

**Computational and Experimental Investigation of CH₄ Adsorption in Pure
and Ionic Liquid Incorporated Metal Organic Frameworks**

by

Kutay Berk Sezginel

**A Thesis Submitted to the
Graduate School of Engineering
in Partial Fulfillment of the Requirements
for the Degree of**

Master of Science

In

Chemical and Biological Engineering

Koç University

July 2015

Koc University
Graduate School of Sciences and Engineering

This is to certify that I have examined this copy of a master's thesis by

Kutay Berk Sezginel

and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

Committee Members:

Assoc. Prof. Seda Keskin Avcı (Advisor, Koç University)

Asst. Prof. Alper Uzun (Advisor, Koç University)

Assoc. Prof. Demircan Canadinç (Koç University)

Asst. Prof. Mehmet Sayar (Koç University)

Prof. Ramazan Yıldırım (Boğaziçi University)

Date:

ABSTRACT

Natural gas is an abundant and relatively clean energy source with a potential to replace petroleum towards a low-carbon energy future. The most challenging part of utilizing natural gas for various applications is the development of a feasible method for its high density storage. Natural gas is commonly stored as compressed or liquefied natural gas which both create economical and safety issues. An alternative approach for safe and efficient storage of natural gas, adsorbed natural gas (ANG), has drawn attention recently. For the efficient implementation of ANG specifically tailored high capacity adsorbents are required. Metal organic frameworks (MOFs) have emerged as crystalline porous materials constructed from organic linkers and metal clusters. MOFs are considered as very promising adsorbents as a result of their extraordinary structural characteristics, such as high surface area, high porosity, low density as well good thermal and mechanical stability.

In the first part of this thesis, grand canonical Monte Carlo (GCMC) simulations were performed to investigate CH₄ (main component of natural gas) storage performance of MOFs. Structural/chemical properties of MOFs were calculated and simple multivariate linear models were constructed to predict CH₄ uptake of over 1500 different MOF structures using these properties. Moreover, the structural/chemical characteristics resulting in high CH₄ uptake were identified and optimum ranges for these properties were presented. In the second part, experimental characterization and high pressure adsorption measurements for CH₄, CO₂, N₂, and H₂ were performed for one of the top performing MOFs, HKUST-1 (commercially available as Basolite C300). Incorporation of ionic liquids (ILs) were examined using 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) to enhance gas storage and separation capabilities of Basolite C300. Results suggest that incorporation of ILs in MOFs results in modified adsorption capacities for different gases, with the highest affinity towards CH₄. The high pressure gas storage capacities were lowered with the addition of IL however, improved gas separation performance was observed. As a result, IL-incorporated MOFs are identified as new type of adsorbents with high potential for various gas storage/separation applications.

ÖZET

Doğal gaz bol bulunan ve diğer fosil yakıtlara göre daha temiz yanan düşük karbonlu bir enerji kaynağıdır. Doğal gazın pratikte kullanılabilmesi için yüksek yoğunlukta depolanmasını sağlayacak yöntemler bulunması gerekmektedir. Hali hazırda doğal gaz sıkıştırılmış doğal gaz (CNG) ya da sıvılaştırılmış doğal gaz (LNG) olarak depolanmaktadır. Bu iki yöntem de hem ekonomik açıdan hem de güvenlik açısından elverişli değildir. Yakın zamanda, adsorbe olmuş doğal gaz (ANG) güvenli ve verimli bir alternatif depolama yöntemi olarak ilgi görmüştür. ANG yönteminin uygulanabilmesi için özel olarak tasarlanmış yüksek kapasiteli adsorban malzemelere ihtiyaç vardır. Metal organik kafesli yapılar (MOFlar) organik bağlayıcılar ve metal kümelerden oluşmuş gözenekli kristal malzemelerdir. MOFlar adsorban olarak kullanılmak için önemli olan yüksek yüzey alanı, bol gözenek hacmi, düşük yoğunluk gibi yapısal özelliklerin yanı sıra yüksek termal ve mekanik dayanıklılığa da sahiptirler.

Bu tezin ilk kısmında MOFların doğal gazın büyük bölümünü oluşturan CH_4 gazını depolama performanslarını belirlemek amacıyla grand canonical Monte Carlo (GCMC) simülasyonları yapılmıştır. 1500'ün üzerinde farklı MOFun yapısal/kimyasal özellikleri hesaplanmış ve bu özelliklerden yararlanılarak MOFların CH_4 depolama miktarlarını tahmin eden çok değişkenli doğrusal denklemler çıkarılmıştır. Ayrıca, MOFların yüksek CH_4 depolamasını sağlayan yapısal/kimyasal özellikler belirlenmiş bu özellikler için ideal aralıklar tanımlanmıştır. Tezin ikinci kısmında CH_4 depolama uygulamaları için en ümit verici MOFlardan biri olan HKUST-1 (ticari ismi Basolite C300) deneysel olarak karakterize edilmiş ve yüksek basınçta CH_4 , CO_2 , N_2 ve H_2 gazlarının adsorpsiyon miktarları ölçülmüştür. Gaz depolama ve ayırma özelliklerinin iyileştirilmesi için Basolite C300'ün yapısına yaygın olarak kullanılan iyonik sıvılardan (İS) biri olan 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) dahil edilmiştir. Deney sonuçlarıncı İS-içerikli MOFların gaz depolama özelliklerinin normal MOFlara göre değişiklik gösterdiği saptanmıştır. İS-içerikli MOFların çalışılan gazlar arasında en çok CH_4 'e karşı yatkınlığı artmıştır fakat yüksek basınçlardaki gaz depolama kapasitelerinde düşüş gözlemlenmiştir. Sonuç olarak İS-içerikli MOFlar çeşitli gaz depolama ve gaz ayırma uygulamalarında kullanılmak üzere yüksek potansiyele sahip yeni bir adsorban çeşidi olarak tanımlanmışlardır.

ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to my advisors Dr. Seda Keskin and Dr. Alper Uzun for their endless support and guidance. They have become invaluable mentors to me both in my academic and social life. I attribute special thanks to my committee members Dr. Ramazan Yıldırım, Dr. Demircan Canadınç and Dr. Mehmet Sayar for their valuable time and contribution.

This project is funded by Tübitak 1001 Program (project number: 114R093). I sincerely acknowledge the support from Koç University Seed Program, and Koç University-Tüpraş Energy Center (KÜTEM).

I am very thankful to Koç University Surface Science and Technology Center (KUYTAM) coordinators Barış Yağcı and Cansu Yıldırım for their help in elemental analysis, XRD, SEM and BET measurements. I also want to thank Dr. Ahmet Kerim Avcı for providing the Basolite C300.

Working in two research laboratories, I had the opportunity to meet a lot of great people. I would like to thank Nanomaterials, Energy and Molecular Modeling Research Group (NEMO) and KÜTEM members for their friendship and support.

I am grateful to my parents Ahmet and Nur Sezginel for supporting me in every way possible and guiding me through life with their wisdom and knowledge. I also want to express my love for my little sister Dilay Naz for her friendship and sympathy for times we stayed apart.

TABLE OF CONTENTS

ABSTRACT.....	iii
ÖZET	iv
ACKNOWLEDGEMENTS.....	v
LIST OF TABLES.....	viii
LIST OF FIGURES	x
NOMENCLATURE	xvii
Chapter 1: Introduction	1
Chapter 2: Literature Review.....	5
2.1 Metal-Organic Frameworks (MOFs) for CH ₄ Storage.....	5
2.1.1 Computational Investigation of CH ₄ Storage in MOFs.....	8
2.1.2 Experimental Investigation of CH ₄ Storage in MOFs.....	11
2.3 Gas Solubility in Ionic Liquids	13
2.4 Ionic Liquid-Incorporated MOFs	18
Chapter 3: Methods.....	21
3.1 Computational Methods	21
3.1.1 Grand Canonical Monte Carlo (GCMC) Simulations	21
3.1.1.1 Theoretical Background	21
3.1.1.2 Computational Details.....	25
3.1.2 Computational Tools for the Calculation of Structural Properties of MOFs	27
3.2.1.1 Surface Area Calculations.....	27
3.2.2.2 Pore Size Distribution and Pore Volume Calculations	29
3.1.3 Quantitative Structure-Property Relationship (QSPR) Analysis.....	31
3.1.4 Computational Tools for Large Scale Screening of MOFs	32
3.2 Experimental Methods	33
3.2.1 Materials and Sample Preparation	33
3.2.2 Characterization Methods	34
3.2.2.1 X-Ray Diffraction	34
3.2.2.2 Thermal Gravimetric Analysis.....	35
3.2.2.3 Scanning Electron Microscopy.....	36
3.2.2.4 Brunauer–Emmett–Teller (BET) Surface Area.....	36
3.2.2.5 Infrared Spectroscopy.....	38
3.2.2.6 Elemental Analysis	39

3.2.3 High Pressure Volumetric Adsorption Analysis	40
Chapter 4: Computational Studies for CH ₄ Storage of MOFs	43
4.1 Validation of GCMC Simulations	45
4.2 QSPR Analysis and Regression Models for the Prediction of CH ₄ Storage	47
4.2.1 Comparison of Regression Models with Experimental Results	54
4.2.2 Comparison of Regression Models with Models Proposed by Other Studies	56
4.3 Large Scale Screening of MOFs for CH ₄ Storage	58
Chapter 5: Preparation, Characterization, and Adsorption Measurements of Ionic Liquid (IL) Incorporated MOFs	67
5.1 Material Handling	67
5.2 Characterization of as-purchased Basolite C300	68
5.2.1 Powder X-Ray Diffraction (XRD)	68
5.2.2 Thermal Gravimetric Analysis (TGA)	69
5.2.3 Scanning Electron Microscopy (SEM)	72
5.2.4 Brunauer–Emmett–Teller (BET) Surface Area	74
5.3 Preparation and Characterization of IL-Incorporated MOFs	75
5.3.1 Powder X-Ray Diffraction (XRD)	76
5.3.2 Thermal Gravimetric Analysis (TGA)	78
5.3.3 Scanning Electron Microscopy (SEM)	80
5.3.4 Infrared (IR) Spectroscopy	81
5.3.5 Brunauer–Emmett–Teller (BET) Surface Area	83
5.3.6 Elemental Analysis	85
5.4 Gas Adsorption Measurements	88
5.4.1 Gas Adsorption Analysis of Basolite C300	88
5.4.2 Gas Adsorption Analysis of IL-Incorporated MOFs	90
Chapter 6: Conclusions and Outlook	97
BIBLIOGRAPHY	100
APPENDIX A: Supplementary Information for Computational Methods	110
APPENDIX B: Supplementary Computational Results	136
APPENDIX C: Supplementary Experimental Results	176
APPENDIX D: Full names of Ionic Liquids	180

LIST OF TABLES

Table 2.1: Gas solubility data in ILs at temperatures close to ambient and various pressures [62]. Data at different temperatures and pressures can be found in related references.	16
Table 3.1: Simulation parameters for MOFs with modified force fields.....	26
Table 3.2: Input Parameters for PoreBlazer [128] Software.....	31
Table 4.1: Structural properties, isosteric heat of adsorption and excess CH ₄ uptake at 298 K, 5 and 35 bar for MOFs used in this study (sorted by alphabetical order of common names). ..	44
Table 4.2: Parameters of the QSPR multivariate linear regression models and their statistical model analysis for 5 and 35 bar. Statistical parameters of models at other pressures are given in Appendix B.	49
Table 4.3: Statistical parameters of the 4-variable models Model-1 and Model-2. The results for models at pressures other than 5 and 35 bar are given in Appendix B.	62
Table 4.4: Statistical parameters and formulas for pressure-independent models Model-3 and Model-4.....	65
Table 5.1: Onset temperatures and normalized wt% losses due to decomposition calculated from TGA experiments. Data for [BMIM][BF ₄] is adapted from literature [167].	79
Table 5.2: BET surface areas calculated from N ₂ adsorption measurements at 77 K.	85
Table 5.3: Experimental (Exp) and theoretical (Theo) weight percent of N, C, and H atoms in the structures.	86
Table A.1: CCDC refcodes for all MOFs considered in Chapter 4.3.	131
Table B.1: Simulated excess CH ₄ uptake at 298 K and all pressures considered in this study.	136
Table B.2: Simulated isosteric heat of adsorption values at 298 K and all pressures considered in this study.	138

Table B.3: Parameters of the QSPR multivariate linear regression models (Model-0) and their statistical model analysis.....	140
Table B.4: Minimum and maximum values for the parameters of the models (model restrictions).	151
Table B.5: Parameters of the simple linear regression models to predict isosteric heat of adsorption (Q_{st}) and their statistical model analysis.	152
Table D.1: Full names of ionic liquids mentioned in this thesis.....	180

LIST OF FIGURES

Figure 2.1: CH ₄ uptake (65 bar) and working capacity (difference between the uptake values at 65 and 5 bar) of top performing MOFs [18].	7
Figure 2.2: (a) Relationship between the deliverable capacity and the largest included sphere diameter; the horizontal line indicates the deliverable capacity of an empty tank; (b) Fractional deliverable capacity f plotted against the saturation loading M for each material. Hyperbolas indicate lines of constant deliverable capacity. The bottom and top hyperbolas give the deliverable capacity of a free space tank and the APRA-E target, respectively; (c) Relationship between the deliverable capacity and the crystal density [53].	10
Figure 2.3: Total gravimetric uptake, pore volume V_{pore} , and total volume V_{total} ($1/\rho$) as a function of BET surface area. The horizontal gray line indicates the DOE's gravimetric target 0.5 g/g [18].	12
Figure 2.4: [HMIM][Tf ₂ N]-monoethanolamine solution (a) CO ₂ -lean; (b) CO ₂ -rich [29].	15
Figure 2.5: (a) CO ₂ adsorption isotherms of the parent HKUST-1 (Cu-BTC in the figure) and impregnated HKUST-1-PF ₆ -5% and HKUST-1-Tf ₂ N-5% samples at 298 K; (b) Adsorption isotherms of parent HKUST-1 and impregnated HKUST-1-PF ₆ -10% at 298 K [98].	18
Figure 3.1: The difference between probe molecule orientation for accessible and Connolly surface area calculations [127].	28
Figure 3.2: (a) Schematic depiction of the accessible surface; (b) schematic depiction of the geometric pore. [128].	30
Figure 3.3: (a) N ₂ adsorption isotherm at 77 K between 0-1 bar; (b) BET equation fit used for the calculation of surface area between relative pressure of 0.05-0.3.	38
Figure 3.4: Schematic of High Pressure Volumetric Analyzer (HPVA) system [142].	40
Figure 3.5: CH ₄ adsorption isotherm for Basolite C300 at 298 K, Langmuir fit (red line) Inset: linearized Langmuir fit and regression equation.	42

Figure 4.1: Comparison of experimental and simulated CH ₄ uptake at 298 K in the range of 0.1 – 35 bar. Corresponding experimental references are given in Table 4.1.	47
Figure 4.2: Comparison of models and simulations for CH ₄ uptake at 298 K and 5 bar. Regression coefficients are given in Table 4.2.	51
Figure 4.3: Comparison of models and simulations for CH ₄ uptake at 298 K and 35 bar. Regression coefficients are given in Table 4.2.	53
Figure 4.4: Comparison of experiments and models for CH ₄ uptake at 298 K, (a) 5 bar; and (b) 35 bar. Corresponding experimental references are given in Table 4.1.....	55
Figure 4.5: Comparison of experiments and predictions of different models [50,60] for CH ₄ uptake at 298 K, (a) 1; and (b) 35 bar.	57
Figure 4.6: Comparison of Model-0 and simulations for CH ₄ uptake at 298 K and (a) 5 bar; and (b) 35 bar. Statistical parameters provided in Table 4.2. Model results at other pressures are given in Appendix B.	59
Figure 4.7: Comparison of Model-1 and simulations for CH ₄ uptake at 298 K and (a) 5 bar; and (b) 35 bar. Statistical parameters are provided in Table 4.3. Model results at other pressures are given in Appendix B.	60
Figure 4.8: Comparison of Model-2 and simulations for CH ₄ uptake at 298 K and (a) 5 bar; and (b) 35 bar. Statistical parameters are provided in Table 4.3. Model results at other pressures are given in Appendix B.	61
Figure 4.9: The model results and equations for pressure-indepent models (a) template model; (b) Model-3. Statistical parameters of the models are given in Table 4.4.	63
Figure 4.10: (a) Relation between average CH ₄ uptake and pressure, and equation of logarithmic fit; (b) Comparison of model results with simulations and equation for Model-4. Statistical parameters of Model-4 are given in Table 4.4.	64

Figure 5.1: X-ray diffraction pattern of Basolite C300 in this work (red) and its comparison with XRD pattern adapted from literature (black) [161].	69
Figure 5.2: Thermal gravimetric analysis results for Basolite C300. Red line and left y-axis shows weight percent change with temperature and dashed black line and right y-axis shows derivative weight percent change with temperature.	70
Figure 5.3: Thermal gravimetric analysis results for Basolite C300 adapted from work by Gimeno-Fabra et al. [162]. Straight line and left y-axis shows weight percent change with temperature and dashed line and right y-axis shows derivative weight percent change with temperature.	71
Figure 5.4: Morphology of Basolite C300 crystals at different magnifications: (a) 20,000x; (b) 10,000x; (c) 2,000x; and (d) 500x determined by SEM analysis.....	72
Figure 5.5: SEM Image of Basolite C300 obtained from Ref. [163].....	73
Figure 5.6: Morphology of old Basolite C300 crystals at different magnifications: (a) 20,000x; (b) 2,000x determined by SEM analysis.....	73
Figure 5.7: N ₂ adsorption isotherm at 77 K between 0-1 bar. Inset: fit used for the calculation of BET surface area between relative pressures of 0.05-0.3.....	74
Figure 5.8: Morphology of untreated Basolite C300 crystals at (a) 20,000x; (b) 10,000x; (c) 2,000x; magnifications, ethanol dipped Basolite C300 crystals at (c) 20,000x; (d) 10,000x; (e) 2,000x; magnifications, and acetone dipped Basolite C300 crystals at (g) 20,000x; (h) 10,000x; (i) 2,000x magnifications determined by SEM analysis.....	76
Figure 5.9: X-ray diffraction pattern of Basolite C300 (black), IL/C300 (5 wt%) (red), IL/C300 (20 wt%) (blue), and IL/C300 (30 wt%) (purple).	77
Figure 5.10: Thermal gravimetric analysis results for Basolite C300 and IL/C300: (a) weight percent change with temperature; and (b) derivative weight percent change with temperature.	78

Figure 5.11: Isothermal TGA results for Basolite C300 and IL/C300 (20 wt%) at 175 °C for 15 h.....	80
Figure 5.12: Morphology of (a) Basolite C300; (b) IL/C300 (5 wt%); (c) IL/C300 (20 wt%); and (d) IL/C300 (30 wt%) crystals determined by SEM analysis.	81
Figure 5.13: IR Spectra for Basolite C300, IL-incorporated C300 samples, and [BMIM][BF ₄] between (a) 3300-2800 cm ⁻¹ ; and (b) 1700-500 cm ⁻¹ . ν : stretching, γ : bending, δ : deformational, subscripts sym and asym are symmetric and asymmetric vibrations, respectively.	82
Figure 5.14: N ₂ adsorption isotherm at 77 K between 0-1 bar for (a) Basolite C300; (b) IL/C300 (5 wt%); (c) IL/C300 (20 wt%); and (d) IL/C300 (30 wt%).....	84
Figure 5.15: Correlation between BET surface area and IL loading of Basolite C300.	85
Figure 5.16: High pressure adsorption isotherms of Basolite C300 and their comparison with literature for (a) CH ₄ [1]; (b) CO ₂ [172]; (c) N ₂ [173]; and (d) H ₂ [173]. Measurement temperatures are given in legends of each plot.	89
Figure 5.17: High pressure gas adsorption isotherms of Basolite C300 and IL/C300 samples at room temperature for (a) CH ₄ ; (b) CO ₂ ; (c) N ₂ ; and (d) H ₂	90
Figure 5.18: Low pressure (0 – 1 bar) gas adsorption isotherms of Basolite C300 and IL/C300 samples at room temperature for (a) CH ₄ ; (b) CO ₂ ; (c) N ₂ ; and (d) H ₂	91
Figure 5.19: Adsorption capacity change of all gases at different IL loadings at 1 bar.	92
Figure 5.20: Ideal adsorption selectivities for (a) CO ₂ /CH ₄ ; (b) CO ₂ /N ₂ ; (c) CO ₂ /H ₂ ; (d) CH ₄ /N ₂ ; (e) CH ₄ /H ₂ ; and (f) N ₂ /H ₂ at room temperature up to 5 bar. The first component is the more selective over the second component. The x-axes are given in log scale for clear representation of the data at low pressures.	93
Figure A.1: Pore size distribution of HKUST-1 calculated by PoreBlazer.	110
Figure B.1: Comparison of models and simulations for CH ₄ uptake at 298 K and 1 bar.....	141

Figure B.2: Comparison of models and simulations for CH ₄ uptake at 298 K and 5 bar.....	142
Figure B.3: Comparison of models and simulations for CH ₄ uptake at 298 K and 10 bar....	143
Figure B.4: Comparison of models and simulations for CH ₄ uptake at 298 K and 15 bar....	144
Figure B.5: Comparison of models and simulations for CH ₄ uptake at 298 K and 20 bar....	145
Figure B.6: Comparison of models and simulations for CH ₄ uptake at 298 K and 25 bar....	146
Figure B.7: Comparison of models and simulations for CH ₄ uptake at 298 K and 30 bar....	147
Figure B.8: Comparison of models and simulations for CH ₄ uptake at 298 K and 35 bar....	148
Figure B.9: Comparison of models and simulations for CH ₄ uptake at 298 K and 50 bar....	149
Figure B.10: Comparison of models and simulations for CH ₄ uptake at 298 K and 65 bar..	150
Figure B.11: Comparison of models and simulations for Q_{st} at 298 K, 1 and 5 bar.....	152
Figure B.12: Comparison of models and simulations for Q_{st} at 298 K, 10 and 15 bar.....	153
Figure B.13: Comparison of models and simulations for Q_{st} at 298 K, 20 and 25 bar.....	153
Figure B.14: Comparison of models and simulations for Q_{st} at 298 K, 30 and 35 bar.....	154
Figure B.15: Comparison of models and simulations for Q_{st} at 298 K, 50 and 65 bar.....	154
Figure B.16: Binary relations of crystallographic density with other structural parameters.	155
Figure B.17: Binary relations of crystallographic density with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH ₄ uptake at (c) 5 bar; (d) 35 bar.....	156
Figure B.18: Binary relations of pore volume with other structural parameters.	157
Figure B.19: Binary relations of pore volume with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH ₄ uptake at (c) 5 bar; (d) 35 bar.....	158
Figure B.20: Binary relations of void fraction with other structural parameters.....	159
Figure B.21: Binary relations of void fraction with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH ₄ uptake at (c) 5 bar; (d) 35 bar.....	160
Figure B.22: Binary relations of gravimetric surface area with other structural parameters.	161

Figure B.23: Binary relations of gravimetric surface area with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.....	162
Figure B.24: Binary relations of pore limiting diameter with other structural parameters....	163
Figure B.25: Binary relations of pore limiting diameter with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.....	164
Figure B.26: Binary relations of maximum pore diameter with other structural parameters.	165
Figure B.27: Binary relations of maximum pore diameter with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.....	166
Figure B.28: Binary relations of dominant pore diameter with other structural parameters.	167
Figure B.29: Binary relations of dominant pore diameter with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.....	168
Figure B.30: Binary relations between Q_{st} and CH_4 uptake at (a) 5 bar; and (b) 35 bar.	169
Figure B.31: Comparison of Model-0 and simulations for CH_4 uptake at 298 K and (a) 1; (b) 10; (c) 15; (d) 20 bar.	170
Figure B.32: Comparison of Model-0 and simulations for CH_4 uptake at 298 K and (a) 25; (b) 30; (c) 50; (d) 65 bar.	171
Figure B.33: Comparison of Model-1 and simulations for CH_4 uptake at 298 K and (a) 1; (b) 10; (c) 15; (d) 20 bar.	172
Figure B.34: Comparison of Model-1 and simulations for CH_4 uptake at 298 K and (a) 25; (b) 30; (c) 50; (d) 65 bar.	173
Figure B.35: Comparison of Model-1 and simulations for CH_4 uptake at 298 K and (a) 1; (b) 10; (c) 15; (d) 20 bar.	174
Figure B.36: Comparison of Model-2 and simulations for CH_4 uptake at 298 K and (a) 25; (b) 30; (c) 50; (d) 65 bar.	175

Figure C.1: XRD results for Basolite C300 with background signal.	176
Figure C.2: Determination of T_{onset} and T'_{onset} values on a representative TGA data obtained for Basolite C300.	176
Figure C.3: Full range ($4000\text{-}500\text{ cm}^{-1}$) IR spectra for all samples.	177
Figure C.4: Deconvolution of IR spectra for 30 wt% IL-incorporated Basolite C300 sample between (a) $1400\text{-}1500\text{ cm}^{-1}$; (b) $625\text{-}675\text{ cm}^{-1}$	177
Figure C.5: IR spectra of 20 wt% IL-incorporated Basolite C300 before (black) and after (red) adsorption measurements.	178
Figure C.6: IR spectra of 30 wt% IL-incorporated Basolite C300 before (black) and after (red) adsorption measurements.	178
Figure C.7: XRD results of 20 wt% IL-incorporated Basolite C300 before (black) and after (red) adsorption measurements.	179

NOMENCLATURE

BET: Brunauer–Emmett–Teller	R_c : Cut-off radius (Å)
CCDC: Cambridge Crystallographic Data Centre	SEM: Scanning electron microscope
DPD: Dominant pore diameter (Å)	S_g : Gravimetric surface area (m ² /g)
GCMC: Grand canonical Monte Carlo	STD: Standard deviation
IL: Ionic liquid	STP: Standard temperature and pressure
k_B : Boltzman constant	S_v : Volumetric surface area (m ² /cm ³)
LJ: Lennard-Jones	TGA: Thermal gravimetric analysis
MOF: Metal organic framework	T_{onset} : Onset temperature (°C)
MPD: Maximum pore diameter (Å)	T'_{onset} : Derivative onset temperature (°C)
N_i : Adsorbed amount for component i	UFF: Universal force field
PCN: Porous coordination network	V_p : Pore volume (cm ³ /g)
PLD: Pore limiting diameter (Å)	XRD: X-Ray Diffraction
PPN: Porous polymer network	ZIF: Zeolitic imidazolate framework
PSD: Pore size distribution	ε : LJ potential parameters (J/mol)
QSPR: Quantitative Structure-Property Relation	μ : Chemical potential (J/mol)
Q_{st} : Isosteric heat of adsorption (kJ/mol)	σ : LJ distance parameter (Å)
R^2 : Coefficient of determination	ρ_{cryst} : Crystal density (g/cm ³)

Chapter 1: Introduction

Natural gas, comprising mainly CH_4 , has the potential to replace petroleum and become the primary fuel for transportation. It is naturally abundant and it has the highest H/C ratio of all hydrocarbons, and therefore it emits less carbon than other fossil fuels [1]. However, the low volumetric energy density of CH_4 creates a major challenge for its utilization as a fuel. There are several ways to store high densities of CH_4 . Adsorbed natural gas (ANG), one promising option, offers a safer and relatively inexpensive solution compared to other methods, such as compressed natural gas (CNG) and liquefied natural gas (LNG) [2]. In order to successfully implement ANG, adsorbent materials that can efficiently store and deliver CH_4 must be developed. For this purpose, various studies focused on porous materials such as zeolites [3], activated carbons [4], carbon nanotubes (CNTs) [5], porous polymer networks (PPNs) [6] and metal-organic frameworks (MOFs) [1,2]. Among these porous materials, MOFs have been examined extensively for their CH_4 storage applications.

MOFs are a type of highly porous material formed typically from metal clusters and organic linkers. They show a high potential for use in a wide range of applications, such as

gas storage [2,7-9], gas separation [10-13] and catalysis [14]. Compared to traditional nanoporous materials, MOFs exhibit several advantages, such as ease of synthesis, good thermal and mechanical stability, high permanent porosity, and large surface area. Moreover, as a result of their tunable chemistry, it is possible to obtain an almost unlimited number of different MOFs with a wide range of pore sizes and framework structures by changing the combination of metal centers and organic linkers [15].

In order to assess the viability of using adsorbent materials for CH₄ storage, Advanced Research Projects Agency-Energy [16] of U.S. Department of Energy (DOE) has set targets for volumetric and gravimetric adsorbent CH₄ working capacity. The working capacity is defined as the difference between the adsorbed amounts at storage and delivery pressures at 298 K. The volumetric working capacity target between a delivery pressure of 5 bar and moderate storage pressures corresponds to 350 cc(STP)/cc CH₄. When adsorbent material packing loss is ignored, the working capacity target becomes 263 cc(STP)/cc (corresponding to CNG at 250 bar and 298K) [2]. Two storage pressures of 35 and 65 bar were considered in previous studies as they correspond to the upper limits achievable with single-stage and two-stage compressors, respectively [17,18]. Both pressures require relatively inexpensive equipment whereas multi-stage compressors needed to reach high pressures (250 bar) of CNG tanks are more costly.

To date, no MOFs were able to reach this working capacity target at either of these storage pressures. For the purpose of increasing adsorption performance, creating stronger adsorption sites by functionalization of MOFs has been successfully applied for various MOFs [19-21]. One of the promising candidates to incorporate with MOFs is ionic liquids (ILs). ILs are salts that have melting points below 100 °C. They are composed of ions and they offer wide range of physical and chemical properties by means of different anion-cation pairs [22]. Moreover, ILs have been considered as green solvents due to their desirable

properties, such as high thermal stability, negligible volatility and non-flammability [23]. These properties enable them to be considered for applications in catalysis [24,25], extraction [26,27] and gas absorption [28,29]. It is possible to obtain ILs with high solubility towards gases, such as CH₄, CO₂ and this solubility can be modified by changing ion pairs. As a result, one approach to increase CH₄ storage performance or CH₄ selectivity of MOFs is to incorporate ILs with high CH₄ solubility into MOF structures.

In this thesis, CH₄ adsorption in MOFs has been studied using both computational and experimental methods. Initially, a detailed investigation of the relations between structural properties and CH₄ storage performance on a dataset of 45 MOFs were carried out using computational methods. Quantitative structure property relationship (QSPR) analysis was performed to determine which structural parameters are more correlated with CH₄ uptake. Using the most correlated properties, simple multivariable linear models were constructed using one, two, three, and four variables to predict CH₄ storage at ambient temperature and at a wide range of pressures 1, 5, 10, 15, 20, 25, 30, 35, 50, and 65 bar. To extend this study the predictive abilities of the models were tested on ~1500 MOFs, the model coefficients were updated and a new model was proposed using the same analyses. The viability of using a single pressure-independent model to predict CH₄ uptake of MOFs was examined by constructing models that include an additional parameter to account for pressure change. In the experimental part, one of the top performing materials, HKUST-1 (commercially available as Basolite® C300), has been characterized extensively and its high pressure CH₄, CO₂, N₂ and H₂ adsorptions have been measured. The viability of enhancing adsorption performance of this MOF with ILs has been tested by incorporating 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) into Basolite C300 at different loadings. Same characterizations and adsorption measurements have been performed for the IL-incorporated Basolite C300 samples and outcomes have been investigated.

In Chapter 2, a detailed literature survey for CH₄ storage on MOFs, gas solubility in ILs and IL-incorporated MOFs has been provided. In Chapter 3, computational and experimental methods used in this study are described. In Chapter 4, results obtained from computational screening of MOFs for CH₄ storage are presented. In Chapter 5, experimental characterization and adsorption measurements of MOF and IL-incorporated MOFs are given. Finally, outcomes of the research have been summarized in Chapter 6.

Chapter 2: Literature Review

In the first part of this chapter, background of CH₄ storage in MOFs is given focusing on computational and experimental studies unraveling the structural/chemical properties effective for high CH₄ uptake. In the second part, summaries of studies concentrating on CH₄ and CO₂ solubility in ILs are discussed. And finally, previous studies of IL incorporated MOFs focusing on adsorption related applications are introduced.

2.1 Metal-Organic Frameworks (MOFs) for CH₄ Storage

Triggered by the depletion of fossil fuels and increasing threat of global warming search for clean energy carriers such as H₂ and CH₄ in addition to the need for the reduction of CO₂ emissions has critical importance. The most challenging part of utilizing these gases for various applications is seen as the development of a feasible method for their storage in a confined space [30]. Highly porous materials have been considered as means to increase the storage density of gases via adsorption. If porous materials are utilized, high pressures required to store large amounts of gases can be avoided which would bring important safety advantages. For a successful application, the adsorbent material should be carefully tailored

to have sufficient adsorption capacity, controllable delivery rates, suitable lifetimes, and good recharging characteristics [31].

MOFs have been extensively examined as adsorbents thanks to their useful structural properties such as ultrahigh porosity, very large surface area, and pore volume. These crystalline materials are formed from various metal clusters and organic linkers providing an extraordinary degree of structural variability. MOFs have been considered for many applications including gas storage [1,2,7,8,30,32], gas separation [10-12,33-36], catalysis [14,37-39], and chemical sensing [40-45]. Among these applications, remarkable structural properties and highly tunable nature of MOFs excelled them as high-capacity adsorbents for both gas storage and separation requirements.

Among the gas storage applications CO_2 , H_2 , and CH_4 have been studied in detail using both computational and experimental methods. CH_4 , as the main component of natural gas, has been considered as an environmental friendly alternative fuel for vehicular transportation. Natural gas is typically stored in cylindrical containers compressed up to 250 bar. However, compressed natural gas (CNG) has low energy content per volume, approximately one third of gasoline, therefore CNG fuel tanks should be three times larger than gasoline tanks to provide the same driving range [46]. Additionally, at 250 bar, CNG tanks also generate safety and economic issues for use in vehicular applications due to the required high pressures. Adsorbed natural gas (ANG) has been considered as a promising approach to safely storage high densities of natural gas using porous adsorbent materials. Advanced Research Projects Agency-Energy (ARPA-E) division of U.S. Department of Energy (DOE) has initiated a program that investigates the viability of using porous adsorbents as storage media for CH_4 storage [16]. ARPA-E has set targets for adsorptive CH_4 storage at ambient temperature and relatively low pressures, which are seen as benchmarks to actualize ANG related applications. The volumetric CH_4 storage target corresponds to 315 cc(STP)/cc, and

263 cc(STP)/cc if the adsorbent packing loss is ignored. The adsorption unit, cc(STP)/cc, indicates cm^3 of CH_4 gas at standard temperature and pressure per cm^3 of adsorbent. The target is determined for working capacity which is defined as the difference between adsorbed amounts at storage pressure and delivery pressure. Generally, a delivery pressure of 5 bar and two storage pressures of 35 and 65 bar were considered in previous studies [17,18]. Both pressures can be achieved with relatively inexpensive equipment and provide safety advantages compared to high pressures required for CNG.

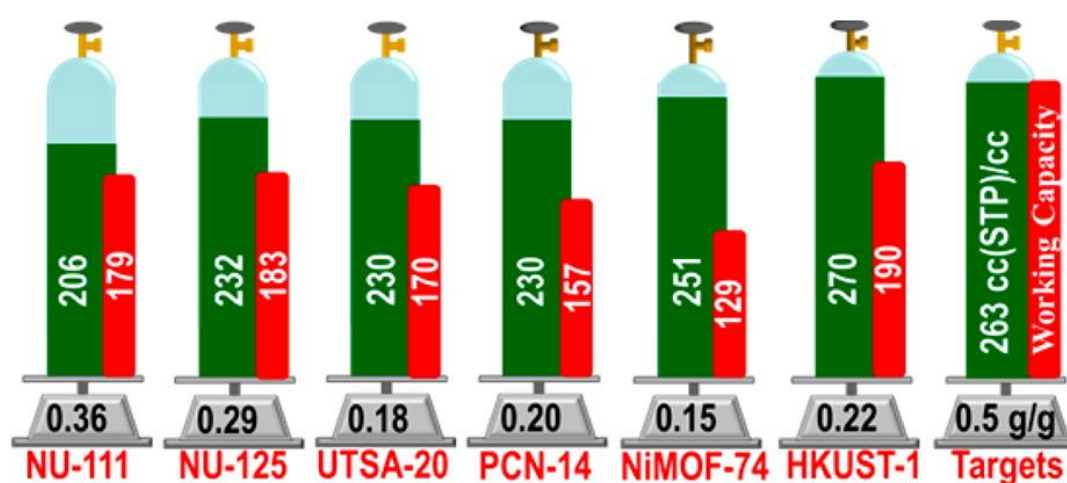


Figure 2.1: CH_4 uptake (65 bar) and working capacity (difference between the uptake values at 65 and 5 bar) of top performing MOFs [18].

MOFs have been investigated in detail for ANG storage [1,2], however none of synthesized structures were able to satisfy the CH_4 working capacity target so far. As seen in Figure 2.1, MOFs can provide high CH_4 storage at 65 bar and even exceed the target of 263 cc(STP)/cc CH_4 [18]. However, as well as high uptake at storage pressure, low uptake at delivery pressure is also required to achieve the working capacity target. The highest working capacity recorded for a delivery pressure of 5 bar was 211 and 151 cc(STP)/cc for MOF-519 [47], 197 and 151 cc(STP)/cc for UTSA-76a [48] followed by 190 and 150 cc(STP)/cc for HKUST-1 [18] for storage pressures of 65 and 35 bar, respectively. Even though the target has not been reached yet, the highly tunable nature of MOFs provides opportunities to design

materials that may reach the target. For optimal material design, it is required to examine structural and chemical properties that are controlling the CH₄ storage and working capacity.

2.1.1 Computational Investigation of CH₄ Storage in MOFs

Molecular simulations have been extensively used to study CH₄ adsorption in MOFs. Compared to experimental methods, simulations provide detailed molecular understanding of the chemical phenomena. This enables determination of structural/chemical properties that lead to high CH₄ storage performance. Additionally, construction of MOF structures and measurement of high pressure adsorption are much simpler with simulations. This enables fast and effortless examination of large number of structures to identify top performing materials at high pressures, which are difficult to achieve experimentally [49].

Large scale computational screening studies were performed to predict CH₄ uptake at storage and delivery pressures as well as the working capacity. Fernandez et al. [50] performed a large-scale quantitative structure-property relationship (QSPR) analysis on approximately 130,000 hypothetical MOFs to predict CH₄ uptake at 1, 35, and, 100 bar focusing on structural properties, such as dominant pore diameter (DPD), gravimetric surface area (S_g), and void fraction (V_f). They concluded that for high CH₄ storage at 35 bar, crystal density (ρ_{cryst}) and V_f should be greater than 0.43 g/cm³ and 0.52, respectively. Gomez-Gualdron et al. [51] followed this study by performing simulations on 122,835 hypothetical MOFs to elucidate the viability of reaching volumetric CH₄ storage and delivery targets (between 5.8 and 65 bar). Their results revealed the recommended parameters as volumetric surface area (S_v) between 2100-2300 m²/cm³, largest cavity diameter (LCD) between 10-12 Å, and, isosteric heat of adsorption (Q_{st}) between 10.5-13.0 kJ/mol. Another large scale screening study [52] was performed by Martin et al. for porous polymer networks (PPNs), where structure-property relationships for CH₄ storage performance was investigated on

approximately 18,000 hypothetical PPN structures. They found out that pore size is the primary structural property that determines the CH₄ uptake performance of PPNs and they also discovered that in all best-performing materials cooperative CH₄-CH₄ interactions were present, therefore they suggested CH₄ adsorption sites should be optimized by adjusting the pore size to enhance CH₄ uptake.

Recently, Simon et al. [53] evaluated CH₄ working capacity between 5.8 and 65 bar at 298 K in 650,000 structures including 139,407 predicted zeolite structures [54, 55], 10,000 hypothetical MOF structures randomly selected from a set of 137,953 materials [56], 17,970 predicted PPN structures [52], 20,000 hypothetical zeolitic imidazolate framework (ZIF) structures randomly selected from a set of 381,178 structures [57], and 5,109 experimental MOF structures [58]. They found out that PPNs and MOFs have significantly higher working capacities than zeolites, however the maximum deliverable capacity for all materials investigated was 196 cc(STP)/cc CH₄ which is far from the DOE target of 315 cc(STP)/cc.

As seen in Figure 2.2 (a) and (c) the optimal pore diameter and crystal density were found to be ~ 11 Å and ~ 450 kg/m³, respectively. They also investigated optimum working capacity by comparing fractional deliverable capacity (f), defined as the ratio of working capacity to CH₄ loading at storage pressure, and saturation loading (M), defined as the maximum amount of CH₄ stored at saturation pressure. The resulting plot (given in Figure 2.2 (b)) suggested a trade-off between density of adsorption sites and the density of the material. They proposed that the ideal material should have the largest density of adsorption sites which have optimum methane interactions. Considering previous experimental studies and computational screening of 650,000 materials, they concluded that there might be a physical limitation for CH₄ storage around 200 cc(STP)/cc.

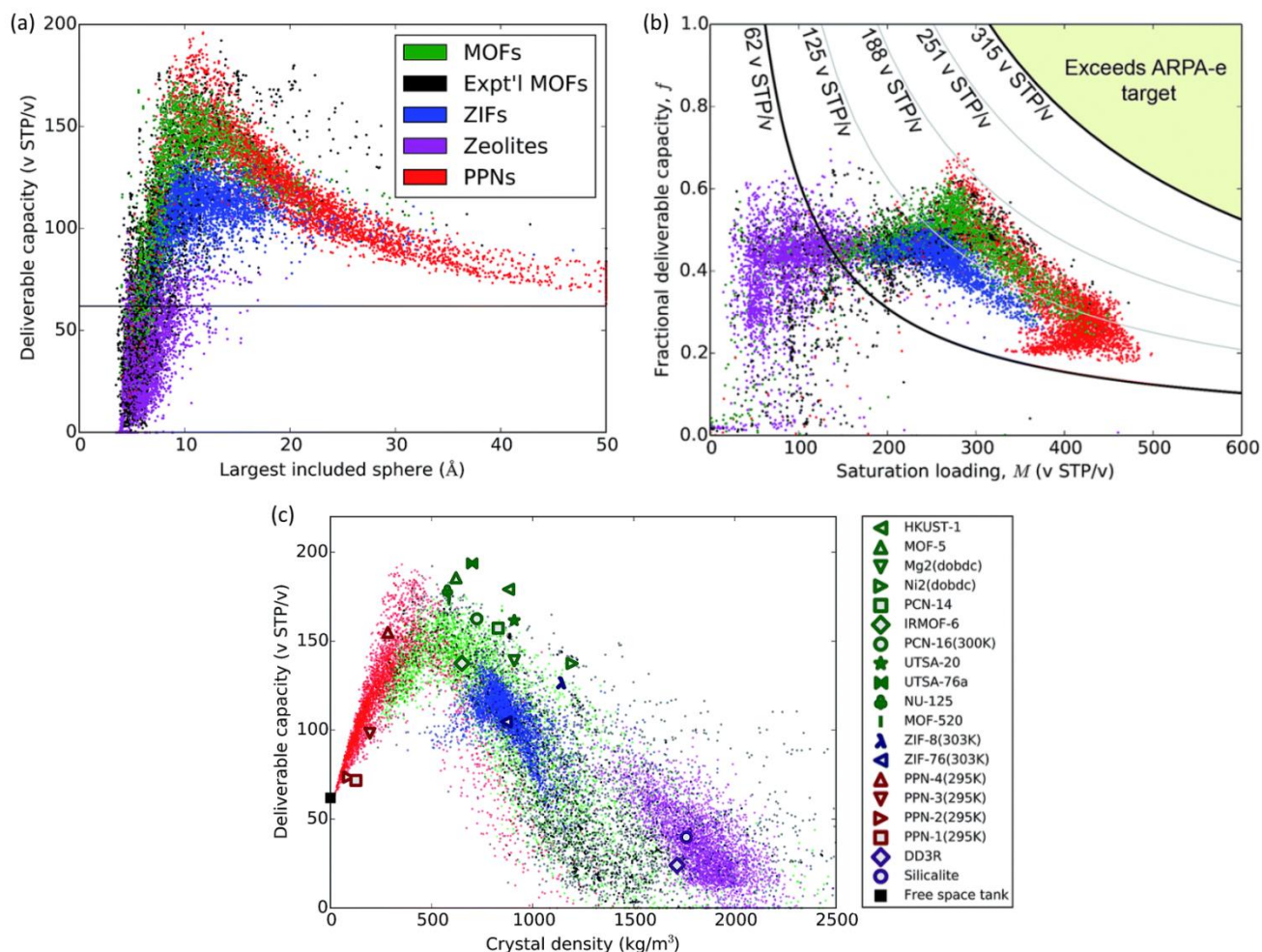


Figure 2.2: (a) Relationship between the deliverable capacity and the largest included sphere diameter; the horizontal line indicates the deliverable capacity of an empty tank; (b) Fractional deliverable capacity f plotted against the saturation loading M for each material. Hyperbolas indicate lines of constant deliverable capacity. The bottom and top hyperbolas give the deliverable capacity of a free space tank and the APRA-E target, respectively; (c) Relationship between the deliverable capacity and the crystal density [53].

These large scale studies provide very important information regarding which routes to take to design new materials that can reach set CH_4 storage target. However, structures considered in most of these studies are hypothetical, thus these works are limited in accurately representing the performance of actual synthesized MOFs. One successful approach on this regard was reported by Farha et al. [59] which used computational modeling to design and characterize a hypothetical MOF followed by synthesis of the designed structure. After synthesis of the tailored material, they found very similar characterization and

uptake properties (H_2 and CO_2) with the predicted structure. Even though this is a very promising result CH_4 uptake properties of the synthesized material were not measured and no other hypothetical MOF structure has been investigated experimentally for CH_4 storage purposes.

2.1.2 Experimental Investigation of CH_4 Storage in MOFs

Relations between structural properties of MOFs and CH_4 uptake were studied experimentally by several groups. Identifying these relations is beneficial for making preliminary evaluation of the material for CH_4 storage before going through high pressure adsorption experiments. Several studies have identified linear relationships with structural properties of MOFs and their CH_4 uptake at high pressures. Making use of these correlations characterization of the X-ray crystal structure and porosity of the MOF would be sufficient to approximately predict CH_4 storage performance [2].

He et al. [60] investigated five MOFs of the same family (NOTT-100, NOTT-101, NOTT-102, NOTT-103 and NOTT-109) having variable open Cu sites and systematically varied porosities for CH_4 storage at 35 bar. They found a linear correlation between gravimetric CH_4 uptake and pore volume (V_p) for the MOFs considered in this study and they proposed the following empirical equation to predict excess CH_4 uptake (N) at 35 bar and ambient temperature:

$$N_{CH_4} (cm^3(STP)/g) = -126.69 \times V_p^2 + 381.62 \times V_p - 12.57$$

where V_p indicates pore volume in cm^3/g .

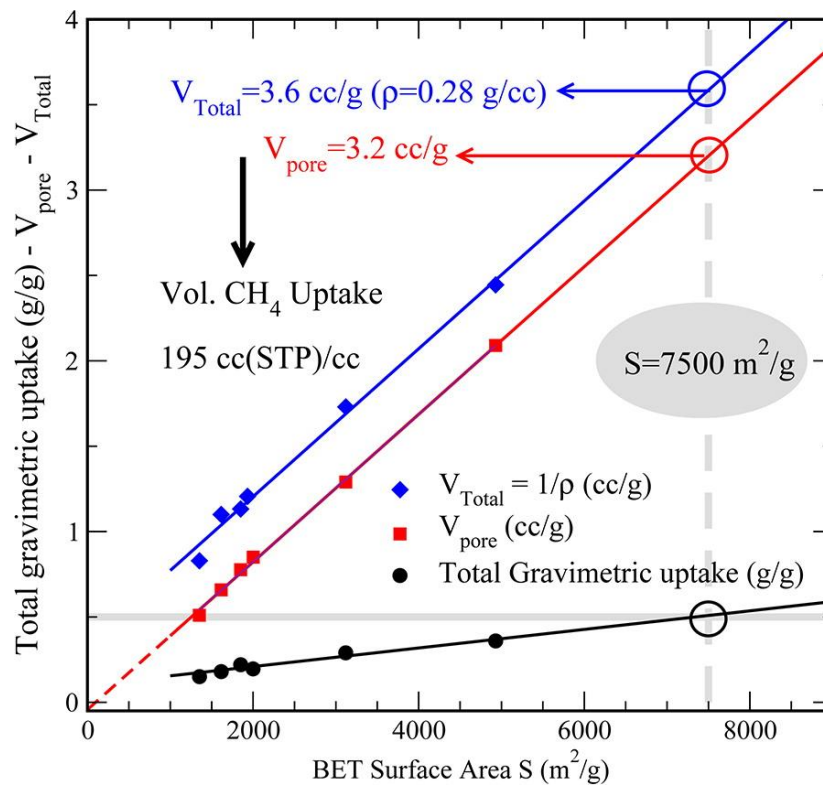


Figure 2.3: Total gravimetric uptake, pore volume V_{pore} , and total volume V_{total} ($1/\rho$) as a function of BET surface area. The horizontal gray line indicates the DOE's gravimetric target 0.5 g/g [18].

Peng et al. [18] studied six promising MOFs for CH_4 storage (PCN-14, UTSA-20, HKUST-1, CPO-27-Ni, NU-111, and NU-125) at 65 bar. As can be seen in Figure 2.3, they identified linear correlations between gravimetric CH_4 uptake and V_p , and between gravimetric surface area (S_g) and total volume V_{total} (i.e. one over crystal density $1/\rho_{\text{cryst}}$). From these correlations the corresponding values for S_g , V_p , and ρ_{cryst} of MOFs were suggested to be in the order of $7500 \text{ m}^2/\text{g}$, $3.2 \text{ cm}^3/\text{g}$, and $0.28 \text{ g}/\text{cm}^3$, respectively, to exceed the gravimetric DOE target. Moreover, correlations indicated that CH_4 storage capacity (N) at 65 bar and ambient temperature can be approximated using the equation:

$$N_{\text{CH}_4} (\text{cm}^3(\text{STP})/\text{g}) = 0.07958 \times S_g + 127.1,$$

where S_g indicates gravimetric BET surface area in m^2/g .

Kong et al. [61] investigated the relation between S_g and CH_4 uptake at 60 bar using previously reported experimental results for 25 MOFs and reported that CH_4 uptake is linearly correlated with S_g and, V_p linearly varies with $1/\rho_{\text{cryst}}$. Based on the revealed correlations, CH_4 uptake at 60 bar and ambient temperature can be approximately calculated using following equation:

$$N_{\text{CH}_4} (\text{cm}^3(\text{STP})/\text{g}) = 0.06526 \times S_g + 147.2.$$

These studies give valuable information about the relation of structural properties and CH_4 uptake, however, the limited number of MOFs (≤ 25) used in these studies and the fact that these studies focused solely on storage pressures prevent utilization of these outcomes extensively. Therefore, investigation of structural/chemical properties of a large number of real MOF structures is required to both understand the underlying structural/chemical factors affecting CH_4 storage and construct models for the accurate prediction of CH_4 uptake.

2.3 Gas Solubility in Ionic Liquids

Ionic liquids (ILs) possess remarkable properties such as non-volatility, non-flammability, high chemical and thermal stability, which facilitate them as good alternatives to conventional liquid solvents [22]. As a result, gas solubility data in ILs is essential in assessing a variety of chemical processes, such gas separations, gas-liquid reactions, and liquid-liquid extractions. Among the gas solubility studies of ILs CO_2 solubility has been widely studied especially for CO_2 capture. CH_4 generally has much lower solubility compared to CO_2 , however its higher than that of H_2 , CO , N_2 , and O_2 [62]. When other gaseous hydrocarbons (ethane, propane, butane) are considered CH_4 is significantly less soluble in ILs [63]. As expected, CH_4 solubility increases at low temperatures [62], and increasing the alkyl chain length on the cation of IL was found to increase CH_4 solubility as

well [64]. In this section gas solubility in ILs will be introduced focusing on CO₂ and CH₄ solubility.

Bates et al. [28] discovered a novel task-specific IL which reversibly reacts with CO₂ and enables sequestration of the gas as a carbamate salt. They incorporated an ammine group (which reacts with CO₂) into the cation of the IL by the reaction of 1-butyl imidazole with 3-bromopropylamine hydrobromide, followed by purification and anion exchange. The resulting IL was proposed as an alternative to commercial amine sequestering agents due to its comparable efficiency, non-volatility and recyclability. Camper et al. [29] studied the viability of using mixtures of ILs and commercial ammine solutions for the capture of CO₂ as carbamate salts. 50:50 (mol/mol) solutions of [HMIM][Tf₂N] monoethanolamine (MEA) and [C₂OHMIM][Tf₂N] diethanolamine (DEA) were found to outperform previously proposed “task-specific” ILs and show similar performance as widely used aqueous amine solutions. They discovered a significant advantage of [HMIM][Tf₂N]-(MEA) mixture as the insolubility of resulting carbamate in the mixture. This allowed the precipitation of carbamate to favor the formation of more carbamate as opposed to aqueous ammine solutions in which the carbamate salt remains soluble, thereby slowing the rate of the CO₂ capture reaction. The precipitated carbamate salt in [HMIM][Tf₂N]-MEA solution can be seen in Figure 2.4, where the carbamate formation and the capture of CO₂ can be easily reversed by increasing temperature or decreasing pressure.

Anthony et al. [65] studied anion effects of [BF₄], [Tf₂N], and [PF₆] with [BMIM] cation for solubilities of CO₂, C₂H₄, C₂H₆, N₂O, C₆H₆ vapor, H₂O vapor, CO, and O₂. They ordered the solubility of gases in these ILs as H₂O and C₆H₆ followed by N₂O and CO₂, then C₂H₄, C₂H₆ and O₂. They found out that anion appears to play the most significant role in determining the gas solubilities and [Tf₂N] anion increases all gas solubilities relative to ILs with [BF₄] and [PF₆] anions.

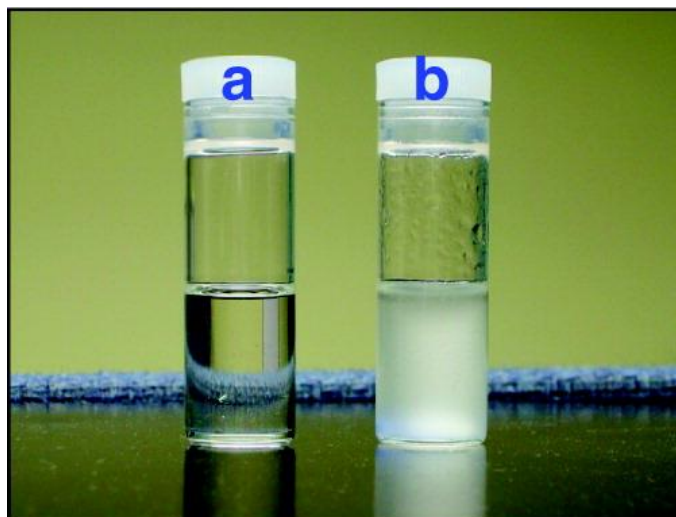


Figure 2.4: [HMIM][Tf₂N]-monoethanolamine solution (a) CO₂-lean; (b) CO₂-rich [29].

Mortazavi-Manesh et al. [66] calculated pure solubilities of CO₂, CH₄, H₂S, and C₂H₆ for 425 ILs at 298 K and 2000 kPa using conductor-like screening model for real solvents (COSMO-RS) [67]. They determined that ILs containing the [doc], [FEP], and [Tf₂N] anions show the highest average solubility of all gases whereas ILs containing [Cl], [NO₃], [BF₄], and [lactate] anions show the lowest average solubilities. Moreover they observed that ILs containing [C₆H₄F₉mim], [N₄₄₄₄], and [b₂Nic] cations show highest average solubilities for all gases considered in their study. They have also calculated binary selectivities for all four gases and identified most promising 58 IL candidates for sour gas treatment.

Ramdin et al. [68] measured solubility of pure CO₂ and CH₄ gases for a temperature range of 303.15–363.15 K and for pressures up to 14 MPa for 10 ILs: [EMIM][DEP], [THTDP][PHOS], [THTDP][DCA], [AMIM][DCA], [BMPYRR][DCA], [CPROP][DCA], [CPROP][Tf₂N], [BMPIP][Tf₂N], [TES][Tf₂N], and [TOA][Tf₂N]. They calculated CO₂/CH₄ selectivities from Henry's constants and found out that selectivities change between 6-22 at 313 K and decrease with increasing temperature and increasing IL's molecular weight. In a different study Ramdin et al. [69] measured solubilities in the binary mixture of CO₂ and CH₄ at the same temperature range and pressures as in their previous study [68] using 4 ILs:

[BMIM][Tf₂N], [EMIM][DEP], [THTDP][PHOS], and [THTDP][DCA]. They calculated the CO₂/CH₄ selectivity for different compositions of gas mixtures and showed that the real selectivity values do not differ significantly from the ideal selectivity regardless of the gas phase composition.

In Table 2.1 gas solubility data for CH₄, N₂, H₂, and CO₂ in imidazolium ILs are provided at temperatures and pressures close to ambient. For studies where ambient pressure data were not available solubility data at lowest and highest pressures were given. For studies where both sub-ambient and above ambient pressures are available solubility data at the lowest pressure, ambient pressure and highest pressure are given. The gas solubilities of these ILs at other temperatures and pressures can be found in references provided in Table 2.1.

Table 2.1: Gas solubility data in ILs at temperatures close to ambient and various pressures [62]. Data at different temperatures and pressures can be found in related references.

