Pressure and temperature influence the efficacy of metal-organic frameworks for carbon capture and conversion

Taohan Lin[1], Thomas J. Webster[2]

[1]Thomas Jefferson High School for Science and Technology, Alexandria, Virginia
[2]Division of Pre-college and Undergraduate Programs, Brown University, Providence, Rhode Island

SUMMARY

Carbon dioxide (CO_2) is a major contributor to global warming, which has led to irreversible environmental and socio-economic damage. Metal-organic frameworks (MOFs) are promising new nanomaterials for use in the fight against climate change that can efficiently capture and convert CO_2 to other useful carbon products, such as ethanol, methanol, and cyclic carbonates. However, the large-scale production of MOFs for industrial use is limited because of their high porosity and customizability making their development, synthesis, and use expensive. The purpose of our research was to use computational models to determine the reaction conditions under which MOFs can more efficiently capture and convert CO_2. We used Python programming to examine current data presented in the literature, encompassing various MOFs with a range of pore sizes and different substrates to determine the optimal conditions for MOFs to capture and convert CO_2 into useful products. Our results showed that pressure was significantly correlated in convex quadratic models with the selective capture of carbon and temperature was significantly correlated in a concave quadratic model with carbon conversion. Optimal reaction conditions were approximately 80°C ($R^2 = 0.376$) and 0-1 atm or 11-12 atm of pressure ($R^2 = 0.210$). In a cost-efficient manner, this analysis tested the hypothesis that pressure and temperature affect the efficacy of carbon capture and conversion, and contribute to understanding the optimal conditions for MOF performance to improve the use of MOFs for controlling greenhouse CO_2 emissions.

INTRODUCTION

Greenhouse gas emissions are main contributors to climate change and global warming. Emission of the most abundant greenhouse gasses, specifically carbon dioxide (CO_2), has grown by almost 6 times in the past 70 years (1). The current concentration of CO_2 in the atmosphere is over 400 parts per million (ppm), 30 % higher than the highest CO_2 level prior to the industrial revolution (2). The main sources of CO_2 emission include human transportation, energy production, and commercial heating and cooling (3). Climate change and global warming have led to both widespread ecological damage to plants and animals as well as significant socio-economic losses. In the United States alone, the total cost of the 332 weather and climate-related disasters sustained since 1980 exceeds $2 trillion, according to a recent estimate by the National Centers for Environmental Information (4). Globally, according to estimates by the World Bank, climate change may push over 130 million people into poverty by 2030 and cause over 200 million people to migrate within their own countries by 2050 (5).

Carbon capture and conversion aim to reduce atmospheric CO_2 levels and mitigate climate change (6, 7). According to estimates by the Center for Climate and Energy Solutions, carbon capture and storage technologies can capture more than 90 % of CO_2 emissions from power plants and industrial facilities and reduce 14 % of global greenhouse gas emissions by 2050 (3).

Several methods exist for carbon capture focused on using absorption, distillation, adsorption, and membrane-based technologies (8). Each technology has advantages and disadvantages. Absorbents represent a more advanced technology with a high CO_2 removal rate but suffer from high regeneration costs and corrosion. Distillation is similarly beneficial for its strong CO_2 removal capacity, but also has the problem of prohibitive costs. Membranes are cheap and easy to operate but have high material costs and are not ideal for elevated temperatures. A variety of adsorbents are available, but adsorption is sensitive to impurities within the gas (8). Innovative technologies with fewer drawbacks that function strongly under different reaction conditions must be developed, including the use of metal-organic frameworks (MOFs).

MOFs are promising materials for carbon capture and conversion due to their repetitive lattice structures, ultra-high surface areas, and significant CO_2 selectivity (9, 10). MOFs consist of metallic clusters and organic ligands bonded to each other in a crystal lattice (11). They capture carbon mainly through physical, instead of chemical, means by "trapping" processes that require lower energy input for regeneration. MOFs can also have open metal sites, which are unbonded parts of the metal clusters to allow for greater interaction between the MOF and CO_2. In addition, MOFs are inherent catalysts and convert the CO_2 they capture into useful carbon products, such as methanol and acetic acid, through electric and photic means (11). Altogether, MOFs are a more energy-

efficient carbon capture and conversion technology compared to other methods because they can achieve both steps in this process.

