbonate minerals, thus fixing CO_2 into a rock (Strandmann et al., 2019).

In other areas, the geothermal plants in Turkey that have the high GHG emissions are capturing CO_2 gas and selling it as liquid CO_2 or dry ice (Reynir et al., 2010). Germany is currently investigating the use of CO_2-plume as the heat carrier in low temperature geothermal systems that have high porosity and permeability (Mcdonnell et al., 2020). In New Zealand, two-phase fluids from the Tauhara geothermal field are used to dry timber and was observed to reduce emissions by 20,000 CO_2e/kWh (Mclean et al., 2020). While these technologies effectively decrease CO_2 emissions, they are energy intensive, require additional infrastructure and sometimes specific geological conditions. Thus, there is a need to look for alternative methods to help the decarbonization of the geothermal energy sector.

2. POROUS MATERIALS AS ADSORBENTS

There has been a lot of studies focused on developing adsorbents for removing CO_2 from flue gas - which contains 12-15% CO_2 – produced by coal and gas powerplants (McDonald et al., 2012). Stationary sorbents operate either under: (a) Temperature Swing Adsorption (TSA) – wherein it adsorbs gases at a low temperature (55-60°C) and is regenerated (desorb gas) by increasing temperatures (up to 150°C) at a constant pressure (1.01 bar); (b) Pressure Swing Adsorption (PSA) – wherein gases are adsorb at high pressures (6 bar) and gets desorbed by lowering the pressures (1.5 bar) at a constant temperature; or (c) Vacuum Swing Adsorption (VSA) – another version of PSA but the pressure is lowered below 1.01 bar and a vacuum is applied to facilitate desorption (Figure 3) (Espinal et al., 2013). Several liquid and solid adsorbents have been developed and were found to be cheaper and easy to use (McDonald et al., 2012). To get the overall efficiency of the adsorbent, one of the parameters used is the %total uptake (%wt) – the ratio of the total weight of the adsorbed gas and the sum of the weight of the adsorbed gas and the adsorbent (Yaghi et al., 2019).

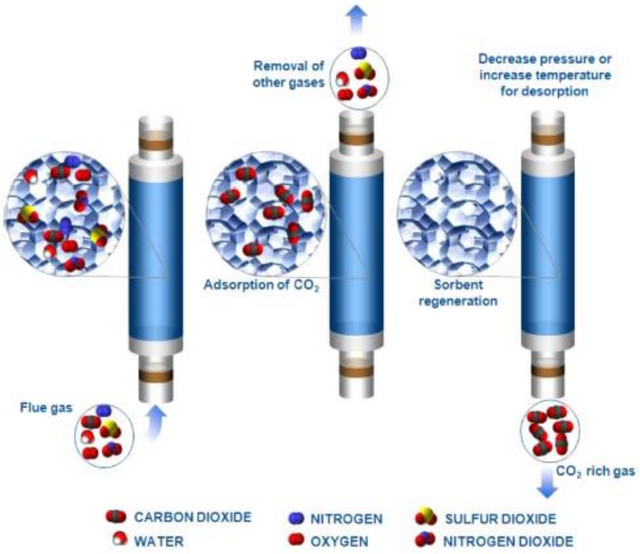

Figure 3. Diagram on how a stationary solid sorbent works and how it is regenerated (Espinal et al., 2013)**.**

Most of the liquid adsorbents that have been studied and used are aqueous alkanolamine solutions, wherein the lone electrons present in the amine group perform a nucleophilic attack on the carbon in CO_2 which either results to a carbamate of bicarbonate by-product (Sumida et al., 2012). The chemisorption of CO_2 occurs via bubbling the cooled down flue gas (40-60°C) into these aqueous amine solutions; afterwards, the CO_2-saturated amine solution is pumped through a desorber column to regenerate the amine solution (Figure 4) (Espinal et al., 2013). This regeneration process requires an energy input (mainly from steam) as it is done at 100-140°C; thus, while it has a high CO_2 uptake of 8-13 wt%, the regeneration process has been regarded to be costly (Adil et al., 2017). The amine solution also has a limit of regeneration and requires to be regularly replenished, for example 1 ton of CO_2 will use up 2.2kg of monoethanolamine (MEA) solution (Adil et al., 2017).