Cation	Anion	Gas	T (K)	P (bar)	Solubility	Ref
					x (mole fraction)	
[BMIM]	[BF ₄]	CH ₄	303.38	0.88	0.0011	[70]
[BMIM]	[MeSO ₄]	CH ₄	293.15	13.63	0.0094	[71]
[BMIM]	[MeSO ₄]	CH ₄	293.15	85.10	0.0461	[71]
[BMIM]	[Tf ₂ N]	CH ₄	313.15	15.01	0.0298	[72]
[BMIM]	[Tf ₂ N]	CH ₄	313.15	160.27	0.2245	[72]
[EMIM]	[EtSO ₄]	CH ₄	293.14	1.98	0.0013	[73]
[EMIM]	[EtSO ₄]	CH ₄	292.37	101.50	0.0405	[73]
[HMIM]	[Tf ₂ N]	CH ₄	293.30	8.86	0.0275	[71]
[HMIM]	[Tf ₂ N]	CH ₄	293.30	82.52	0.1860	[71]
[BMIM]	[BF ₄]	N ₂	303.38	0.87	0.0006	[70]
[BMIM]	[PF ₆]	N ₂	308.33	0.86	0.0007	[74]
[BMIM]	[BF ₄]	H ₂	298.34	0.82	0.0005	[70]
[BMIM]	[MeSO ₄]	H ₂	293.30	14.57	0.0021	[75]
[BMIM]	[MeSO ₄]	H ₂	293.30	86.17	0.0125	[75]
[BMIM]	[PF ₆]	H ₂	313.05	16.95	0.0040	[76]
[BMIM]	[PF ₆]	H ₂	313.05	90.85	0.0216	[76]
[BMIM]	[Tf ₂ N]	H ₂	303.24	0.81	0.0007	[77]
[EMIM]	[PF ₆]	H ₂	298.00	26.82	0.0058	[78]
[EMIM]	[Tf ₂ N]	H ₂	303.38	0.80	0.0007	[77]

[HMIM]	[Tf ₂ N]	H ₂	303.41	0.83	0.0008	[79]
[BMIM]	[Ac]	CO ₂	298.10	0.10	0.1880	[80]
[BMIM]	[Ac]	CO ₂	298.10	1.00	0.2740	[80]
[BMIM]	[Ac]	CO ₂	298.10	19.99	0.4550	[80]
[BMIM]	[BF ₄]	CO ₂	298.15	0.10	0.0012	[65]
[BMIM]	[BF ₄]	CO ₂	298.15	1.00	0.0161	[65]
[BMIM]	[BF ₄]	CO ₂	298.15	13.00	0.1850	[65]
[BMIM]	[DCA]	CO ₂	298.20	12.71	0.1598	[81]
[BMIM]	[DCA]	CO ₂	298.20	59.43	0.5149	[81]
[BMIM]	[MeSO ₄]	CO ₂	293.20	9.08	0.1118	[82]
[BMIM]	[MeSO ₄]	CO ₂	293.20	41.20	0.3997	[82]
[BMIM]	[PF ₆]	CO ₂	298.15	0.50	0.0080	[83]
[BMIM]	[PF ₆]	CO ₂	298.15	1.00	0.0170	[83]
[BMIM]	[PF ₆]	CO ₂	298.15	12.99	0.2000	[83]
[BMIM]	[Tf ₂ N]	CO ₂	298.15	0.10	0.0032	[65]
[BMIM]	[Tf ₂ N]	CO ₂	298.15	1.00	0.0308	[65]
[BMIM]	[Tf ₂ N]	CO ₂	298.15	13.00	0.2960	[65]
[BMIM]	[TfO]	CO ₂	303.85	8.50	0.2182	[84]
[BMIM]	[TfO]	CO ₂	303.85	85.00	0.6325	[84]
[EMIM]	[Ac]	CO ₂	298.10	0.10	0.1890	[85]
[EMIM]	[Ac]	CO ₂	298.10	1.00	0.2670	[85]
[EMIM]	[Ac]	CO ₂	298.10	20.00	0.4280	[85]
[EMIM]	[BF ₄]	CO ₂	298.15	2.51	0.0330	[86]
[EMIM]	[BF ₄]	CO ₂	298.15	8.75	0.1060	[86]
[EMIM]	[DCA]	CO ₂	303.20	1.48	0.0205	[87]
[EMIM]	[DCA]	CO ₂	303.20	54.47	0.2174	[87]
[EMIM]	[Tf ₂ N]	CO ₂	298.15	2.13	0.0500	[86]
[EMIM]	[Tf ₂ N]	CO ₂	298.15	9.03	0.2090	[86]
[EMIM]	[PF ₆]	CO ₂	313.12	71.60	0.4490	[88]
[EMIM]	[PF ₆]	CO ₂	313.04	793.00	0.6190	[88]
[EMIM]	[TfO]	CO ₂	303.85	8.00	0.1794	[84]
[EMIM]	[TfO]	CO ₂	303.85	149.00	0.6268	[84]
[HMIM]	[BF ₄]	CO ₂	298.15	3.12	0.0710	[86]
[HMIM]	[BF ₄]	CO ₂	298.15	8.99	0.1630	[86]
[HMIM]	[PF ₆]	CO ₂	298.15	2.96	0.0580	[86]
[HMIM]	[PF ₆]	CO ₂	298.15	9.27	0.1670	[86]
[HMIM]	[Tf ₂ N]	CO ₂	298.15	2.42	0.0930	[86]
[HMIM]	[Tf ₂ N]	CO ₂	298.15	8.59	0.2360	[86]
[HMIM]	[TfO]	CO ₂	303.85	12.50	0.2885	[84]
[HMIM]	[TfO]	CO ₂	303.85	180.00	0.7171	[84]

2.4 Ionic Liquid-Incorporated MOFs

Majority of the studies incorporating ILs and MOFs consist of ionothermal synthesis of MOFs, where ILs have been used as both reaction media and structure-directing agents due to their good solvent properties [89-96]. Other studies that include MOFs and ILs were focused on CO₂ capture and separation [97-102], desulfurization [103,104], catalysis [105-108], ionic conductivity [109], and phase behavior [110]. There are limited studies involving MOFs and ILs other than MOF synthesis and nearly all of these studies were carried out after 2013 suggesting that new applications for these IL/MOF materials are yet to be discovered. Only a handful of studies were performed on the adsorption performance of IL-incorporated MOFs and their main outcomes are described in the following paragraphs.

In a recent study Silva et al. [98] studied CO₂ adsorption on [BMIM][Tf₂N] and [BMIM][PF₆] incorporated HKUST-1 using both computational and experimental methods. They performed GCMC simulations on the IL incorporated MOF structures and found out that until 30 wt% IL loading CO₂ adsorption increased at pressures up to 2 and 3 bar for [BMIM][Tf₂N] and [BMIM][PF₆] loaded structures, respectively.

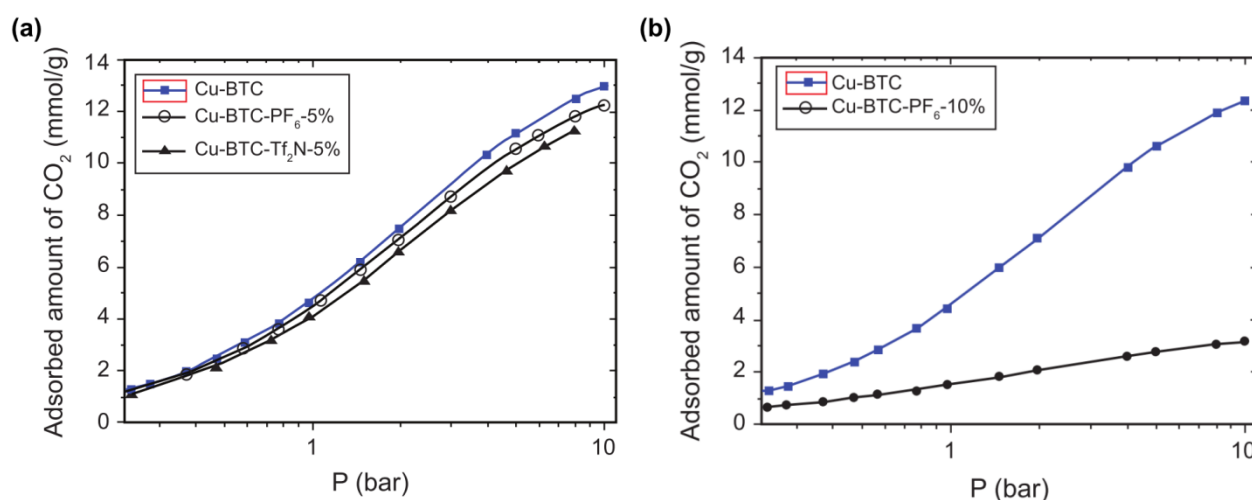


Figure 2.5: (a) CO₂ adsorption isotherms of the parent HKUST-1 (Cu-BTC in the figure) and impregnated HKUST-1-PF₆-5% and HKUST-1-Tf₂N-5% samples at 298 K; (b) Adsorption isotherms of parent HKUST-1 and impregnated HKUST-1-PF₆-10% at 298 K [98].

They have also experimentally impregnated HKUST-1 with both ILs at 1, 5, and 10 wt% loadings. All impregnated HKUST-1 samples had significantly lower Brunauer-Emmett-Teller (BET) surface area and pore volume, inversely proportional with IL loading. As seen in Figure 2.5, CO₂ adsorption was measured for IL impregnated samples with 5 and 10 wt% loadings and realized that none of the samples were able to outperform parent HKUST-1 at any pressure. Sample with 5 wt% [BMIM][PF₆] impregnation showed a slight decrease in CO₂ uptake, whereas sample with 10 wt% impregnation showed a much significant decrease. They concluded that even though the addition of ILs creates stronger adsorption sites for CO₂, the decrease in the free volume inhibits adsorption performance especially at higher pressures.

Chen et al. [101] examined [BMIM][PF₆] incorporated IRMOF-1 for CO₂ capture using molecular simulations. They discovered that CO₂ adsorption increased up to 0.5 bar for IRMOF-1/[BMIM][PF₆] sample with 40% loading and decreased after that pressure. For other samples at higher loadings the CO₂ uptake values decreased compared to IRMOF-1. They also found out that even though CO₂ uptake decreased, CO₂/N₂ selectivity of IRMOF-1 increased from ~6 to ~50 at ambient conditions for IRMOF-1/[BMIM][PF₆] with 150% loading. Vicent-Luna et al. [97] studied effect of ILs with [EMIM] cation and various anions namely, [SCN], [Tf₂N], [BF₄], [NO₃], and [PF₆] on CO₂ adsorption and selectivity towards CH₄ and N₂. They performed GCMC simulations and observed that CO₂ uptake increases in IL-incorporated samples up to 5 bar for [EMIM][SCN] and up to 2 bar for [EMIM][Tf₂N] whereas other samples' uptake remains between these pressure values. They also revealed that CH₄ and N₂ adsorption remains almost unchanged; therefore CO₂ selectivity towards these gases increases greatly. Lei et al. [99] investigated the solubility of CO₂ in mixtures of ILs ([OMIM][Tf₂N] and [OMIM][PF₆]) and ZIFs (ZIF-7 and ZIF-8). First, they measured CO₂ solubility in pure ILs and performed GCMC simulations to predict CO₂ adsorption in

ZIFs. Using these results, they employed lever rule to predict CO₂ solubility in IL/ZIF mixtures and found out that individual CO₂ solubility of ILs and CO₂ adsorption of ZIFs can be used to predict CO₂ solubility in IL/ZIF mixtures. Aijaz et al. [102] fabricated nanoporous carbons by impregnation of ILs ([EMIM][DCN] and [EMIM][TCB]) within MIL-100(Al) framework followed by carbonization of the impregnated samples. The resulting carbon materials had BET surface area between 1525-2731 m²/g and promising CO₂ and H₂ uptakes. They also showed high selectivity (between 22-57) for CO₂ adsorption over N₂.

Li et al. [103] carried out molecular simulations to investigate the performance of Cu-TDPAT/IL samples for the separation of H₂S/CH₄ mixture. [BMIM] cation with four types of anions ([Cl], [Tf₂N], [PF₆], and [BF₄]) were incorporated into Cu-TDPAT framework at different loadings and it was found out that all samples had significantly higher affinity towards H₂S compared to pristine Cu-TDPAT. The highest performing material was identified as Cu-TDPAT/[BMIM][Cl] with a H₂S/CH₄ selectivity at 1 bar reaching 1302, nearly 10 times of unmodified Cu-TDPAT which has a H₂S/CH₄ selectivity of 141. Khan et al. [104] investigated potential of IL supported MOFs for adsorptive desulfurization using [BMIM][Cl] and MIL-101. They found out that adsorption capacity for benzothiophene was increased up to 71% in [BMIM][Cl]/MIL-101 compared to virgin MIL-101.

As discussed here, there is limited number of studies on IL-incorporated MOFs and none of these studies investigated CH₄ storage and separation capabilities of these materials. In this study, gas storage and separation abilities of IL-incorporated MOFs have been investigated experimentally focusing on CH₄. The results are given in Chapter 5.

Chapter 3: Methods

This chapter focuses on computational and experimental methods utilized in this thesis study. In the first part, computational methods are explained in detail and in the second part experimental methods are described extensively.

3.1 Computational Methods

3.1.1 Grand Canonical Monte Carlo (GCMC) Simulations

3.1.1.1 Theoretical Background

CH₄ adsorption can be measured by volumetric/gravimetric adsorption experiments or it can be calculated with computer simulations. Grand canonical Monte Carlo (GCMC) simulations are extensively used to calculate adsorption of gases in porous materials and especially in metal organic frameworks. It is important to understand basic principle of classical Monte Carlo simulations before focusing on the grand canonical Monte Carlo simulations. In classical Monte Carlo Ensemble, number of particles (N), volume (V), and temperature (T) are kept constant and chemical potential of the material is allowed to

fluctuate. This fluctuation is based on random sampling that is called as the natural ensemble where the chemical potential fluctuates to achieve the lowest energy level. In grand canonical Monte Carlo Ensemble, chemical potential (μ), temperature (T), and volume (V) are kept constant and the number of molecules is allowed to fluctuate to obtain the lowest energy level. In adsorption studies, GCMC is widely used as natural ensemble because understanding the average number of particles adsorbed in a system as a function of external conditions such as pressure is important [111].

There are three different particle moves in a GCMC simulation: particle insertion, particle deletion, and particle displacement. For a GCMC simulation probability of the insertion moves and the probability of deletion moves are kept constant and they are calculated as follows:

$$P_{insertion} = P_{deletion} = \frac{1}{2} [1 - P_{displacement}] \quad (3.1)$$

For a single GCMC event, a number between 0 and 1 is chosen randomly and according to the probabilities assigned to each move (Equation 3.1) this number determines which move to attempt. If the random number is lower than the probability of the displacement move, a particle is randomly selected and the system attempts to perform a displacement move. If the number chosen is between the probability of displacement move and the probability of insertion move plus the displacement move, then the system attempts to insert a new particle randomly. If the number is larger than the probability of insertion move plus the displacement move, the system attempts to delete a randomly chosen particle. For all three types of moves, particles in the simulation box are exchanged with a reservoir containing the same gas molecules with the same chemical potentials and at the same temperature. After deciding on the type of movement, it is important to check the acceptance

criteria of the movement performed. For particle displacement and particle insertion/deletion there exists two different acceptance criteria, which can be found in the literature [111].

One of the most important steps in a GCMC simulation is the calculation of the chemical potential. Chemical potential should be related to pressure in order to compute gas adsorption isotherm of a material. There are three different ways to estimate the chemical potential of a system. First, chemical potential can be set equal to fugacity. In a system where the pressure is low and the bulk phase can be assumed as ideal, this assumption is valid. For systems having higher pressures, chemical potential can be calculated if an equation of state is known. If not, a test method named as *widom test particle insertion method* [112] can be used. In this method a particle is assumed as a ghost particle and inserted into the system without changing the overall energy of the system. The insertion of the particle does not affect the structure therefore the energy does not change due to particle insertion. Using this method, chemical potential of the system can be calculated.

The calculation of the energy between particles is performed using intermolecular interactions. In this study, attractive dispersion and short-range repulsive forces, commonly named as Van der Waals forces, are considered [113]. CH₄ is a nonpolar molecule with an overall dipole moment of zero, therefore van der Waals forces are sufficient to represent intermolecular interactions. These interactions are calculated by using Lennard-Jones 12-6 type potential for all non-bounded pair atoms. Lennard-Jones (LJ) potential can be calculated with the following equation:

$$U_{LJ} = 4 \times \varepsilon_{ij} \times \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3.2)$$

where r represents the distance between two molecules and U is the internal energy. In order to use this equation σ and ε parameters should be known where the σ value represents the size

parameter interpreting distance and ε is the energy parameter. In this equation the term with magnitude 12 represents repulsive potential resulting from electron overlap and the term with magnitude 6 represents long-range attractive forces. A cut off radius is determined for each simulation where the distance between particles bigger than the cut off radius results in negligible interactive forces. In this study, cut off radius was set to 13 Å, which suggests that atom pairs whose distances are greater than 13 Å have van der Waals interaction energy of zero.

Another important step in GCMC simulations is the calculation of isosteric heat of adsorption (Q_{st}). Q_{st} by definition is the difference in the partial molar enthalpies of gas molecules between bulk and adsorbed phase, which corresponds to change in enthalpy with the adsorption process. If ideal gas assumption is used for the adsorbed gas phase, than the change in the enthalpy is calculated using the Van't Hoff equation. Q_{st} , which is equal to negative of change in the enthalpy during adsorption, is commonly reported as a positive thermodynamic quantity to simplify the calculations. The Q_{st} values in this work were calculated at the same pressures with adsorption calculations using the fluctuation method [114]:

$$Q_{st} = R \times T - \frac{\langle U \times N \rangle - \langle U \rangle \times \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (3.3)$$

where R is the ideal gas constant, T is the temperature, N is the number of molecules in the system, U is the potential energy and the brackets denote ensemble averages.

For the comparison of simulated adsorption isotherms with experimental results further calculations are needed. Experimental results are commonly reported in excess adsorption isotherms whereas GCMC simulations report absolute adsorption. It is important

to convert absolute adsorption to excess adsorption before making any comparison. The following equation is used for the conversion:

$$N_{excess} = N_{absolute} - \rho_{gas} \times V_p \quad (3.4)$$

where N indicates adsorbed amount, ρ_{gas} is the density of gas and V_p is the pore volume of the adsorbent. GCMC simulations produce absolute adsorption because adsorption occurring on the external surface is also accounted. When the gas molecules stay in the pores of an adsorbent, GCMC simulation includes these molecules in the adsorption amount. This difference is negligible at low pressures however it becomes considerable at high pressures. More detailed explanation for the conversion between excess and absolute adsorption can be found in the literature [115].

3.1.1.2 Computational Details

X-ray diffraction measurements enable the generation of crystal files which contain lattice parameters, symmetry group and individual coordinates of each atom. All the crystal information used in this work is extracted from the Cambridge Crystallographic Data Center (CCDC) [116]. A total of 45 metal organic frameworks (MOFs) were studied in the first part of computational studies. To obtain LJ potentials for the framework atoms various force fields were used. For 28 MOFs UFF [117], for 10 MOFs DREIDING [118] force fields, which are the most widely used force fields for simulating gas adsorption in MOFs, were used in GCMC simulations based on the results of this study and previous simulation studies [119, 120] that show a good agreement with the available experimental data. For ZIF-68, ZIF-69, ZIF-78, ZIF-81 force field parameters proposed by Liu and Smit [121] and for ZIF-79 force fields parameters proposed by Perez-Pellitero et al. [122] were used. For PCN-80 [123] and PCN-26 [124] materials, modified force fields were adapted from literature since they show better agreement with the experimental results. These modified force field

parameters are given in Table 3.1. For the simulations of 1514 MOFs presented in Chapter 4.3, UFF was used to obtain potential parameters since it is a widely used generic force field.

Spherical LJ 12-6 potential is used to model the adsorbed gas molecule (CH_4) as a single sphere using united atom model [125] ($\epsilon/k_B = 148 \text{ K}$, $\sigma = 3.73 \text{ \AA}$). In order to calculate cross interactions between unlike LJ sites, the Lorentz-Berthelot mixing rules [126] were employed and the intermolecular potentials were truncated at $13 \text{ \AA}$ for adsorption simulations. Periodic boundary conditions were applied and simulation box of $2 \times 2 \times 2$ crystallographic unit cell was used for GCMC 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 all simulations random insertion, deletion, and translation moves were used.

Table 3.1: Simulation parameters for MOFs with modified force fields

MOF	Atom	$\epsilon/k_B \text{ (K)}$	$\sigma \text{ (\AA)}$	$R_c \text{ (\AA)}$	Force Field	Reference
PCN-26	C	41.86	3.47	13	C atom ϵ modified	[124]
	Cu	2.51	3.11	13		
	H	7.65	2.85	13		
	O	48.19	3.03	13		
PCN-80	C	23.95	3.47	13	C atom ϵ modified	[123]
	Cu	2.51	3.11	13		
	H	7.65	2.85	13		
	N	38.98	3.26	13		
	O	48.19	3.03	13		
ZIF-68	C	40.27	3.43	13	Liu	[121]
	H	14.14	2.57	13		
	N	22.72	3.26	13		
	O	21.75	3.12	13		
	Zn	53.40	2.46	13		
ZIF-69	C	40.27	3.43	13	Liu	[121]
	H	14.14	2.57	13		
	N	22.72	3.26	13		
	O	21.75	3.12	13		
	Zn	53.40	2.46	13		
ZIF-78	C	40.27	3.43	13	Liu	[121]
	H	14.14	2.57	13		
	N	22.72	3.26	13		
	O	21.75	3.12	13		

	Zn	53.40	2.46	13		
ZIF-79	C	36.48	3.26	13	Perez	[122]
	H	15.29	2.44	13		
	N	23.97	3.10	13		
	O	20.85	2.96	13		
	Zn	43.08	2.34	13		
ZIF-81	C	40.27	3.43	13	Liu	[121]
	H	14.14	2.57	13		
	N	22.72	3.26	13		
	O	21.75	3.12	13		
	Zn	53.40	2.46	13		
	Br	126.39	3.732	13		

3.1.2 Computational Tools for the Calculation of Structural Properties of MOFs

3.2.1.1 Surface Area Calculations

Surface area is one of the most important characteristic properties of a porous material. There are two different surface areas reported in the literature namely Brunauer–Emmett–Teller (BET) and Langmuir surface areas. These are experimentally determined structural properties from N₂ adsorption isotherms of a material at 77 K and details are described in Chapter 3.2. Two methods are very similar and they both assume close packing of molecules however, BET equation assumes multilayer adsorbed phase while Langmuir method assumes monolayer. For structures like MOFs having large enough pores, BET surface area is more commonly used to make calculations.

BET surface area can also be calculated mathematically using two different methods. First method is the Connolly surface area where the bottom of the probe molecule is used to calculate the surface area as illustrated in Figure 3.1. Other method is to calculate the accessible surface area where the center of the probe molecule is rolled across the surface.

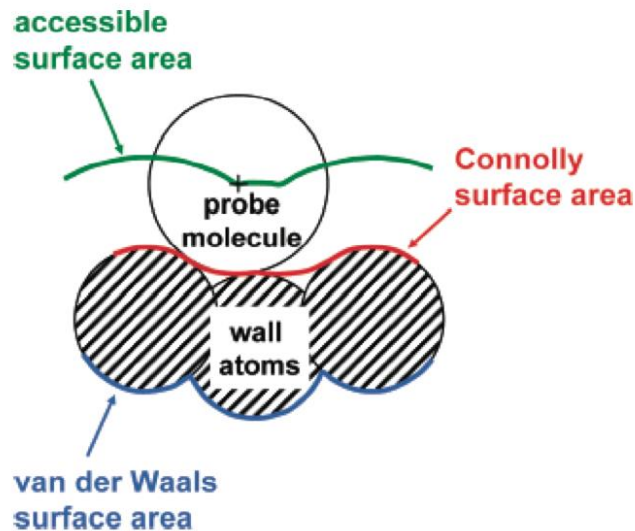


Figure 3.1: The difference between probe molecule orientation for accessible and Connolly surface area calculations [127].

In this work accessible surface area calculations were carried out with N_2 as a probe molecule which has a kinetic diameter of 3.681 Å. In order to calculate the accessible surface area as explained above, a computational tool proposed by Düren et al. [127] is employed. This algorithm assumes a probe molecule is placed on a location at a distance r_c to the framework atom and considers all the framework atoms separately while calculating the surface area. The distance between the centers of the two molecules is calculated as:

$$r = r_p + r_f \quad (3.5)$$

where r_p is the diameter of the probe molecule and r_f is the diameter of the framework atom in consideration. The algorithm selects a random framework atom on the structure and places the probe molecule. The placed probe molecule is tested for overlaps. Accessible surface area for a randomly selected single framework atom (S_i) can be calculated as follows:

$$S_i = \pi \times f \times r^2 \quad (3.6)$$

where the f represents the fraction of points that do not cause overlap between the probe molecule and other framework atoms. Similarly, the total accessible surface area of the structure can be calculated as:

$$S_{\text{Accessible Surface}} = \sum_{i=1}^N S_i \quad (3.7)$$

Both volumetric (S_v) and gravimetric surface area (S_g) can be calculated with this method where S_v indicates total area per volume of material and S_g indicates total area per mass of material. For the calculation of the surface areas in this study default parameters suggested by Düren et al. was used [127]. More details about the calculation of surface area can be found in Düren et al.'s work [127].

3.2.2.2 Pore Size Distribution and Pore Volume Calculations

Pore size distribution and pore volume of a material can be calculated using various methods such as mercury porosimetry, N_2 physisorption at 77 K, or through adsorption of other gases. For microporous adsorbents, such as MOFs, generally N_2 adsorption at 77 K is employed at very low pressures. After the adsorption isotherm is generated different theoretical calculations such as Horváth-Kawazoe (HK) method, Barrett-Joiner-Halenda (BJH) method and Broekhoff-de Boer (BdB) method are conducted to obtain the pore size distribution and pore volume [128]. The calculation of pore sizes from experimental data requires extensive experimental measurements at very low temperatures (77 K) and very low pressures (10^{-6} bar) [129]. Therefore, theoretical calculations of pore size distribution can be performed using molecular simulations effortlessly. Before explaining the calculation of the pore size distribution of individual materials, it is important to understand the definition of a pore in a porous material.

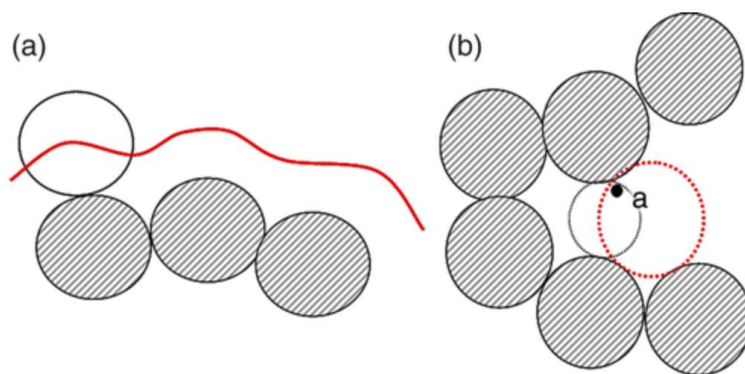


Figure 3.2: (a) Schematic depiction of the accessible surface; (b) schematic depiction of the geometric pore. [128].

Figure 3.2 represents a porous structure where the grey shaded circles are the framework atoms and point “a” belongs to the spherical pore with largest spherical diameter r producing no overlaps with the atoms of the structure.

To calculate the pore size distribution a Monte Carlo algorithm is used. Point “a” is randomly selected on the framework and checked for overlaps to avoid randomly selecting a particle that is inside the framework rather than on the surface of the framework. If there are no overlaps observed in the first round of the Monte Carlo procedure than a second round is conducted where a sphere is introduced on point “a” and the sphere diameter is increased until overlap is observed. The largest diameter of the sphere without overlap gives the pore size of the identified point.

In this work, crystal density (ρ_{cryst}), pore volume (V_p), pore limiting diameter (PLD), maximum pore diameter (MPD) and pore size distribution of all the structures were calculated by an algorithm (PoreBlazer) developed by Sarkisov and Harrison [128]. The input parameters for PoreBlazer can be found in Table 3.2.

Table 3.2: Input Parameters for PoreBlazer [128] Software.

PoreBlazer Input Parameters	
Default Force Field	UFF
Temperature	298 K
He atom (σ)	2.58 Å
He atom (ϵ)	10.22
Nitrogen atom (σ)	3.314 Å
Cubelet Size	0.2 Å
Largest anticipated pore diameter	20 Å, 100 Å ^a
Size of the bin for PSD ^b	0.1 Å ^a
Random number seed	21908391

^a Non-default values^b PSD: Pore Size Distribution

The calculation of void fraction (V_f), also called as porosity (ϕ), was performed by multiplication of V_p and ρ_{cryst} . The dominant pore diameter (DPD) was calculated from the pore size distribution as the diameter of the pore that occurs most frequently. An example pore size distribution for HKUST-1 is provided in Appendix A.

3.1.3 Quantitative Structure-Property Relationship (QSPR) Analysis

The relation between CH₄ adsorption and eight structural/chemical properties described earlier was investigated using a computational QSPR tool [130] (Appendix A) that selects a small set of variables that give the smallest standard deviation (STD) of a multivariate linear regression. The objective of the QSPR theory is to predict chemical properties of frameworks gathered from the molecular structures. The main assumption of the QSPR theory is that such properties are completely determined by the molecular structure.

This method was used for one-, two-, three-, and four-variables for pressures of 1, 5, 10, 15, 20, 25, 30, 35, 50, and 65 bar. The resulting multivariable linear QSPR model was

constructed as: $N = a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + b$ where N represents the excess CH₄ uptake in cc(STP)/g, a_1 , a_2 , a_3 , a_4 represent the coefficients of the model parameters, X_1 , X_2 , X_3 , X_4 represent the model parameters and b represents the constant. The statistical parameters of all models are provided in relevant chapters and in Appendix B. The predictions of these models were compared with GCMC results and they were also compared with the available experimental results.

3.1.4 Computational Tools for Large Scale Screening of MOFs

Large scale screening of 1514 MOFs (list provided in Appendix A) were performed using the MOF database provided by Chung et al. [58]. Simulations were performed using the same source codes explained previously in this chapter however, creation of the simulation files, submission of the simulations and collection of the results were performed by writing several MATLAB scripts provided in Appendix A.

First, the space groups of MOFs provided in the database [58] were converted to their native space group as they were deposited in Cambridge Crystallographic Data Centre (CCDC) [116]. The symmetry conversion was performed using Materials Studio program by Accelrys [131]. The “Find Symmetry” tool was used with 0.1 Å tolerance and symmetry conversion was performed automatically by writing a Perl script given in Appendix A. Resulting structures were packed by excluding all atoms outside the simulation box and the coordinates were saved in “.mol2” file format using Mercury software by CCDC [132]. The files were then converted to simulation input files using MATLAB codes given in Appendix A. The validation of the MATLAB codes was tested by comparing the results of the simulations performed by using input files generated by MATLAB and input files generated by hand. The submission and file handling of the simulations were also automatically performed by using several UNIX shell scripts provided in Appendix A. After the simulations

were completed the results of all simulations were collected by writing other MATLAB codes that read the output files of the simulations. The validations of the results were also tested by comparing with results collected using conventional methods.

3.2 Experimental Methods

In this section experimental methods used for the characterization and adsorption performance analyses of the samples will be explained in detail.

3.2.1 Materials and Sample Preparation

Materials used in this study ([BMIM][BF₄], acetone ($\geq 99.5\%$), ethanol ($\geq 99.8\%$), Basolite C300) were purchased from Sigma-Aldrich with the highest purity commercially available. [BMIM][BF₄] and Basolite C300 were stored in Ar glovebox (Labconco) and fresh materials were used for sample preparation. Basolite C300 was dehydrated at 105 °C overnight before sample preparation and no further purification was performed for other materials. For gas adsorption measurements CH₄ (99.95 vol%), N₂ (99.998 vol%) and CO₂ (99.9 vol%) gases were purchased from Linde gas company and H₂ (99.999 vol%) and He (99.999 vol%) gases were purchased from Messer gas company with purities indicated in brackets.

IL-incorporated Basolite C300 samples were prepared in open atmosphere and the samples were dried after preparation and stored in sealed glass containers in desiccator to minimize water and impurity content. Effects of long term humidity on Basolite C300 are discussed in Chapter 5.1.3. Two solvents were considered for sample preparation and acetone was selected as ethanol had destructive effects on the structure (Chapter 5.3). As an example for the preparation of IL/C300 samples, 0.15 g of [BMIM][BF₄] was dissolved in 15 ml of acetone in an empty glass container. 0.35 g of dehydrated Basolite C300 was added into the

solution and the resulting mixture was continuously stirred at 30 °C for 6 hours. The solvent was evaporated and the resulting sample was dried in vacuum oven at 105 °C overnight. The resultant blue solid was labeled as IL/C300 (30 wt%) according its weight percent. Other samples with 5 and 20 wt% loadings of [BMIM][BF₄] were prepared in a similar manner. The samples were kept sealed in desiccator to minimize their humidity and impurity contents.

3.2.2 Characterization Methods

3.2.2.1 X-Ray Diffraction

X-Ray Diffraction (XRD) is a method used to identify and quantify crystalline phases and determine their atomic structure. X-ray beams are first sent to the crystal atoms to diffract in different directions depending on the spacing between different planes and detected by the detector of the instrument. The angles and intensities of the diffracted beams enable determination of many properties of the studied material including: crystal structure, lattice parameters, atomic positions and chemical bonds.

In the XRD experiments Bruker D8 Advance with DAVINCI design [131] is used with Cu K α_1 radiation source employing a wavelength of 1.5418 Å. The power rating of X-ray generator was adjusted to 40 kV and 40 mA and Vantec-1 detector was used with a slit size of 1 mm. The measurement was performed between 2 Θ values of 2-90° with a step size of 0.01263°.

For the sample preparation, approximately 10 mg of sample was placed on a double-sided tape attached on a glass slide. The glass slide was placed on a gum and leveled with the sample holder using a smooth glass piece. The sample was spread thoroughly to cover double-sided tape to prevent amorphous signals coming from the tape. In measurements where a slight background is observed due to tape, background subtraction was performed.

A comparison between XRD results with and without background subtraction is provided in Appendix C. All samples were prepared in a similar manner and same parameters were used for the measurements.

3.2.2.2 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) can provide information on many physical/chemical phenomena by investigating the change in the weight of the material either during temperature ramp or isothermal temperature treatments under any gas flow. The basic instrumental requirements for thermal gravimetric analysis are a high precision balance and a programmable furnace to control temperature.

For TGA experiments TA Instruments Q500 [133] was used with a platinum pan. Initially, a clean pan was placed on the balance and set to tare. Approximately 15 mg of sample was weighed and the furnace was closed. Constant temperature ramp rate of 2 °C/min was employed up to 700 °C under N₂ flow of 40 and 60 ml/min for balance and purge gases respectively. For isothermal treatment measurements, first a constant temperature ramp rate of 10 °C/min was employed up to 175 °C and then the temperature was kept constant for 15 h under same N₂ flow conditions. After experiment was finished, platinum pan was cleaned carefully to get rid of any residuals. For the comparison of thermal decomposition temperatures, the onset (T_{onset}) and derivative onset (T'_{onset}) temperatures were determined by extrapolation (within an error range of ± 3 °C) from TG and derivative TG curves as shown in Appendix C. T_{onset} generally overestimates thermal decomposition temperature compared to T'_{onset} values. Thus, in this study mainly T'_{onset} values were considered.

3.2.2.3 Scanning Electron Microscopy

Scanning electron microscopes are used to produce high resolution images up to nanometer scales by scanning materials with a focused beam of electrons. The signals produced by the interaction of electrons and atoms of the material are detected to obtain micrographs that contain information about the material's surface topography and composition.

For SEM analyses discussed in Chapter 5.1 and beginning of Chapter 5.2, Zeiss FESEM Ultra Plus [134] was used. Samples were analyzed under vacuum with an accelerating voltage of 1 kV and working distance around 4 mm. Micrographs of the samples were obtained at different magnifications including: 20Kx, 10Kx, 2Kx, and 500x. For SEM analyses discussed in Chapter 5.2.3, Zeiss Evo LS 15 [135] was used. Samples were analyzed under vacuum with an accelerating voltage of 1 kV and working distance around 10 mm. SEM images were obtained up to 2Kx magnification due to limitations of the instrument. For both instruments secondary electron detectors were used.

The sample preparation was performed in a similar manner for both equipment and for all samples investigated in this thesis. Approximately 5 mg of samples were placed on carbon tape and excess samples on the carbon tape surface were discarded. The samples were placed in the instrument and measurements were performed under high vacuum to remove impurities on the surface.

3.2.2.4 Brunauer–Emmett–Teller (BET) Surface Area

BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured at 77 K as a function of relative pressure (p/p°).

Using N_2 physisorption isotherm between relative pressure of 0.05 – 0.3 bar, surface area of the sample is calculated using the BET equation [136] provided below:

$$\frac{1}{N(p^\circ/p - 1)} = \frac{C - 1}{N_m C} \left(\frac{p}{p^\circ} \right) + \frac{1}{N_m C} \quad (3.8)$$

where N is the adsorbed amount at each relative pressure, N_m is monolayer adsorbed amount, and C is BET constant. Making use of the data points obtained from adsorption measurements between 0.05 – 0.3 bar, the adsorbed amounts are entered in N and “ $1/[N(p^\circ/p - 1)]$ ” is plotted against “ p/p° ”. A linear equation is fitted to the plot and the regression parameters are used to calculate N_m and C . Then the BET surface area is calculated using equation below:

$$S_{BET} = \frac{N_m \times N_A \times s}{V_M} \quad (3.9)$$

where N_A is Avogadro constant, s is molecular cross-sectional area of adsorbate and V_M is the molar volume at standard temperature and pressure.

For BET analysis, Micromeritics ASAP 2020 - Physisorption Analyzer [137] was used. For each measurement approximately 100 mg of sample was used and the samples were activated under vacuum in two steps at 90 °C and 150 °C for 1 h and 10 h, respectively. After activation, sample was cooled down to 77 K using liquid nitrogen and free space measurement was performed with helium gas. The sample was then held under vacuum for an additional 10 h to remove residual helium gas. Then the volumetric N_2 adsorption was measured between 10^{-6} – 1 bar. As an example, the resulting N_2 adsorption isotherm and BET equation fit for Basolite C300 are provided in Figure 3.3.

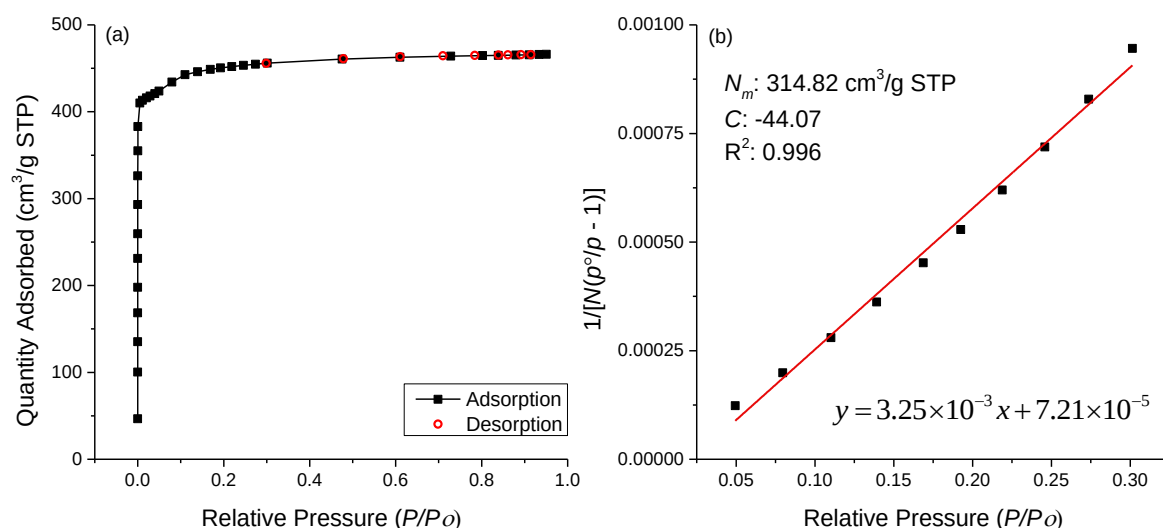


Figure 3.3: (a) N₂ adsorption isotherm at 77 K between 0-1 bar; (b) BET equation fit used for the calculation of surface area between relative pressure of 0.05-0.3.

As seen in Figure 3.3 (b) the BET equation was plotted and from the resulting regression equation N_m and C were calculated. Then using Equation 3.9 and calculated parameters (N_m and C), BET surface area was calculated as $1370.5 \pm 43.3 \text{ m}^2/\text{g}$ by entering s as 0.1620 nm^2 , V_M as $22400 \text{ cm}^3/\text{mol}$ and N_A as 6.02×10^{23} . The same procedure and calculations were adopted for all samples considered in this study.

3.2.2.5 Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy is a widely used method for materials analysis especially in organic chemistry. The IR spectrum represents the fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum.

FT-IR measurements were performed on a Bruker Vertex 80v FT-IR [138] spectrometer equipped with an attenuated total reflection (ATR) cell and a room temperature DLaTGS detector. The data was collected between spectral range of $4000\text{-}500 \text{ cm}^{-1}$ with 4

cm⁻¹ resolution. For both background and sample measurements 128 scans were obtained with a scanner velocity of 10 kHz. Approximately 10 mg sample was placed on top of ATR crystal and measurements were performed at ambient conditions. The ATR crystal and the tip of the compression rod were cleaned gently with ethanol before each measurement. Extended ATR correction, atmospheric compensation, and baseline correction were performed for each IR spectrum. The deconvolution of the signals were performed using Fityk software [139].

3.2.2.6 Elemental Analysis

Elemental analysis is used to determine elemental composition of a material. Elemental analysis, a commonly used method for protein/organic compound analyses, is performed by means of a combustion analysis to determine C, H, and N atoms. In this method sample is burned with oxygen and the combustion products such as CO₂, H₂O, and NO are quantified using chromatographic methods.

For elemental analyses in this study Thermo Scientific Flash 2000 CHNS/O analyzer [140] was used to determine C, H, and N contents of the materials. The sample was weighed in a tin capsule and then placed into an oxidation/reduction reactor kept at a temperature of 900 – 1000 °C. The exact amount of oxygen required for optimum combustion of the sample was delivered into the combustion reactor at a precise time. The reaction of oxygen with the tin capsule at elevated temperature generates an exothermic reaction which raises the temperature to 1800 °C. At this high temperature both organic and inorganic substances are converted into elemental gases which were separated in a chromatographic column and finally detected by a highly sensitive thermal conductivity detector.

3.2.3 High Pressure Volumetric Adsorption Analysis

Adsorption performance analyses were performed to measure gas storage and separation capabilities of the materials. For the measurements and activation (degassing) of the samples, High Pressure Volumetric Analyzer HPVA II-200 [141] from Particulate Systems (Micromeritics) was used. HPVA II uses the static volumetric method to obtain high-pressure adsorption and desorption isotherms. In the volumetric method a known amount of gas is dosed into the chamber containing the adsorbent sample. When the adsorbent reaches equilibrium with the adsorbate gas the final equilibrium pressure is recorded. Using the difference between dosing and equilibrium pressures the quantity of gas adsorbed by the sample is calculated. Same process is repeated for each pressure point until maximum adsorption pressure is reached. Then the pressure is decreased to measure desorption and resulting adsorption/desorption data is plotted as an isotherm. The schematic for HPVA II is given in Figure 3.4.

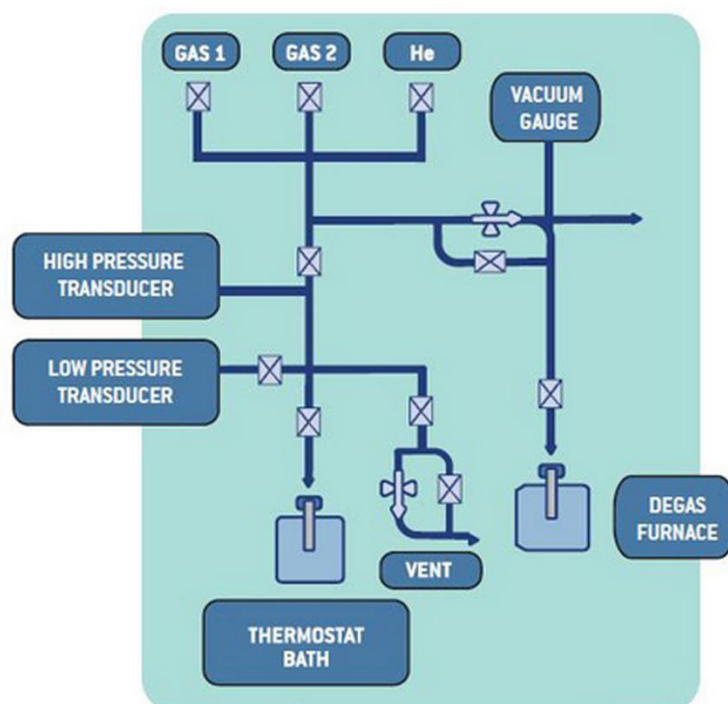


Figure 3.4: Schematic of High Pressure Volumetric Analyzer (HPVA) system [142].

For sample preparation, activation of the sample and adsorption analysis following procedure is used for all samples. Approximately 0.45 g of sample was weighed (designated as wet sample weight) and placed in the sample holder. The sample holder was assembled and connected to the degas port. The sample was activated at 150 °C for Basolite C300 and 125 °C for IL/C300 materials under vacuum for at least 12 h until the pressure reached 10^{-6} bar. After activation, the sample holder was cooled and connected to the analysis port inside a water bath at ambient temperature. Before running the experiment all gas lines were evacuated and flushed with helium three times to get rid of any residual gases from earlier measurements. The analysis gas was connected to either one of gas inputs (Figure 3.4) and the regulator on the gas cylinder was set to maximum adsorption pressure which was 100 bar for CH₄, N₂, H₂, and 35 bar for CO₂. The wet sample weight and requested pressure points were entered into the software and adsorption measurement was started. The analysis is performed automatically by HPVA II as follows: (1) Evacuation of the system for 10 min (2) Free space measurement using helium gas at 0.8 bar (3) Evacuation of the system for 30 min (4) Adsorption/Desorption analysis at given pressure points (5) Flushing of the system with helium gas to dispose of adsorbate gas.

After the completion of the measurements, the adsorption isotherm was obtained using the Excel macro provided with HPVA II. Moreover, Langmuir fit for the adsorption isotherm can also be obtained using this software. As an example, CH₄ adsorption for Basolite C300 at 298 K and the resulting Langmuir fit is given in Figure 3.5. The linearized version of Langmuir fit is provided in the inset and using regression coefficients of this fit equation Langmuir fit can be calculated using the relation:

$$N_{ads} = \frac{P}{a \times P + b} \quad (3.10)$$

where N_{ads} is the adsorbed amount in cm^3/g STP, P is pressure in bar, a is the slope and b is the y-intercept of the linearized Langmuir fit (Figure 3.5 Inset). The Langmuir fit is provided up to saturation pressure which corresponds to surface coverage (θ) of 1.

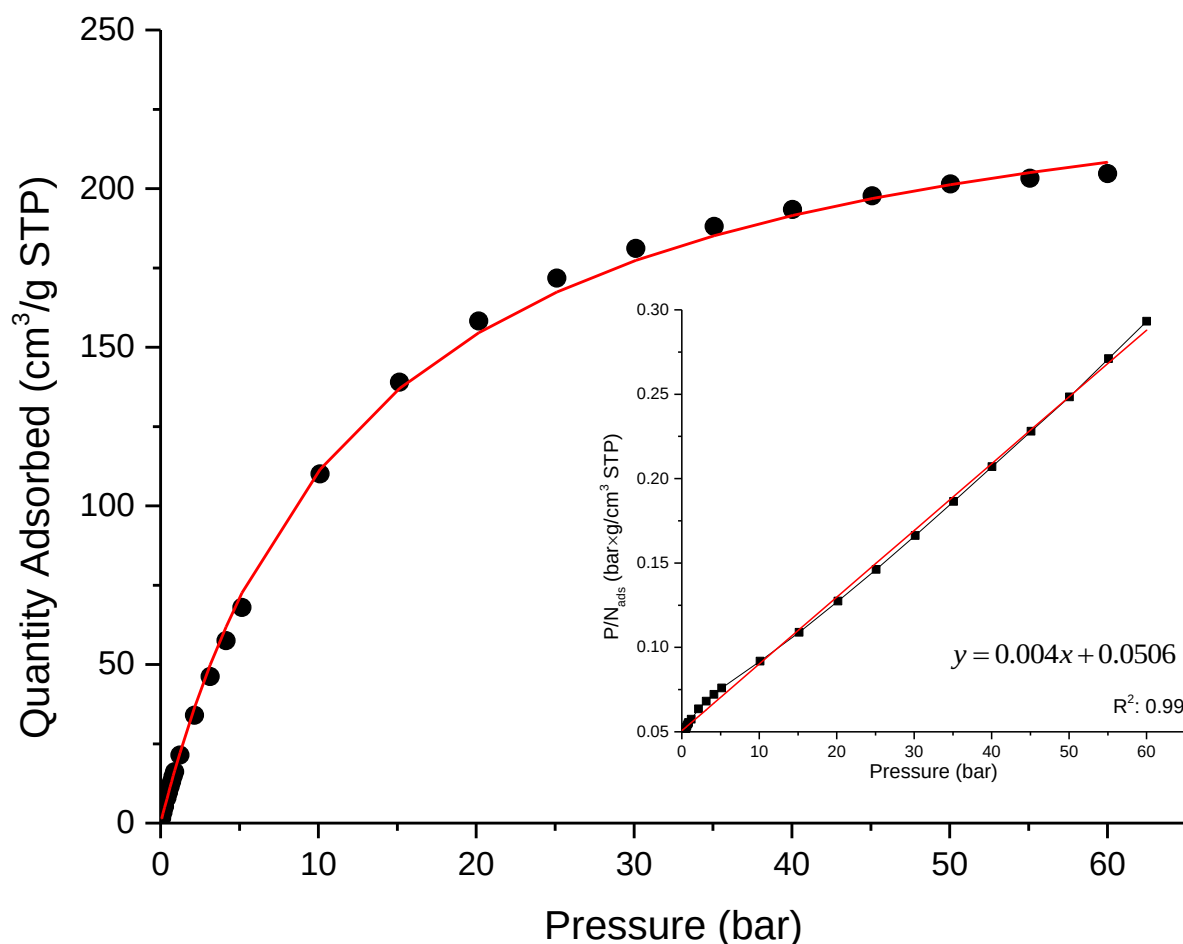


Figure 3.5: CH_4 adsorption isotherm for Basolite C300 at 298 K, Langmuir fit (red line)

Inset: linearized Langmuir fit and regression equation.

The ideal gas selectivities of the samples were calculated as the ratio of adsorbed amounts at exactly same pressures. All selectivities were calculated by dividing more selective component (higher adsorbed amount) to less selective component (lower adsorbed amount). For pressures between 0 and 1 bar, pressure points showed deviations between measurements. Therefore, polynomial interpolation was performed on adsorption isotherms between 0 and 1 bar using fourth-order polynomial fits with R^2 values of at least 0.99.

Chapter 4: Computational Studies for CH₄ Storage of MOFs

In this chapter, the results of a detailed investigation on the structural properties of MOF materials determining the CH₄ storage performance are provided focusing on 45 real MOF structures which were chosen to represent a diverse set of MOFs with pore diameters large enough to accommodate CH₄ molecules. CH₄ adsorption and isosteric heat of adsorption (Q_{st}) values were calculated at 298 K and at a wide range of pressures 1, 5, 10, 15, 20, 25, 30, 35, 50, and 65 bar using grand canonical Monte Carlo (GCMC) simulations. The validity of these simulations was tested by comparing the results with available experimental data from the literature. In order to understand the most prominent factors affecting MOF CH₄ storage performance, seven structural characteristics: crystal density (ρ_{cryst}), void fraction (V_f), pore volume (V_p), gravimetric surface area (S_g), pore limiting diameter (PLD), maximum pore diameter (MPD), dominant pore diameter (DPD) and Q_{st} values were calculated using computational tools. Quantitative structure property relationship (QSPR) analysis was performed to determine which parameters are more correlated with CH₄ uptake. Using the most correlated properties, simple multivariable linear models were constructed using four variables to predict CH₄ storage at ambient temperature. Later on, the data set was increased

to approximately 1500 MOFs and same analyses were performed for these structures. The parameters for the predictive models were updated and a pressure-independent model to predict CH₄ uptake was proposed.

Results of these simulations at 298 K, 5 and 35 bar together with the working capacity and Q_{st} values at these conditions as well as the important structural features are given in Table 4.1. Excess CH₄ uptakes and Q_{st} values at other pressures are given in Appendix B. The volumetric CH₄ uptake values change between 13.00 cc(STP)/cc for NUJCIE and 100.06 cc(STP)/cc for UTSA-20 at 5 bar and 21.87 cc(STP)/cc for NUJCIE and 180.31 cc(STP)/cc for CPO-Co at 35 bar, the working capacities calculated between 5 and 35 bar vary between 5.93 cc(STP)/cc for UHAXUW and 117.01 cc(STP)/cc for MOF-5.

Table 4.1: Structural properties, isosteric heat of adsorption and excess CH₄ uptake at 298 K, 5 and 35 bar for MOFs used in this study (sorted by alphabetical order of common names).

Common Name	CCDC ^a				Excess CH ₄ Uptake ^e							
	Reference	S_g^b	ρ_{cryst}	V_p^c	PLD ^c	MPD ^c	DPD ^c	Q_{st} (kJ/mol) ^d		cc(STP)/cc		WC ^f
	Code	(m ² /g)	(g/cm ³)	(cm ³ /g)	(Å)	(Å)	(Å)	5 bar	35 bar	5 bar	35 bar	cc(STP)/cc
Bio-MOF-1	NUDLAA	1262	1.02	0.57	9.52	9.83	9.63	16.48	16.56	96.00	153.38	57.38
Bio-MOF-11	YUVSUE	585	1.23	0.41	4.24	5.36	4.63	19.54	18.55	73.18	97.47	24.29
Bio-MOF-12	BEYSEF	916	1.18	0.43	4.18	5.16	4.88	21.40	21.76	85.46	129.01	43.55
COF-10[143]	YUTYOC	2376	0.60	1.21	29.91	30.08	28.88	10.95	9.23	15.38	62.92	47.54
COF-5[143]	RAYQAK	1969	0.58	1.25	23.23	23.45	22.38	12.74	10.34	33.49	94.03	60.54
COF-6	YUTYIW	1154	1.00	0.53	8.10	8.61	7.88	16.46	17.02	29.98	59.26	29.28
CPO-27-Co[144]	SATNOR	1477	1.18	0.54	7.19	8.30	7.63	16.27	17.28	84.73	180.31	95.58
CPO-27-Ni[144]	LECQEQ	1388	1.19	0.52	7.01	8.36	7.63	15.95	16.80	77.67	172.72	95.05
CuBDC	AJIHOQ	2171	0.88	0.81	6.37	12.74	12.38	14.09	15.38	62.98	178.35	115.37
CuBTC[1]	LUKLIN	2167	0.88	0.81	6.32	12.74	12.38	13.99	14.80	62.20	176.79	114.59
Cu-TDPAT[145]	XALXUF01	2188	0.78	0.91	6.31	16.37	16.13	15.19	15.30	64.98	171.47	106.49
DEFKUU	DEFKUU	661	1.71	0.29	4.11	5.07	5.13	20.91	20.96	93.16	134.16	41.00
IJOMOJ02	IJOMOJ02	320	1.62	0.29	3.56	4.75	4.38	20.08	18.99	48.99	66.22	17.23
JOKYAJ	JOKYAJ	230	1.55	0.32	3.69	4.79	4.63	17.30	17.42	23.14	44.19	21.05
JOKYEN10	JOKYEN10	251	1.55	0.32	3.70	4.93	4.63	17.36	17.52	23.31	43.29	19.98
JOKYIR10	JOKYIR10	228	1.57	0.31	3.69	4.92	4.63	17.47	17.54	22.82	42.87	20.05
JOKYOX	JOKYOX	224	1.57	0.31	3.37	4.77	4.63	17.68	17.84	22.94	42.52	19.58
KEXFIC10	KEXFIC10	182	1.59	0.30	3.54	4.72	4.38	17.71	18.07	21.25	43.81	22.56
LAMGUB	LAMGUB	200	1.57	0.31	3.60	4.80	4.63	17.52	17.93	21.66	44.49	22.83
MOF-5[146]	SAHYIK	1245	0.60	1.32	7.65	14.85	14.63	11.04	12.80	28.10	145.11	117.01
NTU-105	XEVBILOO	3308	0.63	1.18	4.78	18.28	18.13	13.51	13.08	51.97	167.03	115.06

NU-125[17]	REWNEO	3418	0.61	1.24	4.95	19.22	18.88	13.13	12.96	49.66	162.16	112.50
NUJCIE	NUJCIE	159	1.58	0.30	3.76	4.89	4.63	17.19	17.60	13.00	21.87	8.87
OHETIE	OHETIE	1530	0.78	0.95	5.75	7.46	7.13	10.25	12.43	17.71	97.46	79.75
PCN-11[147]	MOCKAR	2187	0.80	0.86	3.49	5.82	10.13	15.49	16.58	66.29	166.08	99.79
PCN-14[1]	XITYOP	2117	0.87	0.74	4.65	6.57	5.88	17.09	16.66	88.78	162.70	73.92
PCN-26[124]	GEGDED	2212	0.90	0.74	5.10	8.33	8.13	14.83	16.03	58.41	151.04	92.63
PCN-46[148]	LUYHAP	3364	0.66	1.12	10.57	10.68	7.13	12.97	13.98	41.71	146.23	104.52
PCN-80[149]	WAMREJ	3644	0.65	1.15	6.35	12.61	11.38	12.14	11.83	28.86	109.71	80.85
SUDBOI	SUDBOI	592	1.23	0.46	3.64	6.20	5.88	18.08	18.26	49.41	81.22	31.81
UHAXUW	UHAXUW	242	1.52	0.27	3.39	4.80	4.63	24.17	22.51	59.46	65.39	5.93
UTSA-20[150]	ONIXOZ	1950	0.91	0.72	8.73	9.42	9.13	18.10	15.42	100.06	171.77	71.71
YARYEV	YARYEV	817	1.12	0.59	3.61	5.27	5.13	13.63	14.52	22.64	80.56	57.92
YIZWIN	YIZWIN	208	1.59	0.31	3.43	4.45	4.13	17.78	17.91	21.26	40.80	19.54
ZIF-10	VEJZIU	2405	0.75	0.95	7.14	12.94	12.63	13.84	14.24	41.66	130.04	88.38
ZIF-2	VEJYIT	1769	0.93	0.69	5.05	6.09	5.38	18.50	18.90	87.53	137.58	50.05
ZIF-3	VEJYOZ	1915	0.88	0.75	5.55	8.04	7.88	17.06	18.19	76.14	150.83	74.69
ZIF-6	EQOCOC01	2803	0.76	0.91	5.05	9.14	8.88	14.14	15.07	49.15	132.35	83.20
ZIF-60	GITSUY	2196	0.77	0.90	7.09	12.09	11.88	13.80	14.92	40.80	130.20	89.40
ZIF-68[151]	GITTUZ	1076	1.03	0.57	7.47	10.25	9.88	15.86	15.17	42.37	93.87	51.50
ZIF-69[151]	GITVAH	857	1.15	0.49	4.74	8.93	7.63	18.37	17.86	43.99	93.03	44.47
ZIF-78[151]	YOZBIZ01	741	1.18	0.45	3.62	8.03	7.88	17.22	17.32	43.11	96.13	53.02
ZIF-79[151]	YOZBOF01	1018	1.07	0.51	4.42	7.91	7.63	17.31	17.21	50.73	100.07	49.34
ZIF-81[151]	YOZCAS	834	1.29	0.43	4.15	8.29	7.88	16.69	16.66	43.24	90.30	47.06
Zn(bdc)(ted) _{0.5}	WAFKAQ	2019	0.89	0.71	5.09	7.56	7.38	17.89	18.43	93.79	156.58	62.79

^a The Cambridge Crystallographic Data Centre (CCDC)

^b Accessible Gravimetric Surface Area computed using the code by Düren et. al using probe diameter of 3.681 Å

^c Computed using PoreBlazer software by Sarkisov. V_p : Pore Volume, PLD: Pore Limiting Diameter, MPD: Maximum Pore Diameter, DPD: Dominant Pore Diameter

^d Q_{st} : Isosteric Heat of Adsorption computed by GCMC simulations at 298 K

^e Excess CH₄ adsorption computed by GCMC simulations at 298 K

^f Working Capacity calculated as the difference between adsorbed amount of CH₄ at 5 and 35 bar

References given for some MOFs represent the source of experimental CH₄ uptake measurement results.