The process of researching and synthesizing MOFs is expensive, leading to a lack of large-scale manufacturing and limited applications in industry (17, 18). MOFs continue to represent a promising energy-efficient pathway to tackle the growing conundrum around increased CO_2 emissions (8). However, the MOF design space is large due to the great versatility of MOFs (such as their chemistry, geometry, percent porosity, size of pores, etc.) and the different combinations of reaction conditions that can impact capture selectivity and conversion (14). These variables render experimental examination for determining the impact of every MOF design features difficult (19). In addition, some MOFs get used up or decay over time and must be regenerated or replaced during use, which has further added to challenges using MOFs (8). These considerations of cost and time make searching for MOFs with specific properties using experimental techniques largely infeasible. In contrast, computational modeling of MOFs can be useful for the discovery of promising new materials for CO_2 capture in a cost-effective manner (20). Computational modeling can efficiently investigate the properties of new materials beyond the limits of experimental techniques and can be used to support, rationalize, and guide experimental efforts (21). For example, through developing computational models and neural networks, a subset of machine learning that mimics biological neuron signals and relies on training data to learn and improve their accuracy over time, researchers can analyze features of a MOF structure to predict its efficacy before costly synthesis and help reduce the development time for new MOFs (22).

The studies existing in the literature suggest that different reaction conditions, such as pressure and temperature, influence the selectivity and conversion rate of CO_2 capture and conversion by MOFs while the optimal conditions have not yet been fully characterized (8). In our study, we computationally analyzed MOF carbon capture selectivity and conversion under different reaction conditions using data compiled from Al-Rowaili *et al.* (12). Some MOF materials, due to their structural flexibility, may undergo changes within their structures and result in "confined" CO_2 adsorption when exposed to external influences, such as pressure and temperature (12). We tested the hypothesis that pressure and temperature affect the efficacy of MOF carbon capture and conversion. Using Python programming, we performed empirical regression between the reaction conditions, including pressure and temperature, and selectivity and conversion ratios. Pressure was significantly correlated in a convex quadratic model with carbon capture selectivity, and temperature was significantly correlated in a concave quadratic model with carbon conversion. Our study contributes to understanding optimal MOF reaction conditions for carbon capture and conversion through computational modeling, increasing the potential use of MOFs in industry.

RESULTS

The efficacy of CO_2 selectivity and conversion is known to vary depending on the chemical and physical properties of the MOFs and the reaction conditions (23). To examine the impact of pressure and temperature on both the selectivity and conversion steps, we analyzed performance data collected by Al-Rowaili *et al* (12), a dataset consisting of 103 observations using a series of MOFs designs. After filtering out observations with incomplete information of pore size, reaction conditions, or performance ratios, 14 observations remained for the analysis of selectivity and 54 for the analysis of conversion. Linear, exponential, logarithmic, and quadratic fits were all tested to determine the relationship between reaction conditions (pressure and temperature) and performance.

Pressure had a significant convex up quadratic relationship with selectivity ($p=0.05$), while the link between temperature and selectivity was not significant (**Table 1**). Most of the MOFs achieved a selectivity of over 90%. However, when the pressure level was in the middle range around 6-8 atm, the selectivity dropped to a low level of 30-70% (**Figure 1a**). Similarly, when the temperature was around 50°C, the

Table 1. Pressure influences CO_2 selectivity.

	Selectivity (1)	Selectivity (2)
Pressure	-13.12**(-2.44)	
Pressure sq.	1.04**(2.57)	
Temperature		0.22 (0.18)
Temperature sq.		- 0.00 (-0.06)
Constant	109.9***(7.24)	72.82 (1.56)
R^2	0.376	0.031
Number of Obs.	14	14

*Note: Quadratic functions were generated with x = pressure or temperature and y = selectivity (%). Coefficients are indicated outside of parentheses and Student's t-values in parentheses with **p<0.05, ***p<0.01.*

Table 2. Temperature influences carbon conversion rate.

	Conversion (1)	Conversion (2)
Pressure	0.65 (1.06)	
Pressure sq.	-0.01 (-1.18)	
Temperature		1.25***(3.55)
Temperature sq.		-0.01***(-3.20)
Constant	81.42***(16.32)	38.44***(2.97)
R^2	0.027	0.210
Number of Obs.	54	54