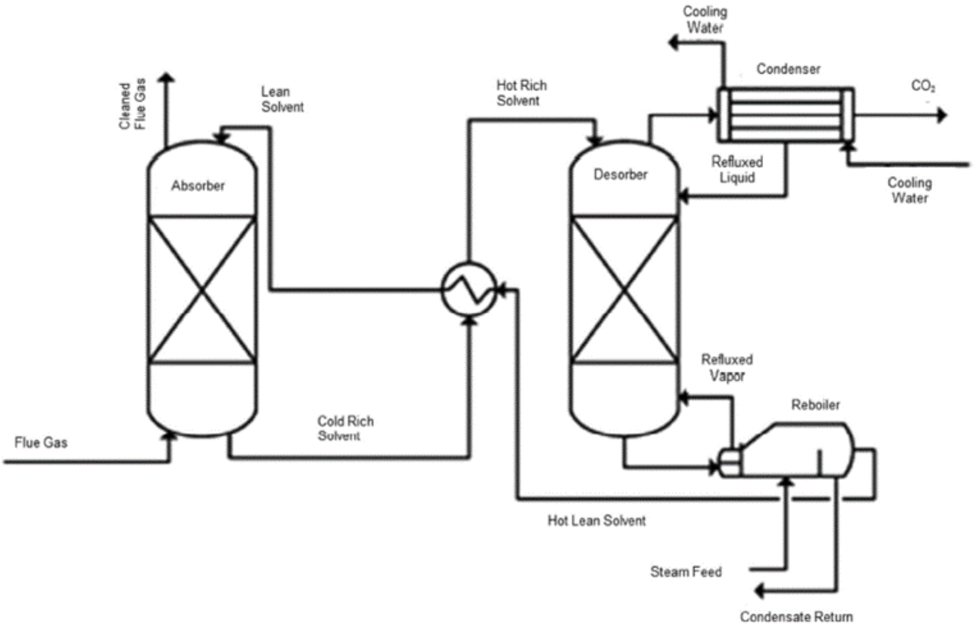

Figure 4. Diagram on how a liquid sorbent works and how it is regenerated (Espinal et al., 2013)**.**

Solid adsorbents were found to be more attractive than their liquid counterparts as they require less heat for regeneration having small heat capacities and do not have corrosion-related issues (McDonald et al., 2012). Once CO_2 is captured, it can be buried at depths where pressures reach 100-150 bars such as dry oil reservoirs or aquifers (Sumida et al., 2012). The solid sorbent types previously used are zeolites, porous carbon and porous silica which had issues such as low surface areas, selectivity and capacity (Schoedel et al., 2016). Porous materials can act as gas adsorbents as gas molecules tend to adhere on the porous surface either through van der Waals interactions, in a process called physisorption or they form new chemical bonds on the surface of the adsorbent via chemisorption (Yaghi et al., 2019).

Metal organic frameworks (MOFs) are a class of crystalline porous materials that are composed of metal ions or clusters and bridging ligands (linkers) connected through coordination bond (Yaghi et al., 2019). One of the first MOFs synthesized and applied for gas storage is MOF-5 (Figure 5) which of synthesized with $Zn_4O(-COO)_6$ clusters linked together by benzene-1,4-dicarboxylate (BDC), resulting to a 3D infinite structure of cubic networks that is highly porous (high surface area) and stable. The yellow sphere represents the space or pore where the gas can be adsorbed (Yaghi et al., 2019).

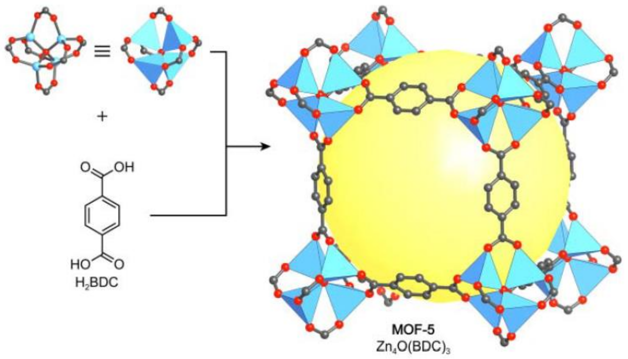

Figure 5. Structure of MOF-5 [(Zn4O(BDC)3] created by Omar Yaghi et. al., in 1999. Legend: Zinc = blue, Carbon = gray, Oxygen – red. Hydrogens are omitted for clarity (Yaghi et al., 2019)**.**

Covalent organic frameworks (COFs) are also crystalline porous materials that are purely composed of non-metals – Carbon, Boron, Nitrogen and Oxygen. The strong covalent bond between these atoms give rise to their thermal and chemical stability (Yaghi et al., 2019). Since non-metals have a lower coordination number, COFs can exist as either a 2D or 3D framework depending on the geometries of their monomers (Figure 6). Due to the stacked framework, 2D COFs have lower porosities compared to 3D COFs. The characteristics of both frameworks are dependent on the monomers that build them up which makes MOFs and COFs very versatile. Post-synthetic modifications can also be done to the framework; thus, making MOFs and COFs tunable to any desired application (Yaghi et al., 2019).