4.1 Validation of GCMC Simulations

Initially, validity of the GCMC simulation results was tested by comparing the data with available experimental results for CH₄ uptake from the literature. This step is crucial before making a detailed analysis about the performances of various MOFs. Wide range of experimental data is collected from the literature and GCMC simulations are performed exactly at the same pressures with the experimental data to be consistent. Figure 4.1 shows the comparison of the experimental data with the simulation results for CH₄ uptake in various

MOFs. The plot is given in log scale to better represent the low pressure uptake data. The root-mean-square deviation (RMSD) of the simulated 267 data points ranging from 0.1 to 35 bar with respect to the corresponding experimental values is calculated as 10.054 cc(STP)/cc with a regression coefficient of 0.972 suggesting that GCMC results represent experimental data very accurately. There are some data points that deviate from experimental measurements by 10% but this deviation is acceptable for the purpose of this work. COF-5 shows the highest deviation from the experimental results as seen in Figure 4.1 and simulation results overestimate the experimental uptake by ~10%.

Various experimental CH₄ uptake data of the same material are reported by different research groups even though measurements were done under the same conditions [1,2]. Any variations in the synthesis or measurement procedure can cause these differences. Synthesis conditions, compounds used in synthesis, activation of the material prior to measurements, equipment used for measuring adsorption are the main factors that can greatly affect experimental results. On the other hand, GCMC simulations have some assumptions that may not be valid in practical conditions. Assumption of rigid framework and using generic force field parameters in simulations can greatly affect the outcome. For example, for ZIF-68, ZIF-69, ZIF-78, ZIF-81 force field parameters proposed by Liu and Smit [121] and for ZIF-79 force fields parameters proposed by Perez-Pellitero et al. [122] were used in GCMC simulations. As it can be seen from Figure 4.1 these specific force fields represent ZIFs accurately. However, if a generic force field such as UFF were used the simulation results would not agree with experimental results.

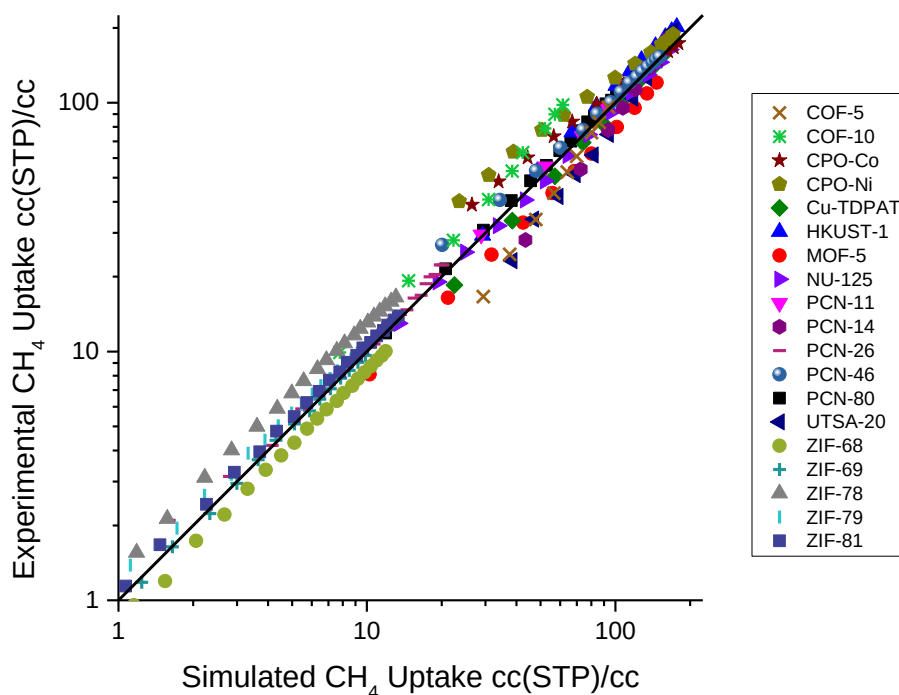


Figure 4.1: Comparison of experimental and simulated CH₄ uptake at 298 K in the range of 0.1 – 35 bar. Corresponding experimental references are given in Table 4.1.

Both experimental methods and simulations take time and effort for assessing CH₄ adsorption capacity of materials and they can contain inconsistencies. Therefore constructing models that make use of easily measurable structural properties to predict CH₄ storage performance of MOFs would be an effective option. Moreover, as the understanding on the relation between structural properties and uptake capacity is developed, more insights are gained regarding optimal material design and development for CH₄ storage.

4.2 QSPR Analysis and Regression Models for the Prediction of CH₄ Storage

The aim of this section is to provide evidence that simple models are useful for predicting the adsorption capacities of different MOFs, and explain how these models are constructed. First of all, in order to understand which parameters express the CH₄ adsorption more accurately, a simple QSPR tool was employed. The objective of a QSPR tool is to

predict a physical/chemical property by utilizing the information obtained from the molecular structure. Before employing the QSPR tool, possible characteristic properties of MOFs that are predicted to have an effect on the adsorption capacity are identified. These chemical and structural properties are as follows; surface area (S_g), crystal density (ρ_{cryst}), pore volume (V_p), void fraction (V_f), pore limiting diameter (PLD), maximum pore diameter (MPD), dominant pore diameter (DPD), and isosteric heat of adsorption (Q_{st}). Then, QSPR analysis was utilized to predict which structural/chemical properties have more significance on the CH₄ uptake values at ambient temperature and 1, 5, 10, 15, 20, 25, 30, 35, 50 and 65 bar. The analysis was performed at each pressure values using one-, two-, three-, and four-variables from those listed above to obtain multivariable linear models in the form of equation given below:

$$N_{CH_4} \left(\frac{cc(STP)}{g} \right) = a \times \rho_{cryst} + b \times V_p + c \times V_f + d \times S_g + e \times PLD + f \times MPD + g \times DPD + h \times Q_{st} + i \quad (4.1)$$

where the coefficients of the unselected parameters would be zero for each model. It is noted that Equation 4.1 contains dependent variables ($V_f = V_p \times \rho_{cryst}$), thus it is possible to rearrange accordingly. For the sake of simplicity this open form is considered. As a representative set, fit parameters of the individual models that predict CH₄ uptake at 5 and 35 bar are given in Table 4.2. These pressures were selected according to the porous material storage target determined by DOE, where 5 bar is considered as a relevant delivery pressure and 35 bar as a storage pressure at ambient temperature. Parameters for other models are also provided in Appendix B.

Table 4.2: Parameters of the QSPR multivariate linear regression models and their statistical model analysis for 5 and 35 bar. Statistical parameters of models at other pressures are given in Appendix B.

Pressure (bar)	# of Variables	Regression Coefficients ^{a,f}									R^2 ^c	$\bar{R}^2$ ^d	STD ^e
		ρ_{cryst} ^b a	V_p ^b b	V_f ^b c	S_a ^b d	PLD ^b e	MPD ^b f	DPD ^b g	Q_{st} ^b h	i			
5	4	-61.67	-60.56	408.66	-	-	-	-	12.32	-290.13	0.85	0.84	11.60
	3	-34.31	-	338.73	-	-	-	-	13.22	-331.37	0.82	0.81	12.56
	2	-	-	462.33	-	-	-	-	13.92	-455.06	0.80	0.79	13.20
	1	-	-	-	0.02	-	-	-	-	27.26	0.38	0.37	22.72
35	4	-	-	676.23	0.03	-	-	2.91	16.70	-620.92	0.92	0.91	21.56
	3	-	-	662.16	0.03	-	-	-	12.76	-527.60	0.90	0.90	23.27
	2	-	-	922.83	-	-	-	-	14.35	-674.21	0.87	0.87	26.53
	1	-	-	-	0.06	-	-	-	-	31.92	0.78	0.77	34.70

^a Multivariable linear models are constructed as in Equation (4.1).^b V_f : Void fraction, see Table 4.1 for other abbreviations^c R -squared^d Adjusted R -squared^e Standard deviation^f Units of regression coefficients are adjusted to give cc/g

As expected, between all trials, models that make use of four-variables predict the CH₄ uptake better than the models with lower number of variables, as evident from their regression coefficient and standard deviation values. Here, the adjusted R -squared ($\bar{R}^2$) values were also included, which indicates whether the parameters used in the model are all needed and whether the addition of a new parameter improves the fit quality. R^2 values increase as a new descriptive parameter is introduced to the model however $\bar{R}^2$ values only increase if the introduced parameter actually improves the fit quality. $\bar{R}^2$ is calculated using the equation:

$$\bar{R}^2 = R^2 - (1 - R^2) \frac{p}{n - p - 1} \quad (4.2)$$

where p is the total number of parameters in the model and n is the sample size.

Data show that $\bar{R}^2$ values are always higher for the models with 4-parameters confirming the necessity of additional parameters. From the properties that are utilized to

construct the model, Q_{st} and V_f are two properties that are consistently present in almost all models. Thus, it is inferred that these two parameters are the most significant parameters determining the CH₄ uptake.

The correlation between CH₄ uptake and Q_{st} was investigated at various pressures and it was found out that a linear QSPR could represent the data more accurately than using Q_{st} exponentially. Previous studies focused on parameters, such as S_g [18, 61] and V_p [60], as one-variable models and S_g , V_f , and DPD [50] as a three-variable model to predict CH₄ uptake. In this study, it is shown that implementation of Q_{st} to the models increases the predictive power of the models for both delivery and storage pressures. However, gathering Q_{st} data can be challenging since it requires atomic simulations. For such cases, additional models which can estimate the Q_{st} by using any of the other easily measurable parameters at considered pressure values were developed and listed in Appendix B.

As shown in Figure 4.2 and Table 4.2, the best model at 5 bar makes use of ρ_{crsyt} , and V_p with negative coefficients and V_f and Q_{st} with positive coefficients. To better understand which one of these parameters were chosen and how they are correlated with CH₄ uptake and each other, their binary relations were investigated and correlation coefficients were calculated. This analysis is given in Appendix B. From the analysis it has been found that at 5 bar, density is negatively correlated with CH₄ uptake and for that reason it has a negative coefficient. However, even though V_p has weak positive correlation, it has a negative coefficient in the model with four-variables. This negative coefficient results from the mathematical expression of the model rather than a physical meaning. The model makes use of the correlation between V_p and other parameters at 5 bar and assigns V_p a negative coefficient to better represent the CH₄ uptake. As the number of variables decrease V_p is dismissed first, then the ρ_{crsyt} is eliminated and finally S_g is selected as the most correlated variable for 5 bar. From the binary relations it is seen that S_g is the most dominant property

with CH₄ uptake at 5 bar and for that reason it is selected in the one-variable model. However, it is interesting to see that S_g is not selected in any other models at 5 bar. This result suggests that binary correlations of properties with CH₄ uptake are not directly related with the selection of model parameters. The parameters should be able to simultaneously represent the data to be selected for the model.

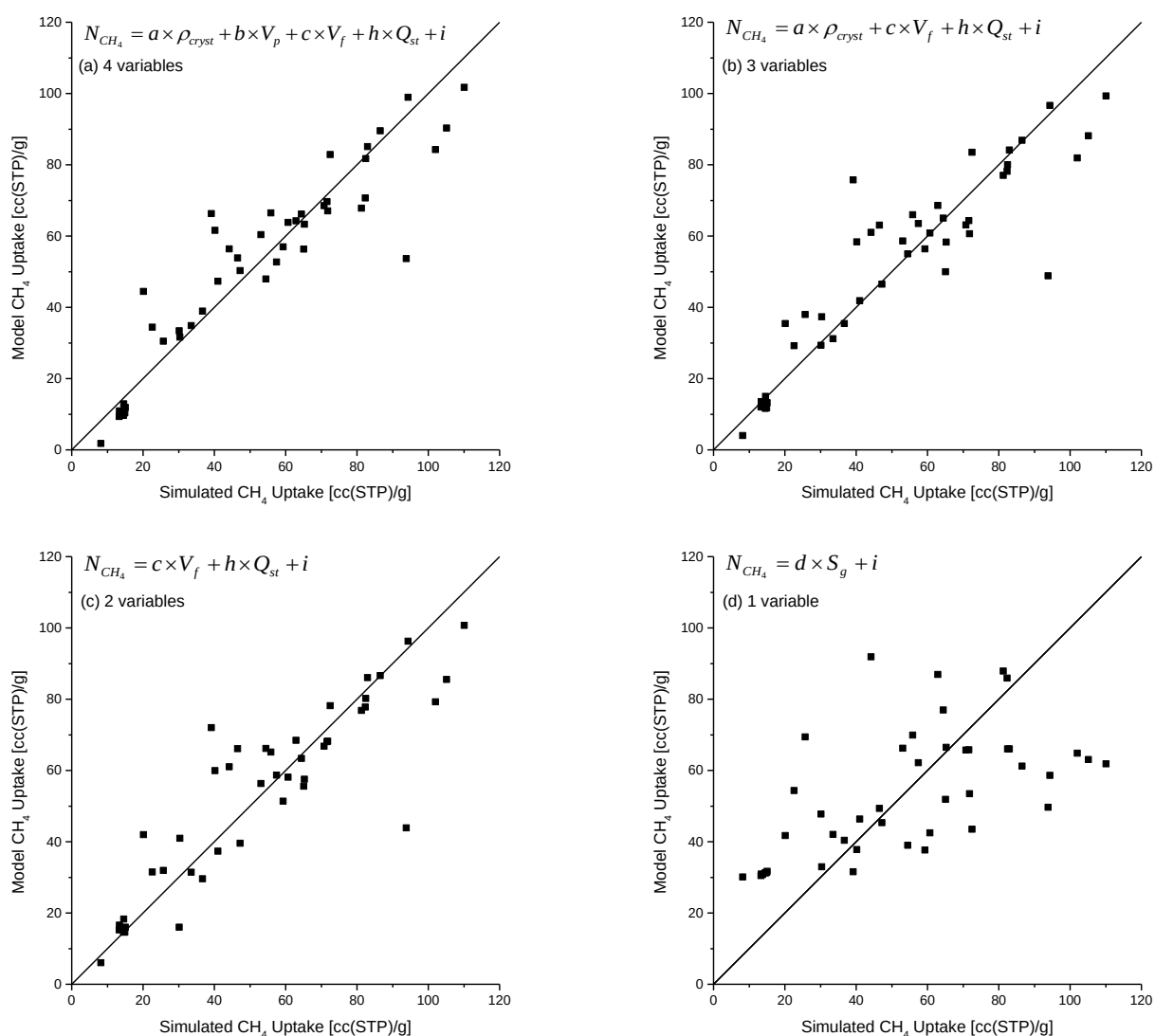


Figure 4.2: Comparison of models and simulations for CH₄ uptake at 298 K and 5 bar. Regression coefficients are given in Table 4.2.

Figure 4.3 represents the model estimated uptake values versus GCMC simulated uptake values for models with one to four-variables at 35 bar. As in the case of 5 bar, the four-variable model performs better than those with less variables. This best performing model at 35 bar makes use of V_f , S_g , DPD and Q_{st} all with a positive coefficient. As the number of variables decrease, DPD is dismissed first then the S_g and, finally only the S_g is selected as the most dominant variable (one-variable model) for 35 bar with a correlation coefficient of 0.78. Similarly at 5 bar, even though S_g is the most correlated parameter at 35 bar, simultaneous representation of other parameters provides better estimation of the simulated uptake values. Moreover, different than the case at 5 bar, S_g and DPD are selected for the four-variable model instead of ρ_{crsyt} and V_p . Even though both V_p and ρ_{crsyt} have better binary correlations with CH₄ uptake at 35 bar the inclusion of DPD results in a better representation of the data.

As it is seen from the model at storage pressure, all the properties have positive correlation with CH₄ uptake values, thus the uptake increases as V_f , S_g , DPD and Q_{st} increase, which is a reasonable outcome. In order for a material to exceed the DOE target of 0.5 g/g CH₄ uptake at a storage pressure of 35 bar, the material should have high S_g , reaching 6000 m²/g, V_f as high as 0.9, DPD approximately 30 Å, and Q_{st} value in the range of 30 kJ/mol. Among these parameters V_f is the most effective one since it has a very high regression coefficient (676.2), thus an increase in the order of 0.1 in this parameter would result in an increase of approximately 68 cc(STP)/g in CH₄ uptake. Even though increasing V_f would enhance CH₄ uptake of the material, improving a single property is not sufficient to optimize CH₄ storage performance, instead all properties of the MOF should be optimized simultaneously [50].

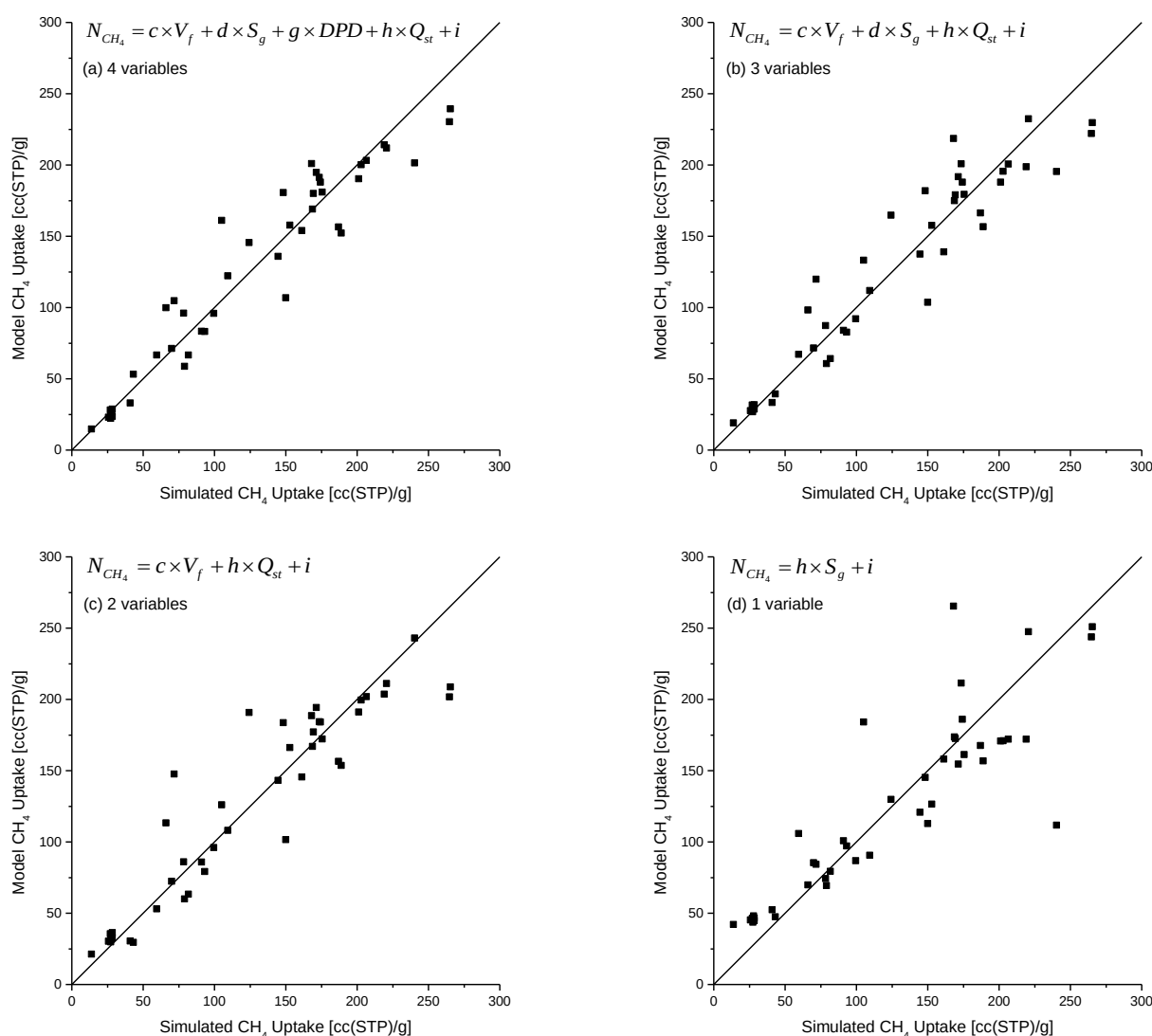


Figure 4.3: Comparison of models and simulations for CH₄ uptake at 298 K and 35 bar. Regression coefficients are given in Table 4.2.

However, when the working capacity is considered for both storage pressures of 35 and 65 bar, the target was not reached by the model predictions as long as the parameters stay in constraints (given in Appendix B) determined by the physical limitations of MOFs. Even though it seems improbable to reach working capacity target more open-metal sites can be incorporated into the materials that possess high S_g and porosities or post-synthetic modifications [152] can be performed that can intensify MOF-CH₄ interactions and increase Q_{st} as well as CH₄ uptake. Newly synthesized NU-140 [153] is a promising option for this

type of application, as it already has good structural properties such as S_g (4300 m²/g), V_p (1.90 cm³/g), V_f (0.82) as well as high gravimetric (0.34 g/g) and volumetric uptake (200 cc(STP)/cc) at 65 bar and from the model if a Q_{st} value of 30 kJ/mol can be obtained the DOE target at 65 bar can be satisfied. However, it should be noted that as the V_f and S_g of a MOF increase, its Q_{st} generally decreases, thus MOFs with very high S_g and V_p do not necessarily have very high CH₄ uptake. In contrast, materials with smaller pores and open-metal sites such as UTSA-76a, HKUST-1, CPO-Ni, PCN-14, UTSA-20 have higher CH₄ uptakes at both low and high pressures. For working capacity between 5 and 35 bar, having lower Q_{st} values would be beneficial, since it would result in a lower uptake at delivery pressure, however, at the same time, it might result in lower uptake at storage pressure as well. Even though these models give insightful information on CH₄ storage and delivery, other parameters that are not covered by the models, such as the flexibility of MOF structures, orientational freedom of organic linkers and other parameters regarding dynamic structure can also be very significant [48].

4.2.1 Comparison of Regression Models with Experimental Results

In order to assess the model accuracy, model predictions were compared with available experimental data. Experimental results for 5 bar and 35 bar were taken directly from the reported values. For cases where data were not reported at these specific pressure values, CH₄ uptakes were interpolated from the adsorption isotherms. The comparison is given in Figure 4.4. Two additional MOFs (MIL-53(Al) and MIL-53(Cr)), which were not present in the data set that was used to generate models, were also included in the experimental comparison since these two MILs have high CH₄ uptake performance. It should be noted that experimental data for these MILs were reported at 303 K, therefore uptake values might be lower than those at 298 K [154,155].

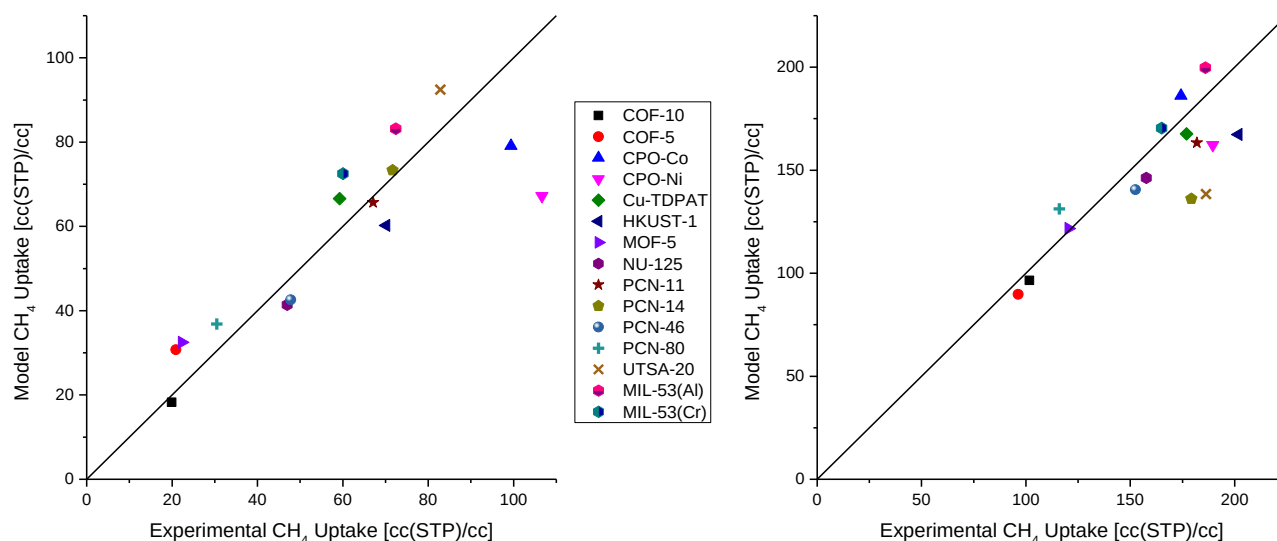


Figure 4.4: Comparison of experiments and models for CH₄ uptake at 298 K, (a) 5 bar; and (b) 35 bar. Corresponding experimental references are given in Table 4.1.

For 5 bar, model results show very good agreement with experimental data except for CPO-Co and CPO-Ni. The model underestimates the CH₄ uptake of these two materials at low pressures and this underestimation becomes less significant at higher pressures. This change might be originating from the fact that CPO-Co and CPO-Ni possess exceptionally high densities of open metal sites and interactions between CH₄ and these unsaturated metal sites results in high uptake values [144]. The primary gas adsorption in these materials occurs directly on open metal sites and as these sites become occupied at higher pressures other structural features become more prominent. Moreover, CH₄ molecules show high affinity towards Co and Ni metals and have high adsorption enthalpies as reported by Rana et al. [156]. Even though this affinity is described in the models via increased Q_{st} values the adsorption mechanism in MOFs with open metal sites might not be described accurately in GCMC simulations causing poor predictions for MOFs with exceptional metal-CH₄ interactions [157].

Similar to 5 bar, model results at 35 bar also show good agreement with the experimental results. There is a slight underestimation of the model which can result from the excess adsorption calculations. There are lots of other parameters that affect CH₄ uptake in MOFs and it is not possible for models to account for all of those. As seen at 5 bar, four-variable model can give inaccurate results for MOFs that have dense open metal sites with metals that show high affinity to CH₄ molecules, such as Mg, Co, Ni, Sr, Sc, Ti, Zn, and Sn. This inaccuracy is especially more dominant in lower pressures since structural features are less significant for CH₄ uptake compared to higher pressures. At lower pressures due to interactions between CH₄ molecules and open metal sites, CH₄ molecules first occupy pockets near metal sites and as the pressure increases these pockets become saturated and the influence of other pores and the overall structural features of the material become more relevant [158]. For that reason as pressure increases the predictive power of the models increases as seen from the larger R-squared values. This increase can also be explained by the improved binary correlations of structural properties with CH₄ uptake. At low pressures, many other parameters are significant for CH₄ storage and the effect of structural properties are hindered by these parameters. At higher pressures effects of these other parameters diminish while those of structural properties dominate. However, both low and high pressure uptakes should be known accurately to calculate working capacity, which is the main property that determines a material's performance. In order to have high working capacities the material should have low uptake at delivery pressure (5 bar) and high uptake at storage pressure (35 bar).

4.2.2 Comparison of Regression Models with Models Proposed by Other Studies

The performance of the previous literature models [50,60] that predict CH₄ uptake were also tested for the materials considered in this study by comparing their results with the available experimental data. Fernandez et al. [50] performed large scale QSPR analysis on

approximately 130,000 hypothetical MOFs and created a web server named MOFIA that predicts CH₄ uptake at 1, 35 and 100 bar using S_g , DPD and V_f . He et al. [60] proposed an empirical equation from experimental results of five MOFs that makes use of V_p to predict CH₄ uptake at 35 bar.

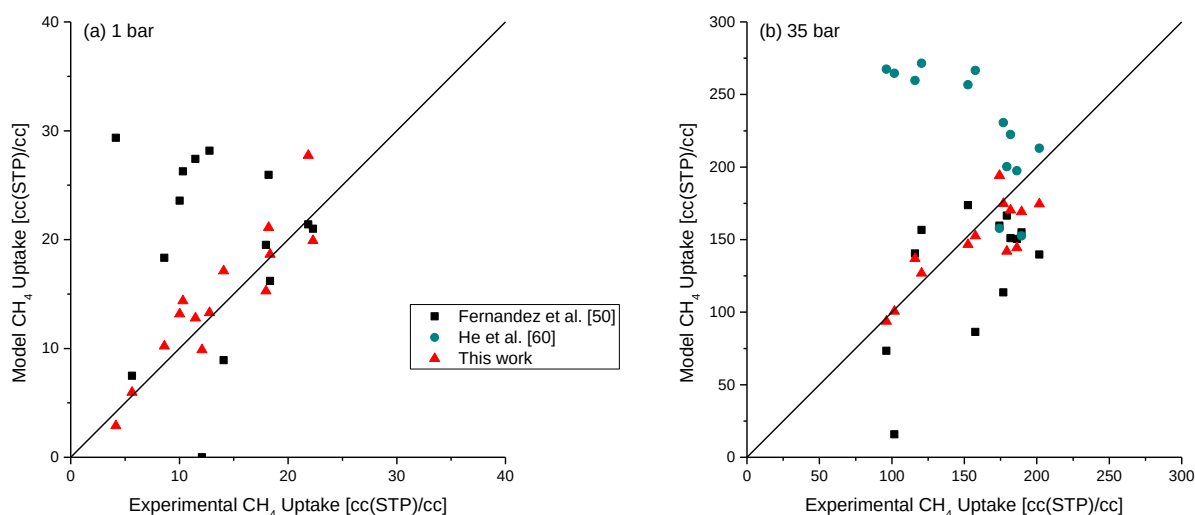


Figure 4.5: Comparison of experiments and predictions of different models [50,60] for CH₄ uptake at 298 K, (a) 1; and (b) 35 bar.

Comparison of these models with four-variable models proposed in this study at 1 and 35 bar was given in Figure 4.5. As evident from Figure 4.5, the models proposed here show better agreement with experimental results at both 1 and 35 bar than the models proposed in the literature. The model by He et al. [60] shows a weak agreement since only five MOFs were used to develop the model and it uses V_p as the only variable. Their model, represent the experimental data well for a certain family of MOFs, which might have high correlation with their V_p and CH₄ uptake, however, it does not correlate well with other MOFs. The model by Fernandez et al. [50] is developed from a library of hypothetical MOFs, therefore its agreement with experimental results of real MOF structures is poor. It shows a better agreement compared to the model by He et al. [60] since it uses three structural parameters that were shown to be significant for CH₄ uptake. The findings on the relations between

structural parameters and CH₄ uptake of real MOFs were compared with hypothetical MOFs: The top 10 performing MOFs in excess CH₄ uptake (cm³/g) had an average S_g around 5000 m²/g, V_f around 0.9 and DPD around 10 Å with an average CH₄ uptake of 427 cm³/g [50]. S_g and V_f values are very well-matched with the values that were found in this work (6000 m²/g and 0.9) to obtain high CH₄ uptake. However, average DPD values of the top performing hypothetical MOFs (10 Å) differ from model predictions (30 Å) of this work. A limited set of building blocks was used in the construction of the hypothetical MOF database and MOFs with DPD > 25 Å were not included. Therefore, the effect of DPD should be investigated in a data set having a wider range of pore structures. When the average structural values of top performing hypothetical MOFs (S_g , V_f , and DPD) are inserted into model proposed at 35 bar with a Q_{st} value of 17 kJ/mol (which is the average value for the data set used in this study), CH₄ uptake value of 416 cm³/g is obtained which is consistent with the uptake reported for hypothetical MOFs (427 cm³/g). The results of this study discussed in Chapter 4.1 and 4.2 were published in Chemical Engineering Science, 2015 [159].

4.3 Large Scale Screening of MOFs for CH₄ Storage

In order to see whether the models proposed earlier in this chapter can be used comprehensively to predict CH₄ uptake of MOFs, same analyses were also performed using a data set of 1514 MOFs from the database of Chung et al. [58]. The simulations and data handling for these structures were performed as described in Chapter 3.1.4. Initially, the regression models proposed in previous section (Model-0) were tested on 1514 MOFs. Later, the regression coefficients of Model-0 were updated and the predictive powers of the resulting models (Model-1) were tested. Moreover, another QSPR analysis was performed to determine new parameters and new four-variable models (Model-2) were constructed. Lastly, viability of using a single model to predict CH₄ uptake at all pressures was examined by constructing pressure-independent models designated as Model-3 and Model-4.

Models proposed in Chapter 4.2 were used to predict CH₄ uptake of 1514 MOFs (Appendix A) and the results for 5 and 35 bar are given in Figure 4.6.

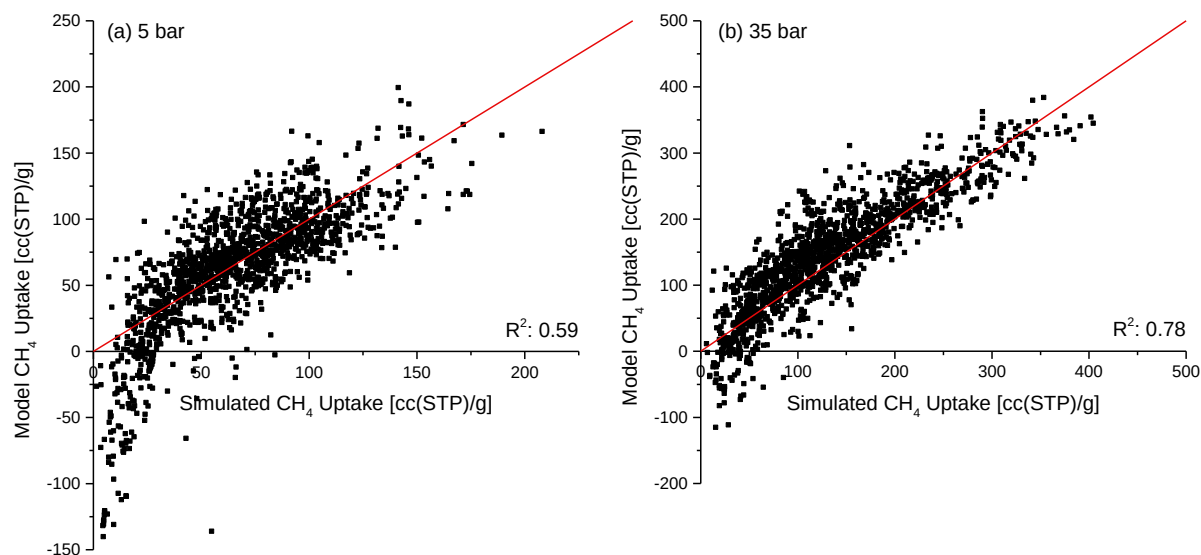


Figure 4.6: Comparison of Model-0 and simulations for CH₄ uptake at 298 K and (a) 5 bar; and (b) 35 bar. Statistical parameters provided in Table 4.2. Model results at other pressures are given in Appendix B.

As seen in Figure 4.6 the predictive power of the model is reduced compared to previous data set of 45 MOFs. This is especially more pronounced at 5 bar since low pressure adsorption is more dependent on distinct framework interactions compared to 35 bar which is more dependent on structural properties. In order to address a bigger data set of MOFs, the regression coefficients of Model-0 have been updated using the same variables and the resulting model (Model-1) predictions for 5 and 35 bar are given in Figure 4.7.

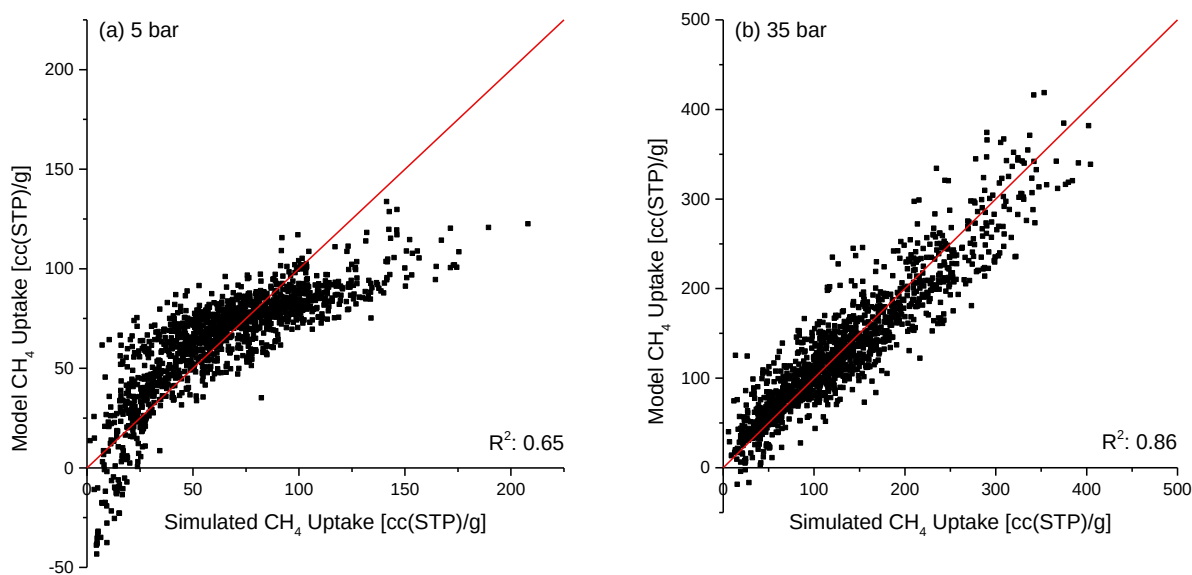


Figure 4.7: Comparison of Model-1 and simulations for CH₄ uptake at 298 K and (a) 5 bar; and (b) 35 bar. Statistical parameters are provided in Table 4.3. Model results at other pressures are given in Appendix B.

With the correction of model coefficients, the predictive capabilities of the models were significantly improved as seen in Figure 4.7. Similar to Model-0, the prediction performance is lower for data at 5 bar as evident from the R^2 values. To improve the model further, another QSPR analysis was performed to construct models with different parameters. An additional parameter, volumetric surface area (S_v), was added to parameter list and four-variable models were constructed (Model-2). The statistical parameters for Model-1 and Model-2 are provided in Table 4.3.

As seen in Figure 4.8 there was no significant improvement due to parameter change between Model-1 and Model-2. The R^2 values were only increased by 0.03 and 0.02 for 5 bar and 35 bar, respectively.

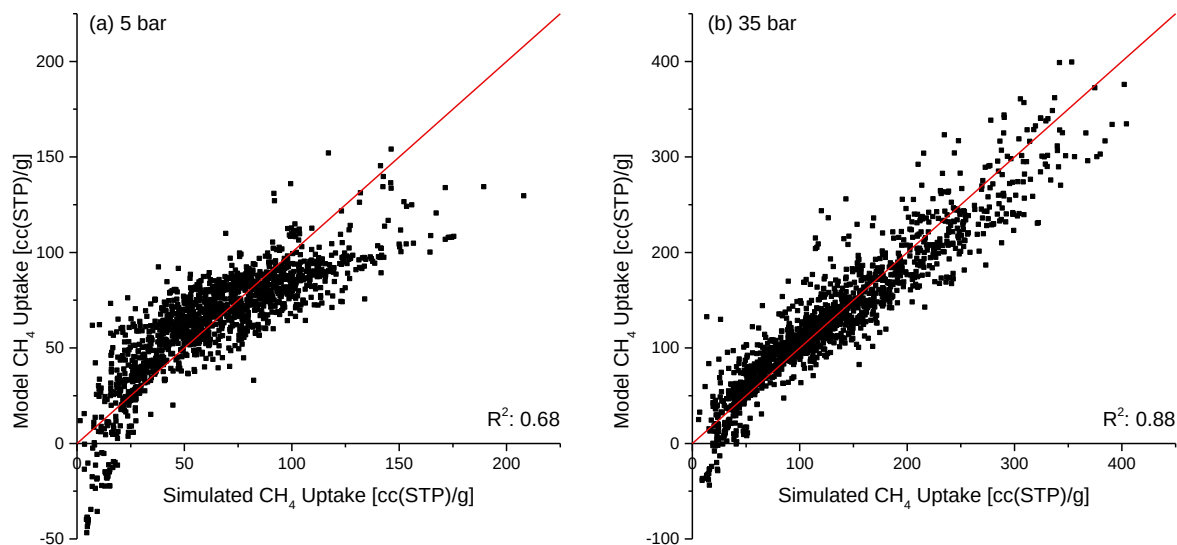


Figure 4.8: Comparison of Model-2 and simulations for CH₄ uptake at 298 K and (a) 5 bar; and (b) 35 bar. Statistical parameters are provided in Table 4.3. Model results at other pressures are given in Appendix B.

Unlike Model-1, S_v was selected at low pressures (1, 5, and 10 bar) instead of V_p in Model-2. At 15 and 20 bar same parameters were selected in both models and at 25, 30, and 35 bar ρ_{cryst} was selected instead of DPD in Model-2. At 50 and 65 bar again S_v was selected in Model-2 as opposed to DPD in Model-1. The R^2 values and standard deviations of both models are comparable and their $\bar{R}^2$ values are same as regular R^2 values because of the large data set used in the construction of these models. The similarity in the predictive power of both models suggests that parameters selected in previous models (Model-0) were able to represent a larger data set when the coefficients were updated in Model-1. However, the predictive powers of previous models (Model-0) on 45 MOFs were fairly higher than the updated versions of these models (Model-1) on ~1500 MOFs. This is expected since the larger number of MOFs brings various specific interactions, especially at lower pressures, and these interactions are not accurately represented using four-variable linear models. Nevertheless, both Model-1 and Model-2 have relatively low standard deviations suggesting the models can be used to predict CH₄ storage capabilities of a newly synthesized structure.

Table 4.3: Statistical parameters of the 4-variable models Model-1 and Model-2. The results for models at pressures other than 5 and 35 bar are given in Appendix B.

		Regression Coefficients ^{a,b}												
	Pressure (bar)	ρ_{cryst} a	V_p b	V_f c	S_g d	S_v e	PLD f	MPD g	DPD h	Q_{st} i	j	R^2	$\bar{R}^2$	STD
Model-1	1	-7.28	-4.21	100.40	-	-	-	-	-	4.82	-110.50	0.73	0.73	10.54
	5	-27.76	-12.88	229.55	-	-	-	-	-	6.49	-146.79	0.65	0.65	19.89
	10	-36.21	-6.83	306.94	-	-	-	-	-	6.50	-162.09	0.69	0.69	25.01
	15	-31.42	-	241.36	0.02	-	-	-	-	6.58	-145.48	0.77	0.77	25.98
	20	-32.55	-	245.74	0.03	-	-	-	-	6.27	-140.18	0.81	0.81	26.56
	25	-	-	280.59	0.04	-	-	-	1.11	6.99	-232.94	0.82	0.82	29.06
	30	-	-	272.17	0.04	-	-	-	1.54	6.83	-229.88	0.84	0.84	28.98
	35	-	-	263.19	0.05	-	-	-	1.94	6.74	-227.90	0.86	0.86	28.83
	50	-	-	226.58	0.06	-	-	-	2.95	6.20	-210.65	0.90	0.90	28.77
	65	-	-	196.68	0.06	-	-	-	3.77	5.82	-198.16	0.91	0.91	29.36
Model-2	1	-7.32	-	61.89	-	0.01	-	-	-	5.06	-104.05	0.75	0.75	9.60
	5	-27.45	-	124.56	-	0.02	-	-	-	6.71	-118.73	0.68	0.68	18.67
	10	-38.43	-	194.29	-	0.02	-	-	-	6.52	-123.41	0.71	0.71	23.63
	15	-31.90	-	252.21	0.02	-	-	-	-	6.99	-158.47	0.77	0.77	25.71
	20	-33.07	-	255.37	0.03	-	-	-	-	6.64	-151.68	0.81	0.81	26.34
	25	-33.57	-	254.76	0.03	-	-	-	-	6.29	-145.05	0.85	0.85	26.48
	30	-33.47	-	250.56	0.04	-	-	-	-	5.86	-136.21	0.87	0.87	26.57
	35	-33.16	-	245.74	0.04	-	-	-	-	5.50	-129.27	0.88	0.88	26.63
	50	-	-	413.48	0.07	-0.04	-	-	-	6.57	-261.65	0.92	0.92	25.84
	65	-	-	432.92	0.08	-0.06	-	-	-	6.17	-259.55	0.94	0.94	24.58

^a Multivariable linear models are constructed as in Equation (4.1).^b Units of regression coefficients are adjusted to give cc/g

In order to assess the feasibility of constructing a single model to predict CH₄ uptake at all pressures and 298 K, pressure-independent models have been constructed. First a QSPR analysis is performed to determine the parameters of the pressure-independent model using four-variables.

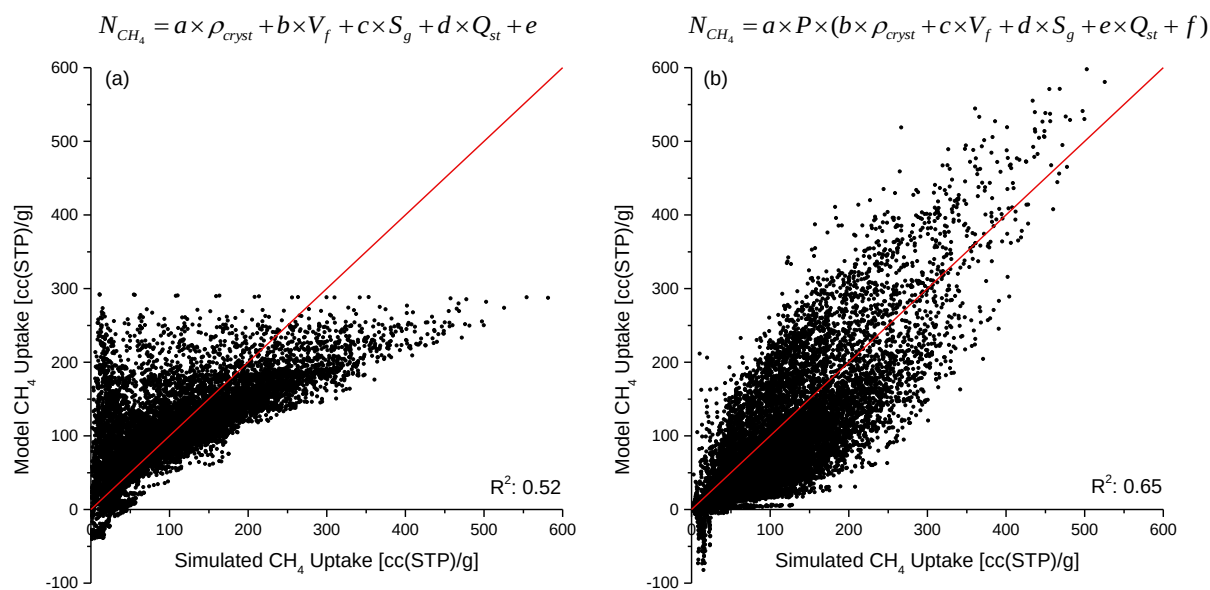


Figure 4.9: The model results and equations for pressure-indepent models (a) template model; (b) Model-3. Statistical parameters of the models are given in Table 4.4.

The resulting four-variable model is constructed by using ρ_{cryst} , V_f , S_g , and Q_{st} (Figure 4.9). The exact same parameters were also selected for 15 and 20 bar and 15, 20, 25, 30, and 35 bar of Model-0 and Model-2, respectively. Thus, it can be inferred that these four parameters are most correlated parameters with CH₄ uptake overall. As seen in Figure 4.9 (a) the model has a very poor prediction of the simulation results since there is only one parameter (Q_{st}) that is a function of pressure. In order to include pressure dependency into the model, a regression constant (a) and pressure variable (P, bar) were added to the equation as seen in Figure 4.9 (b). A significant improvement was observed with the inclusion of pressure term as evident from the increased R^2 value from 0.52 to 0.65. However, this model is not sufficient to accurately predict CH₄ uptake due its high standard deviation of 86.12 (Table 4.4). In order to increase the predictive power of the model, a parameter that accurately introduces the effect of pressure was required. First, to have an average relationship between CH₄ uptake and pressure, the average CH₄ uptake values were calculated at each pressure using simulation data. Then the average uptakes were plotted against pressure and a

logarithmic fit was obtained as seen in Figure 4.10 (a). This resulting fit was used to establish a relation between CH₄ uptake and pressure and it was included in Model-4 (Figure 4.10 (b)).

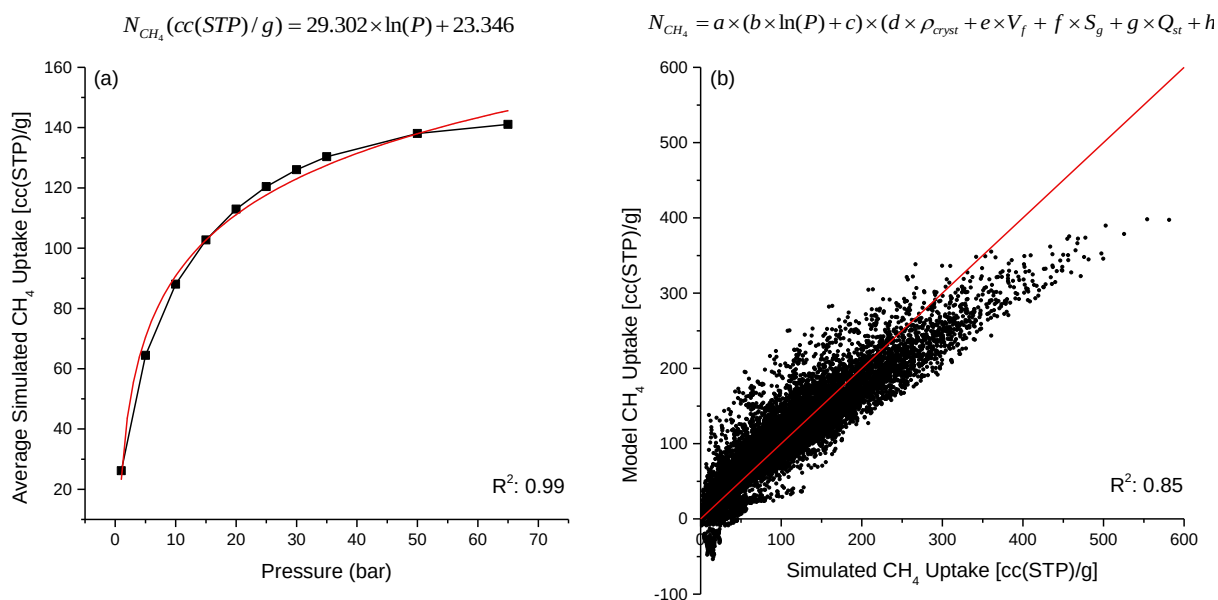


Figure 4.10: (a) Relation between average CH₄ uptake and pressure, and equation of logarithmic fit; (b) Comparison of model results with simulations and equation for Model-4. Statistical parameters of Model-4 are given in Table 4.4.

As seen in Figure 4.10 (b) the inclusion of a logarithmic relation between pressure and CH₄ uptake greatly increased the predictive power of the model (Model-4). However, the standard deviation of Model-4 (Table 4.4) was only decreased to 65.66 indicating a significant error for prediction. Even though Model-4 can give a ballpark idea for CH₄ uptake of a MOF, for more accurate prediction pressure-dependent models (Model-1 or Model-2) should be used. However, these linear models do not provide high enough accuracy to replace GCMC simulations or experimental adsorption measurements. To improve the accuracy for predicting the CH₄ uptake, other methods such as machine learning algorithms can be adopted. Support vector machines, genetic algorithms can be used for a detailed analysis of data and implementation of distinct non-linear models.

Table 4.4: Statistical parameters and formulas for pressure-independent models Model-3 and Model-4.

Regression Coefficients ^{a, b}									R ²	STD
	a	b	c	d	e	f	g	h		
Model-3^c	$N_{CH_4}(cc(STP)/g) = a \times P \times (b \times \rho_{cryst} + c \times V_f + d \times S_g + e \times Q_{st} + f)$								0.65	86.12
	0.03	-28.69	217.18	0.03	5.80	-130.68	-	-		
Model-4^c	$N_{CH_4}(cc(STP)/g) = a \times (b \times \ln P + c) \times (d \times \rho_{cryst} + e \times V_f + f \times S_g + g \times Q_{st} + h)$								0.85	65.66
	0.01	29.30	23.35	-28.69	217.18	0.03	5.80	-130.68		

^a Multivariable linear models are constructed using equations provided in the table^b Units of regression coefficients are adjusted to give cc/g^c b, c, d, e, and f coefficient in Model-3 correspond to d, e, f, g, and h in Model-4, respectively

In summary, successful multivariable linear models were developed on a data set of 45 MOFs to predict CH₄ storage characteristics of MOFs for a wide range of pressures (1-65 bar) using only structural characteristics and Q_{st} values. Models at 5 and 35 bar were examined in detail since these pressures are considered as relevant delivery and storage pressures for vehicular applications as determined by DOE. Model results were compared with both experimental data and previously proposed models and it was found out that models proposed in this study have improved predictive power for experimental data compared to previous models. The prediction capabilities of the models were also investigated on a large set (~1500) of MOF structures. The proposed regression coefficients were updated and new QSPR analyses were also performed. Models with comparable accuracy were constructed for 1500 MOFs using similar parameters with previous models. Moreover, viability of using a single, pressure-independent model was tested by constructing several models. It was found that pressure-independent model can be used to get an approximate estimate of CH₄ uptake at a desired pressure, however for accurate predictions pressure-dependent models should be used. Additionally, it was discovered that V_f and Q_{st} are the most significant parameters for CH₄ uptake since these parameters were included in all the constructed models. The models proposed in this study can be helpful for the estimation

of CH₄ uptake without compelling experimental adsorption measurements. Moreover, benefiting from these models valuable insights can be gained regarding which type of materials should be the targets for synthesis and application. Prior to synthesis, thermal and chemical stability of the MOFs should be examined, as models do not give information regarding stability and it is a crucial factor for practical usage. It should also be noted that for industrial applications, other important factors such as cost of reagents and equipment, ease of experimental synthesis and time constraints should be carefully considered.

Chapter 5: Preparation, Characterization, and Adsorption Measurements of Ionic Liquid (IL) Incorporated MOFs

Following the identification of top performing materials using computational methods, one of the most promising candidates, HKUST-1 (a.k.a CuBTC, and commercially available as Basolite C300), has been investigated experimentally. The IL incorporated Basolite C300 samples have been prepared at different loadings of [BMIM][BF₄]. Later, both unmodified Basolite C300 and IL-incorporated samples have been characterized prior to adsorption performance analysis. In the first part of this chapter, characterization results of Basolite C300 and their comparison with literature are given. In the second part, characterization of Basolite C300 and [BMIM][BF₄] incorporated samples (IL/C300) are provided.

5.1 Material Handling

All materials used in this study (Basolite C300, [BMIM][BF₄], and high purity acetone) have been purchased from Sigma-Aldrich. Basolite C300 and [BMIM][BF₄] were stored in Ar glovebox (Labconco). The preparation of IL-incorporated Basolite C300 samples were performed with fresh materials in open atmosphere (Chapter 3.2.1). After preparation

and drying, the samples were sealed and moved to desiccator to minimize water and impurity content. Humidity has a destructive effect on Basolite C300 when the sample is left in open environment for a long period of time. The effect of humidity can be seen from the SEM results of a previously purchased Basolite C300 which was stored in open environment for ~3 years (Chapter 5.1.3).

5.2 Characterization of as-purchased Basolite C300

Several characterization methods were utilized to characterize Basolite C300 sample, which is commercially produced by BASF company and supplied by Sigma-Aldrich [160]. Basolite C300 is a widely studied MOF and its characterization was investigated in many studies [158, 161]. Firstly, the crystal structure of Basolite C300 was investigated using powder X-ray diffraction. Then, thermal stability limit of the material was determined by thermal gravimetric analysis. Scanning electron microscopy was used to examine the crystal morphology in detail. Finally, N₂ adsorption at 77 K and 0-1 bar was performed to determine the Brunauer–Emmett–Teller (BET) surface area. All the results have been compared with available literature data.

5.2.1 Powder X-Ray Diffraction (XRD)

X-ray diffraction is a widely used method for the characterization of crystalline materials. When crystalline surfaces interact with X-rays, a unique diffraction pattern is obtained which can be used to identify the crystal structure. XRD pattern of Basolite C300 was obtained with measurement parameters provided in Chapter 3. The resulting XRD pattern and its comparison with literature [161] is provided in Figure 5.1.

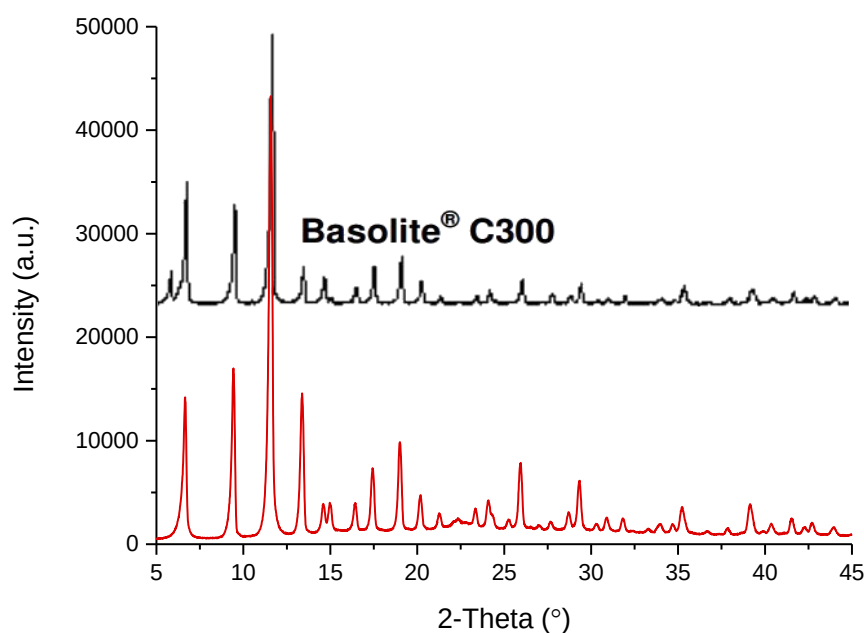


Figure 5.1: X-ray diffraction pattern of Basolite C300 in this work (red) and its comparison with XRD pattern adapted from literature (black) [161].

Basolite C300 has a cubic crystal structure with space group ($Fm\bar{3}m$) [18]. As seen in Figure 5.1, the peaks obtained from the XRD measurement accurately correspond to peaks adapted from literature data. Only one peak around $2\theta = 6^\circ$, which is attributed to (111) plane of the crystal [158] is missing, suggesting the growth of that plane is small. Depending on the synthesis procedure, growth of the planes and consequently peak intensities may vary for different samples [161]. Moreover, as evident from the high intensities seen in small angles it can be inferred that the material is microporous with various small pores and cavities [158].