*Note: Quadratic functions were generated with x = pressure or temperature and y = conversion rate (%). Coefficients are indicated outside of parentheses and Student's t-values in parentheses with ***p<0.01.*
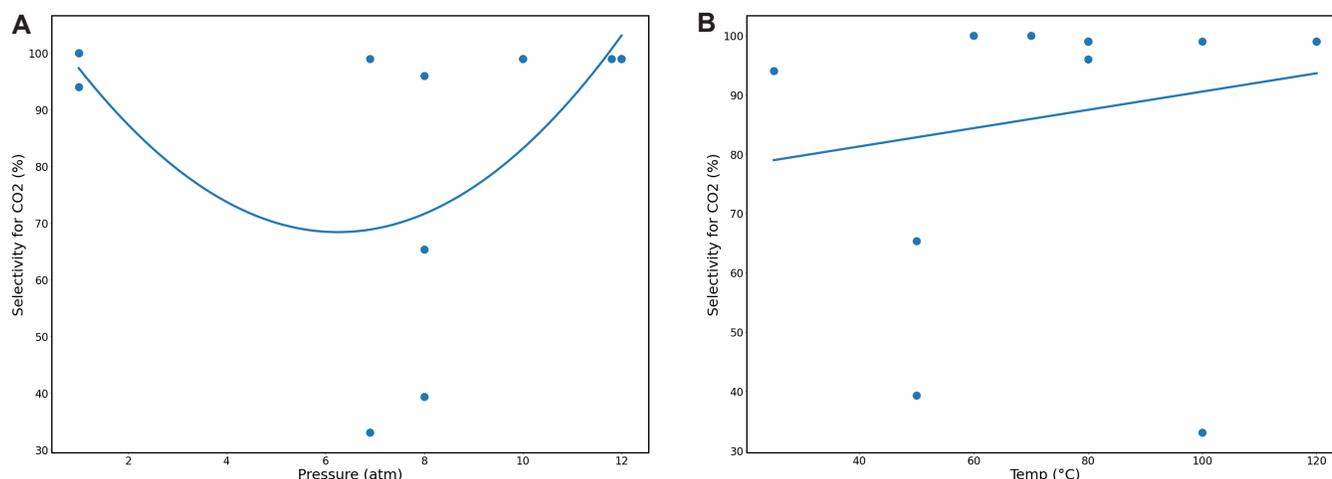
Figure 1. Pressure, not temperature, influences selectivity for CO₂. Scatter plots showing selectivity (%) as a function of **a)** pressure (atm) and **b)** temperature (°C) in 14 MOF samples, fitted with quadratic curves. **A)** {selectivity=109.9-13.12*pressure+1.04*pressure sq. and *p*-value<0.05}, **B)** {selectivity=72.82+0.22*temperature and *p*-value>0.10}.

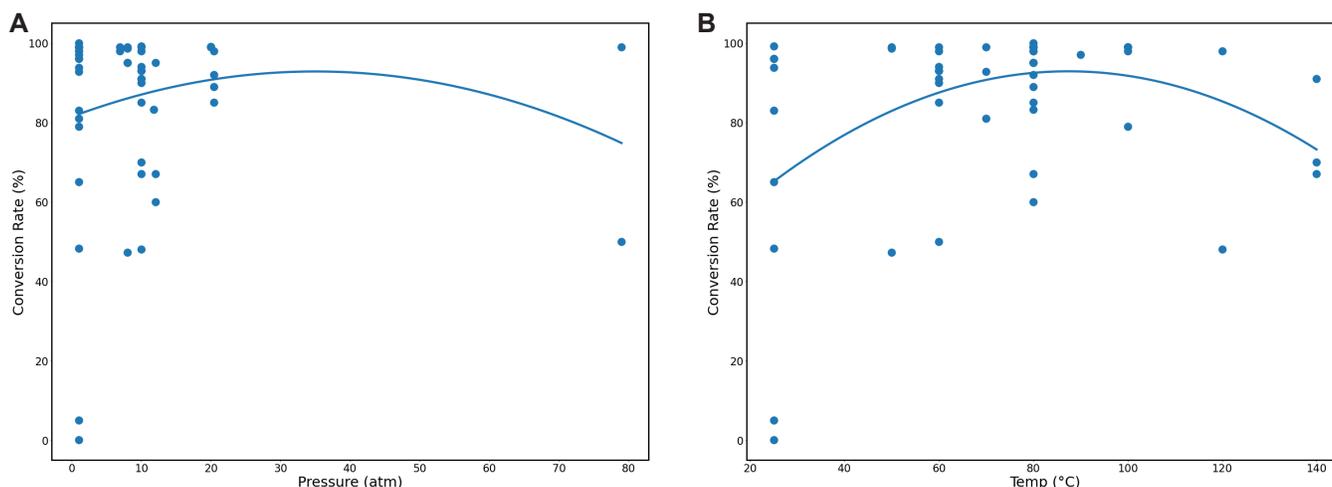**Figure 2. Temperature, not pressure, influences carbon conversion rate. Scatter plots showing conversion rate (%) as a function of a)** pressure (atm) and **b)** temperature (°C) in 54 MOF samples, fitted with quadratic curves. **A)** {conversion=84.24+0.65*pressure-0.01*pressure sq. and *p*-value>0.10}, **B)** {conversion=28.44+1.25*temperature-0.01*temperature sq. and *p*-value<0.01}.

selectivity dropped to 30-70%, although the relationship was not significant (**Figure 1b**). Our results showed that, in a quadratic equation, with 14 observations in the sample from Al-Rowaili *et al*. (12), pressure was significantly associated with selectivity at the 5 % level with a coefficient equaling -13.12 (t=-2.44) and the squared term of pressure was also significantly associated with a selectivity at the 5% level with a coefficient equaling 1.04 (t=2.57). The constant of this equation was 109.9, significant at the 1 % level (t=7.24). Alterations in pressure explained over one-third of the variance observed in selectivity (R^2=0.376). Meanwhile, the associations between temperature or the squared term of temperature and selectivity were not significant (t=0.177 and t=-0.055, respectively) and the alteration in temperature explained little of the variance observed in selectivity (R^2=0.031).