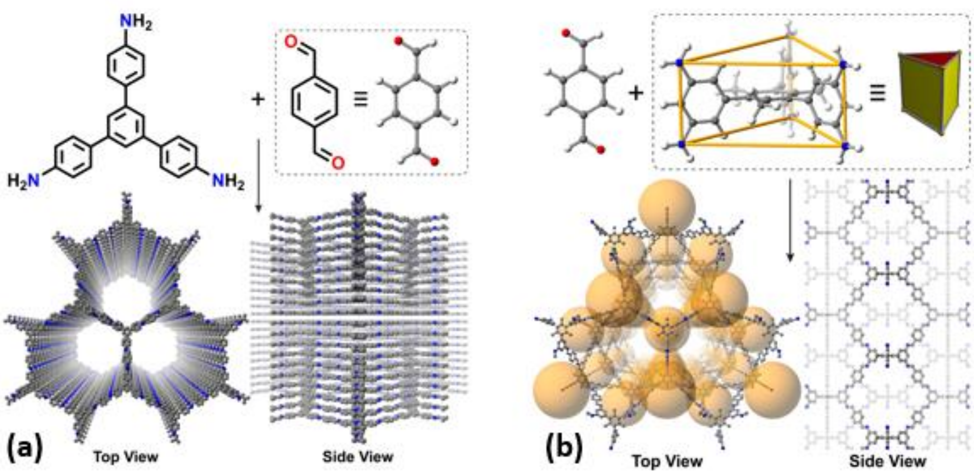

Figure 6. Examples of (a) a 2D COF and (b) a 3D COF. Legend: Black = Carbon, Blue = Nitrogen, Red = Oxygen. The brown spheres in (b) represent the gas molecules adsorbed on the COF.

The target set by the US DOE for solid adsorbents was to obtain 90% CO_2 removal from flue gas during post-combustion which was translates to a minimum of 15% CO_2 uptake (Willis, 2010). In the case of MOFs and COFs, the mass of the adsorbed gas is always smaller compared to the mass of the adsorbent that is sometimes neglected and the %wt is overestimated (Yaghi et al., 2019). A more direct measurement of CO_2 capacity is to get moles of gas adsorb per mass of sorbent which can either be expressed as mol CO_2/kg or mmol CO_2/g. To achieve the US DOE target and to be economically competitive against liquid sorbents, a solid sorbent must have a capacity ranging from 3-6 mmol CO_2/g (Espinal et al., 2013). The present cost of using technologies that perform direct air capture and storage within the range of USD135-345/tCO_2 (IEA, 2020).

2.1 MOFs for CO_2 Capture

There have already been three significant development stages in designing and creating MOFs for CO_2 capture and conversion (Ding et al., 2019). The first stage was to create MOFs that have a high CO_2 adsorption and selectivity – especially in the presence of N_2, and CH_4 – by ensuring a framework that has: (a) available open metal sites, (b) heteroatoms that can act as Lewis bases, and (c) polar functional groups, and (d) very hydrophobic (Ding et al., 2019). The first three parameters are to provide active sites for CO2 to bind to the MOF, thus increasing its capacity. However, the framework cannot be too polar as it must exhibit low affinity for water to increase its selectivity. Figure 7 shows the CO_2 adsorption performance of 125 MOFs at ambient temperature (25°C) and pressure (1 bar) done in 2016 by Schoedel, et. al. Mg-MOF-74 has the highest gas uptake at 37.9%wt and is one of the leading MOFs for CO_2 capture (Schoedel et al., 2016). An updated review by Yaghi, et al., in 2019 added 10 MOFs and 2 MOF-composites that can function at high pressures from 5-40 bars at ambient temperatures with capacities ranging from 3-46mmol CO_2/g (Ding et al., 2019).