5.2.2 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) is performed to determine the weight loss of the sample as a function of temperature. Basolite C300 was treated in a furnace under N_2 flow with a constant temperature ramp at $2^\circ\text{C}/\text{min}$ up to 700°C . The resulting weight percent change and derivative weight percent change with temperature are provided in Figure 5.2.

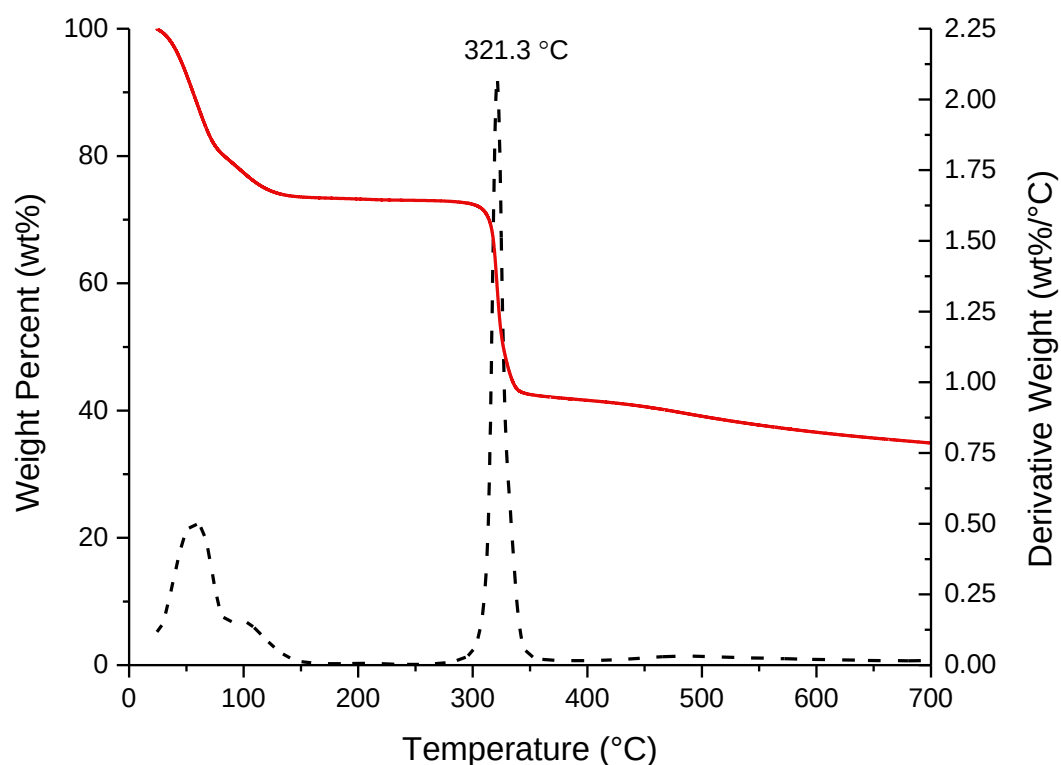


Figure 5.2: Thermal gravimetric analysis results for Basolite C300. Red line and left y-axis shows weight percent change with temperature and dashed black line and right y-axis shows derivative weight percent change with temperature.

As seen in Figure 5.2, an initial weight loss of 27 wt% is observed until 200 °C caused by water desorption from the sample. The weight percent is stable until around 310 °C followed by a sudden loss of 30 wt% because of the decomposition of the framework. After around 350 °C another loss of 7.5 wt% was observed until 700 °C. The derivative onset temperature (T'_{onset}) was measured as 312.3 °C from the derivative TGA curve. These results are comparable with TGA data of Basolite C300 obtained from literature given in Figure 5.3.

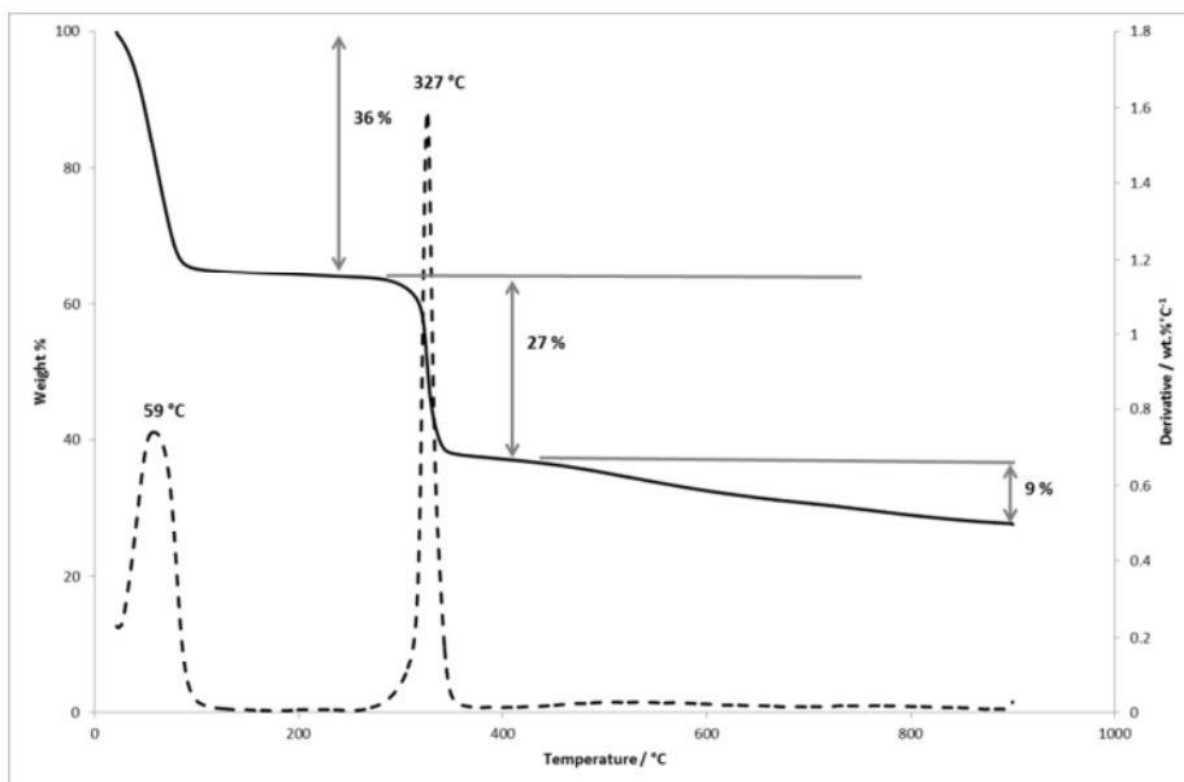


Figure 5.3: Thermal gravimetric analysis results for Basolite C300 adapted from work by Gimeno-Fabra et al. [162]. Straight line and left y-axis shows weight percent change with temperature and dashed line and right y-axis shows derivative weight percent change with temperature.

As seen in Figure 5.3 the initial weight loss until ~ 200 °C is reported as 36 wt% [162] which is greater than our result of 27 wt%. This difference is caused by different water adsorption into the sample because of air exposure. The water content of our sample is apparently lower than sample investigated by Gimeno-Fabra et al. [162] resulting in a decreased weight percent loss. The samples in this thesis study were handled carefully to minimize water content, as described in Chapter 5.1. Other weight percent losses and peak temperature of derivative weight percent change are in agreement with the results obtained in this study.

5.2.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopes are used to produce images at very high magnifications that provide information about surface topography and composition down to nanometer scales. For crystal samples, SEM enables the determination of particle size, crystal shape and surface characteristics. Photomicrographs of Basolite C300 were obtained at different magnifications to examine the morphology and particle size of the sample and results are provided in Figure 5.4. As seen in Figure 5.4, most of the particles are octahedral in shape with sizes averaging around 10 μm . This results are in agreement with the crystal shapes and sizes reported in literature [163] (given in Figure 5.5).

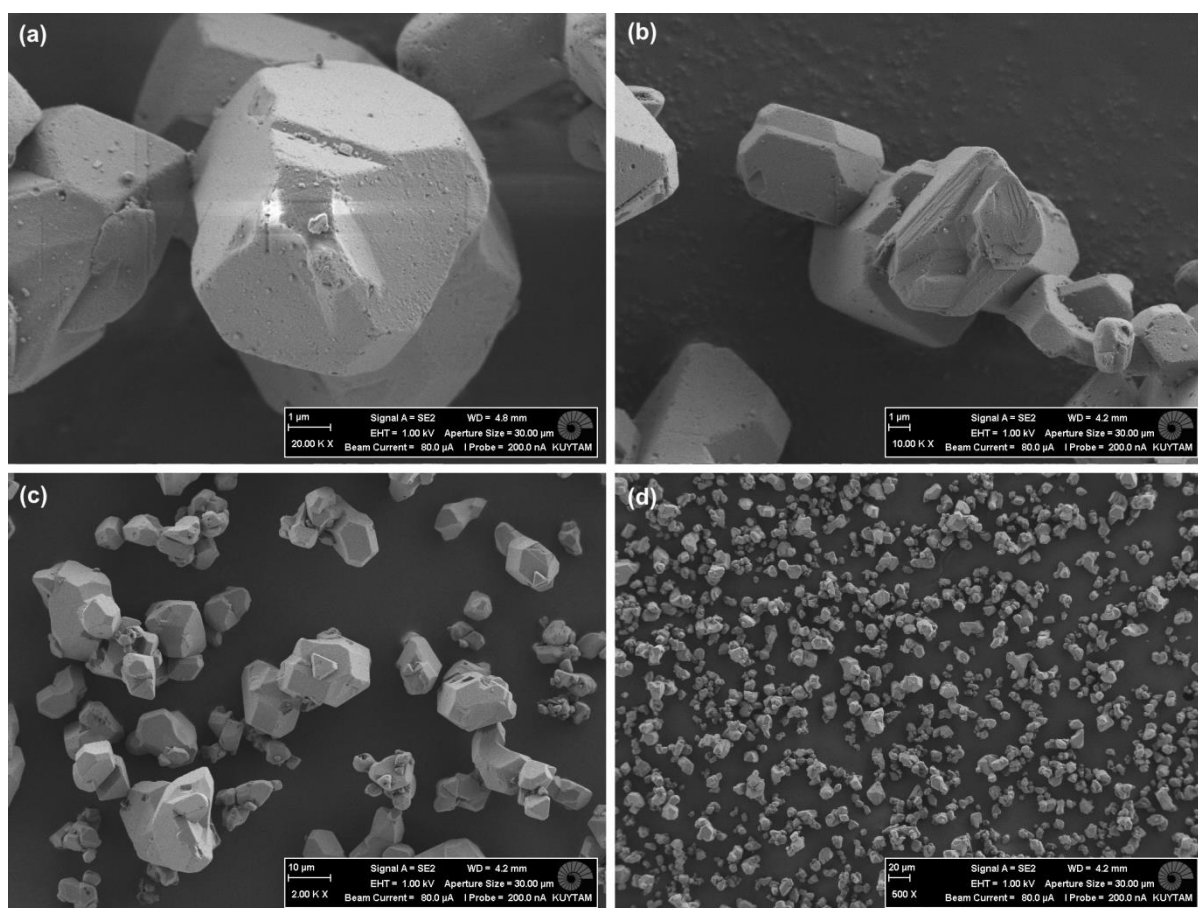


Figure 5.4: Morphology of Basolite C300 crystals at different magnifications: (a) 20,000x; (b) 10,000x; (c) 2,000x; and (d) 500x determined by SEM analysis.

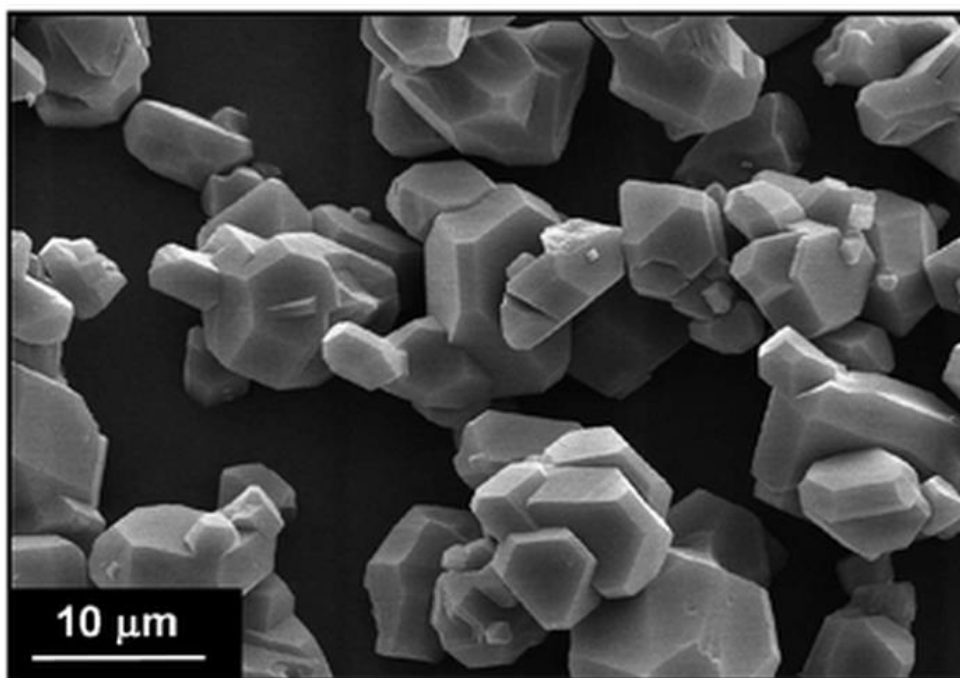


Figure 5.5: SEM Image of Basolite C300 obtained from Ref. [163].

In order to illustrate the effects of humidity on Basolite C300, SEM images of a previously purchased sample which was held in open air for approximately 3 years are given in Figure 5.6. The long term water adsorption in sample has destructive effects on the crystal surface. Even though the crystal planes are preserved the surfaces have significant deformations.

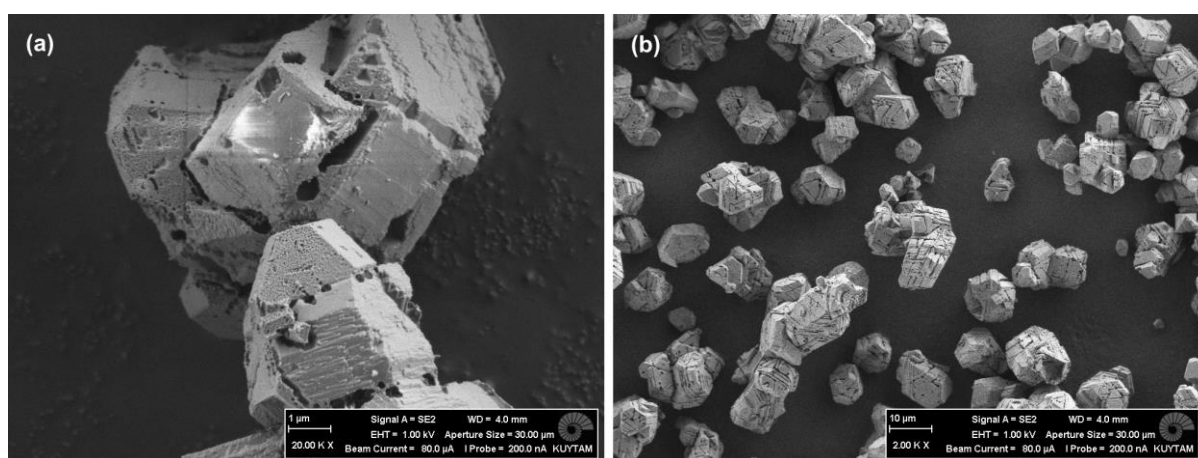


Figure 5.6: Morphology of old Basolite C300 crystals at different magnifications: (a) 20,000x; (b) 2,000x determined by SEM analysis.

5.2.4 Brunauer–Emmett–Teller (BET) Surface Area

Surface area measurements provide important insights regarding the porosity of the material and it is one of the most essential characterization methods used for adsorbent materials. For the determination of the surface area of Basolite C300, N₂ adsorption measurements have been performed at 77 K between 0-1 bar. The resulting isotherm and data fit for the calculation of BET surface area (details provided in Chapter 3) are given in Figure 5.7.

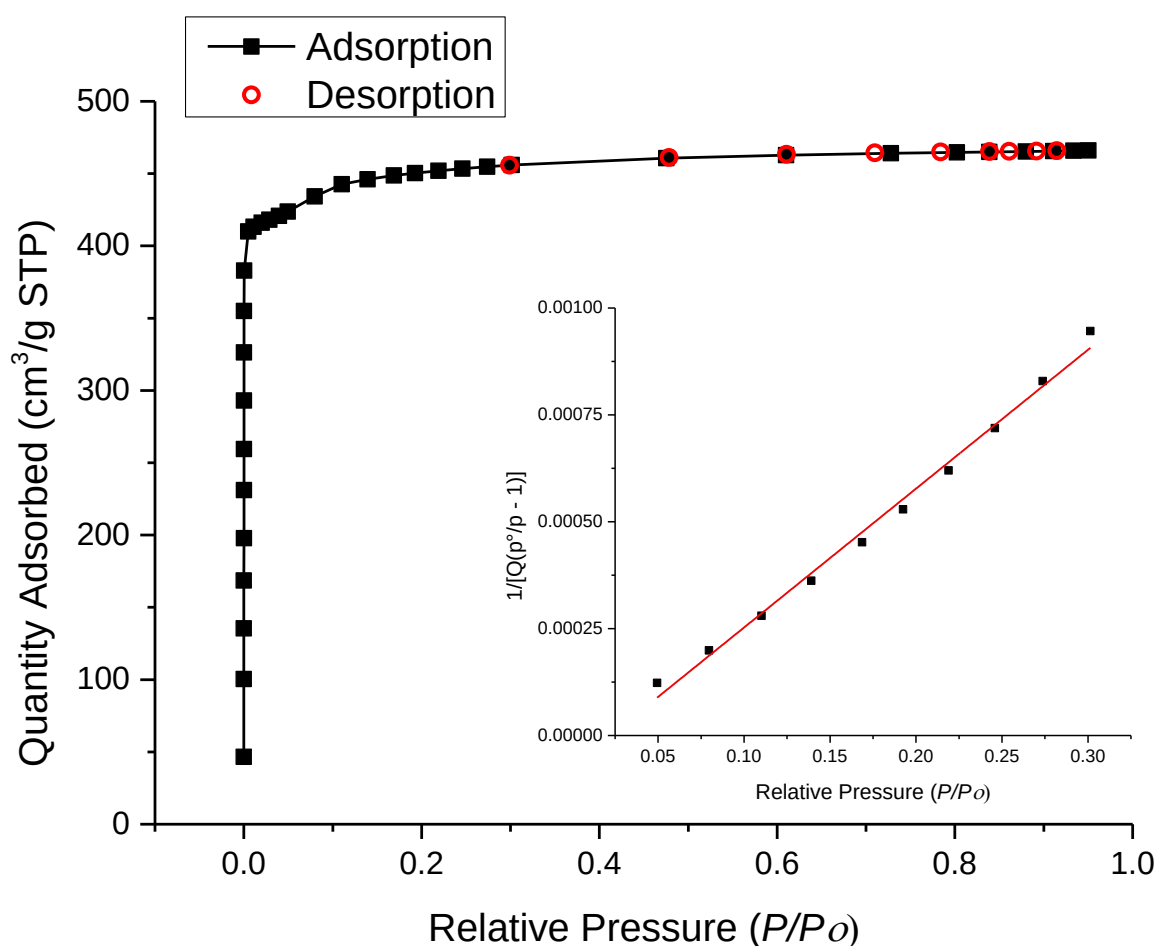


Figure 5.7: N₂ adsorption isotherm at 77 K between 0-1 bar. Inset: fit used for the calculation of BET surface area between relative pressures of 0.05-0.3.

According to the N₂ physisorption isotherm at 77 K between relative pressures of 0.05-0.3 bar, the BET surface area was calculated as $1370.5 \pm 43.3 \text{ m}^2/\text{g}$ for Basolite C300. This is slightly lower than average surface areas reported previously around 1300-1800 m²/g [164]. This difference is likely caused by insufficient activation of the sample prior to the adsorption measurement, which was performed at 150 °C for 10 hours. Yoon et al. [165] activated Basolite C300 at 150 °C for 12 hours and reported a surface area of 1560 m²/g. Another reason for the slightly low surface area of Basolite C300 might be variations in the synthesis procedure as well. Majano and Perez-Ramirez [166] found out that synthesis time significantly affects the BET surface area of this MOF which showed deviations between 1346 m²/g to 1749 m²/g according to time given for crystallization.

5.3 Preparation and Characterization of IL-Incorporated MOFs

Preparation of the IL-incorporated MOFs (IL/C300) have been performed by impregnation of [BMIM][BF₄] molecules in to the Basolite C300 framework using acetone as solvent. Similar procedures have been carried out by Khan et al. [104] and Luo et al. [108] and it was found that IL molecules were successfully impregnated using this procedure. Prior to IL/MOF preparation, two different solvents were considered for impregnation: acetone and ethanol. Both solvents can readily dissolve [BMIM][BF₄] therefore their effects on Basolite C300 structure were investigated by SEM. Different Basolite C300 samples were soaked in ethanol and acetone and the solvents were evaporated. As seen in Figure 5.8, ethanol caused deformation of the crystal structure whereas sample soaked in acetone were almost undamaged. As a result acetone was selected as solvent for impregnation. The preparation of IL/C300 samples are described in Chapter 3.2.1.

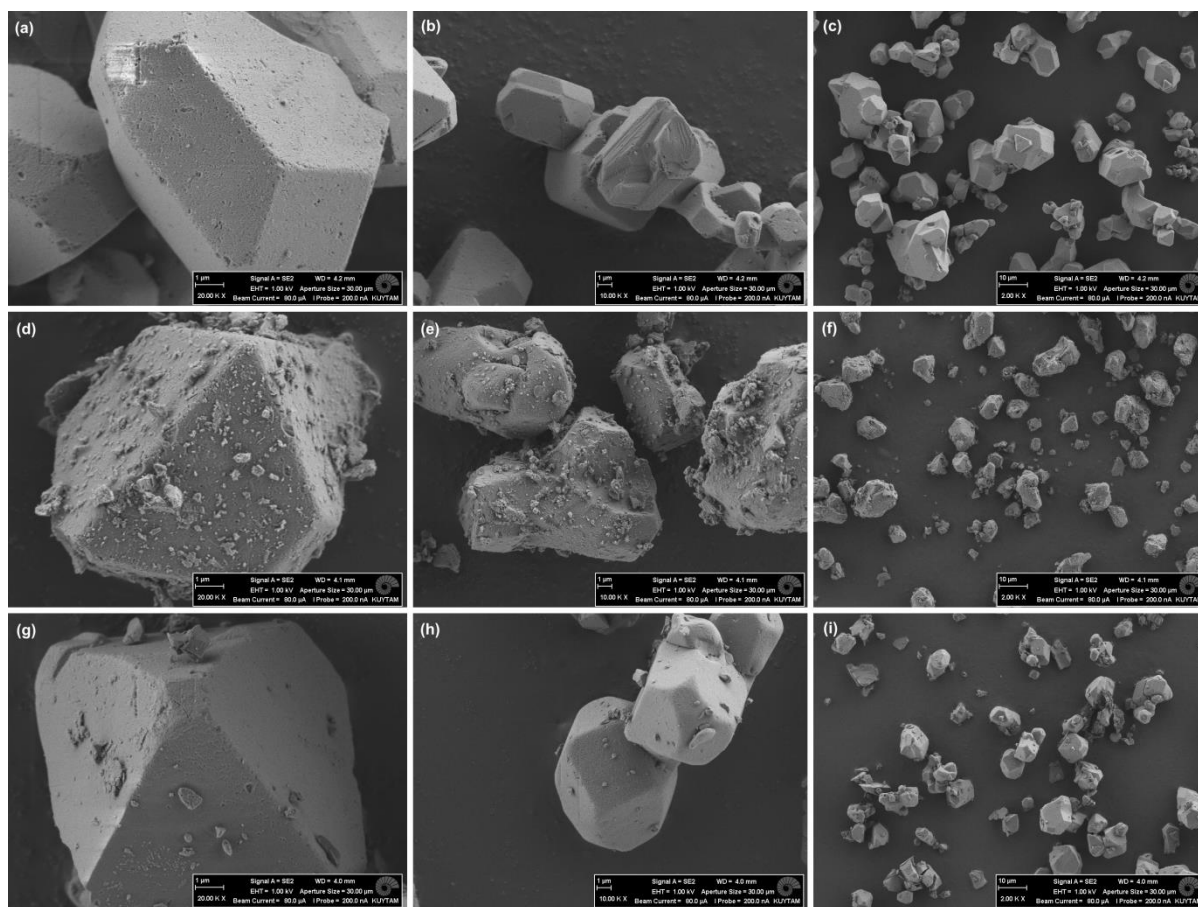


Figure 5.8: Morphology of untreated Basolite C300 crystals at (a) 20,000x; (b) 10,000x; (c) 2,000x; magnifications, ethanol dipped Basolite C300 crystals at (c) 20,000x; (d) 10,000x; (e) 2,000x; magnifications, and acetone dipped Basolite C300 crystals at (g) 20,000x; (h) 10,000x; (i) 2,000x magnifications determined by SEM analysis.

All the characterization measurements discussed in Chapter 5.2 have also been performed on IL/C300 samples with the inclusion of two additional methods: IR spectroscopy and elemental analysis which were used to validate the existence of [BMIM][BF₄] molecules in the IL-incorporated samples.

5.3.1 Powder X-Ray Diffraction (XRD)

X-ray diffraction patterns were determined for IL/C300 samples to investigate the effect of impregnation on the crystal structures. XRD measurements were performed using same parameters (discussed in Chapter 3) for all samples in this study and the results are

given in Figure 5.9. The intensity values were normalized according to the highest peak observed in the measurements to enable accurate comparison of results.

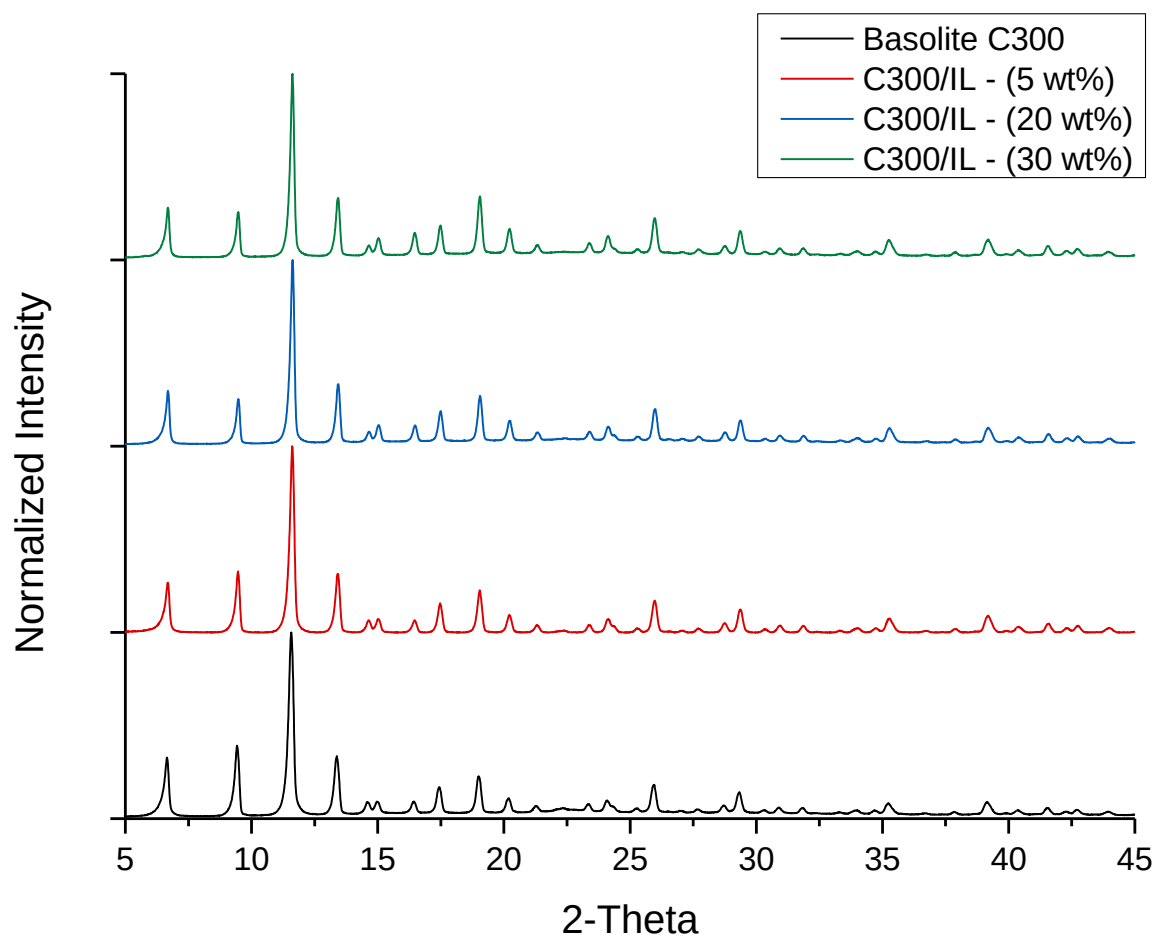


Figure 5.9: X-ray diffraction pattern of Basolite C300 (black), IL/C300 (5 wt%) (red), IL/C300 (20 wt%) (blue), and IL/C300 (30 wt%) (purple).

As evident from Figure 5.9, the crystallinity of the MOF framework was preserved for all loadings after impregnation with IL. Additionally, no peak shifts have been observed for the IL/C300 materials compared to pristine Basolite C300 suggesting that IL molecules resided on the surface of the crystals. As a result it can be inferred that structures did not show deformation and loss of crystallinity after impregnation.

5.3.2 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analyses of the IL/C300 samples were performed to investigate the temperature tolerance and determine the onset and derivative onset temperatures which denote the temperature at which the weight loss due to decomposition begins. The weight percent and derivative weight percent changes for all samples are given in Figure 5.10 (a) and (b), respectively.

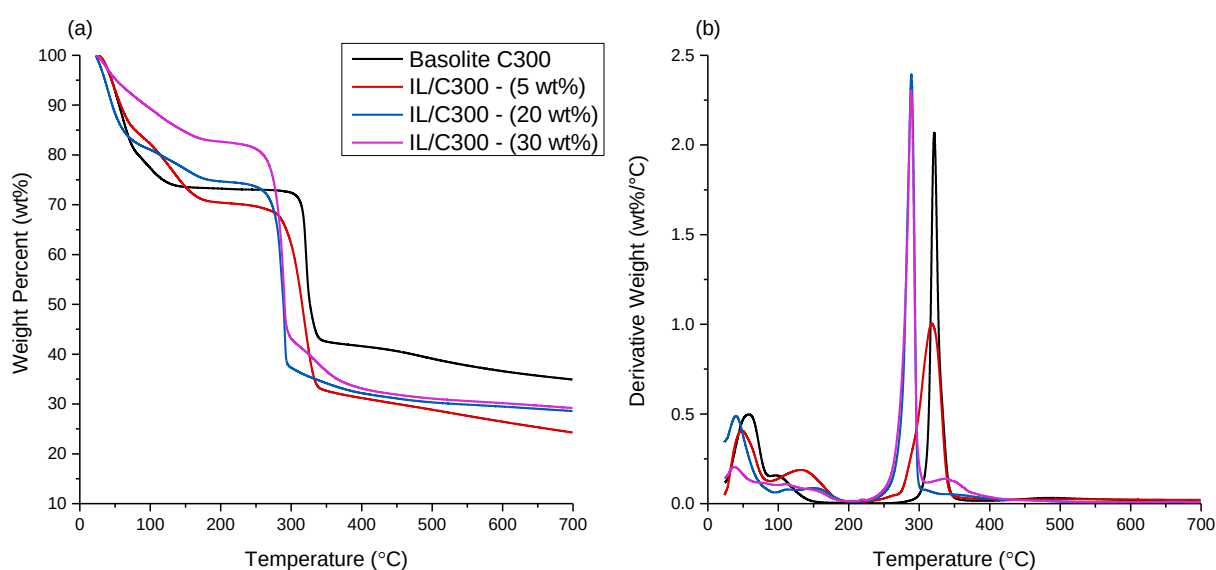


Figure 5.10: Thermal gravimetric analysis results for Basolite C300 and IL/C300: (a) weight percent change with temperature; and (b) derivative weight percent change with temperature.

As seen in Figure 5.10 (a) there is a significant weight loss up to 200 °C for all materials due to water content of the samples. These amounts are different in each sample because of different exposure times to air during sample preparation for the TGA experiments. In order to determine the weight losses due to decomposition of the samples, amounts prior to decomposition and following the drying period have been normalized to 100 wt% and the weight losses due to decomposition have been calculated and given Table 5.1.

Table 5.1: Onset temperatures and normalized wt% losses due to decomposition calculated from TGA experiments. Data for [BMIM][BF₄] is adapted from literature [167].

	[BMIM][BF₄] (Bulk)	Basolite C300	IL/C300 (5 wt%)	IL/C300 (20 wt%)	IL/C300 (30 wt%)
T' _{onset} (°C)	376	312.3	285.9	275.5	275.4
T _{onset} (°C)	381	316.2	293.9	281.1	278.0
Normalized wt% loss	-	42.5	55.1	56.8	58.5

As expected, Basolite C300 has a lower weight percent loss compared to IL/C300 samples and the weight loss slightly increases as the IL loading increases. This increase is because of [BMIM][BF₄] decomposition in addition to the decomposition of the MOF framework. Additionally, onset temperatures calculated from TGA (T_{onset}) and derivative TGA (T'_{onset}) curves for the decomposition of the samples are provided in Table 5.1. The onset temperature decreases around 26 °C and 37 °C for 5 wt% and 20 wt% IL loadings, respectively. After 20 wt% IL loading the onset temperature stays constant. Even though the decomposition of IL/C300 samples occurs at lower temperatures compared to Basolite C300, the structures are still stable up to around 275 °C suggesting good thermal stability.

Additionally isothermal gravimetric analysis was performed to investigate temperature tolerance as a function of time. Basolite C300 and 20 wt% IL-incorporated sample were held at 175 °C for 15 hours and the results are given in Figure 5.11.

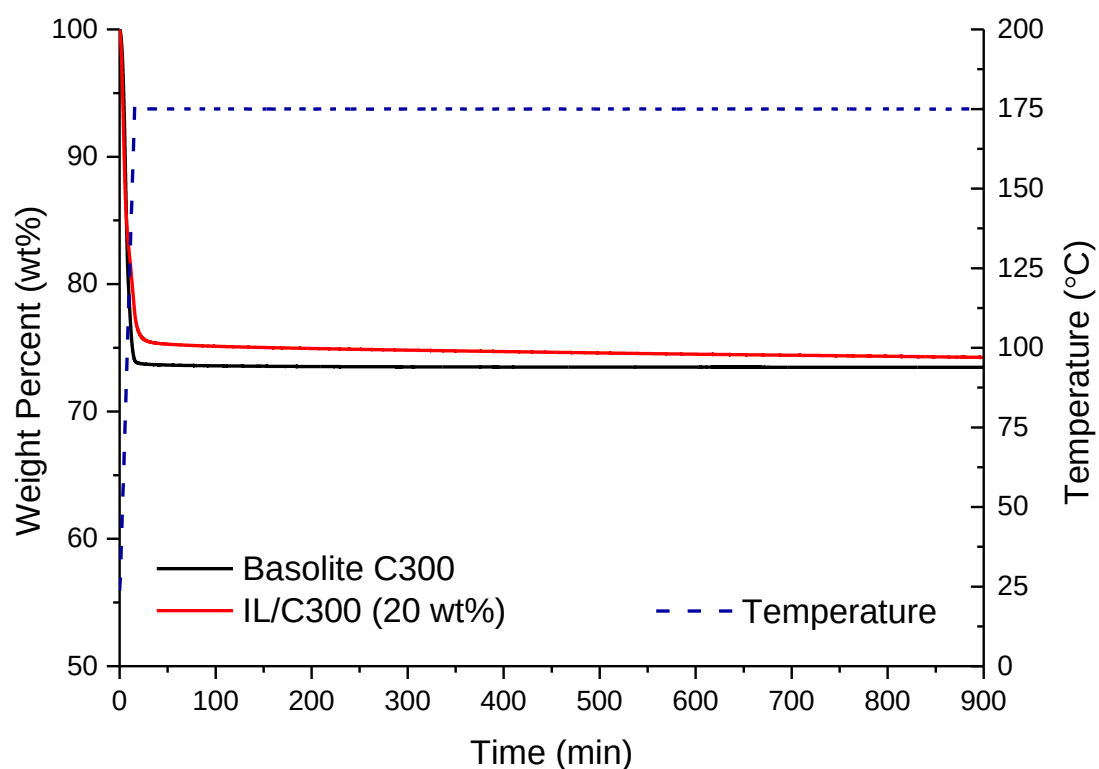


Figure 5.11: Isothermal TGA results for Basolite C300 and IL/C300 (20 wt%) at 175 °C for 15 h.

An initial weight loss around 25 wt% is observed for both samples due to dehydration. Weight loss for Basolite C300 stabilizes around 250 min whereas a slight weight loss can be observed for IL/C300 (20 wt%) throughout the measurement. This slight weight loss is likely resulting from very slow dehydration of the sample. No significant decomposition was observed for both samples at 175 °C for 15 h, suggesting the activation of the samples performed at 150 and 125 °C for Basolite C300 and IL/C300 (20 wt%) were not detrimental.

5.3.3 Scanning Electron Microscopy (SEM)

Photomicrographs of IL/C300 samples were obtained by SEM and they are provided in Figure 5.12. As seen from the images, the size and shape of the particles of IL/C300 are almost identical to those of Basolite C300. Coupled with XRD patterns discussed previously,

it is clearly seen that the crystal structure is preserved during incorporation of IL into Basolite C300.

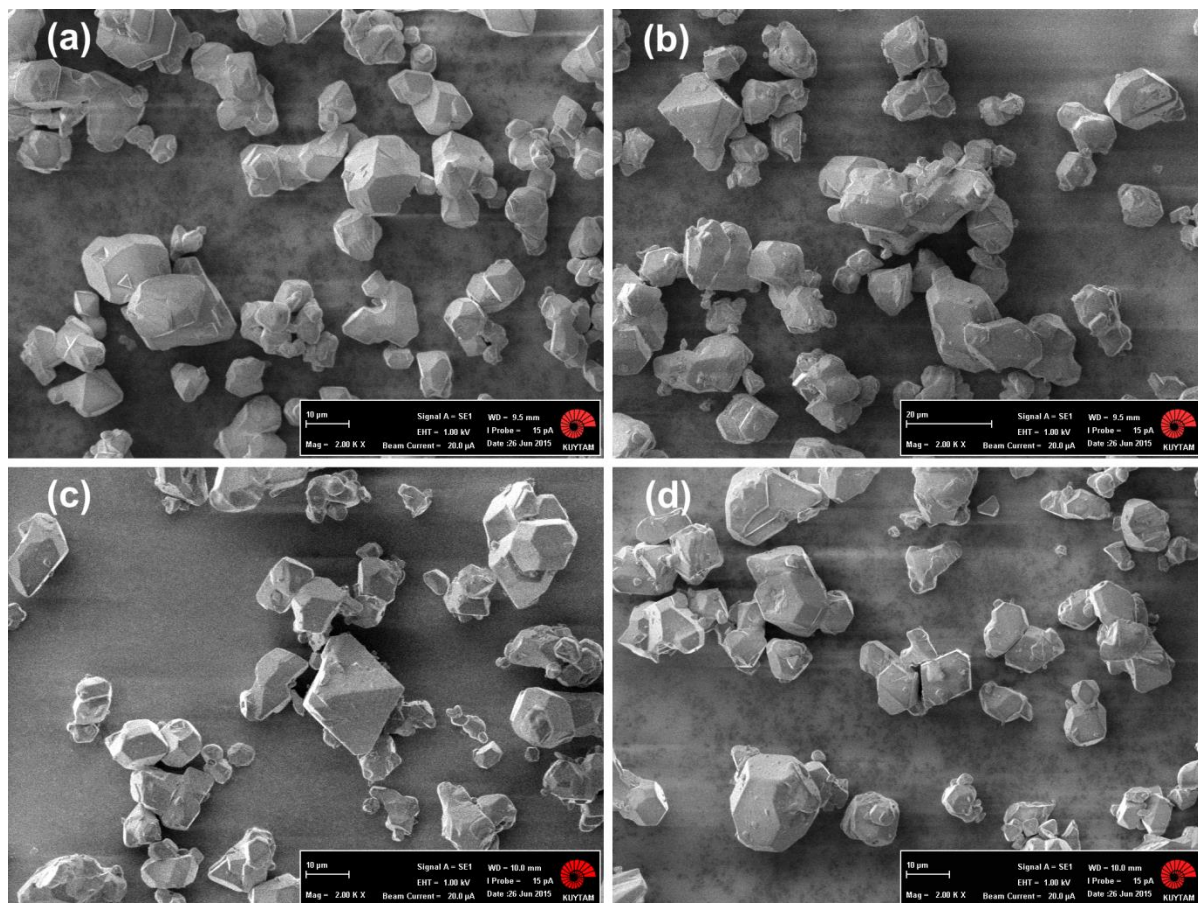


Figure 5.12: Morphology of (a) Basolite C300; (b) IL/C300 (5 wt%); (c) IL/C300 (20 wt%); and (d) IL/C300 (30 wt%) crystals determined by SEM analysis.

5.3.4 Infrared (IR) Spectroscopy

The vibrational properties of Basolite C300 and IL-incorporated C300 samples were studied by collecting the spectra in ATR mode and the spectrum between $3300\text{--}2800\text{ cm}^{-1}$ and $1700\text{--}500\text{ cm}^{-1}$ as given in Figure 5.13. The whole spectrum between $4000\text{--}500\text{ cm}^{-1}$ for all samples and [BMIM][BF₄] is given in Appendix C. The broad IR bands observed in the spectra of hydrated C300 and IL/C300 samples between $2800\text{--}3800\text{ cm}^{-1}$ are assigned to adsorbed H₂O and IR bands between $2200\text{--}2400\text{ cm}^{-1}$ are caused by adsorbed CO₂ and N₂.

from the atmosphere [168,169] (Appendix C). Other peaks resulting from the framework atoms of Basolite C300 between $1700\text{--}1500\text{ cm}^{-1}$ and $1500\text{--}1300\text{ cm}^{-1}$ are assigned to $\nu_{\text{asym}}(\text{C-O}_2)$ and $\nu_{\text{sym}}(\text{C-O}_2)$, respectively [169]. The sharp peaks around 760 cm^{-1} and 730 cm^{-1} are related to out of plane C-H bending.

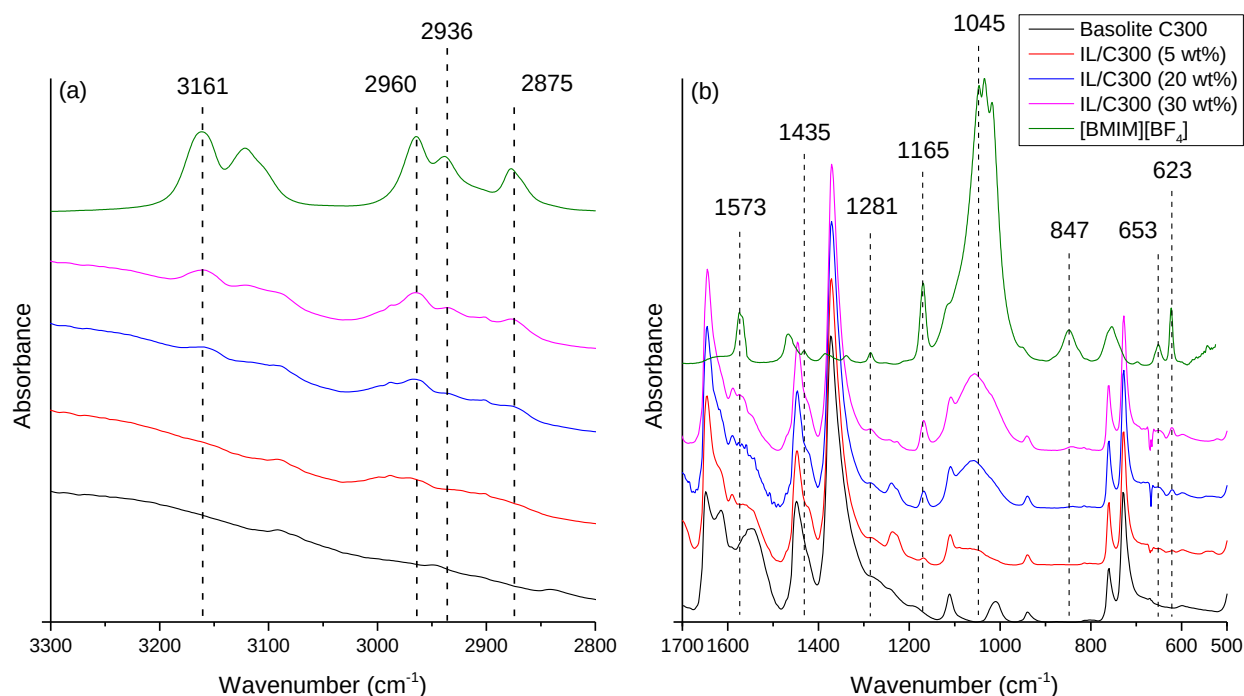


Figure 5.13: IR Spectra for Basolite C300, IL-incorporated C300 samples, and [BMIM][BF₄] between (a) $3300\text{--}2800\text{ cm}^{-1}$; and (b) $1700\text{--}500\text{ cm}^{-1}$. ν : stretching, γ : bending, δ : deformational, subscripts sym and asym are symmetric and asymmetric vibrations, respectively.

As seen in Figure 5.13 (a) four peaks belonging to [BMIM][BF₄] were also observed in IL/C300 samples with increasing absorbance with the IL loading. These peaks at 3161 , 2960 , 2936 , and 2875 cm^{-1} were assigned to $\nu(\text{C}_{4,5}\text{-H})$, $\nu_{\text{asym}}(\text{CH}_2)$, $\nu_{\text{asym}}(\text{CH}_2)$, and $\nu_{\text{sym}}(\text{CH}_2)$ modes respectively [170]. In $1700\text{--}500\text{ cm}^{-1}$ region other peaks were observed with the incorporation of IL (Figure 5.13 (b)). The new peaks resulting from [BMIM][BF₄] incorporation at 1573 , 1281 , 1165 , 1045 , and 623 cm^{-1} are more noticeable compared to others. The peaks at 1573 , and 1165 cm^{-1} are assigned to C=C bond stretching and in plane

HCCH bending of the BMIM cation [170]. Other peaks at 1281 and 1045 cm^{-1} are resulting from the stretching of BF_4 anion. There are two more peaks close to 1045 cm^{-1} which were also assigned to $\nu(\text{BF}_4)$ however these peaks were united in IL/C300 samples. Two peaks at 623 and 653 cm^{-1} were both assigned to in-phase vibrations of $(\text{CH}_2(\text{N}), \text{CH}_3(\text{N}))$ [170]. It is difficult to observe the peak at 653 cm^{-1} in IL/C300 samples. Therefore, deconvolution of peaks was performed on the signal for peaks at 653 cm^{-1} and 1435 cm^{-1} (Appendix C). For wavenumbers around 1450 cm^{-1} , deconvolution revealed three peaks at 1423, 1446, and 1470 cm^{-1} . The peaks at 1470 and 1446 cm^{-1} were assigned to $\delta_{\text{sym}}(\text{CH}_3)$ of [BMIM] cation [170] and $\nu(\text{C-C})$ for Basolite C300 [171]. For wavenumbers at approximately 650 cm^{-1} , deconvolution revealed two peaks at 653 and 662 cm^{-1} suggesting the existence of N atoms. Lastly, the peak at 847 cm^{-1} , assigned to $\gamma(\text{C4,5-H})$ is hardly visible in IL/C300 samples however magnification of the region shows a slight peak especially for IL/C300 (30 wt%).

As a result, [BMIM][BF_4] incorporation can be observed from the IR spectrum in the IL/C300 samples. As the IL loading increases peaks assigned to [BMIM][BF_4] are intensified. Moreover, both Basolite C300 and [BMIM][BF_4] keep characteristic peaks in IL-incorporated samples suggesting both materials were intact after incorporation.

5.3.5 Brunauer–Emmett–Teller (BET) Surface Area

N_2 adsorption measurements were performed for IL/C300 samples at 77 K between 0-1 bar to determine the BET surface areas. The adsorption isotherms and the resulting BET surface areas are given in Figure 5.14 and Table 5.2, respectively.

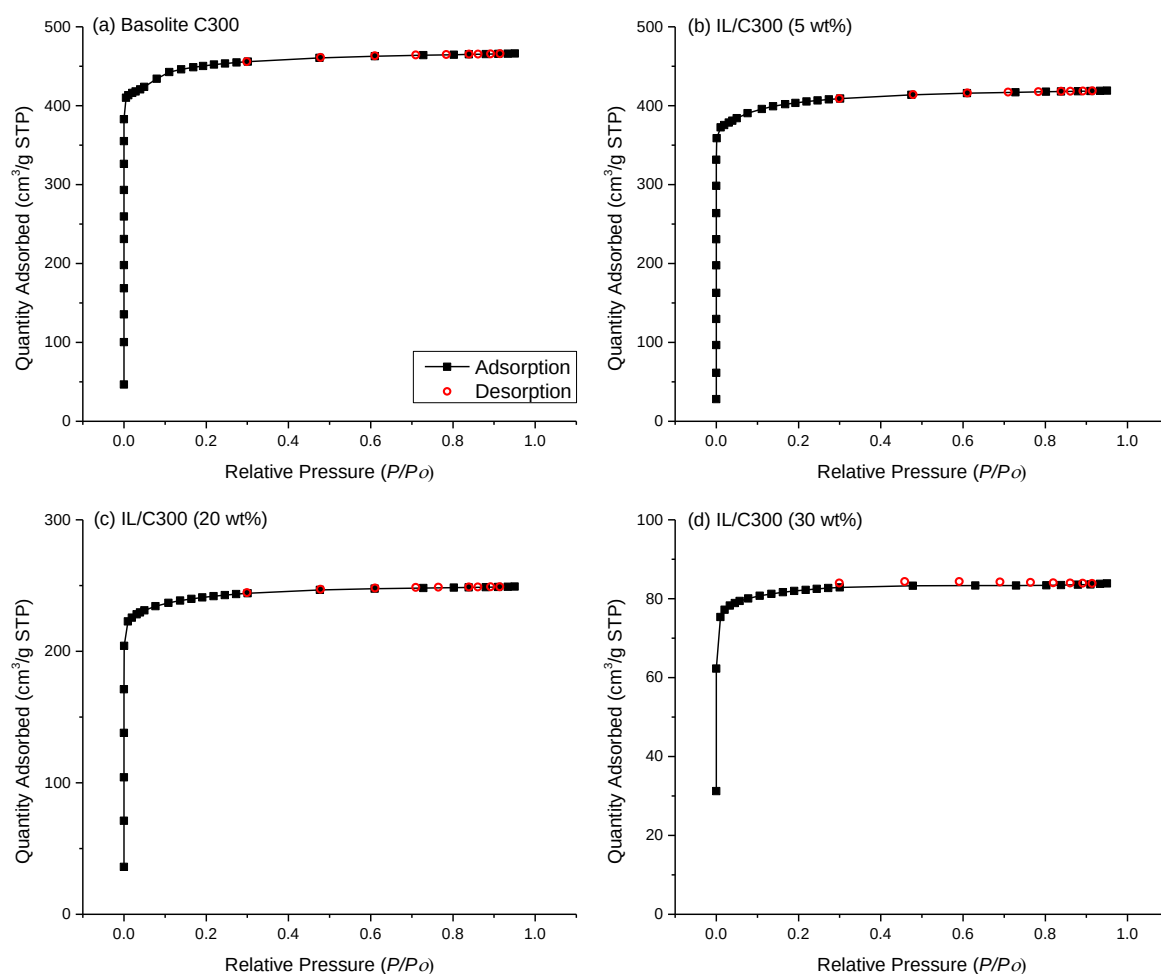


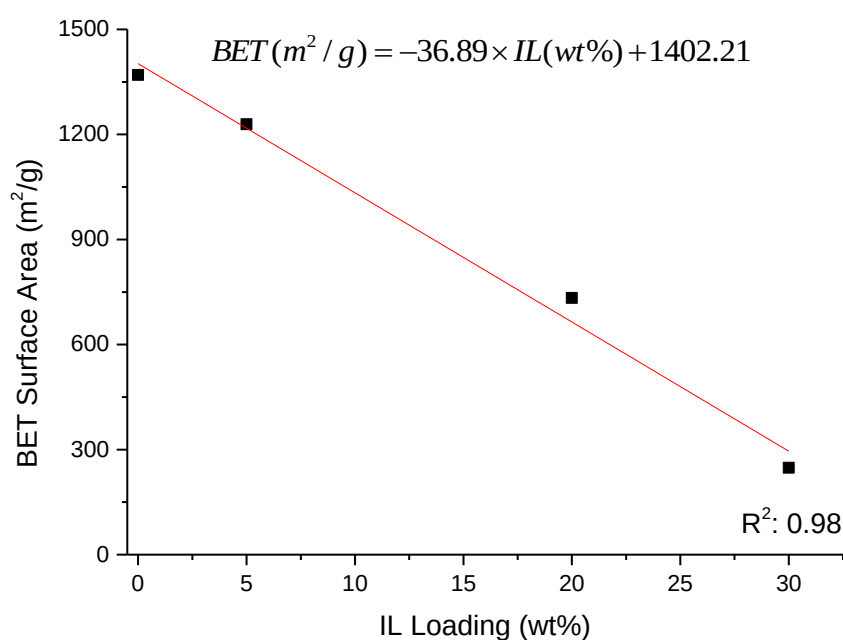
Figure 5.14: N₂ adsorption isotherm at 77 K between 0-1 bar for (a) Basolite C300; (b) IL/C300 (5 wt%); (c) IL/C300 (20 wt%); and (d) IL/C300 (30 wt%).

As expected, N₂ uptake at 77 K and consequently the BET surface areas decrease with IL incorporation, proportional with the amount of IL loaded. The bulky [BMIM][BF₄] molecules decrease the number of accessible pores in the structure resulting in lower surface areas. No hysteresis is observed in the N₂ adsorption isotherms suggesting the microporosity of Basolite C300 is preserved.

Table 5.2: BET surface areas calculated from N₂ adsorption measurements at 77 K.

	Basolite C300	IL/C300 (5 wt%)	IL/C300 (20 wt%)	IL/C300 (30 wt%)
BET Surface Area (m ² /g)	1370.5 ± 43.3	1229.1 ± 37.7	733.2 ± 22.3	247.9 ± 7.3

Additionally, relation between BET surface areas and the IL loadings were investigated and a linear relationship was revealed as seen in Figure 5.15. The BET surface area decreases linearly as the IL loading increases and the correlation is accurately described with the equation provided in Figure 5.15. This correlation suggests that the surface area of the IL/C300 sample can be tailored easily by the amount of IL in the structure.

**Figure 5.15:** Correlation between BET surface area and IL loading of Basolite C300.

5.3.6 Elemental Analysis

The elemental analysis was performed to determine amounts of N, C, and H atoms in the structures of Basolite C300 and IL/C300 samples. Theoretical weight percent for N, C, and H atoms have been calculated using molecular formulas (C₁₈H₆Cu₃O₁₂ and C₈H₁₅BF₄N₂)

and molecular weights (604.9 and 226.0 g/mol) of Basolite C300 and [BMIM][BF₄], respectively. Only N, C, and H atoms were considered for the calculation of theoretical weight percent since the experiments were performed to determine amounts of only these atoms. Experimental results and theoretical weight percent are given in Table 5.3.

Table 5.3: Experimental (Exp) and theoretical (Theo) weight percent of N, C, and H atoms in the structures.

Compound	Nitrogen (wt%)		Carbon (wt%)		Hydrogen (wt%)	
	Exp	Theo	Exp	Theo	Exp	Theo
Basolite C300	0.27	0.00	90.54	97.28	9.19	2.72
IL/C300 (5 wt%)	1.50	1.01	89.47	95.87	9.02	3.13
IL/C300 (5 wt%)*	2.01	1.01	91.37	95.87	6.62	3.13
IL/C300 (20 wt%)	5.74	4.02	85.62	91.63	8.64	4.35
IL/C300 (20 wt%)*	6.24	4.02	86.89	91.63	6.87	4.35
IL/C300 (30 wt%)	8.94	6.04	82.43	88.80	8.63	5.16
IL/C300 (30 wt%)*	9.38	6.04	83.39	88.80	7.24	5.16

*: Results for samples after high pressure gas adsorption measurements

As seen in Table 5.3 the experimentally determined weight percent of N and H atoms are greater than theoretically calculated ones whereas the opposite is observed for C atom. This deviation results from an experimental error caused by water adsorption in samples upon exposure to air during sample preparation for the experiment. The initially weighed sample amount increases before the experiment starts causing the total amount of sample to change. Since the total amount of sample is greater than that initially measured and entered in the equipment for the measurement, the weight percent shows deviations.

As a result, comparing the experimental and theoretical ratios between N atom content of 20 and 5 wt% samples and 30 and 5 wt% samples provides a more accurate determination. The N content ratio between 20 and 5 wt%, and 30 and 5 wt% are determined as 3.82 and 5.95 which are theoretically calculated as 4 and 6, respectively. This shows that [BMIM][BF₄] is properly impregnated into the framework of Basolite C300.

The slight difference between the atomic content of samples before and after adsorption measurements are likely caused by rigorous degassing of samples at low pressures before each adsorption measurement. Samples after adsorption experiments possibly have very little water content therefore in order to saturate these samples from air humidity; longer exposure time is required compared to samples that were not subject to degassing.

In conclusion, both Basolite C300 and IL/C300 samples have been characterized extensively using various methods. It is inferred that Basolite C300 sample possesses identical characteristics with those already reported in the literature. Moreover, characterization on IL/C300 samples revealed that [BMIM][BF₄] molecules were successfully impregnated into Basolite C300 and the IL molecules stayed intact after activation of the samples. Additional IR spectra and XRD results are provided in Appendix C for samples before and after adsorption measurements. These results show that both Basolite C300 framework and [BMIM][BF₄] were undamaged after activation and adsorption measurements. Further experiments on the IL/C300 samples also showed that the crystal structure is preserved after impregnation and thermal stability of the IL/C300 samples are only slightly decreased after addition of IL. As expected, the porosity of the IL/C300 samples was reduced as evident from the BET surface areas.