    Temperature had a significant impact on the ability of MOFs

to convert CO_2 into other carbon products, such as ethanol, methanol, and cyclic carbonates, while the association between pressure and conversion was not significant (**Table 2**). More specifically, temperature had a concave down quadratic relationship (*p*=0.01). In the 54 observations used to analyze conversion, the conversion ratio ranged from approximately 40% to 100% for most samples. Several observations had low conversion ratios around zero (**Figure 2**). The coefficient between temperature and conversion was 1.245, significant at the 1% level (t=3.55) and the coefficient between the squared term of temperature and conversion was -0.0071, also significant at the 1% level (t=-3.20). The constant of the quadratic regression was 38.44, significant at the 1% level (t=2.97). Temperature explained around 20% of the variance of conversion (R^2 = 0.210).

DISCUSSION

The influence of different reaction conditions, such as pressure and temperature, on the selectivity and conversion rate of CO_2 by MOFs has not been fully characterized to date. Here, we analyzed a database presented as **Table 1** in Al-Rowaili *et al.* (12) consisting of MOF characteristics, reaction conditions, and capture outcomes, to determine whether pressure or temperature correlated with CO_2 selectivity or conversion rates. Diverse MOFs were included such as zeolitic imidazolate frameworks, ZnMOFs, University of Oslo MOFs ($Zr_6O_4(OH)_4$ + 1,4-benzodicarboxylic acid), polymer integrated MOFs, Sr-MOFs, Cu-MOFs, and many others (12). Pressure was significantly correlated in convex quadratic models for the selective capture of carbon and temperature was significantly correlated in a concave quadratic model for carbon conversion. Our findings indicated that the reaction conditions of pressure and temperature affected the ability and efficacy of MOFs for carbon capture through CO_2 selectivity and conversion. For a variety of MOF-based materials in the studied samples with different pore sizes for the tested durations, the optimal reaction conditions were around 80°C and at 0-1 atm or 11-12 atm of pressure (R^2 = 0.376 and 0.210, respectively).

Our analysis coincides with previous studies that showed changes in MOF CO_2 selectivity and conversion reacting at different pressures and temperatures (8). Due to their cavity size and surface area, MOFs have a dynamic structure. Variability in reaction conditions can alter the structure, resulting in "confined" CO_2 adsorption (12). At low pressure, the adsorption capability of CO_2 on MOFs is related to the adsorption heat (24), and at high pressure, selectivity depends on pore size. For synthetic MOFs, the pore sizes and channels can reach nanometers and angstroms (11). As the interaction between MOFs and CO_2 at low pressure is relatively weaker, MOFs with high CO_2 uptake at low pressures can help facilitate an effective CO_2 capture process for enclosed localities (11). MOFs can have high CO_2 storage capacity at room temperature (26). However, strong bonds between CO_2 molecules and the adsorbents to achieve selectivity typically require high adsorbent regeneration temperatures (27). As the adsorption capacity and saturated adsorption capacity decrease with an increase in adsorption temperature, low adsorption temperature can help obtain a high CO_2 adsorption capacity (28).

Several limitations of the current study are worth noting. First, samples sizes were low. After dropping unusable data due to incomplete information of pore size, reaction conditions or performance ratios, only 14 data points were left for selectivity tests and 54 data points for conversion tests. While the remaining observations still included a range of different MOF-based materials with different pore sizes and conditions of reaction with no pattern of dominance of any specific MOF types, the datasets may not be representative of diverse experimental parameters and may be skewed by a few observations with extreme values. Furthermore, we could not divide the samples into different sub-groups to capture other common features, such as pore size or MOF-based materials due to the limited number of observations. The R^2 values of 0.376 and 0.210, which explains the share of the variation of selectivity and conversion explained by the changes in temperature and the changes in pressure, respectively, were relatively low. This suggested the selectivity and conversion of carbon dioxide are likely to be determined by other factors besides pressure and temperature. Second, the measures for selectivity and conversion were not standardized across all points as the gas mixture for selectivity and the chosen product for conversion varied. This may limit the comparison across the observations in the sample. Third, different MOF chemistries were not considered during testing and specific arrangements for the reactions to achieve the stated results were not controlled. This may not capture the differences in the ideal reaction conditions for other specific MOF materials.

Future research should focus on testing more MOF characteristics, such as pore size, number of functional groups, and open metal sites, as well as the interplay between the different MOF characteristics and reaction conditions, including the concentrations of reactants, products, and catalysts. Analyses of MOF chemistry and structure should also be implemented with sophisticated models of data analytics, such as machine learning. Finally, it would be useful to test the results on CO_2 selectivity and conversion jointly to reach the ultimate goal of developing specialized and efficient MOFs for carbon capture.