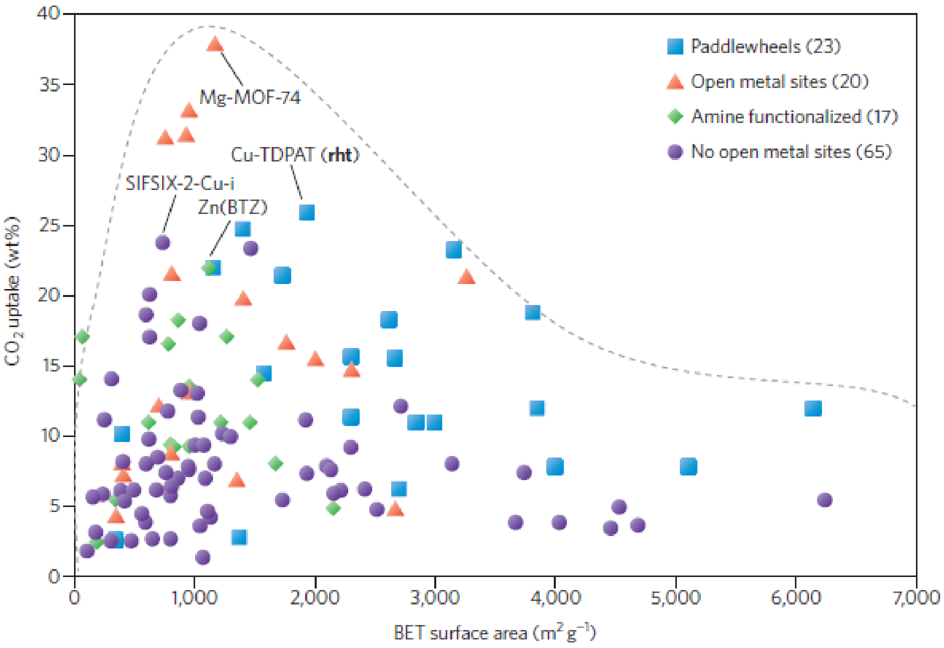

Figure 7. CO_2 uptake vs surface area of 125 MOFs classified based on structure and functionality (Schoedel et al., 2016).

While the metal-ligand bond within the framework is what gives MOFs its porosity and stability, it is highly susceptible to attack by water molecules. Considering that flue gas contains 5-7% water, this presents a big issue in the stability and commercial applicability of MOFs (Ding et al., 2019). However, given the versatility of designing or post-synthetic modification in MOFs, studies have shown that the water stability of MOFs can be improved by either: (a) using highly valent (3^+ or 4^+) metals that are more stable in water, or (b) adding functionalized ligands to protect the metal center (Ding et al., 2019). The functional tunability of MOFs gave rise to the second stage of development focused on the conversion of CO_2 to other organic compounds. As of 2019, there have been seven different carboxylation reactions using MOFs to convert CO_2 into other useful organic compounds in a presence of a catalyst (Ding et al., 2019). This conversion is made possible through the open metal sites or heteroatoms that can act as Lewis acids and bases that serve as active reaction sites in the MOF. MOFs have also been used as heterogeneous catalysts to reduce CO_2 and create feedstock organic compounds such as CH_4, methanol (CH_3OH) and formic acid (CH_3COOH) (Ding et al., 2019). The third stage is focused on increasing the reactive sites in MOFs and exploring the use of MOF-based composites to come-up with a framework that can perform CO_2 adsorption and conversion synergistically (Ding et al., 2019).

2.2 COFs for Carbon Capture

COFs share the same stability and versatility as MOFs. The absence of metals in COFs have resulted in making them more water-resistant compared to some MOFs; thus, making them a more viable alternative for CO_2 capture. However, unlike MOFs that have been extensively studied, COFs is an emerging field in materials science. Several COFs have been synthesized and evaluated for CO_2 adsorption with 2D COFs having a gas uptake ranging from 5.9-9.2 %wt, while the more porous 3D COFs have gas uptakes ranging from 6-17.7 %wt (Huang et al., 2015). Computational simulations and experimental results show that at low pressures, CO_2 uptake between 2D and 3D COFs have no significant difference (Zeng et al., 2016). However, at high pressures, CO_2 uptake is observed to be directly related to porosity, thus 3D COFs exhibited significantly higher adsorption than 2D COFs (Zeng et al., 2016). It was also observed that imine-based and triazine-based COFs have a higher CO_2 uptake and selectivity and are more stable in moisture (Olajire, 2017). The presence of nitrogen within the framework provides an attractive binding site for CO_2. My current project is focused on the design and synthesis of an imine-based 3D COF with a topology (Figure 6b) that is immune to interpenetration to maximize its surface area and achieve high gas uptake and selectivity. As of present time, the monomers needed to make the COF have been successfully synthesized and screening of favorable conditions for the COF synthesis is currently underway.