5.4 Gas Adsorption Measurements

High pressure volumetric adsorption measurements were performed for CH₄, CO₂, N₂, and H₂ at room temperature and from 0.1 to 100 bar for all gases except CO₂ which was measured up to 35 bar. Initially, adsorption measurements of Basolite C300 were compared with the results reported in the literature to assess the gas uptake performance of as is sample. Then, adsorption measurements were done for IL incorporated C300. The ideal gas selectivity of each sample was calculated from the ratio of single-component gas uptake data. It was found out that addition of [BMIM][BF₄] enhances CH₄ selectivity towards all other gases especially at low pressures (0-1 bar).

5.4.1 Gas Adsorption Analysis of Basolite C300

Adsorption measurements were performed for Basolite C300 according to the procedure described in Chapter 3. Prior to gas uptake measurements, the sample was activated at 150 °C overnight (at least 12 h) until vacuum pressure reached to 10⁻⁶ bar. Adsorption of CH₄, N₂, and H₂ gases were measured up to 100 bar and 33 data points were collected throughout the measurement. CO₂ adsorption was measured up to 35 bar (due to cylinder pressure) and 20 data points were collected during measurement. The high pressure volumetric adsorption isotherms and their comparison with literature are provided in Figure 5.16.

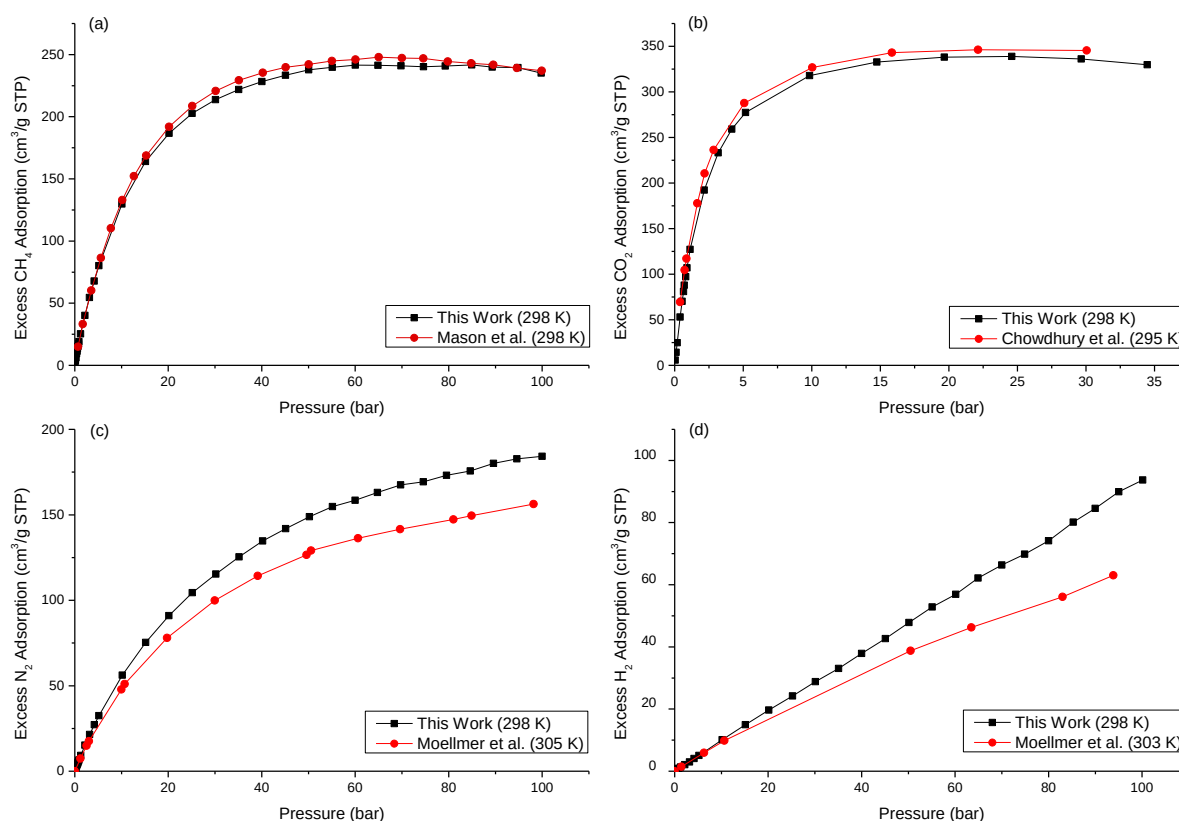


Figure 5.16: High pressure adsorption isotherms of Basolite C300 and their comparison with literature for (a) CH₄ [1]; (b) CO₂ [172]; (c) N₂ [173]; and (d) H₂ [173]. Measurement temperatures are given in legends of each plot.

As seen in Figure 5.16, the adsorption measurements show very good agreement with literature results especially for CH₄ and CO₂ adsorption. The slight differences seen in the uptake amounts can be explained by the different measurement temperatures. Our CO₂ uptake measurements were slightly lower than Chowdhury et al. because of relatively low measurement temperature (295 K) of the work by Chowdhury et al. [172]. The difference is more pronounced for N₂ and H₂ uptake measurements as seen in Figure 5.16 (c) and (d) because of the greater temperature difference between measurements for these gases (7 K for N₂ and 5 K for H₂). Generally, the isotherm trends are in good agreement with measurements obtained in this study suggesting accurate results of adsorption measurements.

5.4.2 Gas Adsorption Analysis of IL-Incorporated MOFs

Volumetric CH_4 , CO_2 , N_2 , and H_2 uptake of all IL-incorporated samples were investigated at ambient temperature (298 K) up to 100 bar except for CO_2 , which was measured up to 35 bar. Figure 5.17 shows the results of these measurements in comparison with those of IL-free Basolite C300.

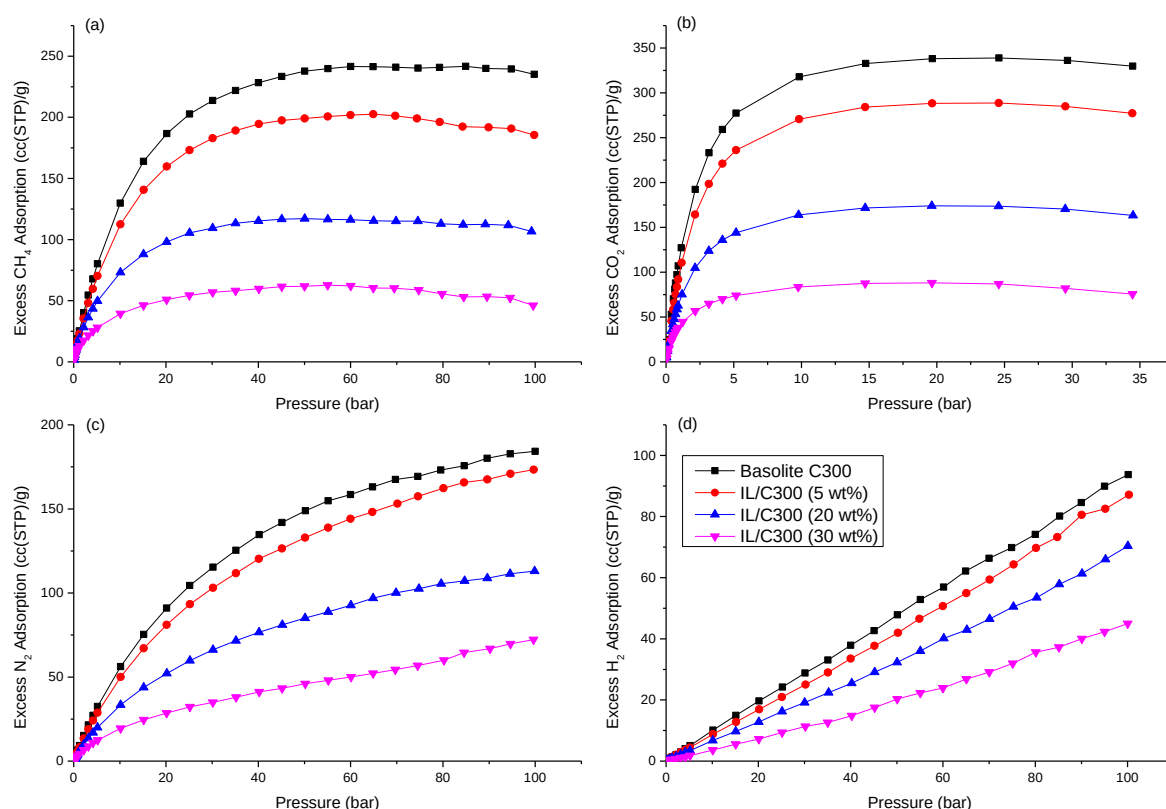


Figure 5.17: High pressure gas adsorption isotherms of Basolite C300 and IL/C300 samples at room temperature for (a) CH_4 ; (b) CO_2 ; (c) N_2 ; and (d) H_2 .

As expected, storage capacity for all gases decreased as the IL loading increased from 5 to 30 wt%. Moreover, the decrease was more pronounced for gas molecules that have stronger interactions with the framework of the structure, i.e., CO_2 followed by CH_4 , N_2 , and H_2 . Additionally, the saturation pressure was decreased from 60 to 50 bar for CH_4 and from 25 to 20 bar for CO_2 in samples with 20 wt% and 30 wt% IL loadings.

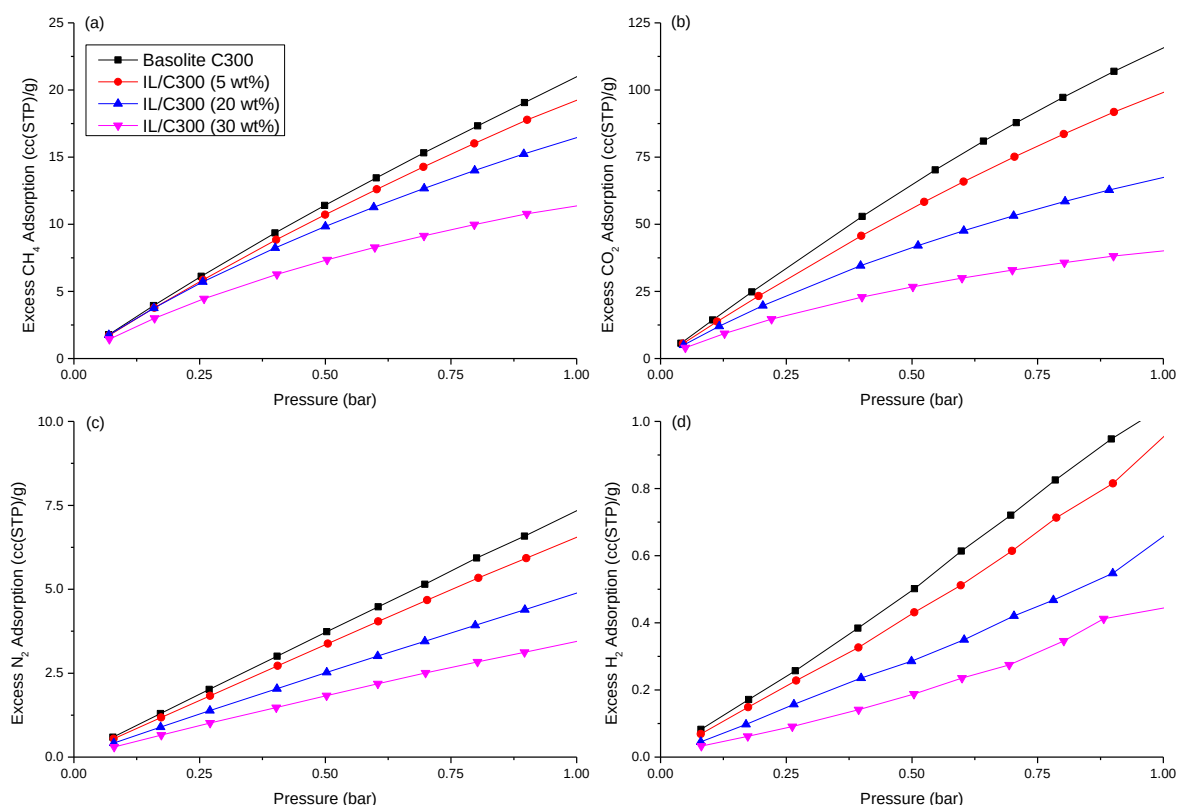


Figure 5.18: Low pressure (0 – 1 bar) gas adsorption isotherms of Basolite C300 and IL/C300 samples at room temperature for (a) CH₄; (b) CO₂; (c) N₂; and (d) H₂.

It is interesting to see that at low pressures, given in Figure 5.18, the decrease in adsorption was not as significant as that in high pressures. This could be related with the decreased porosity (as evident from low surface areas) of IL-incorporated samples because of large IL molecules blocking the micropores of the framework. As the porosity of the framework is reduced, number of adsorption sites is also reduced causing a decrease in the storage capacity. At low pressures there are still many adsorption sites available therefore the decrease is less notable. However, it should be noted that the decrease in gas uptakes at low pressures change significantly for different gases (Figure 5.19). This suggests that even though the adsorption sites are decreased in total, new adsorption sites have also been created with the incorporation of [BMIM][BF₄] into the framework. These new sites have different affinities for each gas, resulting in different reductions in adsorption capacities at low

pressures. As seen in Figure 5.19, the adsorption capacity change compared to Basolite C300 at 1 bar is in the increasing order of $\text{CH}_4 < \text{N}_2 < \text{H}_2 < \text{CO}_2$. The uptake amounts at 1 bar decrease almost linearly with IL loading for N_2 and H_2 whereas different trends were identified for CH_4 and CO_2 . With the addition of $[\text{BMIM}][\text{BF}_4]$, CO_2 uptake shows a significant decrease initially at 5 wt% followed by a linear decrease as the IL amount increased. CH_4 uptake however, exhibits a changing decrease rate in the uptake at 1 bar as a function of IL amount. These trends are significantly different at different pressures.

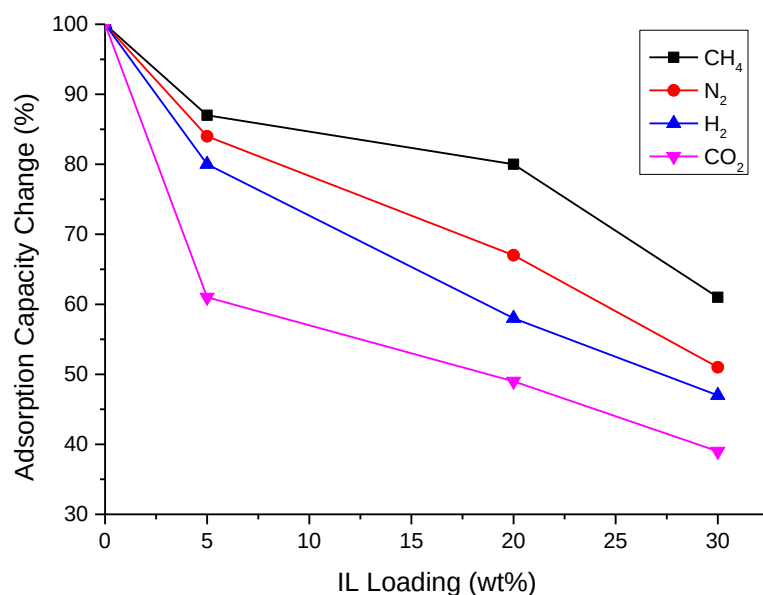


Figure 5.19: Adsorption capacity change of all gases at different IL loadings at 1 bar.

Such distinct behaviors of gases towards IL incorporated C300 samples imply that these materials can be promising towards gas separations by tuning the affinities of each gas by the incorporation of IL into MOFs. Therefore, ideal selectivities of samples for all gas combinations were calculated from the single component gas adsorption isotherms between 0 and 5 bar as the ratio of more selective component to the other (Figure 5.20). Thus, all selectivity values are bigger than 1 suggesting first component is selected over the second.

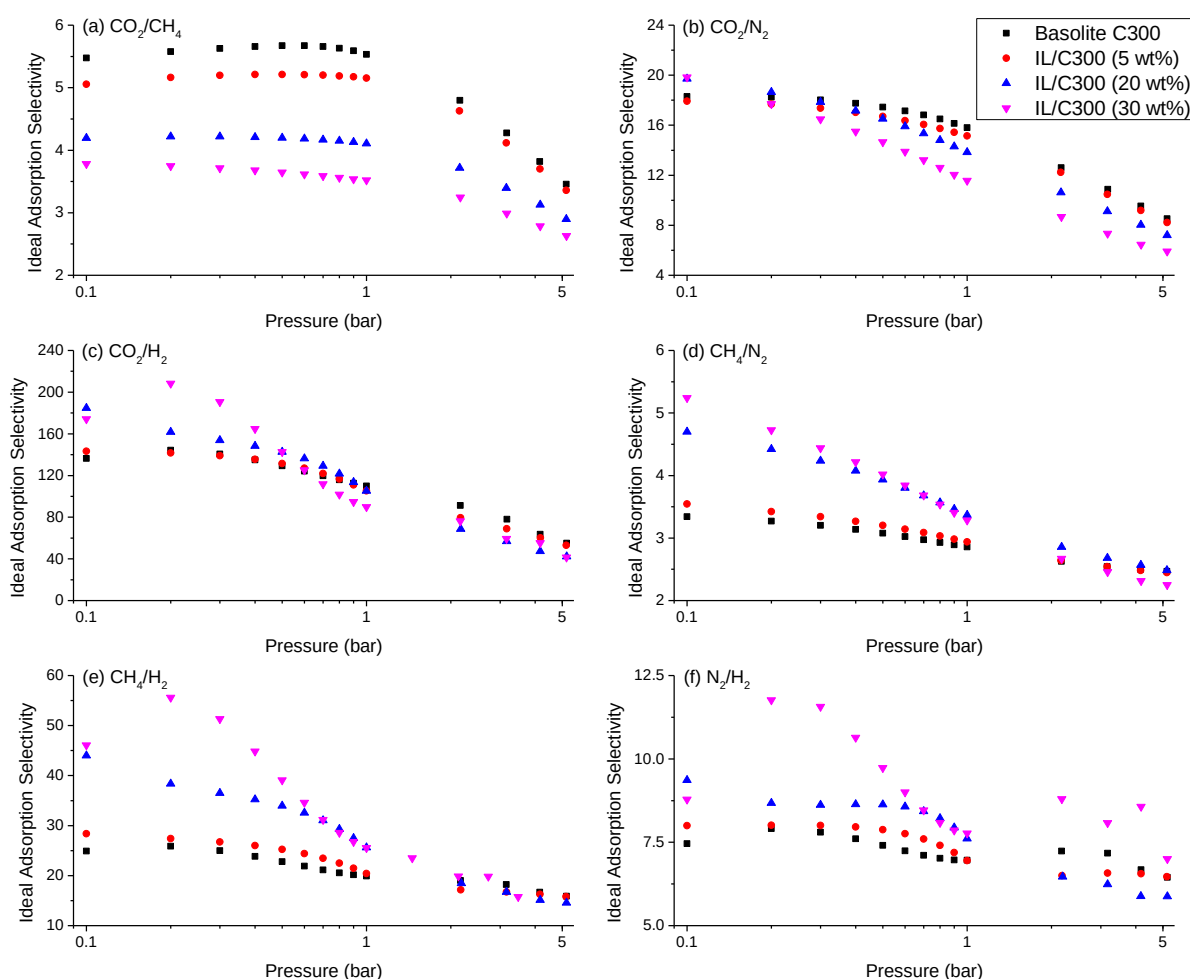


Figure 5.20: Ideal adsorption selectivities for (a) CO_2/CH_4 ; (b) CO_2/N_2 ; (c) CO_2/H_2 ; (d) CH_4/N_2 ; (e) CH_4/H_2 ; and (f) N_2/H_2 at room temperature up to 5 bar. The first component is the more selective over the second component. The x-axes are given in log scale for clear representation of the data at low pressures.

It is seen that selectivities differ significantly especially at pressures up to 1 bar. For instance, the CO_2/CH_4 selectivity decreases to almost half of its value for the IL-free Basolite C300. This result is interesting as $[\text{BMIM}][\text{BF}_4]$ has higher CO_2 solubility compared to CH_4 with a CO_2/CH_4 selectivity of ~ 15 at ambient temperature and pressure [174]. Another interesting behavior was also observed for CO_2/H_2 selectivity as a function of pressure. Data show that at until 0.6 bar CO_2/H_2 selectivity is higher for IL/C300 samples compared to Basolite C300. The CO_2/H_2 selectivity maximizes at 0.2 bar for IL/C300 (30 wt%) sample

reaching 208 almost 1.5 times the selectivity of unmodified Basolite C300. However, after 0.6 bar CO_2/H_2 selectivity of the IL-incorporated samples start to decrease and after 1 bar IL/C300 samples show lower CO_2/H_2 selectivity compared to Basolite C300. A similar behavior was also observed on CO_2/N_2 selectivity of IL/C300, which first starts larger than IL-free Basolite C300 but becomes smaller after around 0.3 bar.

On the other hand, data on IL-incorporated Basolite C300 show that CH_4 selectivity towards all gases increased at all pressures investigated, suggesting an increased CH_4 interaction with IL/C300 compared to IL-free Basolite C300. For instance, the CH_4 selectivity with respect to H_2 increased from 26 to 56 at 0.2 bar when the MOF was coated with 30 wt% IL. At 1 bar the CH_4/H_2 selectivity was increased from 19 to 26 and became comparable with Zeolite 5A and activated carbon which have ideal CH_4/H_2 selectivities of 20 and 25 at 1 bar, respectively [175]. It is observed that higher loading of [BMIM][BF_4] enhances selectivity towards CH_4 at all pressures. As a result it can be inferred that the IL is playing a significant role in determining the selectivity of the MOF material. Similarly, for CH_4/N_2 separation, the material with 30 wt% IL loading becomes almost 1.6 times more selective towards CH_4 at very low pressures, and then this value gradually decreases to the levels of unmodified MOF specifically above 1 bar. The CH_4/N_2 selectivity was only increased from 2.8 to 3.4 for IL/C300 (30 wt%) at 1 bar, however, this value is still higher than 1.1 for MOF-5 [176], 1.7 for Zeolite 5A [175], and 3.0 for activated carbon [175] at around 1 bar. At high IL loadings, data also illustrate that the selectivity for N_2 in N_2/H_2 mixture is always positively influenced at all pressures investigated. The N_2/H_2 selectivity maximizes around 12 at 0.3 bar for IL/C300 (30 wt%), however, it decreases to 8 at 1 bar which is lower than 8.6 for activated carbon [175] and 12 for Zeolite 5A [175] at 1 bar. At lower loadings, the selectivity for N_2 is negatively influenced after approximately 1 bar.

Overall, the changes in gas selectivity values are intensified with the increase of IL amount in the structure. As seen in Figure 5.20 the gas selectivity values for Basolite C300 and IL/C300 (5 wt%) are very similar, however, both IL/C300 (20 wt%) and IL/C300 (30 wt%) show significant deviations in gas selectivities compared to IL-free Basolite C300. These deviations in gas selectivities result from distinct adsorption capacity changes of each gas due to different affinities of adsorption sites for each gas component (Figure 5.19). In general, the adsorption sites established with the incorporation of [BMIM][BF₄] have higher affinity towards CH₄ compared to other gases. As a result, CH₄ selectivity towards all other gases was increased with the incorporation of IL compared to IL-free Basolite C300. The CO₂/CH₄ selectivity was decreased from 5.5 to 3.5 at 1 bar, however, IL/C300 samples remained selective for CO₂. Using a MOF with low CO₂/CH₄ selectivity, such as MIL-101 which has CO₂/CH₄ selectivity of ~3 at 1 bar [177], the material can be made CH₄ selective with the incorporation IL. Moreover, additional XRD and IR results (Appendix C) and elemental analysis (Chapter 5.3.6) investigating the N content of samples before and after gas adsorption measurements show that both Basolite C300 framework and [BMIM][BF₄] molecules stay intact after activation and adsorption measurements.

In summary, data presented here illustrate that the incorporation of IL into the structure of Basolite C300 at different loadings influence the gas storage and separation performance of the MOF significantly. There is a tremendous amount of change in gas selectivity values specifically at low pressures with high IL loading, accompanied by a decrease in the uptake values. It is observed that the IL/C300 show highest affinity towards CH₄ followed by N₂, H₂, and CO₂ especially between 0-1 bar. These promising results present the opportunities for adjusting the gas separation performance of MOFs by the incorporation of ILs into their structures. Moreover, the highly tunable natures of both MOFs

and ILs present almost endless number of possibilities to tailor the IL-incorporated MOF materials for various gas separation applications.

Chapter 6: Conclusions and Outlook

In this study, computational and experimental analyses have been performed to gather insights concerning CH₄ adsorption in metal-organic frameworks. Molecular simulations to assess CH₄ storage capabilities of MOFs revealed that structural properties of MOFs such as surface area, pore volume, crystal density and pore diameter are crucial parameters that affect the CH₄ uptake of a material. Moreover, the affinity of the framework to the CH₄ molecule, determined as isosteric heat of adsorption (Q_{st}), was found to be an essential parameter that determines CH₄ storage. Making use of these structural/chemical parameters multivariable linear models were constructed at 10 different pressures (1, 5, 10, 15, 20, 25, 30, 35, 50, and 65 bar) and ambient temperature. Initial modelling studies on a set of 45 MOFs revealed optimum structural/chemical characteristics to reach CH₄ storage target at 35 bar as: gravimetric surface area (S_g), reaching 6000 m²/g, void fraction (V_f), as high as 0.9, dominant pore diameter (DPD) approximately 30 Å, and Q_{st} value in the range of 30 kJ/mol.

In order to see whether these models can be used comprehensively to predict CH₄ uptake of MOFs, same analyses were also performed using a data set of 1514 MOFs. The model coefficients suggested earlier were updated and new models making use of different variables were constructed at the same temperature and pressure values and similar predictive

capabilities were obtained. To assess the viability of using a single pressure-independent model to predict CH₄ uptake on MOFs new models including a pressure term were considered. The accuracy of the pressure-independent models were lower compared to previous models suggesting that multivariable linear modelling was not a suitable method for constructing a pressure-independent model with high accuracy. Therefore, other methods including more advanced techniques such as machine learning algorithms can be used.

In the second part, experimental investigation of gas storage and separation in pristine and ionic liquid (IL) incorporated MOFs were carried out focusing on CH₄. Basolite C300 was selected as the MOF because of its high CH₄ storage performance and a typical ionic liquid, [BMIM][BF₄], was used. Initially, both MOF and IL/MOF samples were characterized extensively. First, characterization of Basolite C300 was performed and good agreement with literature was found. Later IL/C300 samples were prepared and characterized. Results showed that the incorporation of [BMIM][BF₄] was successful and both Basolite C300 and [BMIM][BF₄] were undamaged after incorporation and activation. Following characterization, high pressure adsorption measurements of CH₄, CO₂, N₂, and H₂ were performed for pristine and IL-incorporated Basolite C300 samples at room temperature. It was found that adsorption capacity of IL/C300 samples were lower compared to IL-free MOF especially at high pressures. However, at low pressures adsorption capacity change showed significant deviations between different gases. The adsorption capacity change of IL/C300 samples compared to Basolite C300 at 1 bar was found to be in the increasing order of CH₄ < N₂ < H₂ < CO₂. Further investigation revealed that with the incorporation of [BMIM][BF₄], CH₄ affinity of C300 was enhanced proportionally with the IL loading, therefore CH₄ selectivity towards other gases were increased.

As a conclusion, IL-incorporated MOFs were identified as new promising adsorbents especially for adsorptive gas separation applications. Moreover, the highly tunable natures of

both MOFs and ILs present almost endless number of possibilities. Making use of this advantage, MOF-IL pairs can be specifically tailored according to the gas storage/separation requirements.

BIBLIOGRAPHY

1. Mason, J.A., M. Veenstra, and J.R. Long, *Evaluating metal-organic frameworks for natural gas storage*. Chemical Science, 2014. 5(1): p. 32-51.
2. He, Y., et al., *Methane storage in metal-organic frameworks*. Chemical Society Reviews, 2014. 43(16): p. 5657-5678.
3. Antoniou, M.K., et al., *Methane storage in zeolite-like carbon materials*. Microporous and Mesoporous Materials, 2014. 188: p. 16-22.
4. Matranga, K.R., A.L. Myers, and E.D. Glandt, *Storage of natural gas by adsorption on activated carbon*. Chemical Engineering Science, 1992. 47(7): p. 1569-1579.
5. Cao, D., et al., *Optimization of Single-Walled Carbon Nanotube Arrays for Methane Storage at Room Temperature*. The Journal of Physical Chemistry B, 2003. 107(48): p. 13286-13292.
6. Lu, W., et al., *Porous Polymer Networks: Synthesis, Porosity, and Applications in Gas Storage/Separation*. Chemistry of Materials, 2010. 22(21): p. 5964-5972.
7. Suh, M.P., et al., *Hydrogen Storage in Metal-Organic Frameworks*. Chemical Reviews, 2012. 112(2): p. 782-835.
8. Sumida, K., et al., *Carbon Dioxide Capture in Metal-Organic Frameworks*. Chemical Reviews, 2011. 112(2): p. 724-781.
9. Chen, E.-Y., et al., *Effects of structure on hydrogen adsorption in zeolitic imidazolate frameworks*. Chemical Engineering Science, 2012. 71: p. 178-184.
10. Li, J.-R., R.J. Kuppler, and H.-C. Zhou, *Selective gas adsorption and separation in metal-organic frameworks*. Chemical Society Reviews, 2009. 38(5): p. 1477-1504.
11. Li, Z., et al., *Computational exploration of metal-organic Frameworks for CO₂/CH₄ separation via temperature swing adsorption*. Chemical Engineering Science, 2014. 120: p. 59-66.
12. Ferreira, A.F.P., et al., *Methane purification by adsorptive processes on MIL-53(Al)*. Chemical Engineering Science, 2014. 124: p. 79-95.
13. Kim, W.-g. and S. Nair, *Membranes from nanoporous 1D and 2D materials: A review of opportunities, developments, and challenges*. Chemical Engineering Science, 2013. 104: p. 908-924.
14. Lee, J., et al., *Metal-organic framework materials as catalysts*. Chemical Society Reviews, 2009. 38(5): p. 1450-1459.
15. Sarkisov, L. and J. Kim, *Computational structure characterization tools for the era of material informatics*. Chemical Engineering Science, 2015. 121: p. 322-330.
16. Available from: <https://arpa-e-foa.energy.gov/Default.aspx?Search=DE-FOA-0000672>.
17. Wilmer, C.E., et al., *Gram-scale, high-yield synthesis of a robust metal-organic framework for storing methane and other gases*. Energy & Environmental Science, 2013. 6(4): p. 1158-1163.
18. Peng, Y., et al., *Methane Storage in Metal-Organic Frameworks: Current Records, Surprise Findings, and Challenges*. Journal of the American Chemical Society, 2013. 135(32): p. 11887-11894.
19. Cohen, S.M., *Postsynthetic Methods for the Functionalization of Metal-Organic Frameworks*. Chemical Reviews, 2012. 112(2): p. 970-1000.
20. Wang, Z. and S.M. Cohen, *Postsynthetic modification of metal-organic frameworks*. Chemical Society Reviews, 2009. 38(5): p. 1315-1329.
21. Zhu, Q.-L. and Q. Xu, *Metal-organic framework composites*. Chemical Society Reviews, 2014. 43(16): p. 5468-5512.

22. Rogers, R.D. and K.R. Seddon, *Ionic liquids - Solvents of the future?* Science, 2003. 302(5646): p. 792-793.
23. Welton, T., *Room-temperature ionic liquids. Solvents for synthesis and catalysis.* Chemical Reviews, 1999. 99(8): p. 2071-2083.
24. Mehnert, C.P., et al., *Supported ionic liquid catalysis - A new concept for homogeneous hydroformylation catalysis.* Journal of the American Chemical Society, 2002. 124(44): p. 12932-12933.
25. Wilkes, J.S., *Properties of ionic liquid solvents for catalysis.* Journal of Molecular Catalysis a-Chemical, 2004. 214(1): p. 11-17.
26. Huddleston, J.G., et al., *Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction.* Chemical Communications, 1998(16): p. 1765-1766.
27. Blanchard, L.A., et al., *Green processing using ionic liquids and CO₂.* Nature, 1999. 399(6731): p. 28-29.
28. Bates, E.D., et al., *CO₂ capture by a task-specific ionic liquid.* Journal of the American Chemical Society, 2002. 124(6): p. 926-927.
29. Camper, D., et al., *Room-Temperature Ionic Liquid-Amine Solutions: Tunable Solvents for Efficient and Reversible Capture Of CO₂.* Industrial & Engineering Chemistry Research, 2008. 47(21): p. 8496-8498.
30. Ma, S. and H.-C. Zhou, *Gas storage in porous metal-organic frameworks for clean energy applications.* Chemical Communications, 2010. 46(1): p. 44-53.
31. Morris, R.E. and P.S. Wheatley, *Gas Storage in Nanoporous Materials.* Angewandte Chemie International Edition, 2008. 47(27): p. 4966-4981.
32. Millward, A.R. and O.M. Yaghi, *Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature.* Journal of the American Chemical Society, 2005. 127(51): p. 17998-17999.
33. Dincă, M. and J.R. Long, *Strong H₂ Binding and Selective Gas Adsorption within the Microporous Coordination Solid Mg₃(O₂C-C₁₀H₆-CO₂)₃.* Journal of the American Chemical Society, 2005. 127(26): p. 9376-9377.
34. Dybtsev, D.N., et al., *Microporous Manganese Formate: A Simple Metal-Organic Porous Material with High Framework Stability and Highly Selective Gas Sorption Properties.* Journal of the American Chemical Society, 2004. 126(1): p. 32-33.
35. Pan, L., et al., *Separation of Hydrocarbons with a Microporous Metal-Organic Framework.* Angewandte Chemie International Edition, 2006. 45(4): p. 616-619.
36. Pan, L., et al., *Zn(tbip) (H₂tbip= 5-tert-Butyl Isophthalic Acid): A Highly Stable Guest-Free Microporous Metal Organic Framework with Unique Gas Separation Capability.* Journal of the American Chemical Society, 2006. 128(13): p. 4180-4181.
37. Cho, S.-H., et al., *A metal-organic framework material that functions as an enantioselective catalyst for olefin epoxidation.* Chemical Communications, 2006(24): p. 2563-2565.
38. Wu, C.-D., et al., *A Homochiral Porous Metal-Organic Framework for Highly Enantioselective Heterogeneous Asymmetric Catalysis.* Journal of the American Chemical Society, 2005. 127(25): p. 8940-8941.
39. Horike, S., et al., *Size-Selective Lewis Acid Catalysis in a Microporous Metal-Organic Framework with Exposed Mn²⁺ Coordination Sites.* Journal of the American Chemical Society, 2008. 130(18): p. 5854-5855.
40. Kreno, L.E., et al., *Metal-Organic Framework Materials as Chemical Sensors.* Chemical Reviews, 2012. 112(2): p. 1105-1125.
41. Seo, J.S., et al., *A homochiral metal-organic porous material for enantioselective separation and catalysis.* Nature, 2000. 404(6781): p. 982-986.

42. Lu, G. and J.T. Hupp, *Metal– organic frameworks as sensors: a ZIF-8 based Fabry–Pérot device as a selective sensor for chemical vapors and gases*. Journal of the American Chemical Society, 2010. 132(23): p. 7832-7833.
43. Lan, A., et al., *A luminescent microporous metal–organic framework for the fast and reversible detection of high explosives*. Angewandte Chemie International Edition, 2009. 48(13): p. 2334-2338.
44. Chen, B., et al., *Luminescent open metal sites within a metal–organic framework for sensing small molecules*. Advanced Materials, 2007. 19(13): p. 1693-1696.
45. Chen, B., et al., *A luminescent microporous metal– organic framework for the recognition and sensing of anions*. Journal of the American Chemical Society, 2008. 130(21): p. 6718-6719.
46. Beckner, M. and A. Dailly, *Adsorbed methane storage for vehicular applications*. Applied Energy, 2015. 149: p. 69-74.
47. Gándara, F., et al., *High Methane Storage Capacity in Aluminum Metal–Organic Frameworks*. Journal of the American Chemical Society, 2014. 136(14): p. 5271-5274.
48. Li, B., et al., *A Porous Metal–Organic Framework with Dynamic Pyrimidine Groups Exhibiting Record High Methane Storage Working Capacity*. Journal of the American Chemical Society, 2014. 136(17): p. 6207-6210.
49. Getman, R.B., et al., *Review and Analysis of Molecular Simulations of Methane, Hydrogen, and Acetylene Storage in Metal–Organic Frameworks*. Chemical Reviews, 2012. 112(2): p. 703-723.
50. Fernandez, M., et al., *Large-Scale Quantitative Structure–Property Relationship (QSPR) Analysis of Methane Storage in Metal–Organic Frameworks*. The Journal of Physical Chemistry C, 2013. 117(15): p. 7681-7689.
51. Gómez-Gualdrón, D.A., et al., *Exploring the Limits of Methane Storage and Delivery in Nanoporous Materials*. The Journal of Physical Chemistry C, 2014. 118(13): p. 6941-6951.
52. Martin, R.L., et al., *In silico Design of Porous Polymer Networks: High-Throughput Screening for Methane Storage Materials*. Journal of the American Chemical Society, 2014. 136(13): p. 5006-5022.
53. Simon, C.M., et al., *The materials genome in action: identifying the performance limits for methane storage*. Energy & Environmental Science, 2015. 8(4): p. 1190-1199.
54. Deem, M.W., et al., *Computational Discovery of New Zeolite-Like Materials*. The Journal of Physical Chemistry C, 2009. 113(51): p. 21353-21360.
55. Pophale, R., P.A. Cheeseman, and M.W. Deem, *A database of new zeolite-like materials*. Physical Chemistry Chemical Physics, 2011. 13(27): p. 12407-12412.
56. Wilmer, C.E., et al., *Large-scale screening of hypothetical metal-organic frameworks*. Nature Chemistry, 2012. 4(2): p. 83-89.
57. Lin, L.-C., et al., *In silico screening of carbon-capture materials*. Nat Mater, 2012. 11(7): p. 633-641.
58. Chung, Y.G., et al., *Computation-Ready, Experimental Metal–Organic Frameworks: A Tool To Enable High-Throughput Screening of Nanoporous Crystals*. Chemistry of Materials, 2014. 26(21): p. 6185-6192.
59. Farha, O.K., et al., *De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities*. Nat Chem, 2010. 2(11): p. 944-948.
60. He, Y., et al., *A series of metal-organic frameworks with high methane uptake and an empirical equation for predicting methane storage capacity*. Energy & Environmental Science, 2013. 6(9): p. 2735-2744.

61. Kong, G.Q., et al., *Expanded Organic Building Units for the Construction of Highly Porous Metal-Organic Frameworks*. Chemistry-a European Journal, 2013. 19(44): p. 14886-14894.
62. Lei, Z., C. Dai, and B. Chen, *Gas Solubility in Ionic Liquids*. Chemical Reviews, 2014. 114(2): p. 1289-1326.
63. Camper, D., et al., *Low Pressure Hydrocarbon Solubility in Room Temperature Ionic Liquids Containing Imidazolium Rings Interpreted Using Regular Solution Theory*. Industrial & Engineering Chemistry Research, 2005. 44(6): p. 1928-1933.
64. Carlisle, T.K., et al., *Interpretation of CO₂ Solubility and Selectivity in Nitrile-Functionalized Room-Temperature Ionic Liquids Using a Group Contribution Approach*. Industrial & Engineering Chemistry Research, 2008. 47(18): p. 7005-7012.
65. Anthony, J.L., et al., *Anion Effects on Gas Solubility in Ionic Liquids*. The Journal of Physical Chemistry B, 2005. 109(13): p. 6366-6374.
66. Mortazavi-Manesh, S., M.A. Satyro, and R.A. Marriott, *Screening ionic liquids as candidates for separation of acid gases: Solubility of hydrogen sulfide, methane, and ethane*. Aiche Journal, 2013. 59(8): p. 2993-3005.
67. Klamt, A., *Conductor-like Screening Model for Real Solvents: A New Approach to the Quantitative Calculation of Solvation Phenomena*. The Journal of Physical Chemistry, 1995. 99(7): p. 2224-2235.
68. Ramdin, M., et al., *Solubility of CO₂ and CH₄ in Ionic Liquids: Ideal CO₂/CH₄ Selectivity*. Industrial & Engineering Chemistry Research, 2014. 53(40): p. 15427-15435.
69. Ramdin, M., et al., *Solubility of CO₂/CH₄ gas mixtures in ionic liquids*. Fluid Phase Equilibria, 2014. 375: p. 134-142.
70. Jacquemin, J., et al., *Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric*. The Journal of Chemical Thermodynamics, 2006. 38(4): p. 490-502.
71. Kumelan, J., et al., *Solubility of the single gases methane and xenon in the ionic liquid [hmim][Tf₂N]*. Industrial & Engineering Chemistry Research, 2007. 46(24): p. 8236-8240.
72. Raeissi, S. and C. Peters, *High pressure phase behaviour of methane in 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide*. Fluid Phase Equilibria, 2010. 294(1): p. 67-71.
73. Bermejo, M.D., T.M. Fieback, and Á. Martín, *Solubility of gases in 1-alkyl-3-methylimidazolium alkyl sulfate ionic liquids: Experimental determination and modeling*. The Journal of Chemical Thermodynamics, 2013. 58: p. 237-244.
74. Jacquemin, J., et al., *Low-pressure solubilities and thermodynamics of solvation of eight gases in 1-butyl-3-methylimidazolium hexafluorophosphate*. Fluid Phase Equilibria, 2006. 240(1): p. 87-95.
75. Kumelan, J., et al., *Solubility of the single gases H₂ and CO in the ionic liquid [bmim][CH₃SO₄]*. Fluid Phase Equilibria, 2007. 260(1): p. 3-8.
76. Kumelan, J., et al., *Solubility of H₂ in the ionic liquid [bmim][PF₆]*. Journal of Chemical & Engineering Data, 2006. 51(1): p. 11-14.
77. Jacquemin, J., et al., *Influence of the cation on the solubility of CO₂ and H₂ in ionic liquids based on the bis (trifluoromethylsulfonyl) imide anion*. Journal of solution chemistry, 2007. 36(8): p. 967-979.
78. Afzal, W., X. Liu, and J.M. Prausnitz, *Solubilities of some gases in four imidazolium-based ionic liquids*. The Journal of Chemical Thermodynamics, 2013. 63: p. 88-94.

79. Costa Gomes, M., *Low-pressure solubility and thermodynamics of solvation of carbon dioxide, ethane, and hydrogen in 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) amide between temperatures of 283 K and 343 K*. Journal of Chemical & Engineering Data, 2007. 52(2): p. 472-475.
80. Shiflett, M.B., et al., *Phase behavior of {carbon dioxide+ [bmim][Ac]} mixtures*. The Journal of Chemical Thermodynamics, 2008. 40(1): p. 25-31.
81. Aki, S.N., et al., *High-pressure phase behavior of carbon dioxide with imidazolium-based ionic liquids*. The Journal of Physical Chemistry B, 2004. 108(52): p. 20355-20365.
82. Kumelan, J., et al., *Solubility of CO₂ in the ionic liquids [bmim][CH₃SO₄] and [bmim][PF₆]*. Journal of Chemical & Engineering Data, 2006. 51(5): p. 1802-1807.
83. Anthony, J.L., E.J. Maginn, and J.F. Brennecke, *Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate*. The Journal of Physical Chemistry B, 2002. 106(29): p. 7315-7320.
84. Shin, E.-K. and B.-C. Lee, *High-pressure phase behavior of carbon dioxide with ionic liquids: 1-alkyl-3-methylimidazolium trifluoromethanesulfonate*. Journal of Chemical & Engineering Data, 2008. 53(12): p. 2728-2734.
85. Yokozeki, A., et al., *Physical and chemical absorptions of carbon dioxide in room-temperature ionic liquids*. The Journal of Physical Chemistry B, 2008. 112(51): p. 16654-16663.
86. Kim, Y., et al., *Solubility measurement and prediction of carbon dioxide in ionic liquids*. Fluid Phase Equilibria, 2005. 228: p. 439-445.
87. Soriano, A.N., B.T. Doma, and M.-H. Li, *Carbon dioxide solubility in some ionic liquids at moderate pressures*. Journal of the Taiwan Institute of Chemical Engineers, 2009. 40(4): p. 387-393.
88. Shariati, A. and C. Peters, *High-pressure phase behavior of systems with ionic liquids: II. The binary system carbon dioxide + 1-ethyl-3-methylimidazolium hexafluorophosphate*. The Journal of supercritical fluids, 2004. 29(1): p. 43-48.
89. Xu, L., et al., *The influence of 1-alkyl-3-methyl imidazolium ionic liquids on a series of cobalt-1,4-benzenedicarboxylate metal-organic frameworks*. CrystEngComm, 2014. 16(46): p. 10649-10657.
90. Peng, L., et al., *Surfactant-directed assembly of mesoporous metal-organic framework nanoplates in ionic liquids*. Chemical Communications, 2012. 48(69): p. 8688-8690.
91. Lin, Z., et al., *Anion Control in the Ionothermal Synthesis of Coordination Polymers*. Journal of the American Chemical Society, 2007. 129(34): p. 10334-10335.
92. Lin, Z., D.S. Wragg, and R.E. Morris, *Microwave-assisted synthesis of anionic metal-organic frameworks under ionothermal conditions*. Chemical Communications, 2006(19): p. 2021-2023.
93. Jin, K., et al., *[Cu(i)(bpp)]BF₄: the first extended coordination network prepared solvothermally in an ionic liquid solvent*. Chemical Communications, 2002(23): p. 2872-2873.
94. Dybtsev, D.N., H. Chun, and K. Kim, *Three-dimensional metal-organic framework with (3,4)-connected net, synthesized from an ionic liquid medium*. Chemical Communications, 2004(14): p. 1594-1595.
95. Zhao, Y., et al., *Metal-Organic Framework Nanospheres with Well-Ordered Mesopores Synthesized in an Ionic Liquid/CO₂/Surfactant System*. Angewandte Chemie International Edition, 2011. 50(3): p. 636-639.
96. Morris, R.E., *Ionothermal synthesis—ionic liquids as functional solvents in the preparation of crystalline materials*. Chemical Communications, 2009(21): p. 2990-2998.

97. Vicent-Luna, J.M., et al., *Effect of Room-Temperature Ionic Liquids on CO₂ Separation by a Cu-BTC Metal–Organic Framework*. The Journal of Physical Chemistry C, 2013. 117(40): p. 20762-20768.
98. Silva, F.d., et al., *CO₂ Adsorption on Ionic Liquid-Modified Cu-BTC: Experimental and Simulation Study*. Adsorption Science & Technology, 2015. 33(2): p. 223-242.
99. Lei, Z., C. Dai, and W. Song, *Adsorptive absorption: A preliminary experimental and modeling study on CO₂ solubility*. Chemical Engineering Science, 2015. 127: p. 260-268.
100. Gupta, K.M., et al., *Metal-organic framework supported ionic liquid membranes for CO₂ capture: anion effects*. Physical Chemistry Chemical Physics, 2012. 14(16): p. 5785-5794.
101. Chen, Y., et al., *Ionic Liquid/Metal–Organic Framework Composite for CO₂ Capture: A Computational Investigation*. The Journal of Physical Chemistry C, 2011. 115(44): p. 21736-21742.
102. Aijaz, A., et al., *From ionic-liquid@metal-organic framework composites to heteroatom-decorated large-surface area carbons: superior CO₂ and H₂ uptake*. Chemical Communications, 2014. 50(49): p. 6498-6501.
103. Li, Z., et al., *Ionic Liquid/Metal–Organic Framework Composites for H₂S Removal from Natural Gas: A Computational Exploration*. The Journal of Physical Chemistry C, 2015. 119(7): p. 3674-3683.
104. Khan, N.A., Z. Hasan, and S.H. Jhung, *Ionic Liquids Supported on Metal-Organic Frameworks: Remarkable Adsorbents for Adsorptive Desulfurization*. Chemistry – A European Journal, 2014. 20(2): p. 376-380.
105. Wu, J., et al., *Deep desulfurization by oxidation using an active ionic liquid-supported Zr metal–organic framework as catalyst*. Applied Organometallic Chemistry, 2015. 29(2): p. 96-100.
106. Wan, H., et al., *Encapsulation of Heteropolyanion-Based Ionic Liquid within the Metal–Organic Framework MIL-100(Fe) for Biodiesel Production*. ChemCatChem, 2015. 7(3): p. 441-449.
107. Luo, Q.-x., et al., *Organic electron-rich N-heterocyclic compound as a chemical bridge: building a Bronsted acidic ionic liquid confined in MIL-101 nanocages*. Journal of Materials Chemistry A, 2013. 1(22): p. 6530-6534.
108. Luo, Q.-x., et al., *Metal–organic frameworks HKUST-1 as porous matrix for encapsulation of basic ionic liquid catalyst: effect of chemical behaviour of ionic liquid in solvent*. Journal of Porous Materials, 2015. 22(1): p. 247-259.
109. Fujie, K., et al., *Low temperature ionic conductor: ionic liquid incorporated within a metal-organic framework*. Chemical Science, 2015. 6(7): p. 4306-4310.
110. Fujie, K., et al., *Introduction of an Ionic Liquid into the Micropores of a Metal–Organic Framework and Its Anomalous Phase Behavior*. Angewandte Chemie International Edition, 2014. 53(42): p. 11302-11305.
111. Frenkel, D. and B. Smit, *Understanding molecular simulation: from algorithms to applications*. Vol. 1. 2001: Academic press.
112. Widom, B., *Some topics in the theory of fluids*. The Journal of Chemical Physics, 1963. 39(11): p. 2808-2812.
113. Stadie, N., *Synthesis and thermodynamic studies of physisorptive energy storage materials*. 2012, California Institute of Technology.
114. Nicholson, D. and N.G. Parsonage, *Computer simulation and the statistical mechanics of adsorption*. 1982: Academic Press.
115. Myers, A. and P. Monson, *Adsorption in porous materials at high pressure: theory and experiment*. Langmuir, 2002. 18(26): p. 10261-10273.

116. Allen, F., *The Cambridge Structural Database: a quarter of a million crystal structures and rising*. Acta Crystallographica Section B, 2002. 58(3 Part 1): p. 380-388.
117. Rappe, A.K., et al., *UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations*. Journal of the American Chemical Society, 1992. 114(25): p. 10024-10035.
118. Mayo, S.L., B.D. Olafson, and W.A. Goddard, *DREIDING: a generic force field for molecular simulations*. The Journal of Physical Chemistry, 1990. 94(26): p. 8897-8909.
119. Keskin, S., *Adsorption, Diffusion, and Separation of CH₄/H₂ Mixtures in Covalent Organic Frameworks: Molecular Simulations and Theoretical Predictions*. The Journal of Physical Chemistry C, 2011. 116(2): p. 1772-1779.
120. Chen, Y.F., et al., *A Highly Hydrophobic Metal–Organic Framework Zn(BDC)(TED)_{0.5} for Adsorption and Separation of CH₃OH/H₂O and CO₂/CH₄: An Integrated Experimental and Simulation Study*. The Journal of Physical Chemistry C, 2010. 114(14): p. 6602-6609.
121. Liu, B. and B. Smit, *Molecular Simulation Studies of Separation of CO₂/N₂, CO₂/CH₄, and CH₄/N₂ by ZIFs*. The Journal of Physical Chemistry C, 2010. 114(18): p. 8515-8522.
122. Pérez-Pellitero, J., et al., *Adsorption of CO₂, CH₄, and N₂ on Zeolitic Imidazolate Frameworks: Experiments and Simulations*. Chemistry – A European Journal, 2010. 16(5): p. 1560-1571.
123. Ozturk, T.N. and S. Keskin, *Predicting Gas Separation Performances of Porous Coordination Networks Using Atomistic Simulations*. Industrial & Engineering Chemistry Research, 2013. 52(49): p. 17627-17639.
124. Zhuang, W., et al., *Robust Metal–Organic Framework with An Octatopic Ligand for Gas Adsorption and Separation: Combined Characterization by Experiments and Molecular Simulation*. Chemistry of Materials, 2011. 24(1): p. 18-25.
125. Jiang, S., K.E. Gubbins, and J.A. Zollweg, *Adsorption, isosteric heat and commensurate-incommensurate transition of methane on graphite*. Molecular Physics, 1993. 80(1): p. 103-116.
126. Allen, P. and D.J. Tildesley, *Computer simulation of liquids*. 1987: Clarendon Press.
127. Dören, T., et al., *Calculating Geometric Surface Areas as a Characterization Tool for Metal–Organic Frameworks*. The Journal of Physical Chemistry C, 2007. 111(42): p. 15350-15356.
128. Sarkisov, L. and A. Harrison, *Computational structure characterisation tools in application to ordered and disordered porous materials*. Molecular Simulation, 2011. 37(15): p. 1248-1257.
129. Horváth, G. and K. Kawazoe, *Method for the calculation of effective pore size distribution in molecular sieve carbon*. Journal of Chemical Engineering of Japan, 1983. 16(6): p. 470-475.
130. Mercader, A.G., et al., *Modified and enhanced replacement method for the selection of molecular descriptors in QSAR and QSPR theories*. Chemometrics and Intelligent Laboratory Systems, 2008. 92(2): p. 138-144.
131. Available from: <https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/x-ray-diffraction/d8-advance/overview.html>.
132. Macrae, C.F., et al., *Mercury CSD 2.0–new features for the visualization and investigation of crystal structures*. Journal of Applied Crystallography, 2008. 41(2): p. 466-470.
133. Available from: <http://www.tainstruments.com/product.aspx?siteid=11&id=20&n=1>.

134. Available from: http://www.zeiss.com/microscopy/en_de/products/scanning-electron-microscopes/ultra-materials.html.
135. Available from: http://www.zeiss.com/microscopy/en_de/products/scanning-electron-microscopes/evo-life-science.html.
136. Brunauer, S., P.H. Emmett, and E. Teller, *Adsorption of Gases in Multimolecular Layers*. Journal of the American Chemical Society, 1938. 60(2): p. 309-319.
137. Available from: <http://www.micromeritics.com/Product-Showcase/ASAP-2020-Physisorption.aspx>.
138. Available from: <https://www.bruker.com/products/infrared-near-infrared-and-raman-spectroscopy/ft-ir-research-spectrometers/vertex-series/vertex-8080v/overview.html>.
139. Wojdyr, M., *Fityk: a general-purpose peak fitting program*. Journal of Applied Crystallography, 2010. 43(5): p. 1126-1128.
140. Available from: <https://www.thermoscientific.com/en/product/flash-2000-chns-o-analyzers.html>.
141. Available from: <http://particulatesystems.com/Products/HPVA-II-High-Pressure-Volumetric-Analyzer.aspx>.
142. Available from: <http://particulatesystems.com/Products/HPVA-II-High-Pressure-Volumetric-Analyzer/HPVA-II-System-Overview.aspx>.
143. Furukawa, H. and O.M. Yaghi, *Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications*. Journal of the American Chemical Society, 2009. 131(25): p. 8875-8883.
144. Wu, H., W. Zhou, and T. Yildirim, *High-Capacity Methane Storage in Metal–Organic Frameworks $M_2(dhtp)$: The Important Role of Open Metal Sites*. Journal of the American Chemical Society, 2009. 131(13): p. 4995-5000.
145. Li, B., et al., *Enhanced Binding Affinity, Remarkable Selectivity, and High Capacity of CO_2 by Dual Functionalization of a rht-Type Metal–Organic Framework*. Angewandte Chemie International Edition, 2012. 51(6): p. 1412-1415.
146. Zhou, W., et al., *Hydrogen and Methane Adsorption in Metal–Organic Frameworks: A High-Pressure Volumetric Study*. The Journal of Physical Chemistry C, 2007. 111(44): p. 16131-16137.
147. Wang, X.-S., et al., *Metal–Organic Frameworks Based on Double-Bond-Coupled Di-Isophthalate Linkers with High Hydrogen and Methane Uptakes*. Chemistry of Materials, 2008. 20(9): p. 3145-3152.
148. Zhao, D., et al., *A NbO-type metal-organic framework derived from a polyyne-coupled di-isophthalate linker formed in situ*. Chemical Communications, 2010. 46(23): p. 4196-4198.
149. Lu, W., et al., *A highly porous and robust (3,3,4)-connected metal-organic framework assembled with a 90 degrees bridging-angle embedded octacarboxylate ligand*. Angew Chem Int Ed Engl, 2012. 51(7): p. 1580-4.
150. Guo, Z., et al., *A Metal–Organic Framework with Optimized Open Metal Sites and Pore Spaces for High Methane Storage at Room Temperature*. Angewandte Chemie International Edition, 2011. 50(14): p. 3178-3181.
151. Banerjee, R., et al., *Control of Pore Size and Functionality in Isoreticular Zeolitic Imidazolate Frameworks and their Carbon Dioxide Selective Capture Properties*. Journal of the American Chemical Society, 2009. 131(11): p. 3875-3877.
152. Tanabe, K.K. and S.M. Cohen, *Postsynthetic modification of metal-organic frameworks-a progress report*. Chemical Society Reviews, 2011. 40(2): p. 498-519.
153. Barin, G., et al., *Isoreticular Series of (3,24)-Connected Metal–Organic Frameworks: Facile Synthesis and High Methane Uptake Properties*. Chemistry of Materials, 2014. 26(5): p. 1912-1917.