MATERIALS AND METHODS
Data

This study analyzed data previously compiled by and presented as **Table 1** in Al-Rowaili *et al* (12). Observations included characteristics of the MOFs, reaction conditions, and performance of the MOFs under those conditions. MOF properties included the MOF name and notes detailing the pore size in angstroms. Reaction conditions were temperature (°C), pressure in atmospheres (atm), and the amount of time (hr) the reaction took place. Pressure and temperature were the focus on this study. Performance was summarized by three measures: i) CO_2 selectivity, ii) conversion, and iii) turnover frequency. CO_2 selectivity and conversion were used in this study, while turnover frequency was dropped due to data limitations. Selectivity, reported as a percentage, measured how well the MOFs trapped CO_2 with relationship to other gasses. Conversion measured the percent of CO_2 that was converted into a different product, such as cyclic carbonates and methanol (29, 30).

Data points without complete data for selectivity or conversion percentages were dropped. For selectivity, only data points that included MOF pore size, reaction temperature, reaction pressure, duration of reaction (time), and selectivity were included, amounting to 14 observations. This selection criteria were applied to conversion data with

conversion values replacing selectivity, amounting to 54 observations. The data, as detailed in Al-Rowaili *et al* in **Table 1** of their publication, included various MOFs, such as zeolitic imidazolate frameworks, ZnMOFs, University of Oslo MOFs ($Zr_6O_4(OH)_4$ + 1,4-benzodicarboxylic acid), polymer integrated MOFs, Sr-MOFs, and Cu-MOFs, with pore sizes ranging from 0.14 to 36 angstroms and tested with different substrates, including epichlorohydrin, styrene oxide, and glycidyl phenyl ether.

Analysis

All data analysis was conducted using Python version 3.9.12 software. Linear and quadratic regressions were performed for all variables x = {temperature, pressure} and y = {selectivity, conversion} using the equations below:

$$y = a + bx$$
$$y = a + bx + cx^2$$

where y stands for the dependent variables, selectivity and conversion; x stands for the independent variables, pressure and temperature; *a* stand for the constant, *b* stands for the coefficient of the independent variable, and *c* stands for the coefficient of the squared term of the independent variable. For each regression, the coefficients were tested for significance using the student's t-test, and the R-squared value was calculated to determine the degree of variability explained by the models. We use t-statistics, defined as the ratio of the departure of the estimated value of a parameter from its hypothesized value to its standard error, to support or reject the null hypothesis that the coefficient of a given independent variable is significant at 1%, 5% or 10%.