While it seems that COFs have a long way to go to become at level with MOFs in terms of CO_2 uptake, several innovations have also been pursued to improve its performance. Jiang et. al. attempted to maximize the stacked geometry of 2D COFs by adding a carboxylic acid groups within the channel walls of the framework and succeeded in increasing the gas uptake of the 2D COF to 18 %wt, making it comparable to a 3D COF (Huang et al., 2015). Smit et al. recently conducted a large-scale computational screening of 69,000 silico-based COF structures as CO_2 adsorbents and identified COF designs that have a comparable performance against Mg-MOF-74, using gas uptake, selectivity, and adsorption regeneration as the main parameters to indicate high performance (Deeg et al., 2020). Since COFs also share the tunability of MOFs, there have also been several studies on the use of COFs for CO_2 conversion. A recent study by Du et. al., showed a bi-functional COF doing the same catalytic cycle as the MOF in Figure 7 but without the need for another catalyst (He et al., 2020). Kong and coworkers also showed that a COF can reduce CO_2 to CO in the presence of water and visible light (Lei et al., 2020).

3. CHALLENGES IN APPLYING MOFS AND COFS FOR CO_2 CAPTURE IN GEOTHERMAL POWERPLANTS

Considering that the vapor phase of geothermal fluids only contains 3-10% CO_2 which is much lower that the CO_2 present in flue gas, it is then possible to use solid adsorbents for CO_2 capture in geothermal powerplants (Fridriksson et al., 2016). The main difference of flue gas and geothermal steam is that the main component of flue gas is N_2, while geothermal steam is mainly H_2O vapor. Thus, the main challenge is to find the right framework that has a high selectivity stability against water combined with sufficient CO_2 uptake. Initial screenings can adapt the target capacities set for flue gas – 15% CO_2 uptake or 3-6mmol CO_2/g sorbent.

Table 1. Gas Composition of Flue Gas (Global CCS Institute, 2012) **against Geothermal Steam** (Fridriksson et al., 2016)

Gas Constituent	Flue Gas		Geothermal Steam*
	Coal-Fired	Gas-Fueled	
Water vapor (H_2O)	8-15%	8-10%	90%
Carbon Dioxide (CO_2)	10-15%	4-5%	9.5%
Nitrogen (N_2)	70-75%	73-76%	<1%
Oxygen (O_2)	3-4%	12-15%	<1%
Trace Gases (others)	<1%	<1%	<1%

* Assumption made was that geothermal steam contained 90% water vapor and 10% NCG.

Another issue would be determining the best location to incorporate the adsorbent – whether before the steam enters the turbine or after it passes the turbine. The easiest way would be treating the steam after it passes the turbine as it would fall within the pressures and temperatures tolerated by the solid sorbents. However, while there is merit in capturing CO_2 altogether with the other non-condensible gases (NCG) prior steam entry to the turbine, this poses problems regarding loss of energy due to a slight pressure change.

4. CONCLUSION

While geothermal energy is significantly cleaner and greener compared to traditional thermal energy powerplants, it cannot be denied that geothermal energy still emits GHG into the atmosphere. Thus, the conscious and growing effort within the geothermal industry towards decarbonisation is a right step towards sustainability. While there have been CCS technologies developed, such as CarbFix and CO2-DISSOLVE, these are energy intensive and require additional infrastructure and sometimes specific geological conditions. Thus, it is proposed to expand the use of solid adsorbents for the selective CO_2 capture not only for flue gas emitted from coal-fired and gas-fueled powerplants but also its applicability for geothermal powerplants. MOFs and COFs are crystalline porous materials that have shown to have high adsorption capacities and selectivity that make them good alternatives for CO_2 capture. The main challenge would be to find a water stable framework that has high CO_2 uptake and selectivity against water vapor. Given the versatility and tunability of MOFs and COFs and the extensive and fast pace research done in this field, it is highly possible to find the best framework for the challenge.

ACKNOWLEDGEMENTS

The authors would like to thank NZ Aid for the scholarship funding, McDiarmid Research Institute and Royal Society Te Aparangi for research funding, and the Energy Development Corporation for the financial support.

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