154. Rallapalli, P., et al., *An alternative activation method for the enhancement of methane storage capacity of nanoporous aluminium terephthalate, MIL-53(Al)*. Journal of Porous Materials, 2010. 17(5): p. 523-528.
155. Bourrelly, S., et al., *Different Adsorption Behaviors of Methane and Carbon Dioxide in the Isotypic Nanoporous Metal Terephthalates MIL-53 and MIL-47*. Journal of the American Chemical Society, 2005. 127(39): p. 13519-13521.
156. Rana, M.K., et al., *Methane Storage in Metal-Substituted Metal-Organic Frameworks: Thermodynamics, Usable Capacity, and the Impact of Enhanced Binding Sites*. Journal of Physical Chemistry C, 2014. 118(6): p. 2929-2942.
157. Uzun, A. and S. Keskin, *Site characteristics in metal organic frameworks for gas adsorption*. Progress in Surface Science, 2014. 89(1): p. 56-79.
158. Sun, B., S. Kayal, and A. Chakraborty, *Study of HKUST (Copper benzene-1,3,5-tricarboxylate, Cu-BTC MOF)-1 metal organic frameworks for CH₄ adsorption: An experimental Investigation with GCMC (grand canonical Monte-carlo) simulation*. Energy, 2014. 76: p.419-427.
159. Sezginel, K.B., A. Uzun, and S. Keskin, *Multivariable linear models of structural parameters to predict methane uptake in metal-organic frameworks*. Chemical Engineering Science, 2015. 124: p. 125-134.
160. Available from: <http://www.sigmaaldrich.com/catalog/product/aldrich/688614?lang=en®ion=TR>.
161. Nobar, S.N., *Adsorption and diffusion of gases in Cu-BTC*. Diss. 2012.
162. Gimeno-Fabra, M., et al., *Instant MOFs: continuous synthesis of metal-organic frameworks by rapid solvent mixing*. Chemical Communications, 2012. 48(86): p. 10642-10644.
163. Czaja, A.U., N. Trukhan, and U. Muller, *Industrial applications of metal-organic frameworks*. Chemical Society Reviews, 2009. 38(5): p. 1284-1293.
164. Yang, Y., et al., *Significant improvement of surface area and CO₂ adsorption of Cu-BTC via solvent exchange activation*. RSC Advances, 2013. 3(38): p. 17065-17072.
165. Yoon, J.W., et al., *Adsorptive separation of propylene and propane on a porous metal-organic framework, copper trimesate*. Bull. Korean Chem. Soc, 2010. 31(1): p. 220-223.
166. Majano, G. and J. Pérez-Ramírez, *Scalable Room-Temperature Conversion of Copper(II) Hydroxide into HKUST-1 (Cu₃(btc)₂)*. Advanced Materials, 2013. 25(7): p. 1052-1057.
167. Akçay, A., V. Balci, and A. Uzun, *Structural factors controlling thermal stability of imidazolium ionic liquids with 1-n-butyl-3-methylimidazolium cation on γ -Al₂O₃*. Thermochimica Acta, 2014. 589: p. 131-136.
168. Szanyi, J., et al., *Well-studied Cu-BTC still serves surprises: evidence for facile Cu²⁺/Cu⁺ interchange*. Physical Chemistry Chemical Physics, 2012. 14(13): p. 4383-4390.
169. Ethiraj, J., et al., *H₂S interaction with HKUST-1 and ZIF-8 MOFs: A multitechnique study*. Microporous and Mesoporous Materials, 2015. 207: p. 90-94.
170. Holomb, R., et al., *Ionic liquid structure: the conformational isomerism in 1-butyl-3-methyl-imidazolium tetrafluoroborate ([bmim][BF₄])*. Journal of Raman Spectroscopy, 2008. 39(7): p. 793-805.
171. Drenchev, N., et al., *CO as an IR probe molecule for characterization of copper ions in a basolite C300 MOF sample*. Physical Chemistry Chemical Physics, 2010. 12(24): p. 6423-6427.
172. Chowdhury, P., et al., *Adsorption of CO, CO₂ and CH₄ on Cu-BTC and MIL-101 metal organic frameworks: Effect of open metal sites and adsorbate polarity*. Microporous and Mesoporous Materials, 2012. 152: p. 246-252.

173. Moellmer, J., et al., *High pressure adsorption of hydrogen, nitrogen, carbon dioxide and methane on the metal–organic framework HKUST-1*. Microporous and Mesoporous Materials, 2011. 138(1–3): p. 140-148.
174. Jacquemin, J., et al., *Solubility of carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon, and carbon monoxide in 1-butyl-3-methylimidazolium tetrafluoroborate between temperatures 283 K and 343 K and at pressures close to atmospheric*. The Journal of Chemical Thermodynamics, 2006. 38(4): p. 490-502.
175. Lopes, F.V.S., et al., *Adsorption of H₂, CO₂, CH₄, CO, N₂ and H₂O in Activated Carbon and Zeolite for Hydrogen Production*. Separation Science and Technology, 2009. 44(5): p. 1045-1073.
176. Saha, D., et al., *Adsorption of CO₂, CH₄, N₂O, and N₂ on MOF-5, MOF-177, and Zeolite 5A*. Environmental Science & Technology, 2010. 44(5): p. 1820-1826.
177. Llewellyn, P.L., et al., *High Uptakes of CO₂ and CH₄ in Mesoporous Metal–Organic Frameworks MIL-100 and MIL-101*. Langmuir, 2008. 24(14): p. 7245-7250.
178. Furukawa, H., et al., *The Chemistry and Applications of Metal-Organic Frameworks*. Science, 2013. 341(6149).

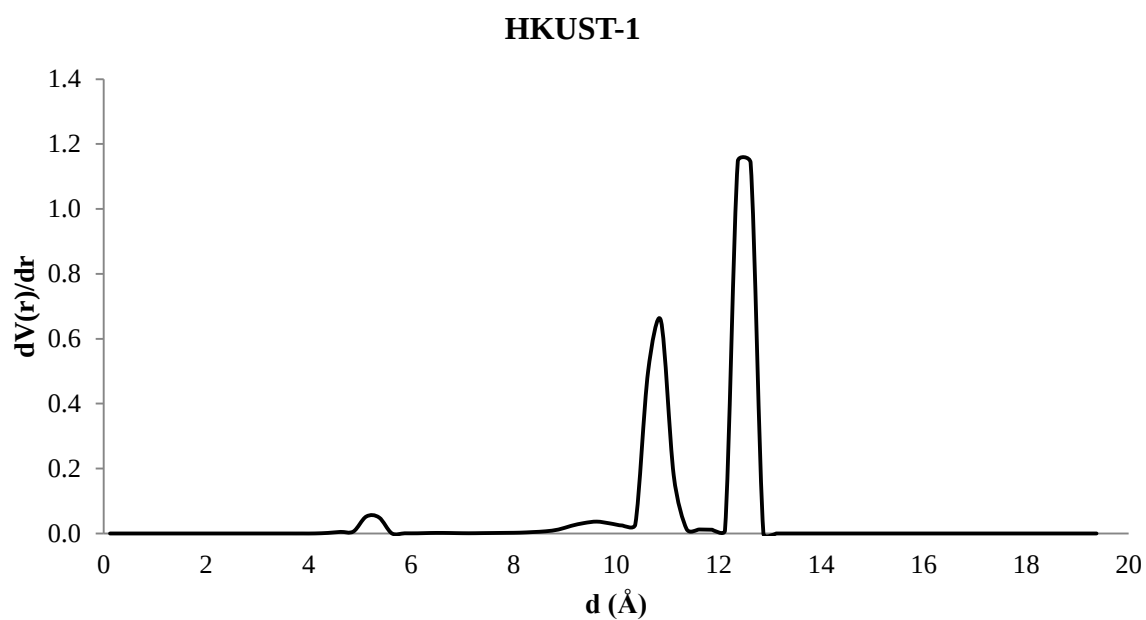
APPENDIX A: Supplementary Information for Computational Methods

Figure A.1: Pore size distribution of HKUST-1 calculated by PoreBlazer.

MATLAB Script for Converting “.mol2” Files to Input Files for GCMC and Poreblazer Simulations

```
% Converts packed mol2 file into crsytal and xyz files
% Creates input.data for GCMC and input.dat for PoreBlazer
% -----INSTRUCTIONS-----
% 1) Change the directories that you want your mol2 file to be read and
%    your simulation files to be saved.
% 2) Change the grid paths.
% 2) If you do not want to create a file type 0 to its "do" entry.
%    Ex: if you do not want crystal file --> crystal_do = 0;
% 3) For input.data you need to enter your simulation conditions that are
%    located at the parameters section. If you want to change
%    additional parameters scroll down the input.data section and modify
%    the relevant section in fprintf comments.
% 4) For the force field parameters you need an excel file named
%    FF_Parameters. Make sure you enter the directory of this file to
%    Excel Force Field Parameter part under input.data. Note that in case
%    you chose DREIDING and an atom does not have parameters in this force
%    field the parameters will be taken from UFF.
% -----
% Version: 1.7
% Input Files: Packed .mol2 file
% Output Files:
%             - GCMC: crystal / input.data / Qtest / run.pl
%             - PoreBlazer: .xyz / input.dat / Qtest
% Gases Available: CH4 / H2
% Mixture Gas: Yes (CH4&H2)
% -----
% -----mol2 and Simulation Files Directories-----
mol2_file = 'C:\Users\WS\Desktop\CoRE Studies\CoRE direct cif to mol2\cif
pack mol2\';
main_dir = 'C:\Users\WS\Desktop\CoRE Studies\CoRE direct cif to
mol2\Simulation\';
% -----
mol2_dir = strcat(mol2_file, '*.mol2');
core = dir(mol2_dir);
[total, jj] = size(core);
for q=1:total
MOFname = strcat(mol2_file, core(q).name);
% -----
fileid = fopen(MOFname);
if fgetl(fileid) == -1
    frewind(fileid);
end

for i = 1:9
    line = fgetl(fileid);
    if i == 1
        if size(line,2) == 6
            MOF = lower(line(1:6));
        elseif ismember(line(7), '0 1 2 3 4 5 6 7 8 9') == 1
            MOF = lower(line(1:8));
        else
            MOF = lower(line(1:6));
        end
    end
    if i == 2
        atomnumber = line(3:6);
        atomnumber = str2num(atomnumber);
    end
end
```

end

```
% Folder to save GCMC files
gcmc_main_dir = strcat(main_dir, '\gcmc\ ', MOF, '\ ');
mkdir(gcmc_main_dir);
% Folder to save PoreBlazer files
pb_main_dir = strcat(main_dir, '\pb\ ', MOF, '\ ');
mkdir(pb_main_dir);
% -----
% ----- PARAMETERS -----
% ----- PoreBlazer -----
% .xyz file
xyz_dir = strcat(pb_main_dir, MOF, '.xyz');
xyz_do = 1;
% PB input.dat file
pb_dir = strcat(pb_main_dir, 'input.dat');
pb_do = 1;
% PB Qtest file
pb_qtest_dir = strcat(pb_main_dir, 'Qtest');
pb_qtest_do = 0;
% ----- GCMC -----
% GCMC Qtest file
qtest_dir = strcat(gcmc_main_dir, 'Qtest');
qtest_do = 0;
% GCMC run.pl file
runpl_dir = strcat(gcmc_main_dir, 'run.pl');
runpl_do = 0;
% GCMC input.data file
inp_dir = strcat(gcmc_main_dir, 'input.data');
input_do = 1;
% Crystal file
cryst_dir = strcat(gcmc_main_dir, MOF);
crystal_do = 1;
% Cluster Selection
cluster = 'scratch';
% Grid Existence
grid_exist_1 = 'No';
grid_exist_2 = 'No';
% Temperature of the simulation
temperature = '298';
temperature = str2double(temperature);
% Adsorbate Species (single or mixture)
gas_species = '1';
gas_species = str2double(gas_species);
gas_1 = 'CH4';
gas_2 = 'H2';
% Force Field Selection ('UFF' or 'DRE')
force_field = 'UFF';
% Pressure Range
p_range = 1;
pressure{1} = '1 65 65';
% -----END OF PARAMETERS-----
% -----
atomname = []; %8-9
coorX = []; %16-22
coorY = []; % 25-31
coorZ = []; %34-40
m = 1;
n = line(10:12);
k = line(1);
while strcmp(n, 'CRY') == 0
    while strcmp(k, ' ') == 1;
```

```

        atomname(m,1:2) = line(8:9);
        coorX(m,1:7) = line(16:22);
        coorY(m,1:7) = line(25:31);
        coorZ(m,1:7) = line(34:40);
        m = m + 1;
        line = fgetl(fileid);
        k = line(1);
    end
    line = fgetl(fileid);
    n = line(10:12);
end

coorX = char(coorX);
coorX = str2num(coorX);
coorY = char(coorY);
coorY = str2num(coorY);
coorZ = char(coorZ);
coorZ = str2num(coorZ);
atomname = char(atomname);

for i = 1:atomnumber
    if ismember(atomname(i,2), '0':'9') == 1
        atomname(i,2)=' ';
    end
end

% Structure Determination
line = fgetl(fileid);
a = line(4:10); a = char(a); a = str2num(a);
b = line(14:20); b = char(b); b = str2num(b);
c = line(24:30); c = char(c); c = str2num(c);
alpha = line(33:40); alpha = char(alpha); alpha = str2num(alpha);
beta = line(43:50); beta = char(beta); beta = str2num(beta);
gamma = line(53:60); gamma = char(gamma); gamma = str2num(gamma);
cellsize = [a b c alpha beta gamma];

% Calculate frequency of each atom and number of species
atoms = cellstr(atomname);
[unique_atoms,junk,ind] = unique(atoms);
freq_atoms = histc(ind,1:numel(unique_atoms));
species = size(unique_atoms);
species = species(1);

% Sorting according to atom name
ksort = {};
ksortX = [];
ksortY = [];
ksortZ = [];
num = 1;
for k=1:species
    for i=1:atomnumber
        if isequal(unique_atoms(k), atoms(i)) == 1
            ksort{num} = atoms(i);
            ksortX(num) = coorX(i);
            ksortY(num) = coorY(i);
            ksortZ(num) = coorZ(i);
            num = num + 1;
        end
    end
end
end
% Create directory to save the files:

```

```

%-----CRYSTAL FILE-----
if crystal_do == 1
cryst_file = fopen(cryst_dir, 'w');

fprintf(cryst_file, 'Species    %d\n', species);
fprintf(cryst_file, 'Structure  Triclinic\n');
fprintf(cryst_file, 'Unit Cell');
fprintf(cryst_file, ' %.4f', cellsize);

freq_ini = [];
freq_ini(1,1)=1;
freq=[];
dummy = 0;
for i=1:species
    dummy = dummy + freq_atoms(i,1);
    freq(i) = dummy;
    if i <= species-1
        freq_ini(i+1) = freq(i) + 1;
    end
end

for i=1:species
    fprintf(cryst_file, '\n%s', char(unique_atoms(i)));
    fprintf(cryst_file, ' %d', freq_atoms(i));
    for k = freq_ini(i):freq(i)
        fprintf(cryst_file, '\n%.4f', ksortX(k));
        fprintf(cryst_file, ' %.4f', ksortY(k));
        fprintf(cryst_file, ' %.4f', ksortZ(k));
    end
end

fclose(cryst_file);
end
%-----XYZ FILE-----
if xyz_do == 1
xyz_file = fopen(xyz_dir, 'w');

fprintf(xyz_file, '%d\n', atomnumber);
fprintf(xyz_file, '%s', MOF);

for k=1:atomnumber
    fprintf(xyz_file, '\n%s ', char(ksort{k}));
    fprintf(xyz_file, ' %.4f', ksortX(k));
    fprintf(xyz_file, ' %.4f', ksortY(k));
    fprintf(xyz_file, ' %.4f', ksortZ(k));
end

fclose(xyz_file);
end
%-----PORE BLAZER INPUT.DAT-----
if pb_do == 1
pb_file = fopen(pb_dir, 'w');

fprintf(pb_file, '%s.xyz\n', MOF);
fprintf(pb_file, '%.4f ', a);
fprintf(pb_file, '%.4f ', b);
fprintf(pb_file, '%.4f\n', c);
fprintf(pb_file, '%.4f ', alpha);

```

```

fprintf(pb_file, '%.4f ', beta);
fprintf(pb_file, '%.4f', gamma);

fclose(pb_file);
end
%-----Q TEST-----
if qtest_do == 1
qtest_file = fopen(qtest_dir, 'w');

fprintf(qtest_file, '#!/bin/bash\n');
fprintf(qtest_file, '#$ -S /bin/bash\n');
fprintf(qtest_file, '#$ -q skeskin.q\n');
fprintf(qtest_file, '#$ -pe smp 1\n');
fprintf(qtest_file, '#$ -M ksezginel@ku.edu.tr\n');
fprintf(qtest_file, '#$ -m n\n');
fprintf(qtest_file, '#$ -cwd\n');
fprintf(qtest_file, '#$ -o $JOB_ID.out\n');
fprintf(qtest_file, '#$ -e $JOB_ID.err\n');
fprintf(qtest_file, './run.pl');

fclose(qtest_file);
end
%-----PoreBlazer Q TEST-----
if pb_qtest_do == 1
pb_qtest_file = fopen(pb_qtest_dir, 'w');

fprintf(pb_qtest_file, '#!/bin/bash\n');
fprintf(pb_qtest_file, '#$ -S /bin/bash\n');
fprintf(pb_qtest_file, '#$ -q skeskin.q\n');
fprintf(pb_qtest_file, '#$ -pe smp 1\n');
fprintf(pb_qtest_file, '#$ -M ksezginel@ku.edu.tr\n');
fprintf(pb_qtest_file, '#$ -m n\n');
fprintf(pb_qtest_file, '#$ -cwd\n');
fprintf(pb_qtest_file, '#$ -o $JOB_ID.out\n');
fprintf(pb_qtest_file, '#$ -e $JOB_ID.err\n');
fprintf(pb_qtest_file, '\n/home/ksezginel/PoreBlazer2/poreblazer.exe <
input.dat > output.txt');

fclose(pb_qtest_file);
end
%-----RUN.PL-----
if runpl_do == 1
runpl_file = fopen(runpl_dir, 'w');

fprintf(runpl_file, '#!/usr/bin/perl\n');
fprintf(runpl_file, '$program="/mnt/projects/ksezginel/Source/run-
1.3.exe";\n');
fprintf(runpl_file, 'system($program);\n');
fprintf(runpl_file, 'exit;');

fclose(runpl_file);
end
%-----INPUT.DATA-----
if input_do == 1

% Grid Existence and Grid Path ('lufer' / 'yunus' / 'scratch')
if strcmp(cluster,'lufer') == 1
grid_path_1 =
strcat('/home/ksezginel/grids/',MOF,'_',gas_1,'_',force_field,'.grid');

```

```

grid_path_2 =
strcat('/home/ksezginel/grids/',MOF,'_',gas_2,'_',force_field,'.grid');
end
if strcmp(cluster,'yunus') == 1
grid_path_1 =
strcat('/mnt/kufs/scratch/ksezginel/grids/',MOF,'_',gas_1,'_',force_field,'
.grid');
grid_path_2 =
strcat('/mnt/kufs/scratch/ksezginel/grids/',MOF,'_',gas_2,'_',force_field,'
.grid');
end
if strcmp(cluster,'scratch') == 1
grid_path_1 =
strcat('/mnt/scratch/ksezginel/grids/',gas_1,'/',MOF,'_',gas_1,'_',force_fi
eld,'.grid');
grid_path_2 =
strcat('/mnt/scratch/ksezginel/grids/',gas_2,'/',MOF,'_',gas_2,'_',force_fi
eld,'.grid');
end

% Excel Force Field Parameter Read -----
[~,~,raw] =
xlsread('C:\Users\WS\Documents\MATLAB\FF_Parameters.xlsx','Sheet1','A3:E105
');
raw(cellfun(@(x) ~isempty(x) && isnumeric(x) && isnan(x),raw)) = {' '};
cellVectors = raw(:,1);
raw = raw(:,[2,3,4,5]);
data = reshape([raw{:}],size(raw));
ff_atoms = cellVectors(:,1);
uff_sigma = data(:,1);
uff_epsilon = data(:,2);
dre_sigma = data(:,3);
dre_epsilon = data(:,4);
clearvars data raw cellVectors;
% -----
% Create input.data file -----
input_data = fopen(inp_dir, 'w');

fprintf(input_data,'#### SIMULATION TYPE
#####\n');
fprintf(input_data,'Request Monte Carlo GCMC\n');
fprintf(input_data,'START FROM BEGINNING Yes\n');
fprintf(input_data,'Request Adsorbent\n');
fprintf(input_data,'#SYSTEM TEMPERATURE \n');
fprintf(input_data,'Global Temperature %d\n', temperature);
% ----- ADSORBATE INFO -----
if gas_species == 1
% CH4 Parameters -----
if strcmp(gas_1,'CH4') == 1
fprintf(input_data,'#### ADSORBATE PHASE
#####\n');
fprintf(input_data,'Species %d\n', gas_species);
fprintf(input_data,'-----
-\n');
fprintf(input_data,'Molecule Name %s\n', gas_1);
fprintf(input_data,'Molecule Type 1\n');
fprintf(input_data,'Number of atoms 1 1\n');
fprintf(input_data,'Atomic Weights \n');
fprintf(input_data,' 1 16d0\n');
fprintf(input_data,'Atomic Names\n');
fprintf(input_data,' 1 CH4\n');

```

```

fprintf(input_data, '#### ADSORBATE - ADSORBATE INTERACTIONS
#####\n');
fprintf(input_data, 'Potential Types\n');
fprintf(input_data, '  1                                     1\n');
fprintf(input_data, 'Self Potential Parameters\n');
fprintf(input_data, '  1 1                                     148.2d0 3.73d0
13d0\n');
end
% H2 Parameters-----
if strcmp(gas_1, 'H2') == 1
fprintf(input_data, '#### ADSORBATE PHASE
#####\n');
fprintf(input_data, 'Species                               %d\n', gas_species);
fprintf(input_data, '-----
-\n');
fprintf(input_data, 'Molecule Name                               %s\n', gas_1);
fprintf(input_data, 'Molecule Type                               1\n');
fprintf(input_data, 'Number of atoms                               1 1\n');
fprintf(input_data, 'Atomic Weights                               \n');
fprintf(input_data, '  1                                     2d0\n');
fprintf(input_data, 'Atomic Names\n');
fprintf(input_data, '  1                                     H\n');
fprintf(input_data, '#### ADSORBATE - ADSORBATE INTERACTIONS
#####\n');
fprintf(input_data, 'Potential Types\n');
fprintf(input_data, '  1                                     1\n');
fprintf(input_data, 'Self Potential Parameters\n');
fprintf(input_data, '  1 1                                     34.2d0 2.96d0
13d0\n');
end
% -----
fprintf(input_data, '#### ADSORBENT SPECIFICATION
#####\n');
fprintf(input_data, 'Structure Datafile                               %s\n', MOF);
fprintf(input_data, 'Adsorbent species                               %d\n', species);
fprintf(input_data, 'Potential Evaluation                               Grid\n');
fprintf(input_data, 'Grid Spacing                               0.2d0\n');
fprintf(input_data, 'Grid Datafile\n');
fprintf(input_data, '1                                     "%s"\n', grid_path_1);
fprintf(input_data, 'Existing Grid Datafile                               \n');
fprintf(input_data, '1                                     %s\n', grid_exist_1);
fprintf(input_data, 'Include Long Range Corrections                     No\n');

fprintf(input_data, '#### ADSORBATE - ADSORBENT INTERACTIONS
#####\n');
fprintf(input_data, 'Potential Types\n');
for i = 1:species
    fprintf(input_data, '  %d                                     1
%s\n', i, char(unique_atoms(i)));
end

fprintf(input_data, 'Self Potential Parameters\n');

lia=[];
loc=[];
for i = 1:species
    [lia(i), loc(i)] = ismember(char(unique_atoms(i)), ff_atoms);
end
liacheck = ones(1, species);
if isequal(lia, liacheck) == 0
    fprintf('Atom not found!\n');

```

```

quit
end

% UFF Parameters for each atom
if isequal(force_field, 'UFF')
for i = 1:species
    fprintf(input_data, ' %d                                %.2fd0 %.2fd0
13d0\n', i, uff_epsilon(loc(i)), uff_sigma(loc(i)));
end
end

% DRE Parameters for each atom
if isequal(force_field, 'DRE')
for i = 1:species
    fprintf(input_data, ' %d                                %.2fd0 %.2fd0
13d0\n', i, dre_epsilon(loc(i)), dre_sigma(loc(i)));
end
end

fprintf(input_data, 'Mixed Potential Parameters\n');
fprintf(input_data, 'Combination Rules                        Yes\n');
fprintf(input_data, 'Type of Combination Rules                Lorenz-Berthelot\n');
fprintf(input_data, '#### FINAL SIMULATION PARAMETERS
#####\n');
fprintf(input_data, 'Simulation Box in Unit cells        2 2 2\n');

fprintf(input_data, '#### MONTE CARLO PARAMETERS
#####\n');
fprintf(input_data, 'Equilibration Steps                    15000000\n');
fprintf(input_data, 'Production Steps                      15000000\n');
fprintf(input_data, 'Types of moves                        2\n');
fprintf(input_data, 'Move Probabilities                    0.3 0.7\n');
fprintf(input_data, 'Pressure Ranges                      %d          \n',
p_range);
for i = 1:p_range
    fprintf(input_data, ' %d
%s\n', i, pressure{i});
end
fprintf(input_data, 'Desorption simulation                No\n');
fprintf(input_data, 'Include Biases                      No\n');
fprintf(input_data, 'MC Trajectory Sampling Rate          -1\n');
fprintf(input_data, '#### EQUATIONS OF STATE
#####\n');
fprintf(input_data, 'EOS types\n');
fprintf(input_data, ' 1                                1\n');
fprintf(input_data, 'Parameters\n');
fprintf(input_data, ' 1                                0d0 0d0  \n');
fprintf(input_data, '##### END OF INPUT
#####\n');
end

% ----- MIXTURE -----
if gas_species == 2
fprintf(input_data, '#### ADSORBATE PHASE
#####\n');
fprintf(input_data, 'Species                                %d\n', gas_species);
fprintf(input_data, '-----
-\n');
fprintf(input_data, 'Molecule Name                        %s\n', gas_1);
fprintf(input_data, 'Molecule Type                        1\n');
fprintf(input_data, 'Number of atoms                      1 1\n');
fprintf(input_data, 'Atomic Weights                       \n');

```

```

fprintf(input_data, ' 1 16d0\n');
fprintf(input_data, 'Atomic Names\n');
fprintf(input_data, ' 1 CH4\n');
fprintf(input_data, '-----
-\n');
fprintf(input_data, 'Molecule Name %s\n', gas_2);
fprintf(input_data, 'Molecule Type 1\n');
fprintf(input_data, 'Number of atoms 1 1\n');
fprintf(input_data, 'Atomic Weights \n');
fprintf(input_data, ' 1 2d0\n');
fprintf(input_data, 'Atomic Names\n');
fprintf(input_data, ' 1 H\n');
fprintf(input_data, '#### ADSORBATE - ADSORBATE INTERACTIONS
#####\n');
fprintf(input_data, 'Potential Types\n');
fprintf(input_data, ' 1 1\n');
fprintf(input_data, ' 2 1\n');
fprintf(input_data, 'Self Potential Parameters\n');
fprintf(input_data, ' 1 1 148.2d0 3.73d0
13d0\n');
fprintf(input_data, ' 2 1 34.2d0 2.96d0
13d0\n');
fprintf(input_data, 'Mixed Potential Parameters\n');
fprintf(input_data, 'Combination Rules Yes\n');
fprintf(input_data, 'Type of Combination Rules Lorenz-Berthelot\n');
fprintf(input_data, '#### ADSORBENT SPECIFICATION
#####\n');
fprintf(input_data, 'Structure Datafile %s\n', MOF);
fprintf(input_data, 'Adsorbent species %d\n', species);
fprintf(input_data, 'Potential Evaluation Grid\n');
fprintf(input_data, 'Grid Spacing 0.2d0\n');
fprintf(input_data, 'Grid Datafile\n');
fprintf(input_data, '1 "%s"\n', grid_path_1);
fprintf(input_data, '2 "%s"\n', grid_path_2);
fprintf(input_data, 'Existing Grid Datafile \n');
fprintf(input_data, '1 %s\n', grid_exist_1);
fprintf(input_data, '2 %s\n', grid_exist_2);
fprintf(input_data, 'Include Long Range Corrections No\n');
fprintf(input_data, '#### ADSORBATE - ADSORBENT INTERACTIONS
#####\n');
fprintf(input_data, 'Potential Types\n');
for i = 1:species
    fprintf(input_data, ' %d 1
%s\n', i, char(unique_atoms(i)));
end
fprintf(input_data, 'Self Potential Parameters\n');
lia=[]; loc=[];
for i = 1:species
    [lia(i), loc(i)] = ismember(char(unique_atoms(i)), ff_atoms);
end
liacheck = ones(1, species);
if isequal(lia, liacheck) == 0
    fprintf('Atom not found!\n');
    quit
end
% UFF Parameters for each atom
if isequal(force_field, 'UFF')
for i = 1:species
    fprintf(input_data, ' %d %.2fd0 %.2fd0
13d0\n', i, uff_epsilon(loc(i)), uff_sigma(loc(i)));
end
end

```

```

% DRE Parameters for each atom
if isequal(force_field, 'DRE')
for i = 1:species
    fprintf(input_data, ' %d %d\n', i, dre_epsilon(loc(i)), dre_sigma(loc(i)));
end
end
fprintf(input_data, 'Mixed Potential Parameters\n');
fprintf(input_data, 'Combination Rules Yes\n');
fprintf(input_data, 'Type of Combination Rules Lorenz-Berthelot\n');
fprintf(input_data, '#### FINAL SIMULATION PARAMETERS
#####\n');
fprintf(input_data, 'Simulation Box in Unit cells 2 2 2\n');
fprintf(input_data, '#### MONTE CARLO PARAMETERS
#####\n');
fprintf(input_data, 'Equilibration Steps 15000000\n');
fprintf(input_data, 'Production Steps 15000000\n');
fprintf(input_data, 'Types of moves 2\n');
fprintf(input_data, 'Move Probabilities 0.3 0.7\n');
fprintf(input_data, 'Composition 0.5 0.5\n');
fprintf(input_data, 'Pressure Ranges %d \n',
p_range);
for i = 1:p_range
    fprintf(input_data, ' %d %s\n', i, pressure{i});
end
fprintf(input_data, 'Desorption simulation No\n');
fprintf(input_data, 'Include Biases No\n');
fprintf(input_data, 'MC Trajectory Sampling Rate -1\n');
fprintf(input_data, '#### EQUATIONS OF STATE
#####\n');
fprintf(input_data, 'EOS types\n');
fprintf(input_data, ' 1 1\n');
fprintf(input_data, ' 2 1\n');
fprintf(input_data, 'Parameters\n');
fprintf(input_data, ' 1 0d0 0d0 \n');
fprintf(input_data, ' 2 0d0 0d0 \n');
fprintf(input_data, '##### END OF INPUT
#####\n');

fclose(input_data);
end
end
fclose all;
% -----
end
% -----

```

MATLAB Script for Converting PoreBlazer Output Files to Input Files for Surface Area Calculations

```
% Converts Pore Blazer input file to Surface Area (Düren) input file
% Requires density information

% Pore Blazer input directory
pb_dir = 'C:\NEMO\Kutay\CoRE\3000\PB_Results_3May15\';
% Surface Area save directory
sa_main_dir = 'C:\NEMO\Kutay\CoRE\3000\SA_Input\';

%Initializing to read Pore Blazer input.dat
PBData = {};
PBData{1,1} = 'MOF';
PBData{1,2} = 'Density';
core_pb = dir(pb_dir);
[total_pb, jjs] = size(core_pb);

for q=3:total_pb

    MOF_pb = core_pb(q).name;
    PBData{q-1,1} = MOF_pb;
    pb_mof = dir(strcat(pb_dir,MOF_pb));
    [totalf, jjf] = size(pb_mof);
    pb_files = {};

    for i=1:totalf
        pb_files{i,1} = pb_mof(i).name;
    end

    %Reading Pore Blazer input.dat for crystal information
    pb_input = strcat(pb_dir,MOF_pb,'\input.dat');
    pb_input_id = fopen(pb_input); frewind(pb_input_id);
    line_pb_input = fgetl(pb_input_id);
    line_pb_input = fgetl(pb_input_id);
    a = str2double(line_pb_input(1:8));
    b = str2double(line_pb_input(9:16));
    c = str2double(line_pb_input(17:end));
    line_pb_input = fgetl(pb_input_id);
    alpha = str2double(line_pb_input(1:8));
    beta = str2double(line_pb_input(9:16));
    gamma = str2double(line_pb_input(17:end));

    %Checking for results' existence
    if ismember('output.txt', pb_files) == 1
        pb_data = strcat(pb_dir,MOF_pb,'\output.txt');
        pb_id = fopen(pb_data); frewind(pb_id);
        line_pb = fgetl(pb_id);

        %Reading density information
        while isequal(line_pb,-1) == 0
            line_pb = fgetl(pb_id);
            if length(line_pb) >= 30
                if strcmp(line_pb(9:15), 'density')
                    density = str2double(line_pb(32:end));
                    PBData{q-1,2} = density;
                end
            end
        end
    end
end
```

```
end
end

% Writing Surface Area input.dat
sa_dir = strcat(sa_main_dir,MOF_pb,'\');
mkdir(sa_dir);
input_dir = strcat(sa_dir,'input.dat');

sa_file = fopen(input_dir, 'w');

fprintf(sa_file, 'UFF.atoms\n');
fprintf(sa_file, '%s.xyz\n', MOF_pb);
fprintf(sa_file, '3.681\n');
fprintf(sa_file, '5000\n');
fprintf(sa_file, '%.4f ', a);
fprintf(sa_file, '%.4f ', b);
fprintf(sa_file, '%.4f\n', c);
fprintf(sa_file, '%.4f ', alpha);
fprintf(sa_file, '%.4f ', beta);
fprintf(sa_file, '%.4f\n', gamma);
fprintf(sa_file, '%.4f\n', density);
fprintf(sa_file, '\n');
fprintf(sa_file, '\n');
fprintf(sa_file, '\n');
fprintf(sa_file, '! file containing the atom types and diameters\n');
fprintf(sa_file, '! file containing the framework coordinates\n');
fprintf(sa_file, '! probe size in A\n');
fprintf(sa_file, '! number of trial insertion\n');
fprintf(sa_file, '! length of unit cell a, b, c in A\n');
fprintf(sa_file, '! unit cell angles alpha, beta, gamma\n');
fprintf(sa_file, '! crystal density in g / cm3\n');

fclose(sa_file);

fclose all;
end
```

MATLAB Script for Reading Output Files of All Simulation Results

```
% GCMC, PB, SA Results Reader
% _____ GCMC _____
% Directory of GCMC Results
gcmc_dir = 'C:\NEMO\Kutay\CoRE\3000\CH4_Results\';
gcmc_do = 1;
mix_do = 0;
adsorbate = 'CH4';
% adsorbate_2 = 'H2';
temperature = '298';
% _____ PoreBlazer _____
% Directory of PoreBlazer Results
pb_dir = 'C:\NEMO\Kutay\CoRE\3000\PB_Results\';
pb_do = 1;
psd_do = 1;
% _____ SurfaceArea (Düren) _____
% Directory of SurfaceArea (Düren) Results
sa_dir = 'C:\NEMO\Kutay\CoRE\3000\SA_Results\';
sa_do = 1;
% _____
```

```
% Data Cell for Results
if gcmc_do == 1
    GCMCData = {};
    GCMCData{1,1} = 'MOF';
    GCMCData{1,2} = 'UCV';
    core_gcmc = dir(gcmc_dir);
    [total_gcmc, jj] = size(core_gcmc);
end
if pb_do == 1
    PBData = {};
    PBData{1,1} = 'MOF';
    PBData{1,2} = 'Density';
    PBData{1,3} = 'He_Vp';
    PBData{1,4} = 'Geo_Vp';
    PBData{1,5} = 'Sg';
    PBData{1,6} = 'PLD';
    PBData{1,7} = 'MPD';
    PBData{1,8} = 'DPD';
    core_pb = dir(pb_dir);
    [total_pb, jjsl] = size(core_pb);
end
if sa_do == 1
    SADATA = {};
    SADATA{1,1} = 'MOF';
    SADATA{1,2} = 'Sv';
    SADATA{1,3} = 'Sg';
    core_sa = dir(sa_dir);
    [total_sa, jjal] = size(core_sa);
end
```

```
% _____ GCMC Read _____
if gcmc_do == 1
    progressbar('gcmc');
    for q=3:total_gcmc
        progressbar(q/total_gcmc);
```

```
MOF_gcmc = core_gcmc(q).name;
GCMCData{q-1,1} = MOF_gcmc;
```

```

gcmc_mof = dir(strcat(gcmc_dir,MOF_gcmc));
[totalf, jjf] = size(gcmc_mof);
gcmc_files = {};

for i=1:totalf
    gcmc_files{i,1} = gcmc_mof(i).name;
end

% Check for results' existence
condition = strcat(adsorbate, '-T', temperature);
if ismember(strcat(condition, '-adsorption.dat'), gcmc_files) == 1

ads_data = strcat(gcmc_dir,MOF_gcmc, '\', condition, '-adsorption.dat');
ucv_data = strcat(gcmc_dir,MOF_gcmc, '\UnitCellVolume.dat');

ads_id = fopen(ads_data); frewind(ads_id);
ucv_id = fopen(ucv_data); frewind(ucv_id);

if mix_do == 0
qst_data = strcat(gcmc_dir,MOF_gcmc, '\', condition, '-Qst.dat');
qst_id = fopen(qst_data); frewind(qst_id);
end

%Name of MOF
MOFnames = {};
MOFnames{q-2,1} = MOF_gcmc;

%Unit Cell Volume
line = fgetl(ucv_id);
ucv = str2double(line(35:end));
GCMCData{q-1,2} = ucv;

%Adsorption and Qst
press = []; ads = []; qst = []; i = 1;
line_ads = fgetl(ads_id);

% GCMC Data Read
while line_ads ~= -1
    press(i,1) = str2double(line_ads(5:20));
    ads(i,1) = str2double(line_ads(25:43));
    if mix_do == 0
        line_qst = fgetl(qst_id);
        qst(i,1) = str2double(line_qst(25:43));
    end
    i = i + 1;
    line_ads = fgetl(ads_id);
end

for i = 1:length(press)
    GCMCData{1,i+2} = strcat('N_',adsorbate, '-', num2str(press(i)));
    if mix_do == 0
        GCMCData{1,i+2+length(press)} = strcat('Qst_',adsorbate, '-',
num2str(press(i)));
    end
    GCMCData{q-1,i+2} = ads(i);
    if mix_do == 0
        GCMCData{q-1,i+2+length(press)} = qst(i);
    end
end
% Result Existence GCMC

```

```

end
% Multiple read for loop
fclose all;
end
% GCMC_DO
end
%
% _____ Pore Blazer Read _____
if pb_do == 1
    progressbar('pb');
    for q=3:total_pb
        progressbar(q/total_pb);
        MOF_pb = core_pb(q).name;
        PBData{q-1,1} = MOF_pb;
        pb_mof = dir(strcat(pb_dir,MOF_pb));
        [totalf, jjf] = size(pb_mof);
        pb_files = {};

        for i=1:totalf
            pb_files{i,1} = pb_mof(i).name;
        end

        if ismember('output.txt', pb_files) == 1
            pb_data = strcat(pb_dir,MOF_pb,'\output.txt');
            pb_id = fopen(pb_data); frewind(pb_id);
            line_pb = fgetl(pb_id);

            while isequal(line_pb,-1) == 0
                line_pb = fgetl(pb_id);
                if length(line_pb) >= 30
                    if strcmp(line_pb(9:15),'density')
                        dens = str2double(line_pb(32:end));
                        PBData{q-1,2} = dens;
                    end
                    if strcmp(line_pb(19:24),'cm^3/g')
                        he_vp = str2double(line_pb(32:end));
                        PBData{q-1,3} = he_vp;
                    end
                    if strcmp(line_pb(7:14),'limiting')
                        pld = str2double(line_pb(35:end));
                        PBData{q-1,6} = pld;
                    end
                    if strcmp(line_pb(2:8),'Maximum')
                        mpd = str2double(line_pb(35:end));
                        PBData{q-1,7} = mpd;
                    end
                end
                if length(line_pb) >= 46
                    if strcmp(line_pb(41:46),'cm^3/g')
                        geo_vp = str2double(line_pb(55:end));
                        PBData{q-1,4} = geo_vp;
                    end
                    if strcmp(line_pb(38:42),'m^2/g')
                        sg = str2double(line_pb(53:end));
                        PBData{q-1,5} = sg;
                    end
                end
            end
        end
    end
end
end

% PSD Calculation

```

```

if ismember('psd.txt', pb_files) == 1
    psd_data = strcat(pb_dir,MOF_pb,'\psd.txt');
    psd_id = fopen(psd_data); frewind(psd_id);
    line_psd = fgetl(psd_id);
    PSD_d = []; PSD_f = []; p = 1;
    while isequal(line_psd,-1) == 0
        PSD_d(p,1) = str2double(line_psd(1:18));
        PSD_f(p,1) = str2double(line_psd(18:end));
        line_psd = fgetl(psd_id);
        p = p + 1;
    end
    [max_freq, freq_ind] = max(PSD_f);
    PBData{q-1,8} = PSD_d(freq_ind,1);
end

fclose all;
end
end

% _____ Surface Area _____
if sa_do == 1
    progressbar('sa');
for q=3:total_sa
    progressbar(q/total_sa);
MOF_sa = core_sa(q).name;
SADData{q-1,1} = MOF_sa;
sa_mof = dir(strcat(sa_dir,MOF_sa));
[total_sa, jjsa] = size(sa_mof);
sa_files = {};

for i=1:total_sa
    sa_files{i,1} = sa_mof(i).name;
end

if ismember('output.txt', sa_files) == 1
    sa_data = strcat(sa_dir,MOF_sa,'\output.txt');
    sa_id = fopen(sa_data); frewind(sa_id);
    for s=1:7
        line_sa = fgetl(sa_id);
    end
    line_sa = fgetl(sa_id);
    sa_v = str2double(line_sa(45:end));
    SADData{q-1,2} = sa_v;
    line_sa = fgetl(sa_id);
    sa_g = str2double(line_sa(45:end));
    SADData{q-1,3} = sa_g;
end

fclose all;
end
end

```

UNIX Shell Script for Automatically Submitting GCMC Simulations

```
cd /mnt/scratch/ksezginel/GCMC/3000/CH4-2
for i in `ls`
do

while [ `qstat -u ksezginel | grep ksezginel | wc -l` -ge 30 ]
do
sleep 10
done

echo $i
cd /mnt/scratch/ksezginel/GCMC/3000/CH4-2/$i

#cp /mnt/scratch/ksezginel/doc/Qtest/auto/long/Qtest .
#cp /mnt/scratch/ksezginel/doc/runpl/scratch/run.pl .

isim=$i"_CH4"
echo "qsub -N `echo $isim` Qtest"
qsub -N `echo $isim` Qtest

echo "----"
done
```

UNIX Shell Script for Automatically Replacing Input Files for Generating Grid with Input Files for GCMC Simulations

```
cd /mnt/scratch/ksezginel/GCMC/3000-YES
for i in `ls`
do

echo $i
cd /mnt/scratch/ksezginel/GCMC/3000/CH4/$i

rm *.err *.out *.data
cp /mnt/scratch/ksezginel/GCMC/3000-YES/$i/input.data .

echo "----"
done
```

UNIX Shell Script for Automatically Submitting PoreBlazer Simulations

```
cd /mnt/scratch/ksezginel/PoreBlazer/3000
for i in `ls`
do

while [ `qstat -u ksezginel | grep ksezginel | wc -l` -ge 40 ]
do
sleep 10
done

echo $i
cd /mnt/scratch/ksezginel/PoreBlazer/3000/$i

#rm *.err *.out defaults.dat new.xyz *.txt

cp /mnt/scratch/ksezginel/PoreBlazer/Qtest .
cp /mnt/scratch/ksezginel/PoreBlazer/defaults.dat .
cp /mnt/scratch/ksezginel/PoreBlazer/UFF.atoms .

isim=$i"_PB"
echo "qsub -N `echo $isim` Qtest"
qsub -N `echo $isim` Qtest

echo "----"
done
```

UNIX Shell Script for Automatically Submitting Surface Area Simulations

```
cd /mnt/scratch/ksezginel/SurfaceArea/3000
for i in `ls`
do

while [ `qstat -u ksezginel | grep ksezginel | wc -l` -ge 50 ]
do
sleep 10
done

echo $i
cd /mnt/scratch/ksezginel/SurfaceArea/3000/$i

#rm *.err *.out *.txt Qtest

#cp /home/ksezginel/PoreBlazer2/ccdc/$i/*.xyz .
#rm new.xyz
#mv input* input.dat

cp /mnt/scratch/ksezginel/SurfaceArea/Qtest .
cp /mnt/scratch/ksezginel/SurfaceArea/UFF.atoms .

isim=$i"_SA"
echo "qsub -N `echo $isim` Qtest"
qsub -N `echo $isim` Qtest

echo "----"
done
```

MATLAB scripts for QSPR calculations can be found in the following website:

<http://www.mathworks.com/matlabcentral/fileexchange/19578-qsar-qspr-search-algorithms-toolbox>

Table A.1: CCDC refcodes for all MOFs considered in Chapter 4.3.

CCDC REFCODE						
ABEMIF	DEZNED	GIWBOE	KUDLUR	OFODET	SADMOB	WAGYUA
ABEXEM	DIBQEM	GIXGOK	KUDMAY	OGAXUR	SAHYAD	WAHNUQ
ABEXIQ	DIBQIQ	GOBGAG	KUGZIW	OGEBAF	SAHYAD01	WAJLEA
ABEXOW	DIBQOW	GOGSIF	KUJNEJ	OGECOUC	SAHYAD02	WAMREJ
ABEXUC	DICKEH	GOGWEF	KUJNUZ	OGIKAR	SAHYAD03	WAMRIN
ABEYAJ	DICVAO	GOJFAN	KUJPAH	OGIYOT	SAHYIL	WAMRIN01
ABEYEN	DICVES	GUKZAO	KUXLUL	OGIYUZ	SAKRAZ	WAMRIN02
ABEYIR	DIDBAV	GULGEZ	LACGED	OGOJOJ	SAKRED	WAQDOJ
ACAJOF	DIDBEZ	GULWAM	LAGBUS	OGURAK	SAPBIW	WAQFAX
ACIBOE	DIHPIU	GULWEQ	LAGCAZ	OHAKIS	SAQZOB	WARJAC
ACUFEK	DIMQOH	GULWIU	LAGCED	OHAQEU	SARGUP	WASTUG
ACUJOZ	DITJIB	GUNFAW01	LAGCIH	OHOFEW	SARHAW	WAVQIV
ADARAA	DITJOH	GUPBOJ01	LAGCON	OHOFIA	SARHEA	WAVQUH
ADASIJ	DOCKOW	GUPCAW	LAGCUT	OHOLIH	SARNOQ	WAVRAO
ADASOP	DOKDEN	GUPDEB	LAGDAA	OJICEQ	SATBEW	WAVROC
ADASUV	DOMCUE	GURPUF	LAGDEE	OJICUG	SATBIA	WAZQIZ
ADATIK	DONNEA	GURTIX	LAGDII	OJIDAN	SATCAT	WEBKIZ
ADOBAX	DOTTUC	GUSMAJ	LAGDOO	OJIWAG	SATCEX	WEBKOD
ADOBEB	DUCGEO	GUVLAL	LAGWUN	OJONOQ	SATNOR	WEBKOF
ADOBOL	DUVNIS	GUXRAT	LAKFIN	OKABAE	SATNOR01	WEHHEY
ADOBUR	DUVNIS01	GUYLOC	LARPOL	OKABEI	SEFBOV	WEHHIC
ADOCAY	DUXKUD	HABREJ	LASDEQ	OKIKEZ	SEHXIN	WEHHOI
ADOCIG	DUXMAL	HAFTOZ	LASMAV	OKILEA	SENVIR	WEHHUO
ADODAA	DUYRAR	HAFVUH	LASWIN	OKITIM	SENWAL	WEHJAW
ADUWIH	DUYREV	HAFWAO	LASYOU	OKITIM01	SENWIT	WEHJEA
AFEJOK	DUYRIZ	HAHPIQ	LAVSUY	OKITIM02	SENWOZ	WEHJIE
AFUKAP	DUYROF	HAJLIO	LAVTAF	OKIVAG	SEQSIS	WEHJOK
AGAXOV	EBATUY	HAJLOU	LAVTEJ	OKIVAG01	SEQSOY	WEMCEY
AGUVOO	EBEVAK	HAJLUA	LAVTEJ01	OKIVIO	SERCEZ	WEMDAV
AJAYIT	EBEWIT	HAJMAH	LAVTIN	OKIVIO01	SERKAC	WEVQIX
AJOVEB	EBEWOZ	HAJMEL	LAVTOT	OKIVIO02	SERKEG	WEVQOD
ALAMUW	EBEWOZ01	HAMREU	LAVTUZ	OKIWEL	SERWAP	WEVQUJ
ALIXAU	EBEXAM	HAMRIY	LAWGEW	OKIWEL01	SETPEO	WEVRUK
ALIXOJ	EBEXEQ	HANWAW	LAWGIA	OKIWEL02	SETSIV	WEZCIO
ALIXUP	EBEXEQ01	HAPHUD	LAWGOG	OKIWUB	SETSOB	WIBSAD
ALOLET	EBIDOK	HAPVAX	LAWGUM	OKIWUB01	SETTAO	WIFBAQ
ALOLIX	EBIHII	HAPVEB	LAZGOK	OKIXIQ	SEVLEM	WIHVEP
ALULEZ	EBIJAC	HAWWIN	LAZXOB	OKIXIQ01	SEWCED	WIKXUJ
ALULID	EBOJOV	HAWWOT	LECFAC	OKIXIQ02	SICZIP	WIKYQA
ALURAB	ECAHAT	HAWWUZ	LECFEG	OKIYAJ	SICZOV	WIYFAM
ALUREF	ECAHEX	HAXMUP	LECQEQ	OKIYIR	SINXET	WIZDAL
ALURIJ	ECAHOH	HEFDED	LEJCAG	OKIYIR01	SIQQEO	WIZDEP
AMAFOK	ECAHUN	HEHCOO	LEJCEK	OKIYIR02	SODZIV	WOBHEB
AMAGAX	ECODEG	HELDOT	LEJCIO	OKIYIR03	SOHGUS	WOBHEB01

AMOFAK	ECOKAJ	HETZUC	LEJRIC	OLEKUM	SOHMEI	WOBHIF
AMUWIP	ECOLEP	HEWFUL	LELDUD	OLUCAZ	SOHMUY	WOBHIF01
AMUWUB	ECUDIR	HEXVEM	LENGAO	OLURUI01	SOJGOO	WOBHIF02
ANUGEW	ECUDOX	HICVOG	LENKIA	ONEYOW	SOKKOT	WOBHOL
ANUGIA	ECUFAL	HIFTOG	LETPOR	ONIXOZ	SOMCON	WOJJOV
AQUCOF	ECUFEP	HIFTOG01	LETPUX	OPOBIF	SONVAT	WOLREV
AQUDAS	EDAVOV	HIFTOG02	LETQAE	OQANIE	SONVEX	WOLRIZ
ASACON	EDEPAG	HIFVOI	LETQAE01	OQEP UW	SONVIB	WOMFIO
ATAFIK	EDOVEA	HIGRIA	LETQEI	OQETEK	SOYWOT	WONZOP
ATIBAG	EDOVIE	HIHGAI	LETRAF	OQIQUB	SUGVUM	WONZUV
ATIBIO	EDUSIF	HIHGEM	LEV DIB	OQIQUB01	SUJNUH	WOQDUB
ATIBOU	EDUVOO	HIHNUJ	LEVLEF	OQIRAI	SUKNOC	WOZSOT
ATICAH	EFOSUO	HIMSAY	LIFWOO	ORAGEU	SUKNUI	WUHJIT
ATICEL	EFOTAV	HOGLEV	LIQCUK	OSIKIL	SUKPAQ	WUNSEE
ATOTIM	EFOTEZ	HOGLEV01	LODPOK	OSILOS	SUKYIH	WUNSEE01
AVAQIX	EFOTID	HOGTOM	LODPUQ	OTATOT	SUKYON	WUNSEE02
AVELOD	EGATEM	HOHMEX	LOFZUB	OTAVUB	SUNLET	WUNSII
AVELUJ	EGATIQ	HOMZEP	LOQLIN	OWAVIS	SUPLOF	WUNSII01
AVEMAQ	EGATOW	HOWPOZ	LOQSIU	OXAPEJ	TACPAP	WUNSII02
AVOSIO	EGEHOO	HOWPUF	LUCDAO	OXOLAP	TADYII	WUNTAB
AVUDAX	EHIAH	HOWQAM	LUCDES	OXUPUT	TAGSEB	WUNVEH
AWAWUR	EHUCOA	HOXGEH	LUCDIW	OYIVEY	TAMJAU	WUNVIL
AWEDOW	EKOPIE	HOZTOG	LUKLIN	OYUJUO	TAMJEY	WUTBES
AWEGEP	EKOPOK	HURGOR	LUMDEC	PADBAZ	TAPXIT	WUTBIW
AXINIF	EKOPUQ	HURGUX01	LUNBIF	PALTON	TAPXIT01	WUTBOC
AXUBOL	EKUPEG	HUXWAY	LUPYAX	PAMHIW	TAPXOZ	WUTBUI
AXUHAD	EMIFOW	HUYJOA	LUQGAG	PAMTII	TARWEO	WUTCAP
AXUHEH	EMIGEN	HUYJUG	LURGEL	PAMTOO	TASVUG	XACZEH
BAEDTA01	EMIGIR	HUYKAN	LUVTAY	PAMTUU	TASWOB	XADCOW
BAKJII	EMIGOX	HUYKUH	LUVTEC	PANYEK	TASYUJ	XADDAJ
BANMAG	EMIGUD	HUZFOY	LUXFEQ	PAPROO	TASZAQ	XADDEN
BARZUR	EMIHEO	HUZSOL	LUYHAP	PAPRUU	TASZEU	XADDIR
BASJUB	ENAFAB	HUZSOL01	MACHIJ	PARHAS	TATPOV	XADDOX
BAXSIE	ENAFOP	IBARUA	MACKAE	PARNIH	TAZLIR	XADDUD
BAZFUF	ENITAX	IBASAH	MAFJIO	PASNAA01	TAZLOX	XAFFAN
BAZGEQ	ENITOL	IBASEL	MAFZIE	PASTOU	TAZLUD	XAFFIV
BAZJET	EPEWAY	IBASOV	MAJHUC	PEGCIP	TEDGOA	XAFFUH
BEDYEQ	EPEWAY01	IBASUB	MAMVED	PEGQUP	TEDGUG	XAHPAZ
BELJIL	EPEWEC	IBATAI	MANLIX	PEJMUN	TEDHAN	XAHPED
BEPLUF	EPISOM	IBATEM	MARDAM	PEJPEB	TEFWIL	XAHPIH
BEPMAM	EQERAU	IBICAZ	MARJAQ	PEJRAZ	TEFWOR	XAHPON
BEPMEQ	EQEREY	IBICED	MARPOL	PELQII	TEMPAE	XAHPUT
BEPMIU	EQERIC	IBICIH	MARXEK	PELRIJ	TENLIJ	XAHQAA
BEPNIV	EQUBIC	IBICON	MAXFIA	PEMGIZ	TEQPAI	XAKQOR
BEPNOB	EQUBOI	IBICUT	MAYKOO	PEMREG	TEQPEM	XAKYUE
BEPNUH	EQUBUO	IBIDAA	MECWIB	PENNON	TEYHIP	XAKZAL
BEPPAP	EREGOY	IBOZIK	MEFJUE	PENNUT	TIRLIQ	XAKZEP

BEPPIX	ESEVIH	ICAGOK	MEGFIN	PEPFAT	TIRQOB	XAKZOZ
BEPPOD	ETAXUT	ICALUV	MEKDUC	PEQRUZ	TISHAF	XALBES
BEPRIZ	ETESIG	ICAMEG	METYIU	PETVEQ	TIVYAZ01	XALBIW
BEPROF	EVAKOB	ICAQIO	MEXJAC	PETWOC	TOHSAL	XALCAP
BEQFEK	EVOTIT	ICAQOU	MIBMER	PEVPUD	TOHYUL	XALCET
BETDIP	EWALUK	ICAREL	MICDEJ	PEVQAK	TOKDON	XALCUJ
BETDUB	EWUCOP	ICAROV	MIDCAF	PEVQIS	TONLOY	XALDAQ
BEWRUR	EXEQII	ICEGED	MIFNUM	PEVQOY	TONQOD	XALDEU
BEWSAY	EXEXAH	ICITEU	MIFPUO	PEWGEF	TUDQOZ	XALDIY
BEXPAX	EXOZIB	ICODIP	MIFQOJ	PEWKOT	UBULIO	XALDOE
BEXRUT	EYULOA	ICODIP01	MIFROK	PEWLUA	UBULUA	XALMII
BEXSAA	EZABEN	IDUDIW	MIFSAX	PEXTUI	UBUMAH	XALMOO
BEYSEF	EZOBUR	IFAGON	MIFSUR	PEYPAM	UCOCUM	XALTIP
BIBXOB	EZOBUR02	IFEHUY	MIFTEC	PEYVEV	UCOJAZ	XALXUF
BIBXUH	EZOFEF	IFENOY	MIFTIG	PIBNUK	UCOJED	XALXUF01
BICDAU	FAGREM	IFENOY01	MIFTUS	PIBNUK01	UDANAQ	XAMDUM
BICPUA	FAHFUR	IFENOY02	MIFVEE	PIBPAS01	UDICAN	XAMDUM01
BIMDOR	FAHGAY	IFENOY03	MIHLAR	PIBPEW	UDIDAO	XAMDUM02
BIWSEG	FAKLIO	IFEPUG	MIKJAR	PIBPEW01	UDOVUG	XAMDUM03
BIWSIK	FAKLOU	IFEQAN	MIMVEJ	PIBPIA	UFEXEJ	XAMDUM04
BOCKOT	FAKMAH	IFEQIV	MITSEO	PIHJOH	UFEXIN	XAMDUM05
BOJCIN	FAPTIB	IFEYIB	MITTAL	PIHWAG	UFIREI	XAMDUM06
BORBEQ	FAPTOH	IGAGUU	MOBBIO	PIJJOI	UFUQIV	XAMDUM07
BOXFOK	FAPTUN	IGAHAB	MOCKAR	PIYZAZ	UGAQEY	XANLUV
BUCSIC	FAPVAV	IJIROI	MOCKEV	POBMOJ01	UGOSOY	XAPDEY
BUFNEW	FAQGEL	IJOMOJ04	MODNOI	POBYAH	UJAQUS	XAVQIU
BUFNOG	FAQGIP	IJOMOJ06	MODNUO	POCPAZ	UJOWEW	XAVQIU01
BUFPAU	FARHIR	IKETOH	MOTMAK	POZHUI	UKIQIP	XAYMUF
BUFPAU01	FARHOX	IKOSOQ	MOXNUJ	PUJQEQ	UKIQOV	XEDGIY
BUKMUQ	FASHAK	IMISED	MOXPOF	PUQXUV	UKUBIM	XEDPED
BUSQEM	FASYUU	IMISIH	MOXPUL	PUQYAC	UKUBOS	XEDPON
BUVXOG	FATKIV	IMUTUG	MOYMET	PURJAO	UKUBUY	XEGKIF
BUVYEX	FAYKOH	IMUVAO	MOYYEF	PUSXIL	UKUCAF	XEJVOZ
BUVYIB	FAYPOM	INAMUG	MOYYIJ	PUSXIL01	UKUPUL	XENKIM
BUYNAL	FAYQUT	IPIDUH	MUDLON	PUTYAE	UMARAC	XESKAJ
CANRIU	FAZFET	IPIFAP	MUGFOK	PUWCEP	UNAZIT	XESKEN
CANROA	FAZPED	IRAGEN	MUJRIT	PUWDOA	UPOZAB	XESKIR
CANYIB	FAZZEM	ISOHEE	MURCIL	PUZLOM	UQULAU	XESKOX
CAVPEW	FEBXIV	ITIWIS	MURCOR	PUZLUS	UTEWOG	XESKUD
CAVPIA	FECKAA	ITIWOY	MUSCIN	QADBII	UTEWUM	XESLAK
CAVPUM	FECXAO	ITIWUE	MUVGOA	QAGQEW	UTEXAT	XIBZUF
CAVRAU	FECXES	IVEHEW	MUVGUG	QAMVEH	UTEXIB	XICNOO
CAVREY	FENVOL	IVETOT	MUVHAN	QAMVEH01	UVEVAT	XICNOO01
CAVSUP	FEQSIF	IWELIG	MUVHER	QASSUZ	UVEVEX	XICNOO02
CAWDOU	FERHAN	IWELIG01	MUWQEB	QATHOK	UVEVUN	XICYEP
CAWDOU02	FERVIJ	IWELOM	NABCEA	QATLEE	UVUFUN	XICYIT
CAWVIH	FERWAC	IXAJUN	NABMUA	QAVBUL	UVUPOR	XICZAM