REFERENCES

1. Ritchie, Hannah, and Max Roser. "CO2 Emissions." *Our World in Data*, 11 May 2020, ourworldindata.org/co2-emissions. Accessed 27 Sept. 2022.
2. "Vital Signs." *Global Climate Change, Vital Signs of the Planet*, NASA, 22 Aug. 2022, climate.nasa.gov/vital-signs/carbon-dioxide/. Accessed 27 Sept. 2022.
3. "Carbon Capture." *Center for Climate and Energy Solutions*, 27 May 2021, www.c2es.org/content/carbon-capture/. Accessed 27 Sept. 2022.
4. National Centers for Environmental Information, "*Billion-Dollar Weather and Climate Disasters*.", NOAA, www.ncei.noaa.gov/access/billions/. Accessed 27 Sept. 2022.
5. The World Bank,"*10 Things You Didn't Know about the World Bank Group's Work on Climate Change*." World Bank Group, 29 Oct. 2021, www.worldbank.org/en/news/factsheet/2021/10/29/10-things-you-didn-t-know-about-the-world-bank-group-s-work-on-climate. Accessed 27 Sept. 2022.
6. Hyseni, Sabina. "*Carbon Capture and Storage as a Method to Mitigate Climate Change*." Inquiries Journal 9.03 (2017). www.inquiriesjournal.com/a?id=1551
7. Farrelly, Damien J., *et al*. "Carbon Sequestration and the Role of Biological Carbon Mitigation: A Review." *Renewable and Sustainable Energy Reviews*, vol. 21, May 2013, pp. 712-27. ScienceDirect, doi.org/10.1016/j.rser.2012.12.038.
8. Demir, Hakan, *et al*. "MOF Membranes for CO2 Capture: Past, Present and Future." *Carbon Capture Science & Technology*, vol. 2, Mar. 2022, p. 100026. Science Direct, doi.org/10.1016/j.ccst.2021.100026.
9. Li, Jian-rong, *et al*. "Carbon Dioxide Capture-related Gas Adsorption and Separation in Metal-organic Frameworks." *Coordination Chemistry Reviews*, vol. 255, nos. 15-16, Aug. 2011, pp. 1791-823. ScienceDirect, doi.org/10.1016/j.ccr.2011.02.012.
10. Rehman, Ayesha, *et al*. "Synthesis and Effect of Metal–organic Frame Works on CO_2 Adsorption Capacity at Various Pressures: A Contemplating Review." *Energy & Environment*, vol. 31, no. 3, 31 July 2019, pp. 367-88. Sage Journals, doi.org/10.1177/0958305X19865352.
11. Elhenawy, Salma Ehab Mohamed, *et al*. "Metal-Organic Frameworks as a Platform for CO2 Capture and Chemical Processes: Adsorption, Membrane Separation, Catalytic-Conversion, and Electrochemical Reduction of CO2." *Catalysts*, vol. 10, no. 11, 9 Nov. 2020, p. 1293. MDPI, doi.org/10.3390/catal10111293.
12. Al-rowaili, Fayez Nasir, *et al*. "A Review for Metal-Organic Frameworks (MOFs) Utilization in Capture and Conversion of Carbon Dioxide into Valuable Products." *Journal of CO2 Utilization*, vol. 53, Nov. 2021, p. 101715. ScienceDirect, doi.org/10.1016/j.jcou.2021.101715.
13. Schaate, Andreas, *et al*. "Modulated Synthesis of Zr-Based Metal-Organic Frameworks: From Nano to Single Crystals." *Chemistry - a European Journal*, vol. 17, no. 24, 5 May 2011, pp. 6643-51. Chemistry Europe, doi.org/10.1002/chem.201003211.
14. Han, Yitong, *et al*. *Synthesis Methods and Crystallization of MOFs*. IntechOpen, 2020. Synthesis Methods and Crystallization. IntechOpen, doi.org/ 10.5772/ intechopen.90435.
15. Reddy, Ch. Venkata, *et al*. "Metal-organic Frameworks (MOFs)-based Efficient Heterogeneous Photocatalysts: Synthesis, Properties and Its Applications in Photocatalytic Hydrogen Generation, CO2 Reduction and Photodegradation of Organic Dyes." *International Journal of Hydrogen Energy*, vol. 45, no. 13, Mar. 2020, pp. 7656-79. ScienceDirect, doi.org/10.1016/j.ijhydene.2019.02.144.
16. Mashhadzadeh, Amin Hamed, *et al*. "Metal–Organic Framework (MOF) through the Lens of Molecular Dynamics Simulation: Current Status and Future Perspective." *Journal of Composites Science,* vol. 4, no. 2, 17 June 2020, p. 75. MDPI, doi.org/10.3390/jcs4020075.
17. Hendon, Christopher H. *et al*. , "Grand Challenges and Future Opportunities for Metal–Organic Frameworks,"

ACS Cent. Sci. 2017, 3, 6, 554–563 Publication Date: June 6, 2017 doi.org/10.1021/acscentsci.7b00197

18. Niklas. 2020, "*Price vs. value of metal-organic frameworks*", Jan. 7, 2020, blog.novomof.com/blog/price-vs-value-of-metal-organic-frameworks

19. Bernales, Varinia, *et al*. "Computational Design of Functionalized Metal–Organic Framework Nodes for Catalysis." *ACS Central Science*, vol. 4, no. 1, 21 Dec. 2017, pp. 5-19. ACS Publications, doi.org/10.1021/acscentsci.7b00500.

20. Avci, Gokay, *et al*. "Do New MOFs Perform Better for CO2 Capture and H2 Purification? Computational Screening of the Updated MOF Database." *ACS Applied Materials & Interfaces*, vol. 12, no. 37, 20 Aug. 2020, pp. 41567-79. ACS Publications, doi.org/10.1021/acsami.0c12330.

21. Keskin, and Alsoy Altinkaya. "A Review on Computational Modeling Tools for MOF-Based Mixed Matrix Membranes." *Computation*, vol. 7, no. 3, 18 July 2019, p. 36. ResearchGate, dx.doi.org/10.3390/computation7030036.

22. "Computation Modeling Guides Development of New Materials." *MIT News*, 11 Mar. 2022, news.mit.edu/2022/metal-oxide-frameworks-model-0311. Accessed 27 Sept. 2022.

23. Gandara-loe, J., *et al*. "Understanding the Opportunities of Metal–organic Frameworks (MOFs) for CO2 Capture and Gas-phase CO2 Conversion Processes: A Comprehensive Overview." *Reaction Chemistry & Engineering*, vol. 6, no. 5, 2021, pp. 787-814. *Royal Society of Chemistry*, doi.org/10.1039/D1RE00034A.

24. Shekhah, Osama, *et al*. "Made-to-order Metal-organic Frameworks for Trace Carbon Dioxide Removal and Air Capture." *Nature Communications*, vol. 5, no. 1, 25 June 2014. PubMed Central, doi.org/10.1038%2Fncomms5228.

25. Gautam, Siddharth, and David Cole. "CO2 Adsorption in Metal-Organic Framework Mg-MOF-74: Effects of Inter-Crystalline Space." *Nanomaterials*, vol. 10, no. 11, 17 Nov. 2020, p. 2274. MDPI, doi.org/10.3390/nano10112274.