CAXTUS	FESBIQ	IXAKAU	NABMUA01	QAYTOZ	UWAFOO	XIGFOJ
CAXVII	FEWQIJ	IXISAJ	NAJMIV	QEBGAH	UWAFUU	XINFUW
CAXVOO	FEWQOP	IXISOX	NAJZII	QEBGEL	UWAGAB01	XINRAP
CAXVUU	FEWWOV	IXUREZ	NALYEG	QEBKUF	UWAGAB02	XITYOP
CAXWAB	FEWWUB	IXUWII	NATXOW	QEFNAQ	UWAGAB04	XOJPIW
CAXWEF	FEXCES	IYIHUU	NAVJAW	QEGGUE	UWUTIQ	XOJWEZ
CAXWIJ	FEZCOD	IYOWID	NAVJAW01	QEPZUH	UXEQOE	XOVQEF
CAXZOS	FEZCUJ	IYUHUG	NAYHAY	QESYOD	UXUNUX	XUGWUS
CAYDEN	FEZREJ	IYUJAO	NAYKAB	QEWDON	UXUPEJ	XUKYEI
CAYDIR	FIDRIV	IYUQEZ	NAYZOE	QIGBIR	UXUPIN	XULCIR
CAYKEU	FIFMIS	IZEBAR	NAYZUK	QOPZIF	UYAPOA	XUTQEI
CAYQUQ	FIFMIS01	IZEPAF	NEDVOJ	QOVDEL	UYOFIY	XUVHEB
CAYSIE	FIFMOX	IZEPEJ	NEDVUP	QOVGOY	UYOXUC	YAPLIM
CAYSOK	FIFMOY	IZOWEA	NEGMUI	QOVGOY01	UZIJJ	YAPLOS
CAYYEG	FIFMUD	IZUMUM	NEGZUW	QOWQUO	VACFOV	YAPLUY
CECVAI	FIFNUE	JASNAT	NEHNEV	QOZDOY	VACFOV01	YAPMAF
CEGDUO	FIFNUE01	JEBCOJ	NEHZIK	QUBZIX	VACFUB	YAPRUE
CEHKUW	FIFPAM	JEJWEB	NEJSOM	QUDJOP	VACFUB01	YAPSAL
CEHLAD	FIFPAM01	JENKET	NENHAQ	QUGPAJ	VAGMEX	YAQDIF
CEKHIL	FIHHUB	JETZAK	NERVAJ	QULMIU	VAGTUU	YARBUQ
CENJIQ	FIJDOS	JEWCAP	NERVEN	QUNMUI	VAHPUR	YARGAB
CENKAJ	FIJFEK	JEWYAM	NESVAK	QUQFIS	VAHQAY	YARSAN
CEQBUV	FIMNIA	JISVAJ	NESVEO	QURSEC	VAKBIU	YAZFOW
CETGOY	FINQOK	JITPOS	NETFAU	QUSBIP	VARJEF	YEGCUJ
CETHEQ	FIQCEN	JIVFUQ	NEVVAM	QUSBIQ	VATXEU	YEGKOM
CETJAN	FIYDOH	JIVHIG	NEVVEQ	RABHIH	VAZROF	YEGTEK
CEXSEE	FONQIJ	JOHFIW	NEXDOK	RACHUA	VAZTOG	YEHGID
CEZFIY	FORWAL	JUCXEK	NEXVUI	RACHUA01	VEBHUG	YEKWOC
CIDKUX	FOXNIQ	JUTCUW	NEXXEV	RASXIT	VECWUX	YEKXET
CIFMEL	FUBDEM	KACZEV	NEYBEZ	RATNIL	VEDFAN	YELYOE
CIGFEF	FUBDIQ	KAGCAY	NIBHOW	RATRUB	VEDFER	YEMJAC
CIJBEE	FULQUZ	KALFIO	NIBHUC	RATSAI	VEDFIV	YEMLUY
CITZIP	FUNBEW	KALGAH	NIBJAK	RAVVUH	VEDFOB	YEMMAF
CIWRAC	FUNBIA	KANCIN	NIGDEO	RAVWAO	VEDGAO	YENLUA
CIWREG	FUNBOG	KANMIX	NIGDIS	RAVWES	VEDGES	YEVQOG
CIWROQ	FUNCEX	KARLIA	NIGNUO	RAVWIW	VEDGIW	YEYCUC
CIWRUW	FUQJUX	KARLUM	NIHBIQ	RAVWOC	VEDVUW	YEYFEP
CIWSAD	FURQOZ	KARMAT	NIHBIQ01	RAVWUI	VEFMAW	YEZFIU
CIXCAO	FURQOZ01	KARNAU	NIHBIQ02	RAVXAP	VEHJOJ	YEZKEV
COCMAJ	FURQUF	KASRAZ	NIJZIP	RAVXET	VEHJUP	YILJAG
COGNAO	FURRUG	KATDAM	NIJZIP01	RAYFAA	VEHKIE	YONNAR
COGWEB	FURRUG01	KAVJAT	NIJZOV	RAYFEE	VEHKOK	YOZBOF
COJHIT	FUSWIA	KAVJEX01	NIKDAM	RAYMIP	VEHNAZ	YOZQAG
COZMUA	FUSYUO	KAYCIY	NIKYUC02	RAYMOV	VEHXEN	YUBFOR
CUHPUR	FUTCAZ	KEBDIG	NINVAI	RAZGOQ	VEJHEZ	YUCZOM
CUNFOH	FUTDII	KEDQAN	NIZZAY	RAZXIA	VEMMAC	YUGLES
CUNFOH01	GACPUX	KEFBEE	NIZZEC	RAZYIC	VEMMEG	YUKBIP01

CUSDIE	GACQAE	KEFBII	NIZZIG	RAZYOI	VEMMIK	YURJUR
CUTFON	GADMAA	KEFBOO	NIZZOM	REBCAE	VEMTAJ01	YUXQIS
CUTFUT	GAJVIY	KEHGAH	NOCLOH	REDYEG	VEPDEB	YUXQOY
CUVHEH	GAMXAV	KEJBOQ	NOCLOH01	REGQUR	VEQBID	ZABQIC
CUVHIL01	GAQYIH	KEJHIQ	NOCLOH02	RESQAJ	VETMIS	ZARLEL
CUVTUJ	GATJIV	KEQDER	NOCLOH03	RESWOC	VETSOE	ZARLUB
CUVXAT	GAXKOH	KESBIU	NOFHOG	RETBEZ	VETTAR	ZARPUF
CUYWUP	GAXKUN	KESBIU01	NOKLIJ	REWLEM	VETTIZ	ZASJAG
DAJHOM	GAYFUJ	KESGAS	NUDLAA	REWNEO	VETVAS	ZASTUK
DAKVOC	GAYPED	KEWZOD	NUFTOY	REWNEO01	VEXTUO	ZECKID
DAKVUI	GAYTEH	KEYDEZ	NUGRIR	REXDOP	VEXVAW	ZECKOJ
DANZAV	GEBCAT	KEYYET	NUGROX	REZVAU	VEXYON	ZEDQEG
DANZEZ	GEDDAW	KIBXUP	NULMAJ	RIBDAJ	VEYREY	ZEDZAL
DANZID	GEDDEA	KIBYAW	NUTQAV	RIBDEN	VEZMIY	ZELROZ
DANZOJ	GEDREO	KIDDIM	NUTQEZ	RICBEM	VEZMOE	ZESFUY
DAPBIH	GEDSUF	KIFKEQ	NUVWEH	RIDCEN	VICYUD	ZESZEE
DAPXID	GEFYUN	KIGCEK	NUVWIL	RIFDUG01	VIDXOX	ZIDVAL
DARDEH	GEFZAU	KIJRUS	OBONUO	RIVDEF	VIGNOQ	ZILBAZ
DARDOR	GEDDED	KINFEU	OBUBOC	RONCIG	VIRPOC	ZILBIH
DATHAJ	GERNOI	KINJUO	OCAQOY	RUBTAK01	VIRVEY	ZILFOR
DAWCIP	GERPUP	KOCWEF	OCIFYUW	RUBTAK02	VIXCUB	ZIMTAS
DAWWEF	GERWEH	KOFPEB	ODIMAQ	RULQIY	VOCXUH	ZINDAD
DAXHUH01	GESBOW	KOFPEB01	ODIXEG	RULXUS	VODQIP	ZISYAD
DEBWAK	GESBUC	KOFPEB02	ODOXEK	RUMWUS	VODSEM	ZUQVAI
DEBWEO	GEVXIQ	KOFPEB03	OFABEZ	RUPRUQ	VUHJAK	ZUQVEM
DEFRIR	GEZRAG	KOFPEB04	OFEHAK	RUTPAY01	VUKHOZ	ZUQVIQ
DEGPEL	GIMSIG	KOFPEB05	OFEREX	RUVKAV	VUQJUN	ZUQVOW
DELGEI	GINLIA	KOHKIC	OFESAU	SACDOR	VUQJUN01	
DEQVIF	GITTUZ	KOHKOI	OFESEY	SACDUX	VUQKAU	
DEYLUQ	GITVEL	KOJZEP	OFESIC	SADLEQ	VUQKAU02	
DEYVUA	GITVEL01	KOJZIT	OFOCUI	SADLIU	VUSQIK	
DEZKAW	GITVIP	KUCDIW	OFODAP	SADLOA	WAFKAQ	

APPENDIX B: Supplementary Computational Results

Table B.1: Simulated excess CH₄ uptake at 298 K and all pressures considered in this study.

Common Name	CCDC Reference Code	Excess CH ₄ Uptake [cc(STP)/g]									
		1 bar	5 bar	10 bar	15 bar	20 bar	25 bar	30 bar	35 bar	50 bar	65 bar
Bio-MOF-1	NUDLAA	44.36	93.84	117.38	130.75	138.64	144.16	147.33	149.94	152.83	152.42
Bio-MOF-11	YUVSUE	21.68	59.30	71.60	76.16	78.13	78.84	79.18	78.98	77.01	74.26
Bio-MOF-12	BEYSEF	27.26	72.49	89.17	98.43	102.86	106.09	108.37	109.42	109.89	107.58
COF-10	YUTYOC	5.84	25.68	44.54	59.94	73.08	84.75	95.81	105.04	130.35	150.87
COF-5	RAYQAK	24.92	57.45	84.67	105.00	122.63	136.95	150.01	161.28	190.34	210.29
COF-6	YUTYIW	9.24	30.13	42.50	49.43	54.05	56.71	58.47	59.56	60.13	58.08
CPO-27-Co	SATNOR	16.89	71.81	107.95	124.20	135.26	142.77	148.11	152.80	159.37	159.72
CPO-27-Ni	LECQEQ	15.42	65.05	99.45	117.52	128.41	135.29	140.83	144.66	150.92	152.43
CuBDC	AJIHOQ	22.48	71.64	115.53	146.05	167.45	182.44	194.94	202.90	219.73	226.37
HKUST-1	LUKLIN	22.78	70.76	113.36	143.55	164.81	179.99	191.50	201.13	217.15	225.29
Cu-TDPAT	XALXUF01	22.28	82.99	129.27	160.38	182.35	196.88	209.42	219.00	234.06	241.81
DEFKUU	DEFKUU	27.26	54.45	64.86	70.19	73.75	75.81	76.81	78.41	79.09	77.85
IJOMOJ02	IJOMOJ02	10.55	30.34	37.57	40.13	41.17	41.41	41.27	41.00	39.00	36.63
JOKYAJ	JOKYAJ	4.25	14.91	21.23	24.52	26.41	27.46	28.30	28.47	27.78	26.68
JOKYEN10	JOKYEN10	4.32	15.08	21.46	24.64	26.60	27.48	28.05	28.00	27.32	25.26
JOKYIR10	JOKYIR10	4.15	14.53	20.83	23.95	25.76	26.74	27.02	27.29	26.47	24.57
JOKYOX	JOKYOX	4.24	14.60	20.99	23.95	25.67	26.61	26.86	27.06	26.16	24.14
KEXFIC10	KEXFIC10	3.58	13.34	19.93	23.43	25.40	26.43	27.11	27.50	26.63	25.00
LAMGUB	LAMGUB	3.74	13.81	20.53	24.09	26.21	27.12	27.90	28.36	27.38	25.60
MOF-5	SAHYIK	9.38	46.53	90.62	131.02	165.89	195.12	219.80	240.25	280.41	302.42
NTU-105	XEBIL00	20.18	82.37	139.23	180.26	210.57	233.38	250.98	264.71	291.19	304.39
NU-125	REWNEO	19.93	81.28	137.37	178.89	210.02	233.06	252.09	265.39	294.94	308.65
NUJCIE	NUJCIE	2.31	8.21	11.76	13.41	14.19	14.49	14.21	13.81	12.03	9.30
OHETIE	OHETIE	4.53	22.59	44.71	64.94	83.09	99.48	112.58	124.32	149.13	162.96
PCN-11	MOCKAR	21.20	82.46	128.46	156.65	175.99	189.42	199.43	206.57	220.28	224.75
PCN-14	XITYOP	34.73	102.05	138.02	157.60	169.30	177.76	182.89	187.01	192.42	193.09
PCN-26	GEGDED	21.99	65.26	100.89	124.37	141.30	152.05	162.05	168.76	179.55	184.02
PCN-46	LUYHAP	15.45	62.92	108.83	143.64	170.59	191.29	207.87	220.56	245.42	255.09
PCN-80	WAMREJ	10.20	44.19	76.87	102.54	123.95	141.65	155.98	168.02	194.40	209.11
SUDBOI	SUDBOI	13.76	40.17	52.82	58.76	62.23	64.32	65.44	66.04	65.51	63.15
UHAXUW	UHAXUW	24.18	39.20	42.82	43.70	44.34	44.02	43.66	43.10	41.35	39.71
UTSA-20	ONIXOZ	39.40	110.07	144.30	161.44	172.46	179.61	185.32	188.97	193.83	194.21
YARYEV	YARYEV	4.53	20.16	35.51	47.01	55.99	62.86	67.60	71.73	78.71	81.85
YIZWIN	YIZWIN	3.75	13.42	19.39	22.33	24.05	24.96	25.59	25.74	24.63	22.75
ZIF-10	VEJZIU	12.46	55.84	95.78	123.19	142.37	155.98	167.04	174.31	188.12	193.49
ZIF-2	VEJYIT	33.35	94.33	121.37	133.62	140.35	144.80	147.65	148.25	149.68	147.33
ZIF-3	VEJYOZ	28.33	86.53	124.36	144.61	156.03	163.74	168.25	171.40	174.28	172.42
ZIF-6	EQOCOC01	16.12	64.42	103.64	129.09	146.20	158.24	166.96	173.46	183.28	186.95
ZIF-60	GITSUY	11.81	53.06	91.38	118.19	137.56	151.41	161.86	169.31	182.69	187.81

ZIF-68	GITTUZ	11.40	41.01	60.20	71.43	79.03	84.32	88.35	90.88	95.47	96.23
ZIF-69	GITVAH	23.54	60.69	78.02	86.93	92.00	95.80	97.82	99.49	101.70	100.74
ZIF-78	YOZBIZ01	10.20	36.69	54.58	65.11	71.65	76.01	79.21	81.81	84.29	84.20
ZIF-79	YOZBOF01	13.45	47.24	67.52	78.34	84.71	89.15	91.29	93.18	94.51	93.78
ZIF-81	YOZCAS	9.50	33.49	48.19	56.54	62.04	65.37	67.93	69.95	72.16	71.83
Zn(bdc)(ted) _{0.5}	WAFKAQ	31.73	105.14	140.27	156.04	164.47	170.11	173.53	175.54	176.30	174.15

Table B.2: Simulated isosteric heat of adsorption values at 298 K and all pressures considered in this study.

Common Name	CCDC Reference Code	Isosteric Heat of Adsorption (kJ/mol)									
		1 bar	5 bar	10 bar	15 bar	20 bar	25 bar	30 bar	35 bar	50 bar	65 bar
Bio-MOF-1	NUDLAA	19.99	16.48	16.39	16.41	16.14	16.64	16.49	16.56	16.82	16.17
Bio-MOF-11	YUVSUE	19.29	19.54	19.35	19.52	19.02	18.70	18.87	18.55	17.87	17.10
Bio-MOF-12	BEYSEF	20.24	21.40	21.69	22.03	21.98	21.78	21.92	21.76	22.03	22.23
COF-10	YUTYOC	11.33	10.95	10.49	10.13	9.87	9.61	9.29	9.23	9.02	9.01
COF-5	RAYQAK	17.33	12.74	11.50	11.25	10.78	10.63	10.48	10.34	10.34	10.47
COF-6	YUTYIW	16.05	16.46	16.69	16.81	17.00	16.95	17.05	17.02	17.12	17.06
CPO-27-Co	SATNOR	15.19	16.27	17.03	17.38	17.56	17.51	17.59	17.28	17.24	17.58
CPO-27-Ni	LECQEQ	15.12	15.95	16.45	16.59	16.89	17.03	17.21	16.80	16.47	16.55
CuBDC	AJIHOQ	15.88	14.09	14.50	14.58	14.67	14.94	15.14	15.38	15.43	15.46
HKUST-1	LUKLIN	15.64	13.99	14.19	14.48	14.40	14.78	14.68	14.80	14.79	15.02
Cu-TDPAT	XALXUF01	15.79	15.19	15.07	15.04	15.00	15.18	15.17	15.30	15.44	15.48
DEFKUU	DEFKUU	21.01	20.91	21.47	21.27	21.72	21.30	21.18	20.96	20.94	20.50
IJOMOJ02	IJOMOJ02	19.68	20.08	20.03	19.90	19.63	19.42	19.31	18.99	18.31	17.83
JOKYAJ	JOKYAJ	17.19	17.30	17.40	17.41	17.47	17.37	17.41	17.42	17.37	17.34
JOKYEN10	JOKYEN10	17.18	17.36	17.51	17.48	17.52	17.45	17.50	17.52	17.44	17.33
JOKYIR10	JOKYIR10	17.28	17.47	17.52	17.58	17.65	17.62	17.56	17.54	17.46	17.43
JOKYOX	JOKYOX	17.52	17.68	17.77	17.83	17.89	17.80	17.83	17.84	17.73	17.71
KEXFIC10	KEXFIC10	17.45	17.71	17.91	17.99	18.16	18.06	18.23	18.07	18.22	17.95
LAMGUB	LAMGUB	17.25	17.52	17.68	17.78	17.86	17.97	17.95	17.93	18.03	18.00
MOF-5	SAHYIK	10.82	11.04	11.33	11.65	11.99	12.27	12.69	12.80	13.49	13.89
NTU-105	XEBIL00	14.16	13.51	13.39	13.15	13.39	13.37	13.46	13.08	13.20	13.05
NU-125	REWNEO	14.24	13.13	12.99	13.03	13.04	12.80	12.79	12.96	12.78	13.04
NUJCIE	NUJCIE	16.92	17.19	17.40	17.59	17.57	17.62	17.60	17.60	17.62	17.10
OHETIE	OHETIE	9.86	10.25	10.71	11.14	11.55	11.85	12.18	12.43	13.03	13.54
PCN-11	MOCKAR	15.49	15.49	15.82	16.25	16.34	16.34	16.74	16.58	16.81	16.98
PCN-14	XITYOP	17.72	17.09	17.26	17.09	17.04	16.86	16.90	16.66	16.97	15.92
PCN-26	GEGDED	16.80	14.83	15.24	15.60	15.72	15.84	15.95	16.03	16.18	16.22
PCN-46	LUYHAP	14.03	12.97	12.99	13.32	13.37	13.56	13.79	13.98	14.40	14.42
PCN-80	WAMREJ	12.38	12.14	11.93	11.68	11.72	11.71	11.63	11.83	11.97	12.12
SUDBOI	SUDBOI	17.58	18.08	18.32	18.50	18.44	18.51	18.42	18.26	17.97	17.86
UHAXUW	UHAXUW	23.91	24.17	23.99	23.65	23.06	23.07	22.65	22.51	21.76	21.53
UTSA-20	ONIXOZ	18.92	18.10	17.08	16.70	15.71	15.56	15.46	15.42	15.49	15.51
YARYEV	YARYEV	13.41	13.63	13.86	14.05	14.21	14.36	14.45	14.52	14.67	14.81
YIZWIN	YIZWIN	17.71	17.78	17.90	17.92	17.85	17.97	17.91	17.91	17.89	17.80
ZIF-10	VEJZIU	13.80	13.84	14.03	13.94	14.00	14.09	14.27	14.24	14.40	14.71
ZIF-2	VEJYIT	17.51	18.50	18.77	19.00	19.05	19.02	18.86	18.90	18.53	18.25
ZIF-3	VEJYOZ	18.06	17.06	17.33	17.68	17.74	17.78	17.87	18.19	17.96	17.92
ZIF-6	EQOCOC01	14.25	14.14	14.24	14.45	14.66	14.78	15.06	15.07	15.46	15.62
ZIF-60	GITSUY	13.59	13.80	13.97	14.06	14.38	14.52	14.61	14.92	14.97	15.25
ZIF-68	GITTUZ	16.13	15.86	15.58	15.28	15.26	15.22	15.38	15.17	15.53	15.52
ZIF-69	GITVAH	19.15	18.37	18.43	18.00	18.38	18.16	18.20	17.86	18.17	18.42

ZIF-78	YOZBIZ01	17.17	17.22	17.09	17.23	16.94	17.11	17.05	17.32	17.35	17.15
ZIF-79	YOZBOF01	17.17	17.31	17.51	17.48	17.26	17.64	17.49	17.21	17.68	17.32
ZIF-81	YOZCAS	16.87	16.69	16.71	16.64	16.47	16.54	16.75	16.66	16.59	16.84
Zn(bdc)(ted) _{0.5}	WAFKAQ	16.87	17.89	18.42	18.62	18.65	18.49	18.55	18.43	18.51	18.23

Multivariable Linear Models (Model-0) for Predicting CH₄ Uptake

Table B.3: Parameters of the QSPR multivariate linear regression models (Model-0) and their statistical model analysis.

Pressure (bar)	# of Variables	Regression Coefficients ^{a,h}										R ² ^e	$\bar{R}^{2f}$	STD ^g
		ρ_{cryst}^b a	V_p^b b	V_f^b c	S_g^c d	PLD ^b e	MPD ^b f	DPD ^b g	Q_{st}^d h	i				
1	4	-20.57	-24.88	126.33	-	-	-	-	4.87	-102.17	0.88	0.86	3.93	
	3	-9.91	-	90.21	-	-	-	-	5.02	-110.57	0.84	0.82	4.44	
	2	-	-	125.44	-	-	-	-	5.24	-146.39	0.82	0.81	4.57	
	1	-	-	-	-	-	-	-	1.65	-10.71	0.18	0.16	9.75	
5	4	-61.67	-60.56	408.66	-	-	-	-	12.32	-290.13	0.85	0.84	11.60	
	3	-34.31	-	338.73	-	-	-	-	13.22	-331.37	0.82	0.81	12.56	
	2	-	-	462.33	-	-	-	-	13.92	-455.06	0.80	0.79	13.20	
	1	-	-	-	0.02	-	-	-	-	27.26	0.38	0.37	22.72	
10	4	-66.67	-57.83	499.09	-	-	-	-	14.02	-355.71	0.86	0.85	13.82	
	3	-	-	447.63	0.01	-	-	-	14.42	-458.02	0.85	0.84	14.39	
	2	-	-	579.26	-	-	-	-	15.71	-542.07	0.82	0.82	15.31	
	1	-	-	-	0.03	-	-	-	-	30.80	0.50	0.57	25.47	
15	4	-36.39	-	407.60	0.01	-	-	-	14.58	-385.35	0.87	0.88	15.81	
	3	-	-	487.25	0.02	-	-	-	14.62	-479.63	0.86	0.87	16.26	
	2	-	-	652.62	-	-	-	-	16.17	-584.02	0.83	0.84	17.61	
	1	-	-	-	0.03	-	-	-	-	32.56	0.58	0.67	27.15	
20	4	-34.93	-	467.75	0.02	-	-	-	14.62	-416.74	0.89	0.88	17.79	
	3	-	-	542.95	0.02	-	-	-	14.62	-505.92	0.88	0.87	18.10	
	2	-	-	756.91	-	-	-	-	16.41	-636.48	0.85	0.84	20.39	
	1	-	-	-	0.04	-	-	-	-	33.80	0.68	0.72	29.17	
25	4	-	-	574.43	0.02	-	-	1.56	15.55	-544.60	0.89	0.90	19.99	
	3	-	-	569.81	0.02	-	-	-	13.78	-502.31	0.88	0.89	20.46	
	2	-	-	813.47	-	-	-	-	15.64	-647.26	0.85	0.86	23.29	
	1	-	-	-	0.05	-	-	-	-	33.84	0.73	0.75	30.64	
30	4	-	-	623.41	0.02	-	-	2.01	16.31	-584.74	0.91	0.91	20.12	
	3	-	-	615.96	0.03	-	-	-	13.87	-526.43	0.90	0.90	21.00	
	2	-	-	871.02	-	-	-	-	15.64	-674.60	0.86	0.86	24.21	
	1	-	-	-	0.06	-	-	-	-	33.38	0.75	0.76	32.01	
35	4	-	-	676.23	0.03	-	-	2.91	16.70	-620.92	0.92	0.91	21.56	
	3	-	-	662.16	0.03	-	-	-	12.76	-527.60	0.90	0.90	23.27	
	2	-	-	922.83	-	-	-	-	14.35	-674.21	0.87	0.87	26.53	
	1	-	-	-	0.06	-	-	-	-	31.92	0.78	0.77	34.70	
50	4	-	-	716.54	0.02	-	-	3.87	16.71	-646.19	0.93	0.92	22.38	
	3	-	158.49	580.07	-	-	-	-	16.44	-596.08	0.92	0.91	24.45	
	2	-	-	961.30	-	-	-	-	12.47	-659.10	0.88	0.88	28.38	
	1	-	-	713.61	-	-	-	-	-	-303.51	0.82	0.82	34.60	
65	4	-	-	684.22	0.02	-	-	3.93	14.24	-585.25	0.93	0.92	24.51	
	3	-	177.76	515.94	-	-	-	-	14.33	-531.29	0.92	0.91	25.78	
	2	-	-	946.10	-	-	-	-	9.67	-600.33	0.88	0.87	30.36	
	1	-	-	768.07	-	-	-	-	-	-333.61	0.85	0.84	33.91	

^a Multivariable linear models are constructed as $N_{CH_4} \left(\frac{cc(STP)}{g} \right) = a \times \rho_{cryst} + b \times V_p + c \times V_f + d \times S_g + e \times PLD + f \times MPD + g \times DPD + h \times Q_{st} + i$

^b Computed using PoreBlazer software by Sarkisov. V_f : Void Fraction, V_p : Pore Volume, PLD: Pore Limiting Diameter, MPD: Maximum Pore Diameter, DPD: Dominant Pore Diameter

^c Accessible Gravimetric Surface Area computed using the code from the work by Düren et. al

^d Q_{st} : Isoteric Heat of Adsorption computed by GCMC simulation at 298 K and 5,35 bar

^e Correlation coefficient (R-squared)

^f Adjusted R-squared (described below)

^g Standard deviation

^h Units of regression coefficients are adjusted to give cc/g

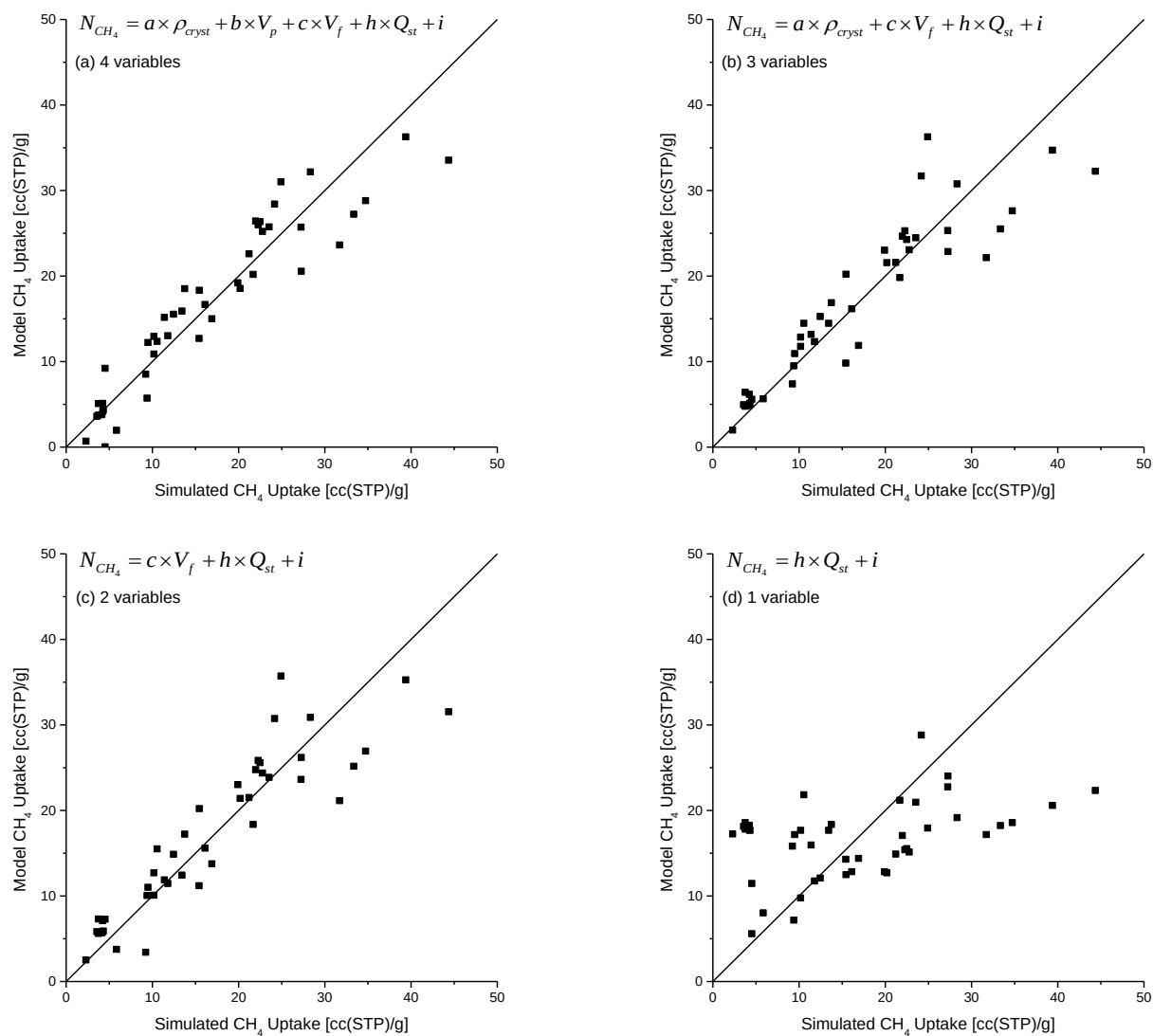


Figure B.1: Comparison of models and simulations for CH_4 uptake at 298 K and 1 bar.

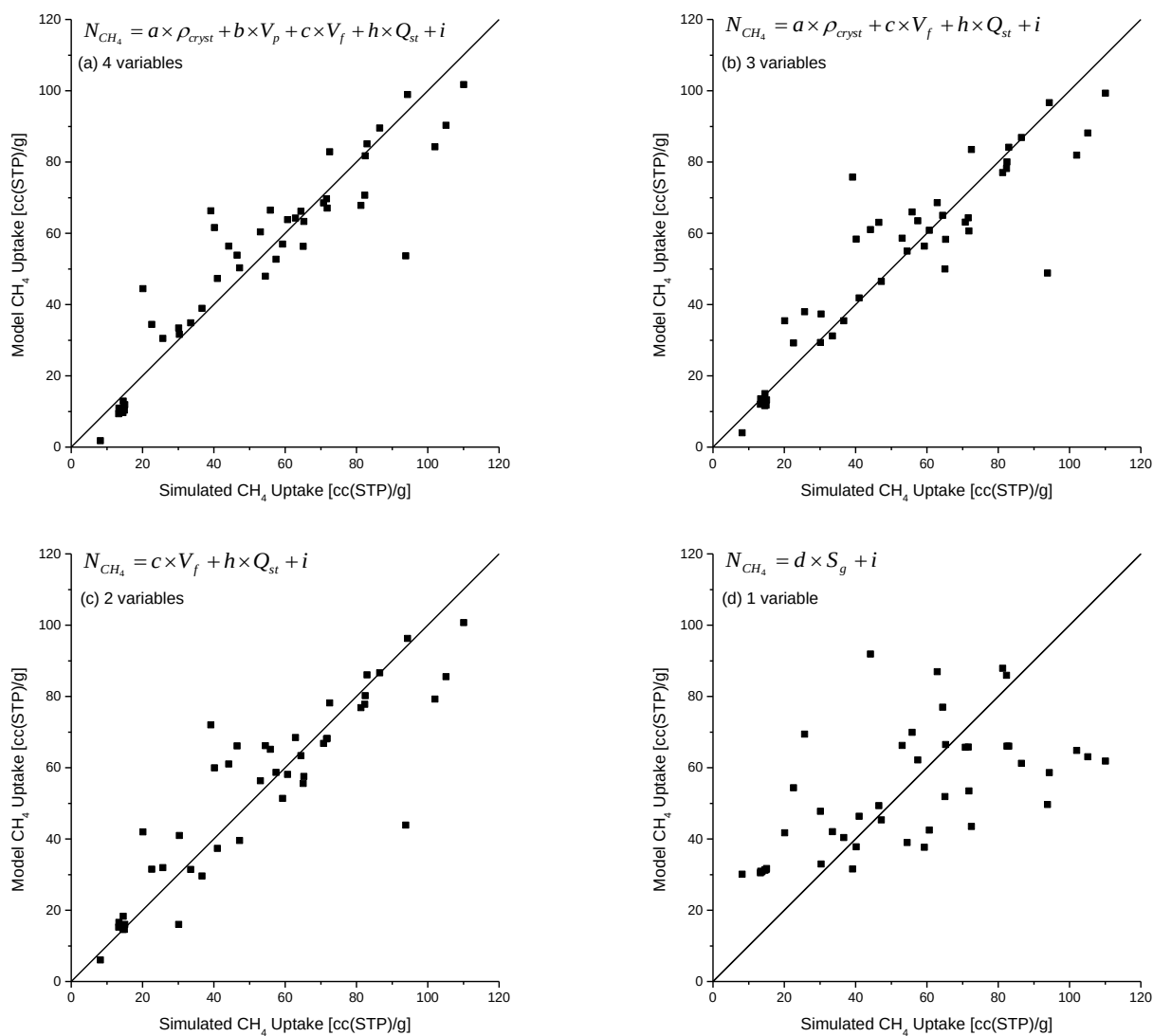


Figure B.2: Comparison of models and simulations for CH_4 uptake at 298 K and 5 bar.

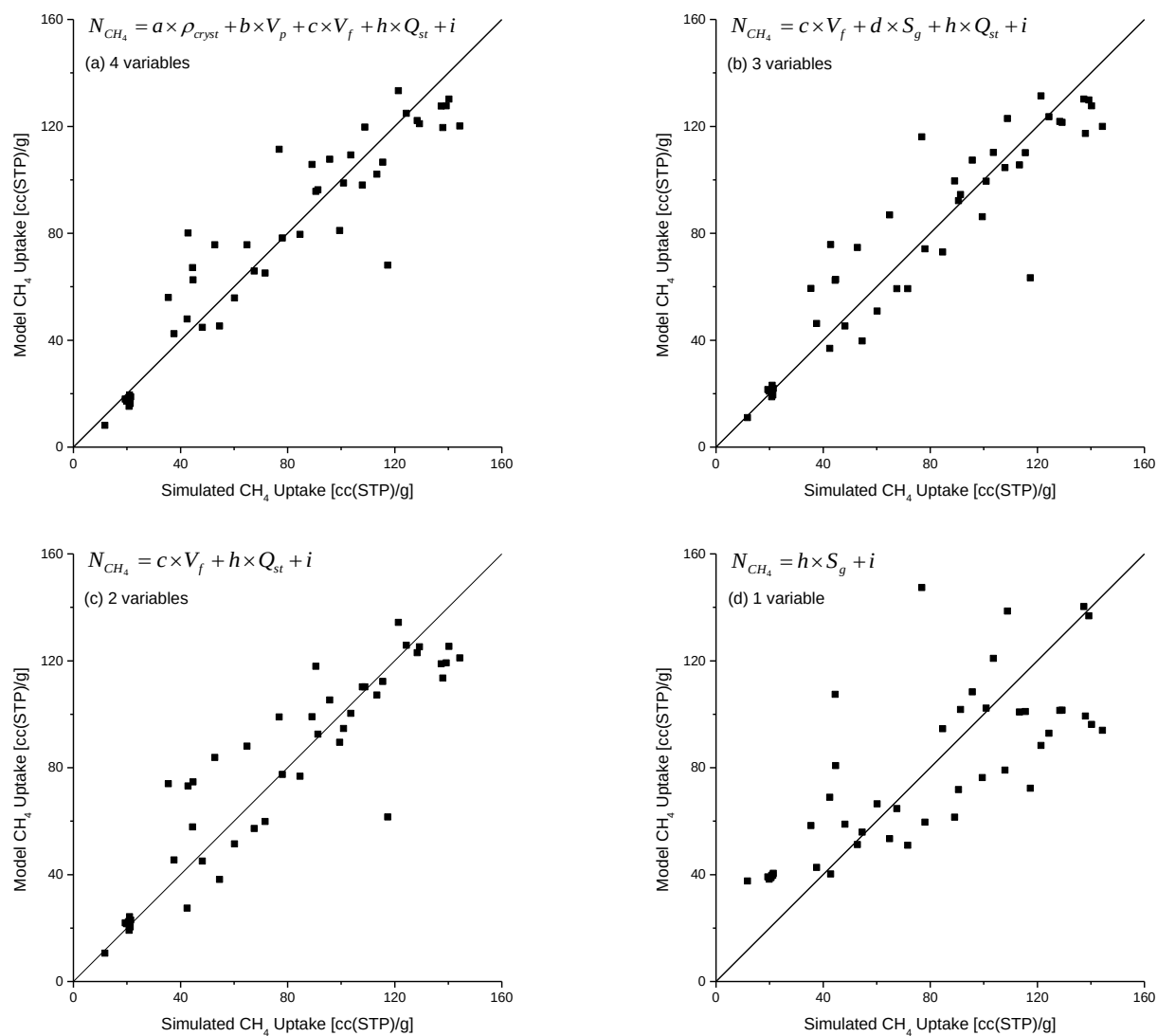


Figure B.3: Comparison of models and simulations for CH_4 uptake at 298 K and 10 bar.

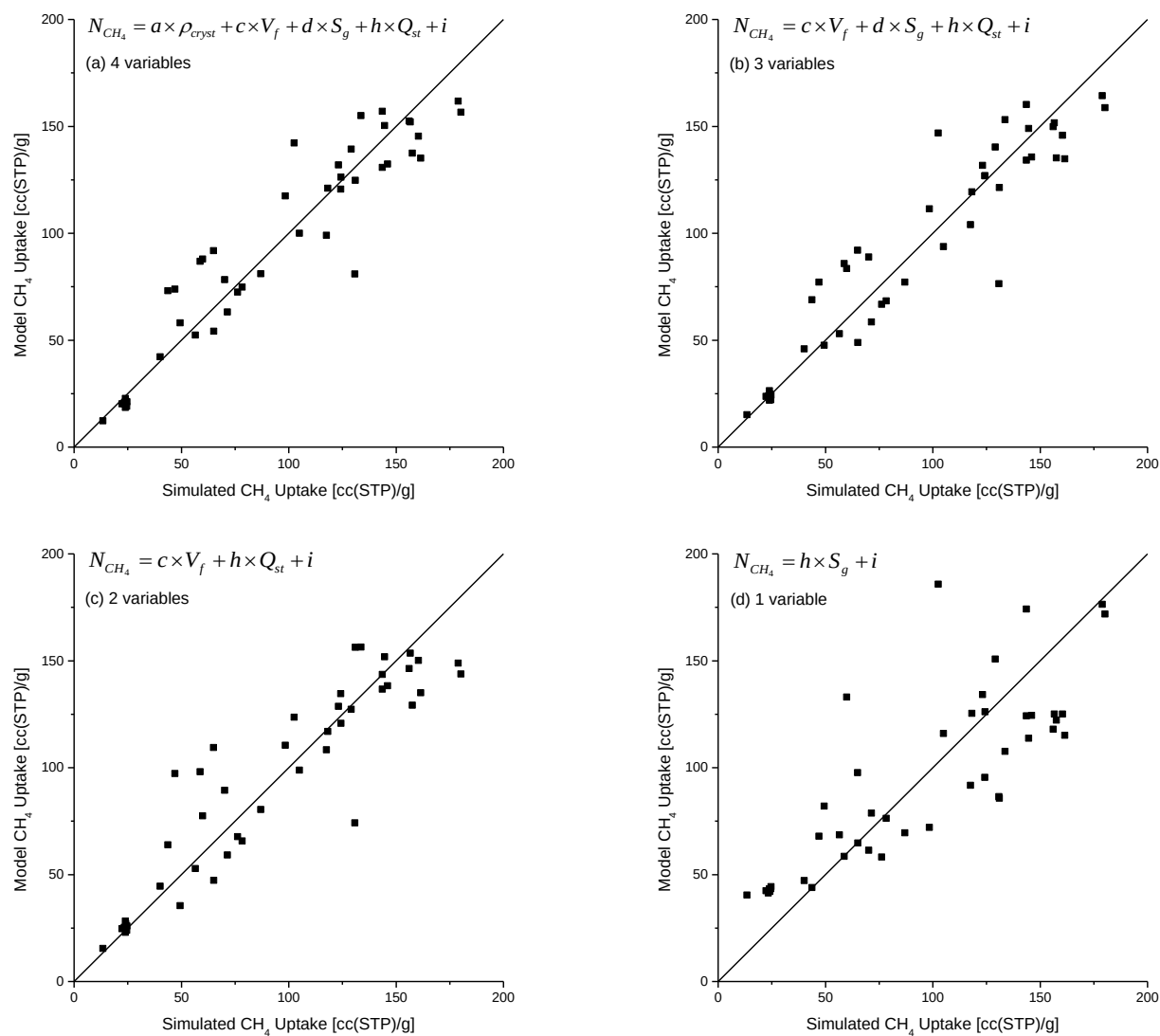


Figure B.4: Comparison of models and simulations for CH_4 uptake at 298 K and 15 bar.

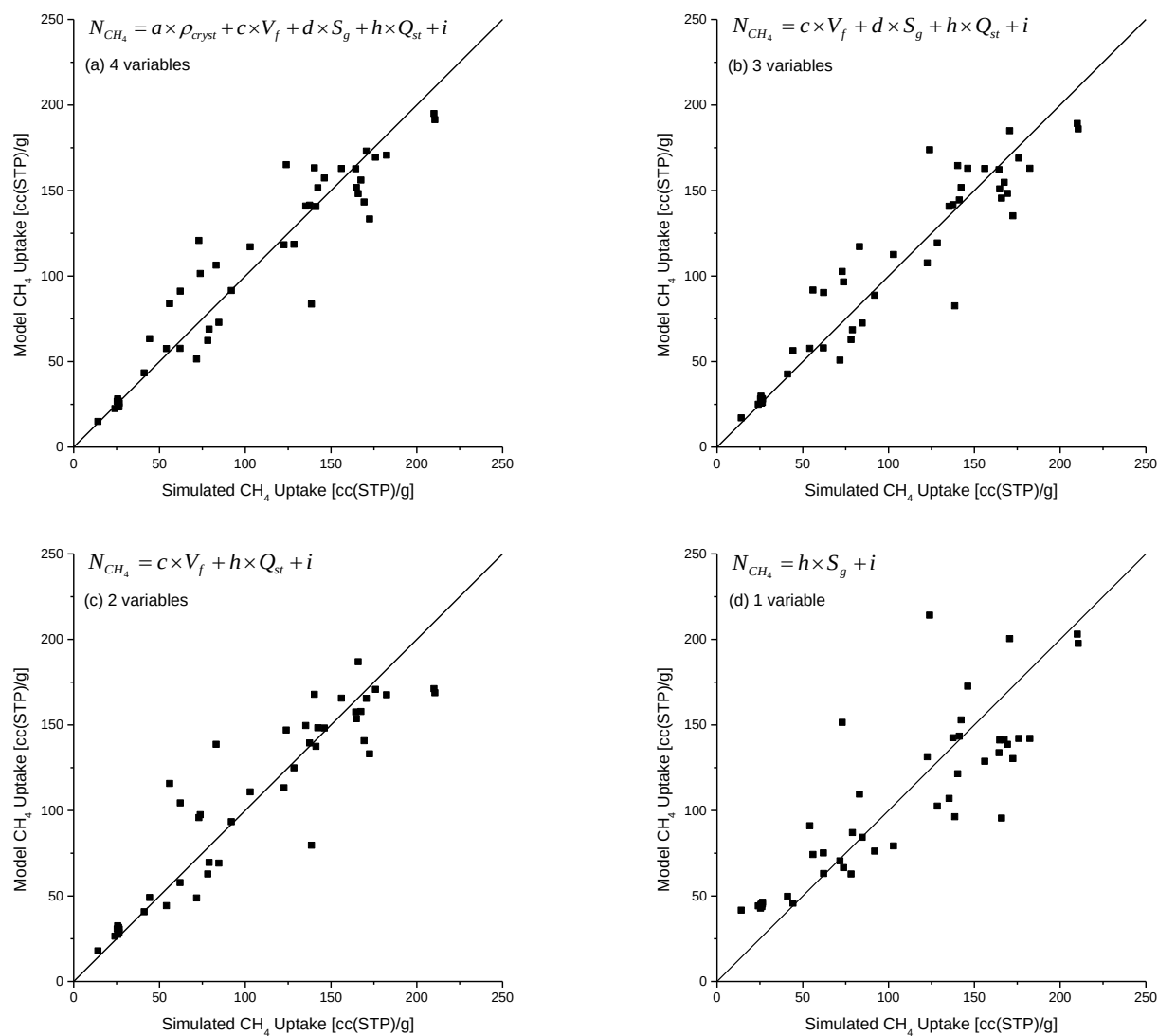


Figure B.5: Comparison of models and simulations for CH_4 uptake at 298 K and 20 bar.

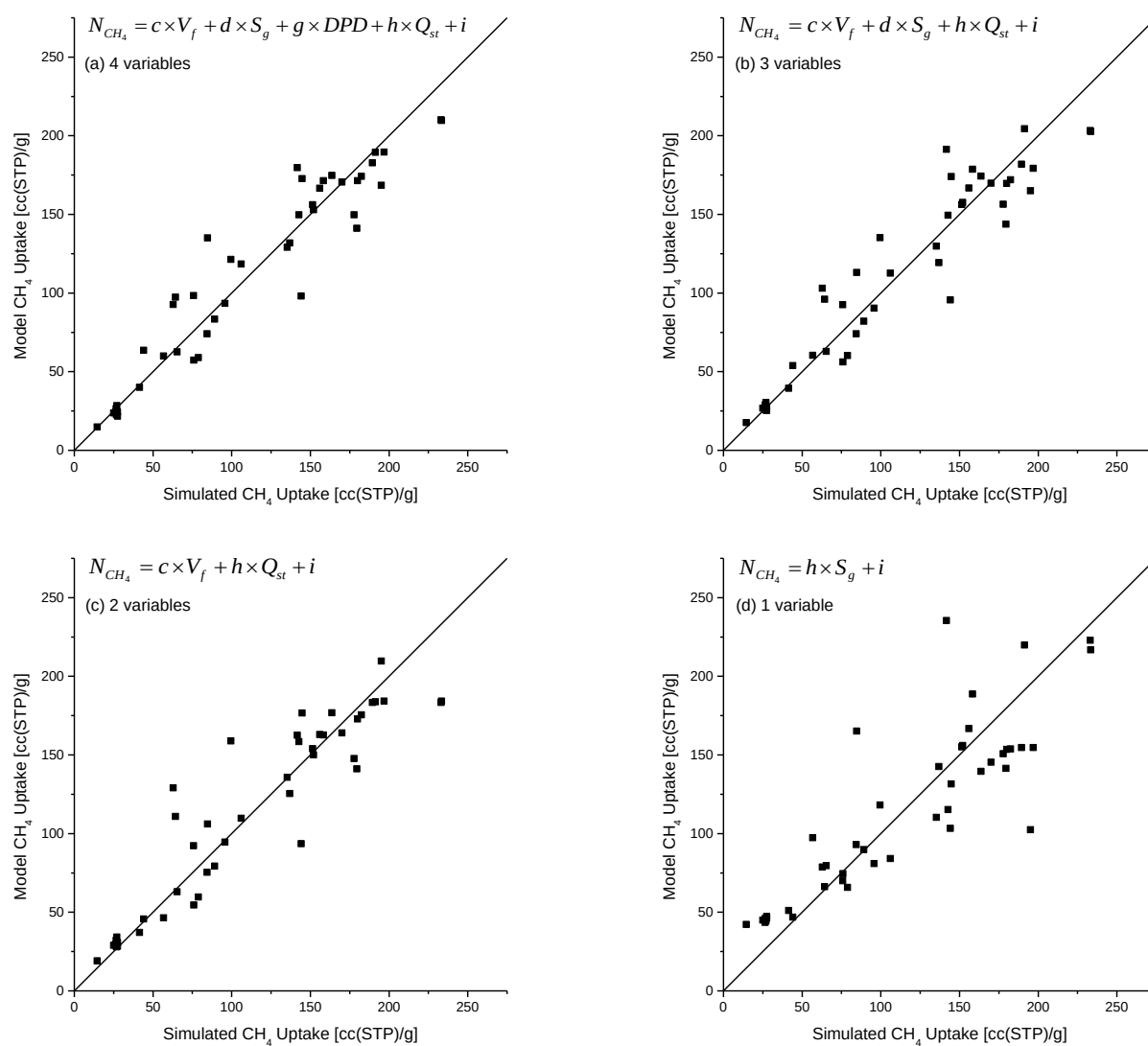


Figure B.6: Comparison of models and simulations for CH_4 uptake at 298 K and 25 bar.

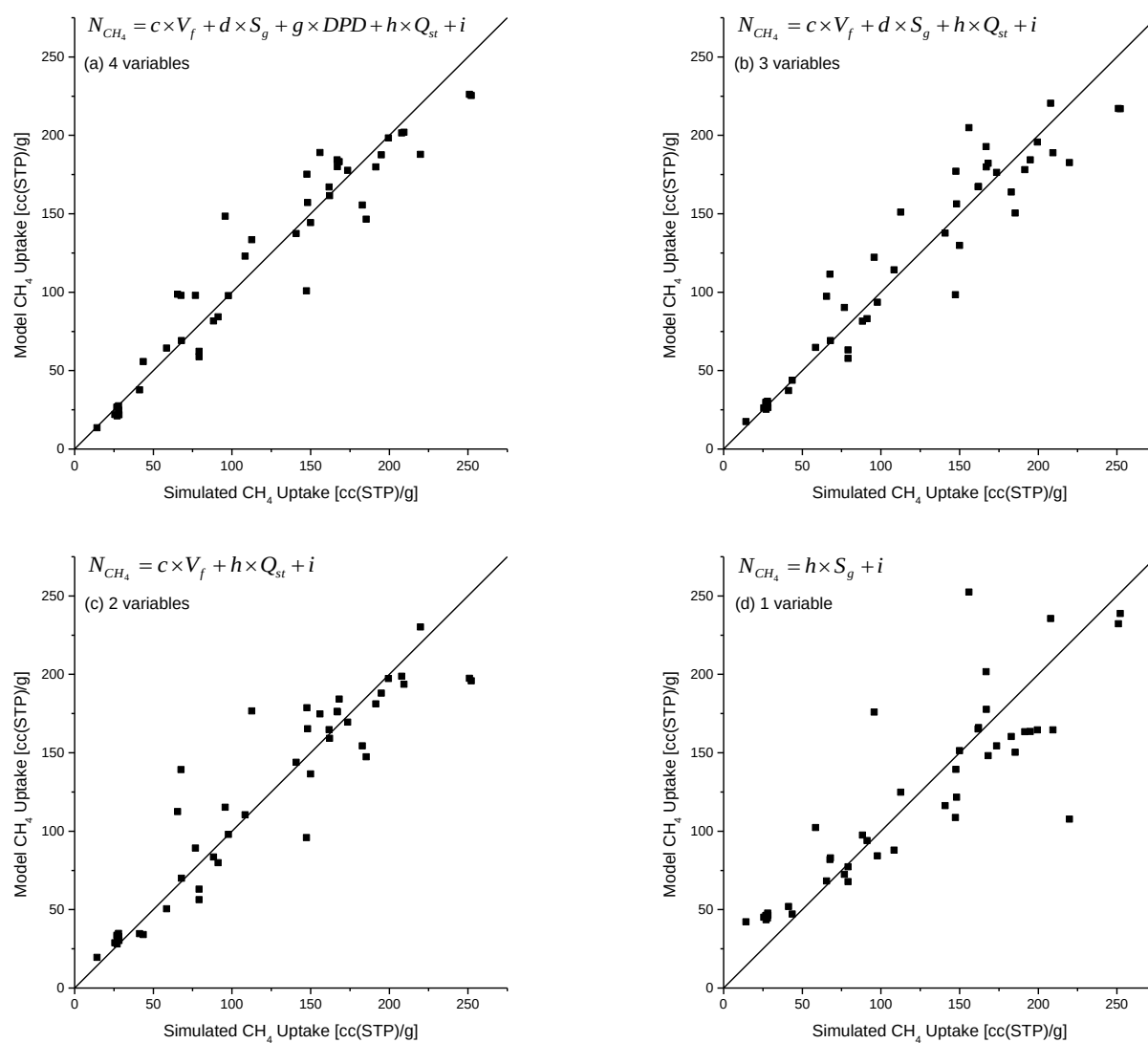


Figure B.7: Comparison of models and simulations for CH₄ uptake at 298 K and 30 bar.

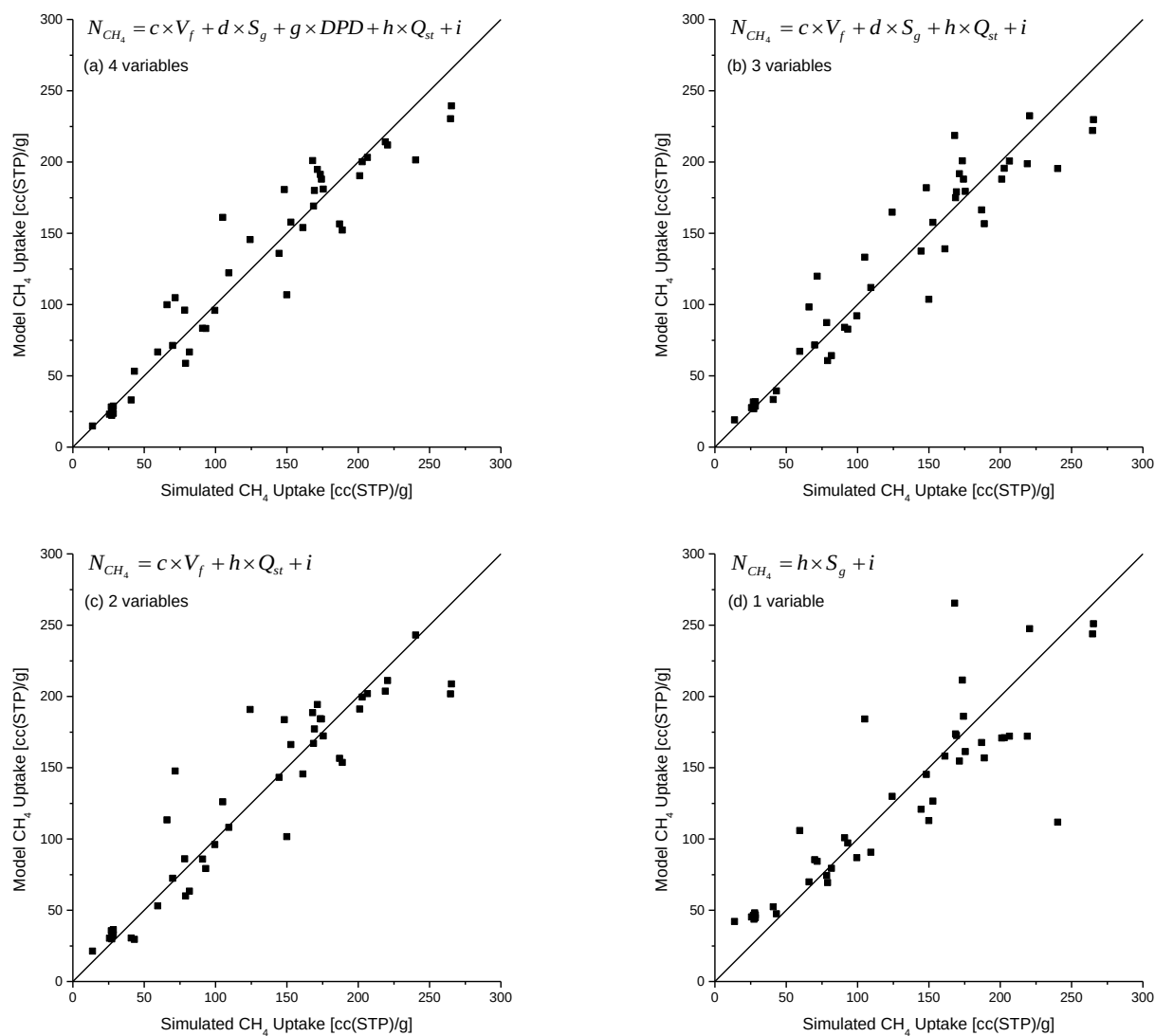


Figure B.8: Comparison of models and simulations for CH_4 uptake at 298 K and 35 bar.