26. Millward, Andrew R., and Omar M. Yaghi. "Metal−Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature." *Journal of the American Chemical Society*, vol. 127, no. 51, 1 Dec. 2005, pp. 17998-99. PubMed, doi.org/10.1021/ja0570032.

27. Ding, Meili, *et al*. "Carbon Capture and Conversion Using Metal-organic Frameworks and MOF-based Materials." *Chemical Society Reviews*. Royal Society of Chemistry, pubs.rsc.org/en/content/getauthorversionpdf/C8CS00829A. Accessed 27 Sept. 2022.

28. Chen, Shaojie, *et al*. "The Effect and Prediction of Temperature on Adsorption Capability of Coal/CH4." *Procedia Engineering*, vol. 26, 2011, pp. 126-31. *ResearchGate*, dx.doi.org/10.1016/j.proeng.2011.11.2149.

29. Zalomaeva, Olga V., *et al*. "Cyclic Carbonates Synthesis from Epoxides and CO2 over Metal–organic Framework Cr-MIL-101." *Journal of Catalysis*, vol. 298, Feb. 2013, pp. 179-85. ScienceDirect, doi.org/10.1016/ j.jcat.2012.11.029.

30. Gutterød, Emil S., *et al*. "Hydrogenation of CO2to Methanol by Pt Nanoparticles Encapsulated in UiO-67: Deciphering the Role of the Metal–Organic Framework." *Journal of the American Chemical Society*, vol. 142, no. 2, 3 Dec. 2019, pp. 999-1009. ACS Publications, doi.org/10.1021/jacs.9b10873.

APPENDIX

Data.csv is taken from Table 1 in Al-Rowaili *et al* (12). The following code takes the data, cleans it for inconsistencies, and then runs all the regressions relevant to this paper. Graphs to visualize results are also generated. Additional explanations on specifics of codes are commented throughout the code below.

```python
#!/usr/bin/env python
# coding: utf-8

# Imports necessary packages
# In[1]:
import pandas as pd
import numpy as np
import statsmodels.api as sm
from sklearn.linear_model import LinearRegression
import matplotlib.pyplot as plt

# Reads in data and cleans out inconsistent character usage within the data and drops datapoints with
missing information. Regenerates squared terms for later use in regression.
def clean(str):
    return str.replace(">", "")

# In[2]:
full = pd.read_csv('Data.csv')

# In[3]:
sel = pd.read_csv('Data.csv', usecols = ['Pore Size (A)', 'Temp (°C)', 'Pressure (atm)', 'Time (hr)',
'Selectivity (%)'])
conv = pd.read_csv('Data.csv', usecols = ['Pore Size (A)', 'Temp (°C)', 'Pressure (atm)', 'Time (hr)',
'Conversion (%)'])

# In[4]:
sel = sel.replace('–')
sel = sel.dropna()
sel = sel.drop([2, 41, 42])
conv = conv.replace('–')
conv = conv.dropna()
conv = conv.drop([2, 41, 42, 43, 67, 68, 98])
sel['Pore Size (A)'] = sel['Pore Size (A)'].map(clean)
sel['Selectivity (%)'] = sel['Selectivity (%)'].map(clean)
conv['Pore Size (A)'] = conv['Pore Size (A)'].map(clean)
conv['Conversion (%)'] = conv['Conversion (%)'].map(clean)
sel = sel.astype('float64')
conv = conv.astype('float64')
for col in sel.columns:
    sel[col + '2'] = np.square(sel[col])
for col in conv.columns:
    conv[col + '2'] = np.square(conv[col])

# Runs linear regression and visualizes results for selectivity variable
# In[5]:
plt.scatter(sel['Pore Size (A)'], sel['Selectivity (%)'])

# In[6]:
sel.columns
```

```
# In[7]:
for col in ['Pore Size (A)', 'Temp (°C)', 'Pressure (atm)', 'Time (hr)']:
    x = sel[col]
    y = sel['Selectivity (%)']
    model = sm.OLS(y, sm.add_constant(x))
    results = model.fit()
    x_pred = np.linspace(sel[col].min(), sel[col].max(), 75)
    y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred})['x']))
    plt.plot(x_pred, y_pred)
    print(results.summary())
    plt.scatter(sel[col], y)
    plt.title(col + ' vs selectivity')
    plt.show()

# Runs quadratic regression and visualizes results for selectivity variable
# In[8]:
for col in ['Pore Size (A)', 'Temp (°C)', 'Pressure (atm)', 'Time (hr)']:
    x = sel[[col, col + '2']]
    y = sel['Selectivity (%)']
    model = sm.OLS(y, sm.add_constant(x))
    results = model.fit()
    x_pred = np.linspace(sel[col].min(), sel[col].max(), 75)
    y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred, 'x2' : np.square(x_
        pred)})[['x', 'x2']]))
    plt.plot(x_pred, y_pred)
    print(results.summary())
    plt.scatter(sel[col], y)
    plt.title(col + ' vs selectivity')
    plt.show()

# Runs linear regression and visualizes results for conversion variable
# In[9]:
for col in ['Pore Size (A)', 'Temp (°C)', 'Pressure (atm)', 'Time (hr)']:
    x = conv[col]
    y = conv['Conversion (%)']
    model = sm.OLS(y, sm.add_constant(x))
    results = model.fit()
    x_pred = np.linspace(conv[col].min(), conv[col].max(), 75)
    y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred})['x']))
    plt.plot(x_pred, y_pred)
    print(results.summary())
    plt.scatter(conv[col], y)
    plt.title(col + ' vs conversion')
    plt.show()

# In[10]:
# Runs quadratic regression and visualizes results for conversion variable
for col in ['Pore Size (A)', 'Temp (°C)', 'Pressure (atm)', 'Time (hr)']:
    x = conv[[col, col + '2']]
    y = conv['Conversion (%)']
    model = sm.OLS(y, sm.add_constant(x))
    results = model.fit()
    x_pred = np.linspace(conv[col].min(), conv[col].max(), 75)
    y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred, 'x2' : np.square(x_
```

```
        pred)})[['x', 'x2']]))
    plt.plot(x_pred, y_pred)
    print(results.summary())
    plt.scatter(conv[col], y)
    plt.title(col + ' vs conversion')
    plt.show()


# Generates more detailed graphs used in this paper
# In[11]:
col = 'Pressure (atm)'
x = sel[[col, col + '2']]
y = sel['Selectivity (%)']
model = sm.OLS(y, sm.add_constant(x))
results = model.fit()
x_pred = np.linspace(sel[col].min(), sel[col].max(), 75)
y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred, 'x2' : np.square(x_pred)})
        [['x', 'x2']]))
plt.plot(x_pred, y_pred)
print(results.summary())
plt.scatter(sel[col], y)
plt.xlabel('Pressure (atm)')
plt.ylabel('Selectivity for CO2 (%)')
plt.show()


# In[12]:
col = 'Temp (°C)'
x = sel[col]
y = sel['Selectivity (%)']
model = sm.OLS(y, sm.add_constant(x))
results = model.fit()
x_pred = np.linspace(sel[col].min(), sel[col].max(), 75)
y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred})['x']))
plt.plot(x_pred, y_pred)
print(results.summary())
plt.scatter(sel[col], y)
plt.xlabel('Temp (°C)')
plt.ylabel('Selectivity for CO2 (%)')
plt.show()


# In[13]:
col = 'Time (hr)'
x = sel[[col, col + '2']]
y = sel['Selectivity (%)']
model = sm.OLS(y, sm.add_constant(x))
results = model.fit()
x_pred = np.linspace(sel[col].min(), sel[col].max(), 75)
y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred, 'x2' : np.square(x_pred)})
        [['x', 'x2']]))
plt.plot(x_pred, y_pred)
print(results.summary())
plt.scatter(sel[col], y)
plt.xlabel('Time (hr)')
plt.ylabel('Selectivity for CO2 (%)')
plt.show()
```

```
# In[14]:
col = 'Pressure (atm)'
x = conv[[col, col + '2']]
y = conv['Conversion (%)']
model = sm.OLS(y, sm.add_constant(x))
results = model.fit()
x_pred = np.linspace(conv[col].min(), conv[col].max(), 75)
y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred, 'x2' : np.square(x_pred)})
        [['x', 'x2']]))
plt.plot(x_pred, y_pred)
print(results.summary())
plt.scatter(conv[col], y)
plt.xlabel('Pressure (atm)')
plt.ylabel('Conversion Rate (%)')
plt.show()


# In[15]:
col = 'Time (hr)'
x = conv[col]
y = conv['Conversion (%)']
model = sm.OLS(y, sm.add_constant(x))
results = model.fit()
x_pred = np.linspace(conv[col].min(), conv[col].max(), 75)
y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred})['x']))
plt.plot(x_pred, y_pred)
print(results.summary())
plt.scatter(conv[col], y)
plt.xlabel('Time (hr)')
plt.ylabel('Conversion (%)')
plt.show()


# In[16]:
col = 'Temp (°C)'
x = conv[[col, col + '2']]
y = conv['Conversion (%)']
model = sm.OLS(y, sm.add_constant(x))
results = model.fit()
x_pred = np.linspace(conv[col].min(), conv[col].max(), 75)
y_pred = results.predict(exog = sm.add_constant(pd.DataFrame({'x': x_pred, 'x2' : np.square(x_pred)})
        [['x', 'x2']]))
plt.plot(x_pred, y_pred)
print(results.summary())
plt.scatter(conv[col], y)
plt.xlabel('Temp (°C)')
plt.ylabel('Conversion Rate (%)')
plt.show()
```