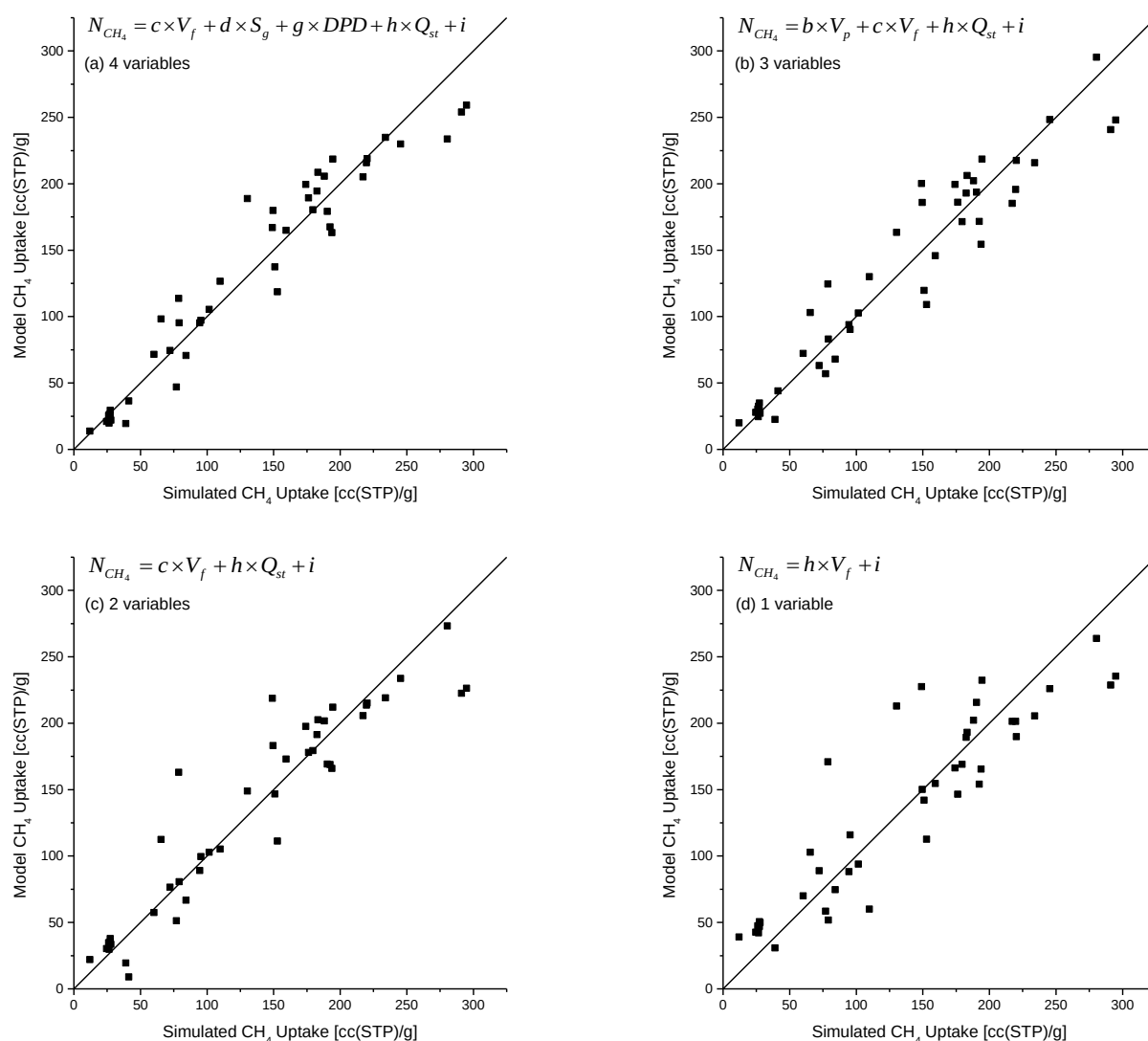


Figure B.9: Comparison of models and simulations for CH₄ uptake at 298 K and 50 bar.

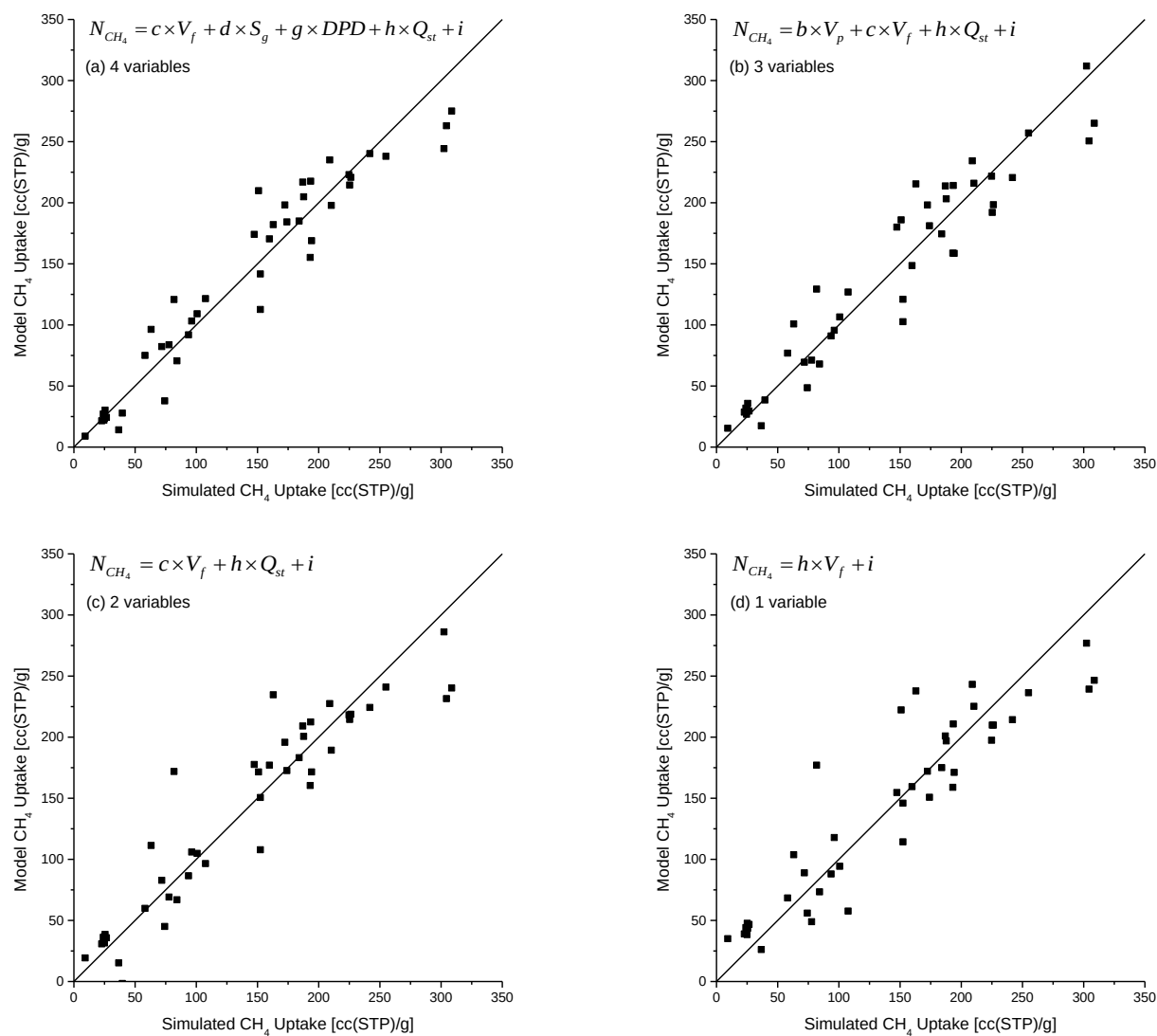


Figure B.10: Comparison of models and simulations for CH_4 uptake at 298 K and 65 bar.

Model Restrictions

The structural and chemical parameters used for the modelling study have physical limitations and when the models are used for the prediction of CH₄ storage these limitations should be considered. As long as the parameters are within restrictions determined by the physical limitations models can perform accurately. The physical limitations for the low bound of density and upper bounds of pore diameter, BET surface area, pore volume, are taken from previously reported typical properties of MOFs by Yaghi et al.[178]. Other limitations are determined from the MOFs examined in this study and conventional properties of MOFs to best of our knowledge.

Table B.4: Minimum and maximum values for the parameters of the models (model restrictions).

Property	Minimum	Maximum	Unit
Density (ρ_{cryst})	0.1	3.0	g/cm ³
Surface Area (S_g)	100	10000	m ² /g
Pore Volume (V_p)	0.1	5.0	cm ³ /g
Void Fraction (V_f)	0.1	1.0	-
Dominant pore diameter (DPD)	4.0	100	Å
Isosteric heat of adsorption (Q_{st})	10	30	kJ/mol

It should be noted that when the minimum values are used simultaneously in the model negative uptake results can be obtained. This arises from the fact that it is not possible for a MOF to have all of these minimum/maximum values for its properties at the same time. There are certain trends such as a negative correlation between Q_{st} and V_f which prevents this type of behavior. Therefore, as long as data belonging to a real MOF structure is used meaningful and accurate results can be obtained.

Simple Linear Regression Models for Predicting Isothermic Heat of Adsorption (Q_{st})

Table B.5: Parameters of the simple linear regression models to predict isothermic heat of adsorption (Q_{st}) and their statistical model analysis.

Pressure (bar)	Regression Coefficients ^{a,e}				R^2 ^c	STD ^d
	V_p ^b a	V_f ^b b	MPD ^b c	d		
1	-	28.46	-	-19.65	0.56	1.80
5	-	30.48	-	-23.38	0.71	1.55
10	-	30.78	-	-23.74	0.71	1.59
15	21.40	-	-	-7.67	0.70	1.62
20	21.34	-	-	-7.58	0.70	1.58
25	21.30	-	-	-7.48	0.71	1.53
30	21.26	-	-	-7.36	0.70	1.53
35	21.08	-	-	-7.16	0.70	1.50
50	20.88	-	-	-6.80	0.68	1.49
65	-	-	19.85	-0.38	0.67	1.44

^a Multivariable linear models are constructed as $Q_{st} \left(\frac{kJ}{mol} \right) = a \times V_p + b \times V_f + c \times MPD + d$

^b V_f : Void Fraction, V_p : Pore Volume, MPD: Maximum Pore Diameter

^c Correlation coefficient

^d Standard deviation

^e Units of regression coefficients are adjusted to give kJ/mol

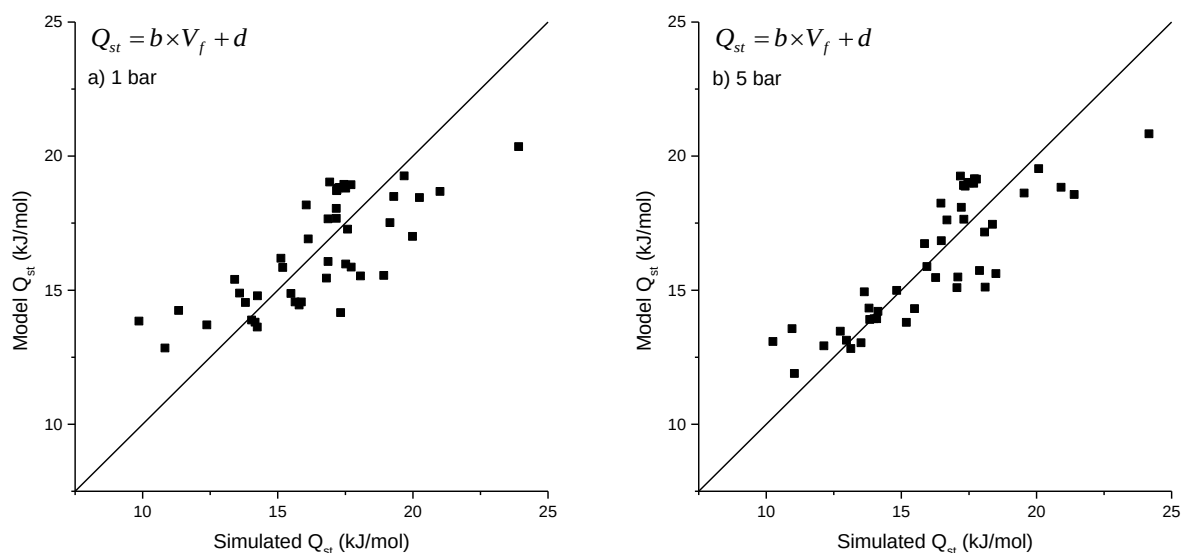


Figure B.11: Comparison of models and simulations for Q_{st} at 298 K, 1 and 5 bar.

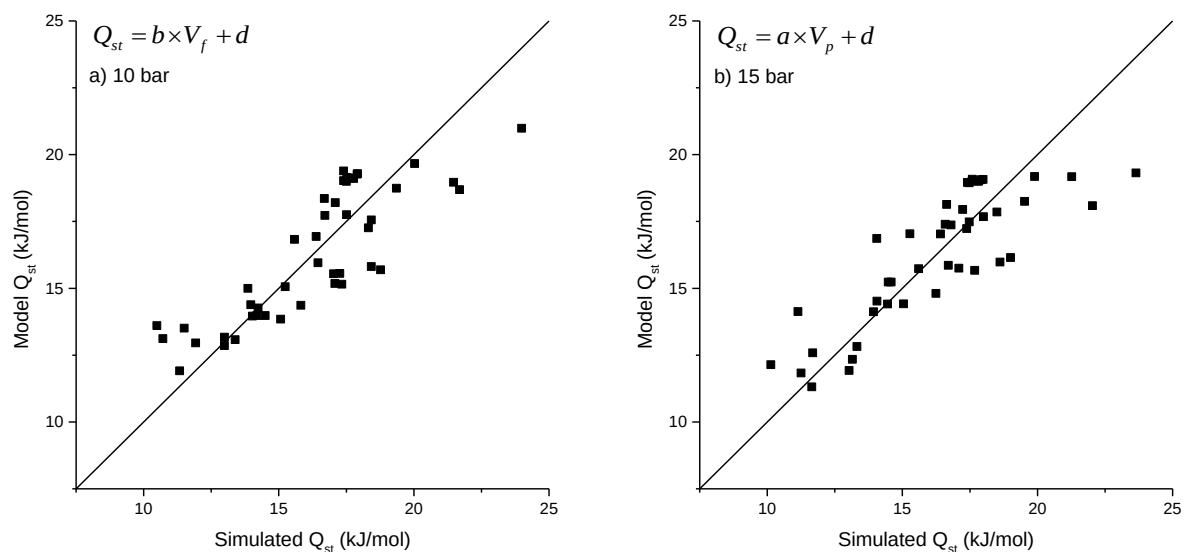


Figure B.12: Comparison of models and simulations for Q_{st} at 298 K, 10 and 15 bar.

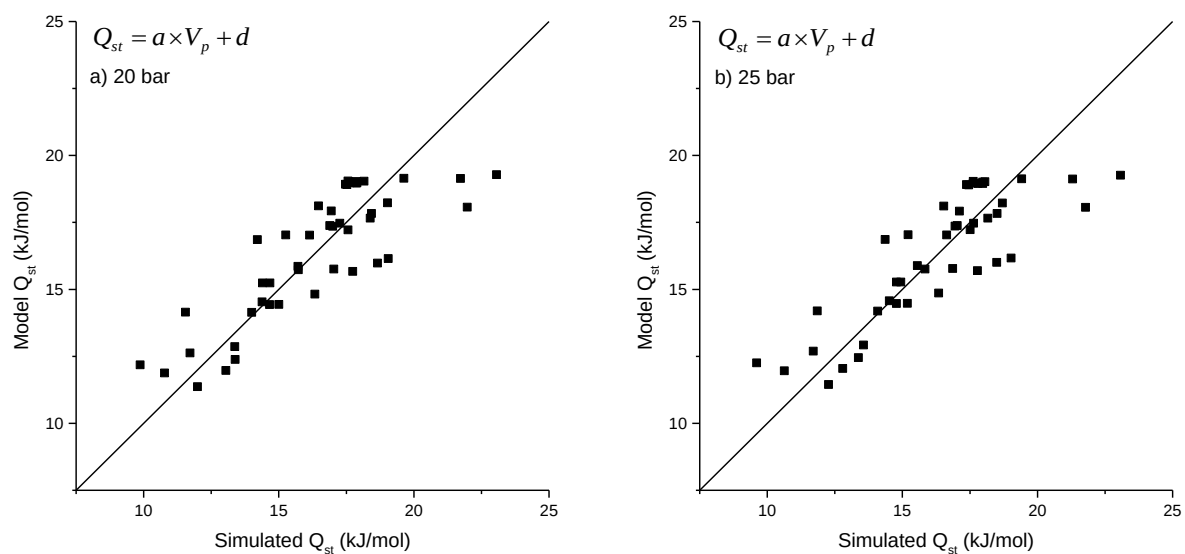


Figure B.13: Comparison of models and simulations for Q_{st} at 298 K, 20 and 25 bar.

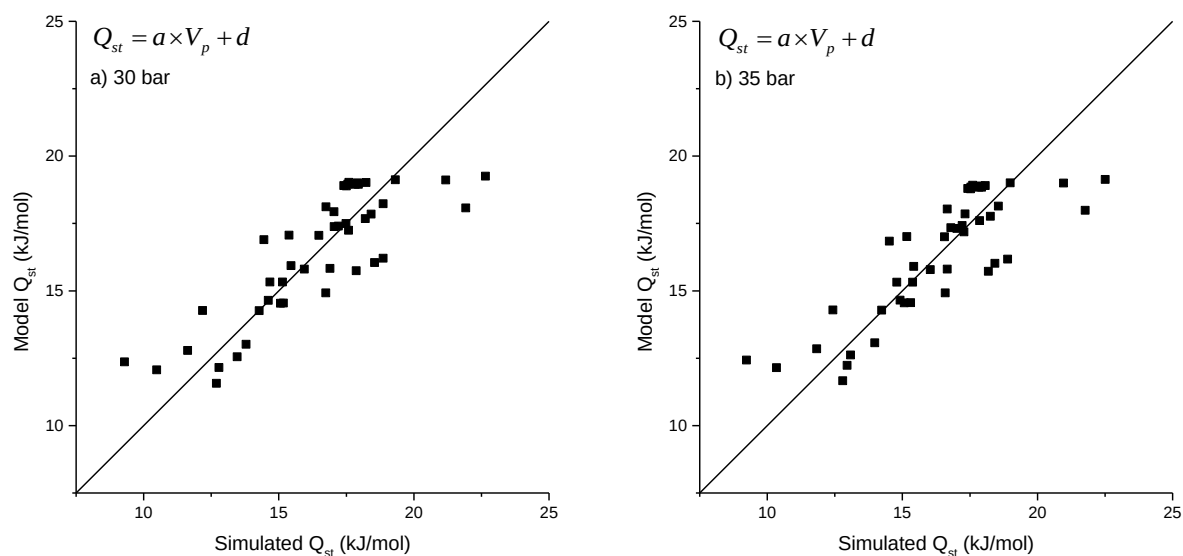


Figure B.14: Comparison of models and simulations for Q_{st} at 298 K, 30 and 35 bar.

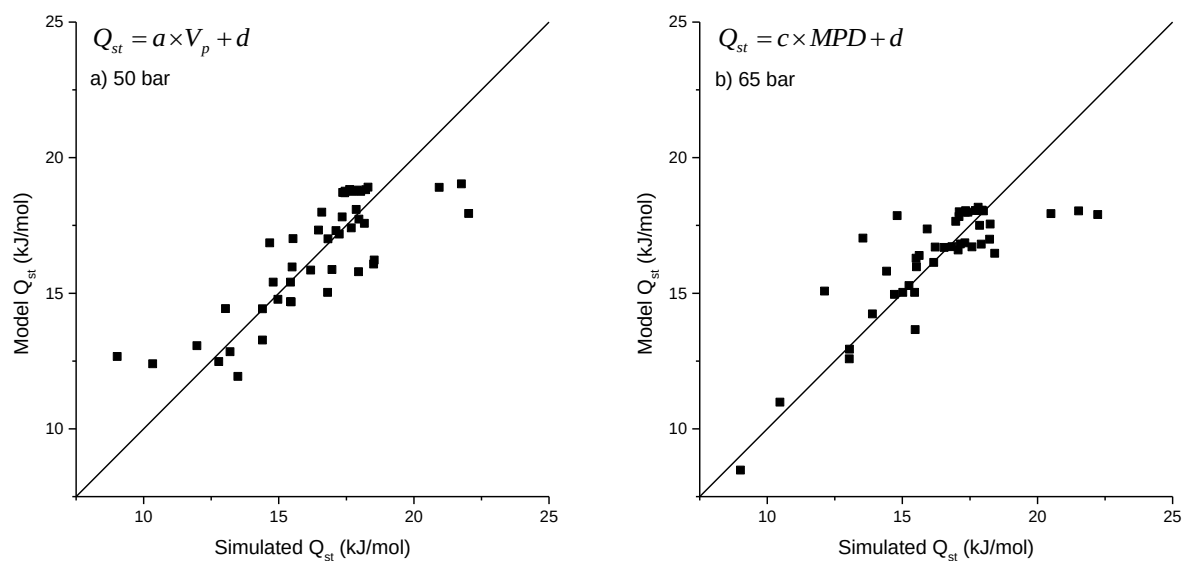
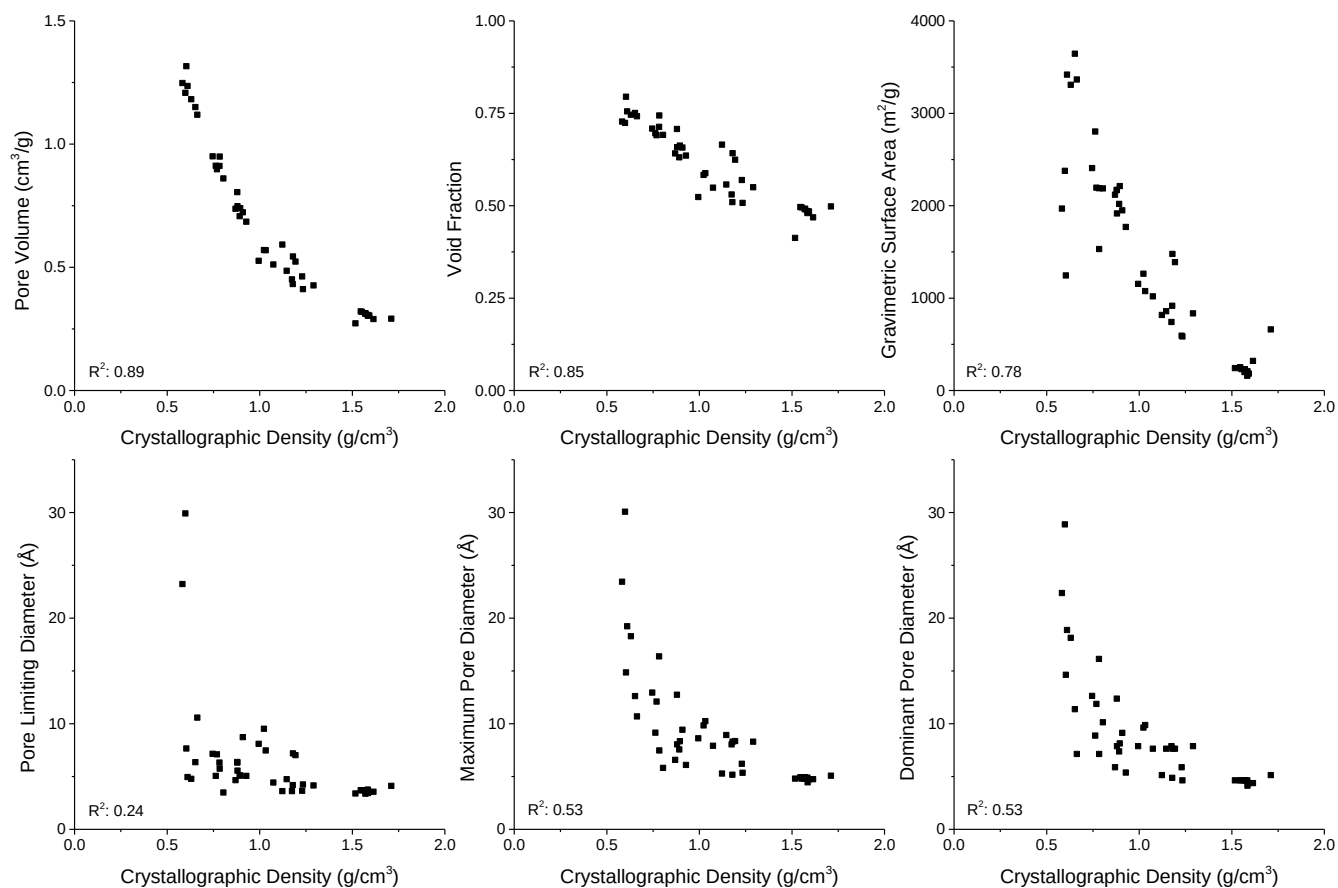


Figure B.15: Comparison of models and simulations for Q_{st} at 298 K, 50 and 65 bar.

Binary Relations of Structural Properties, Q_{st} and CH_4 Uptake**a. Crystallographic Density (ρ_{cryst})****Figure B.16:** Binary relations of crystallographic density with other structural parameters.

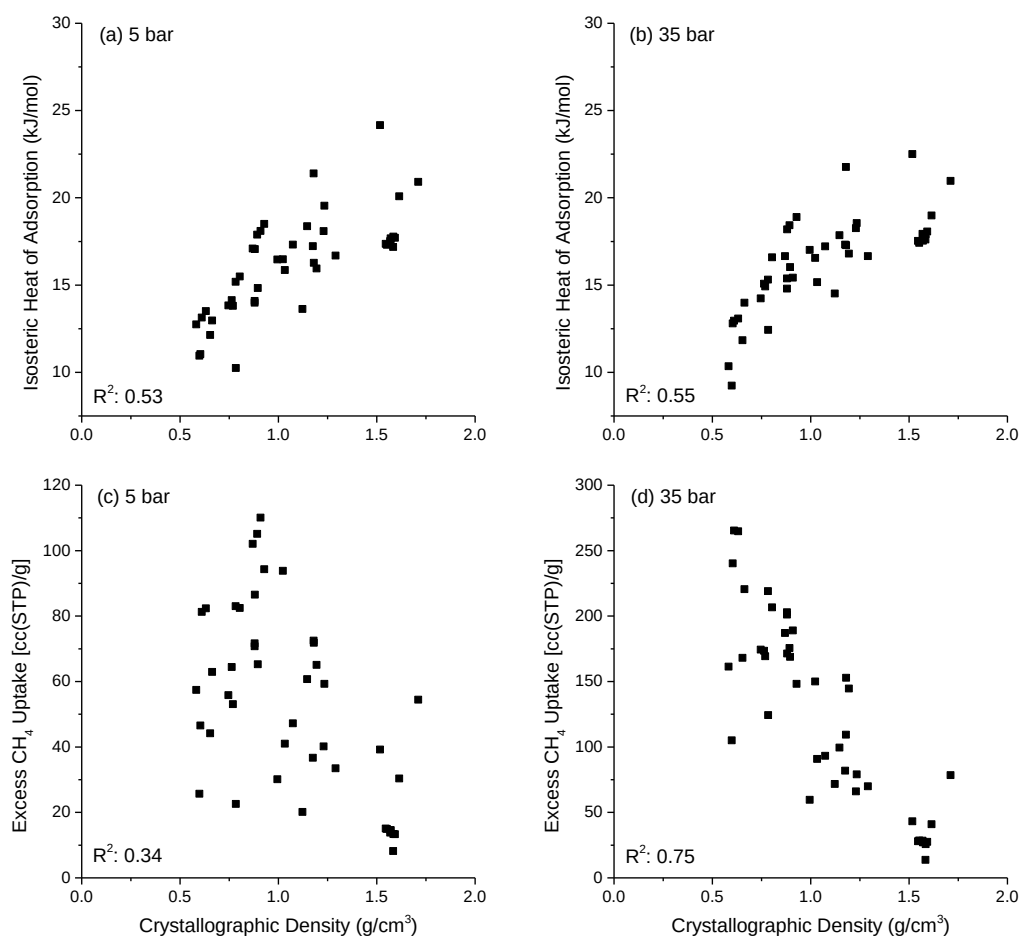


Figure B.17: Binary relations of crystallographic density with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH₄ uptake at (c) 5 bar; (d) 35 bar.

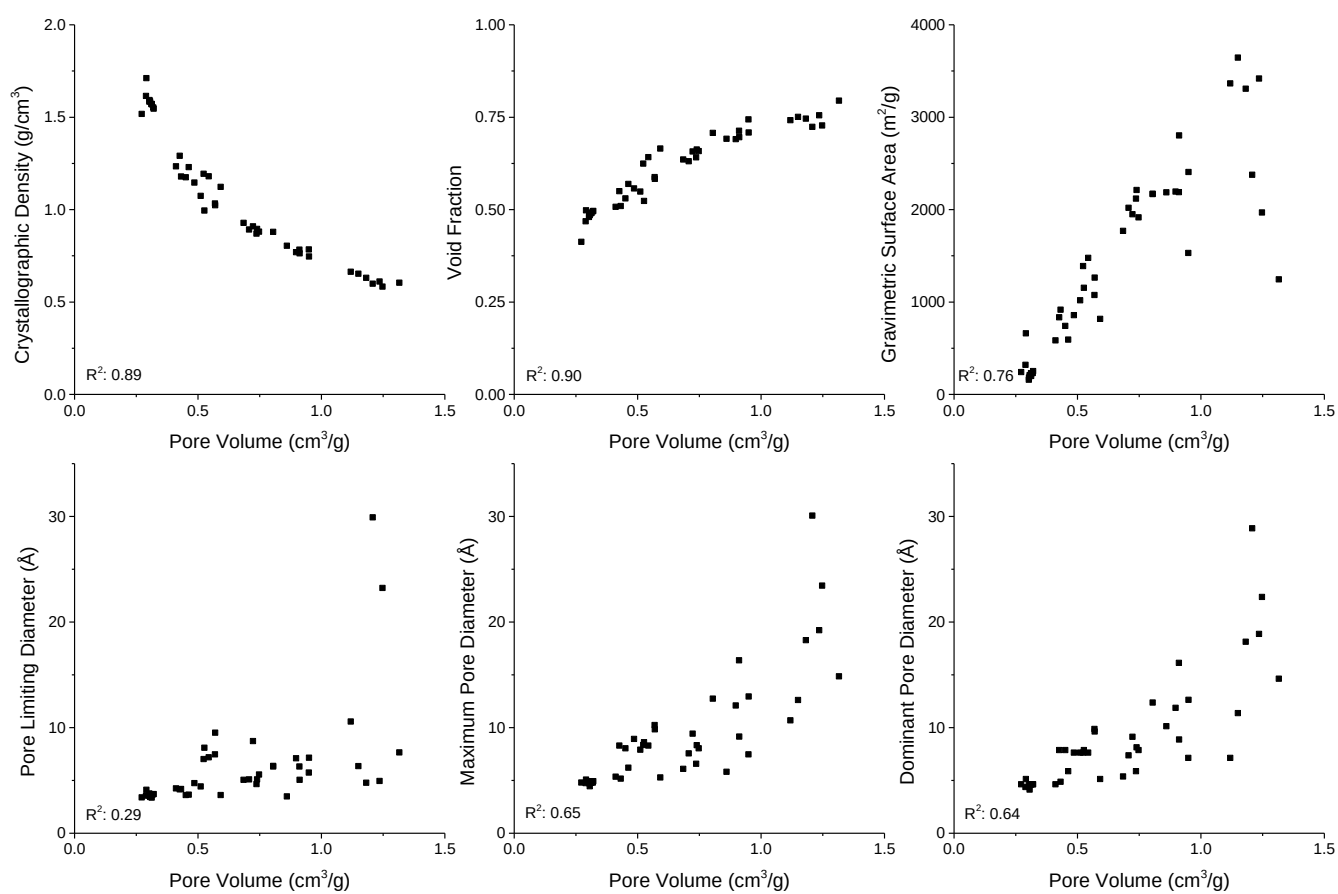
b. Pore Volume (V_p)

Figure B.18: Binary relations of pore volume with other structural parameters.

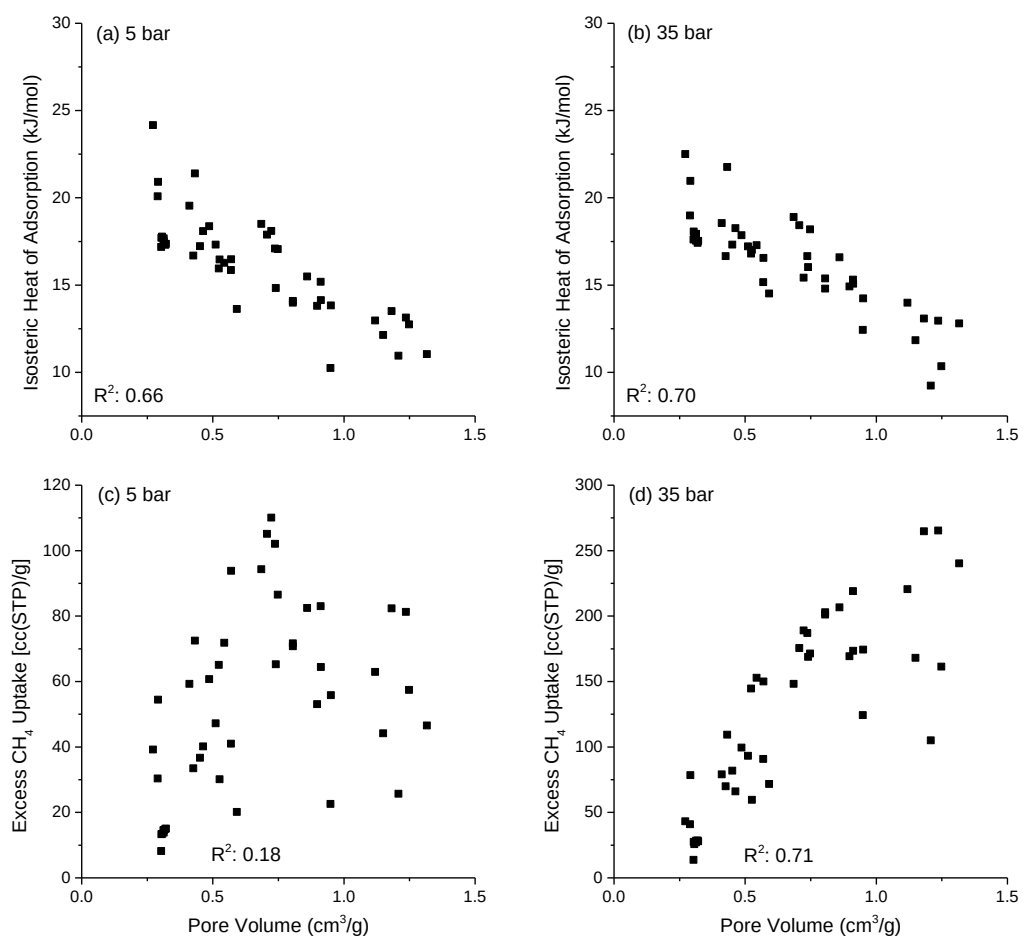
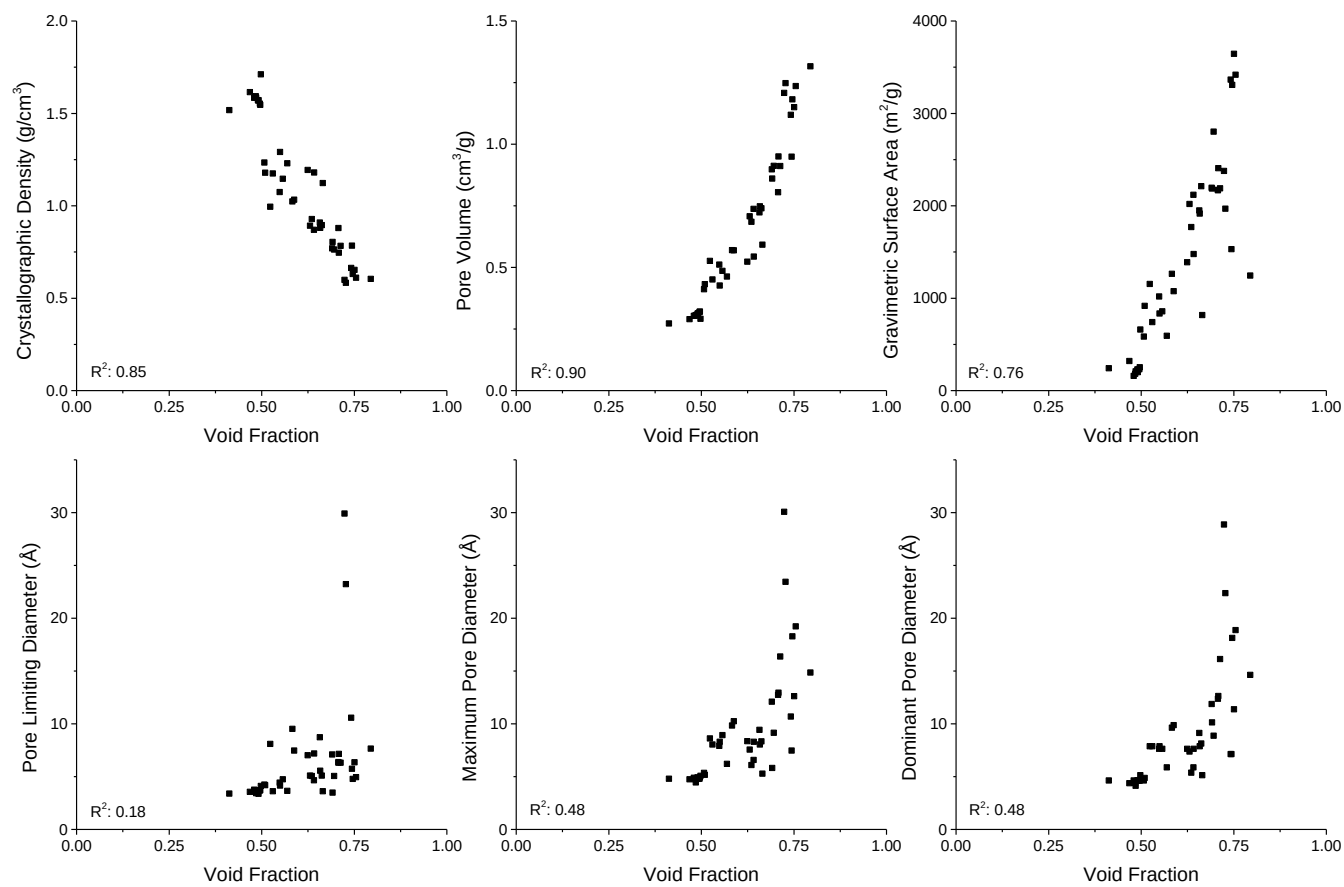


Figure B.19: Binary relations of pore volume with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.

c. Void Fraction (V_f)**Figure B.20:** Binary relations of void fraction with other structural parameters.

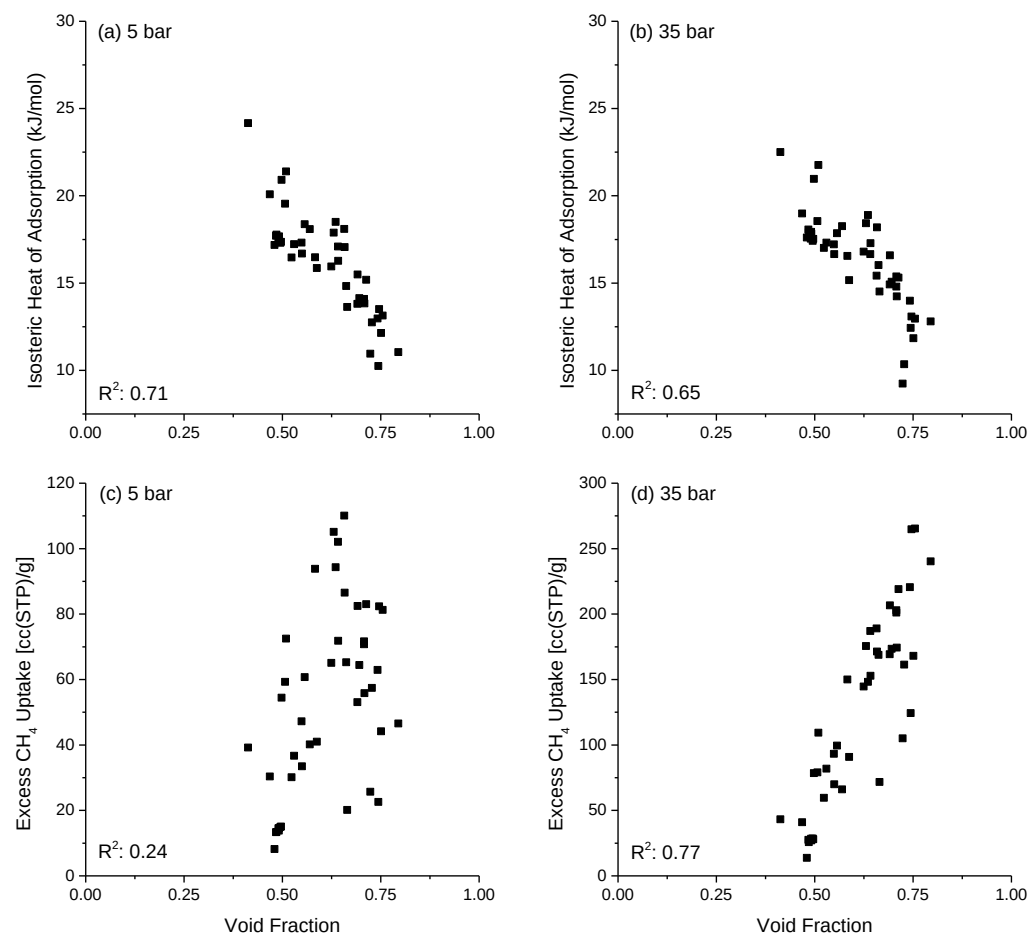


Figure B.21: Binary relations of void fraction with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.

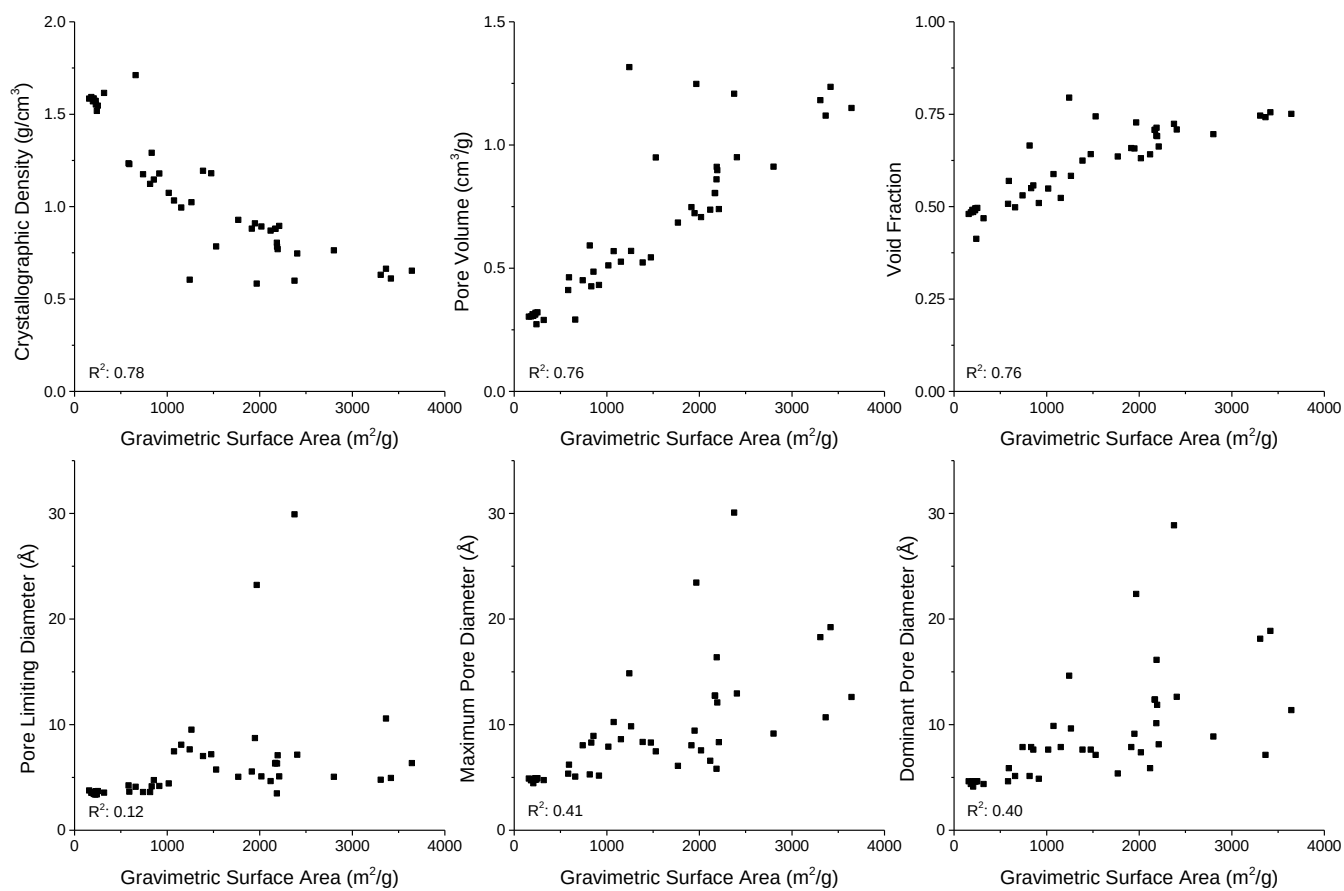
d. Gravimetric Surface Area (S_g)

Figure B.22: Binary relations of gravimetric surface area with other structural parameters.

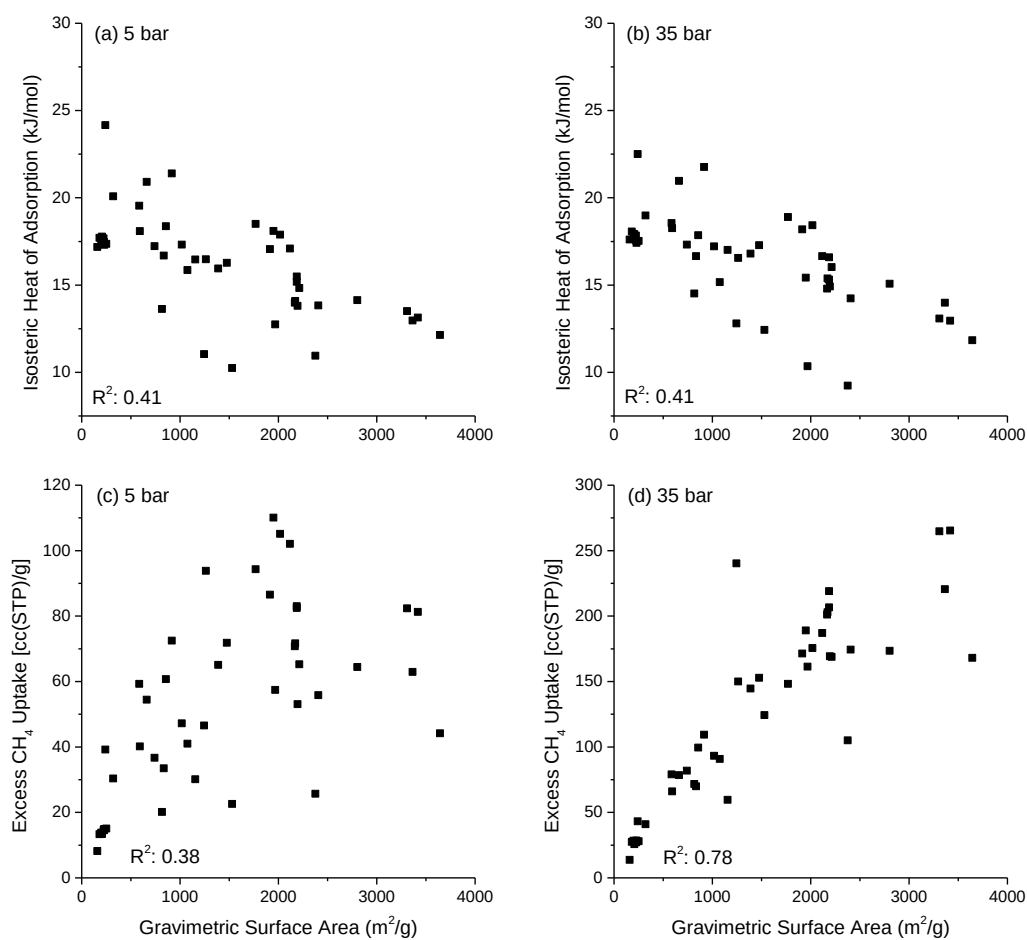


Figure B.23: Binary relations of gravimetric surface area with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar, (d) 35 bar.

e. Pore Limiting Diameter (PLD)

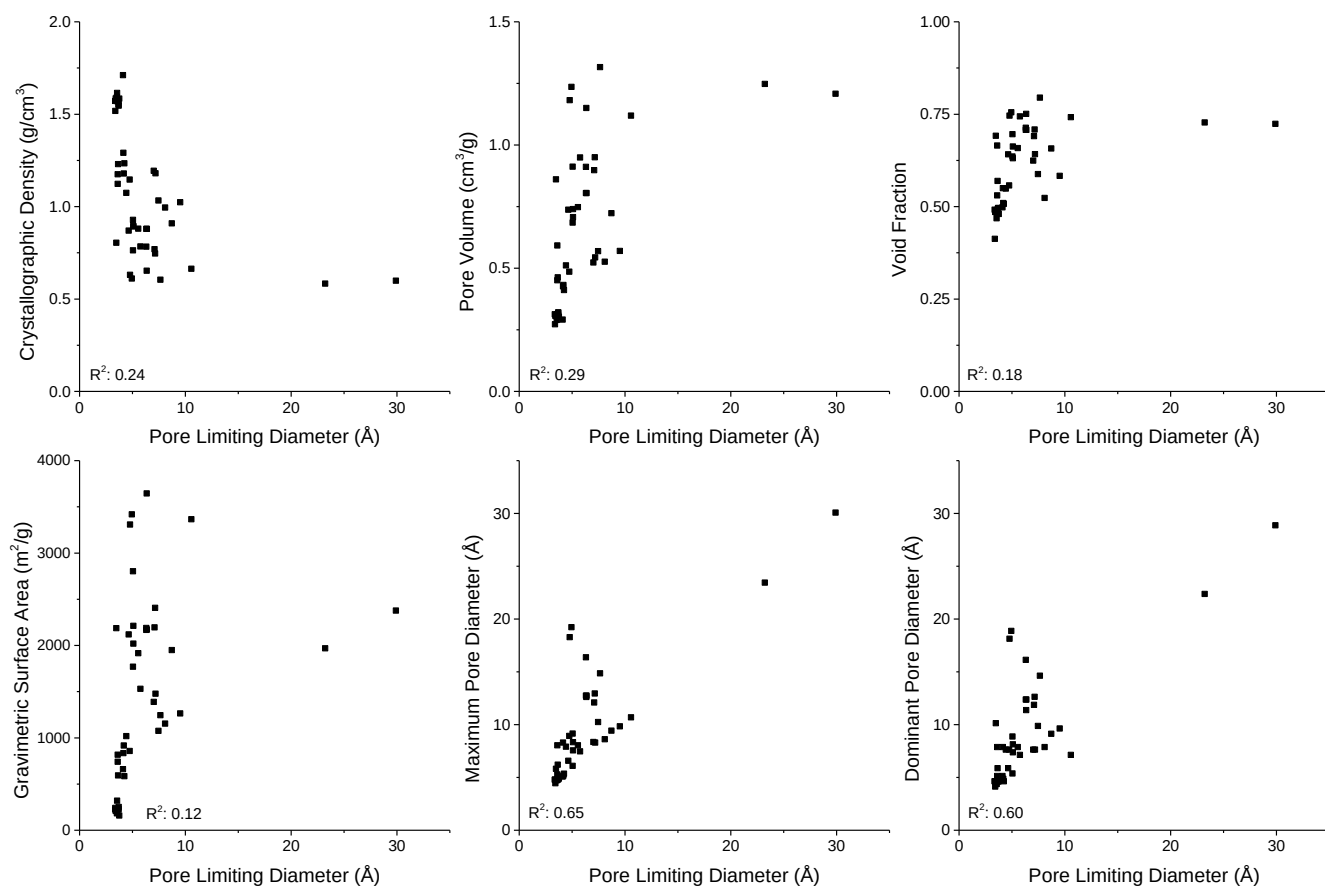


Figure B.24: Binary relations of pore limiting diameter with other structural parameters.

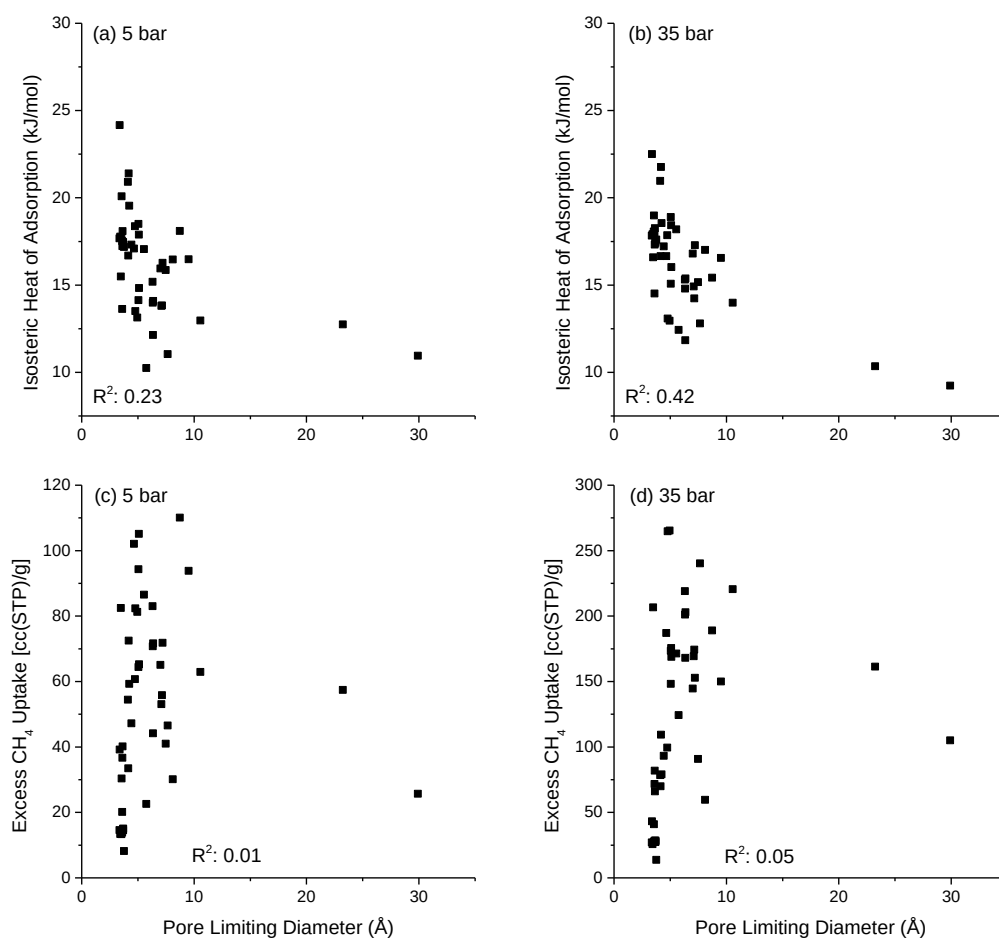
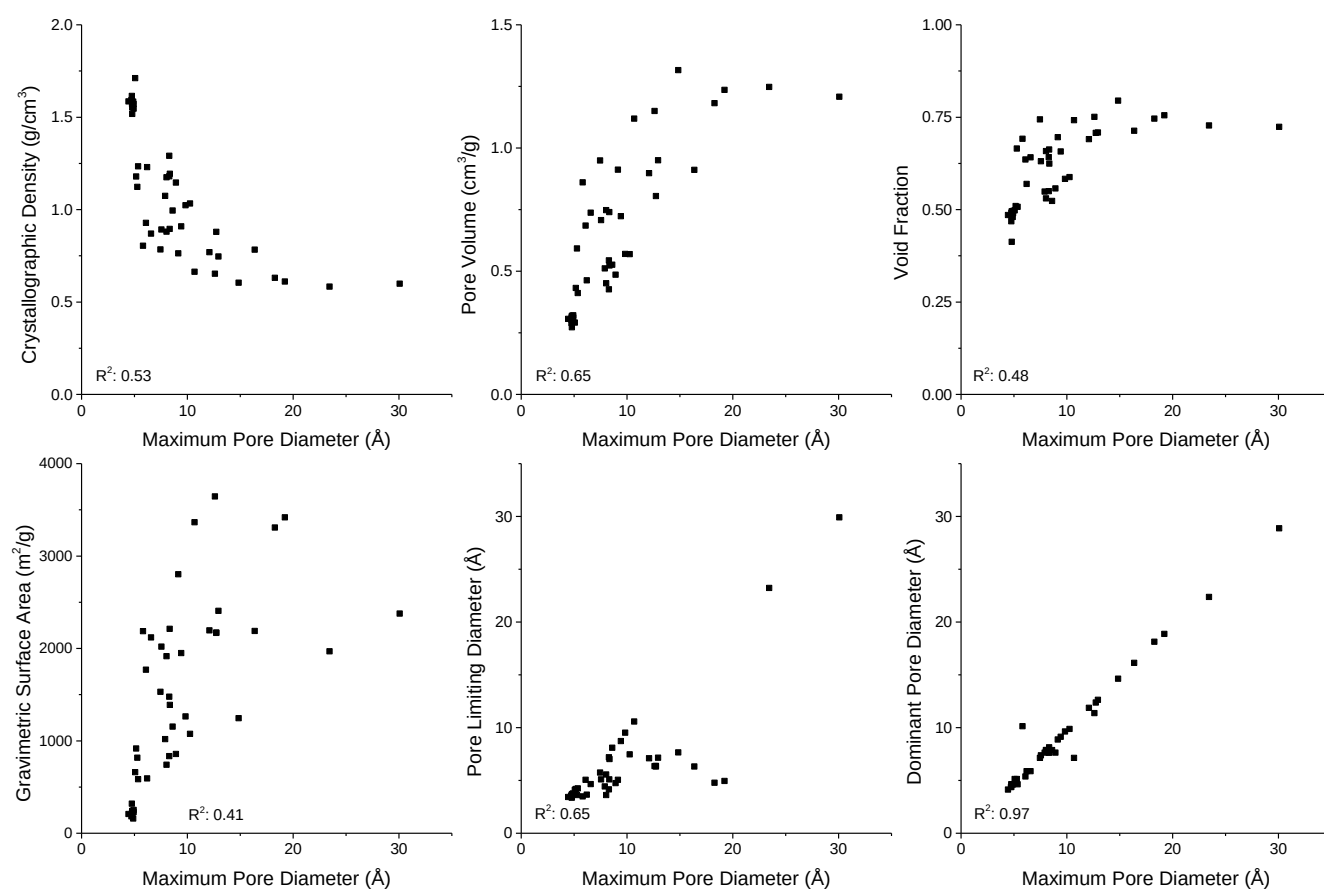


Figure B.25: Binary relations of pore limiting diameter with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.

f. Maximum Pore Diameter (MPD)

**Figure B.26:** Binary relations of maximum pore diameter with other structural parameters.

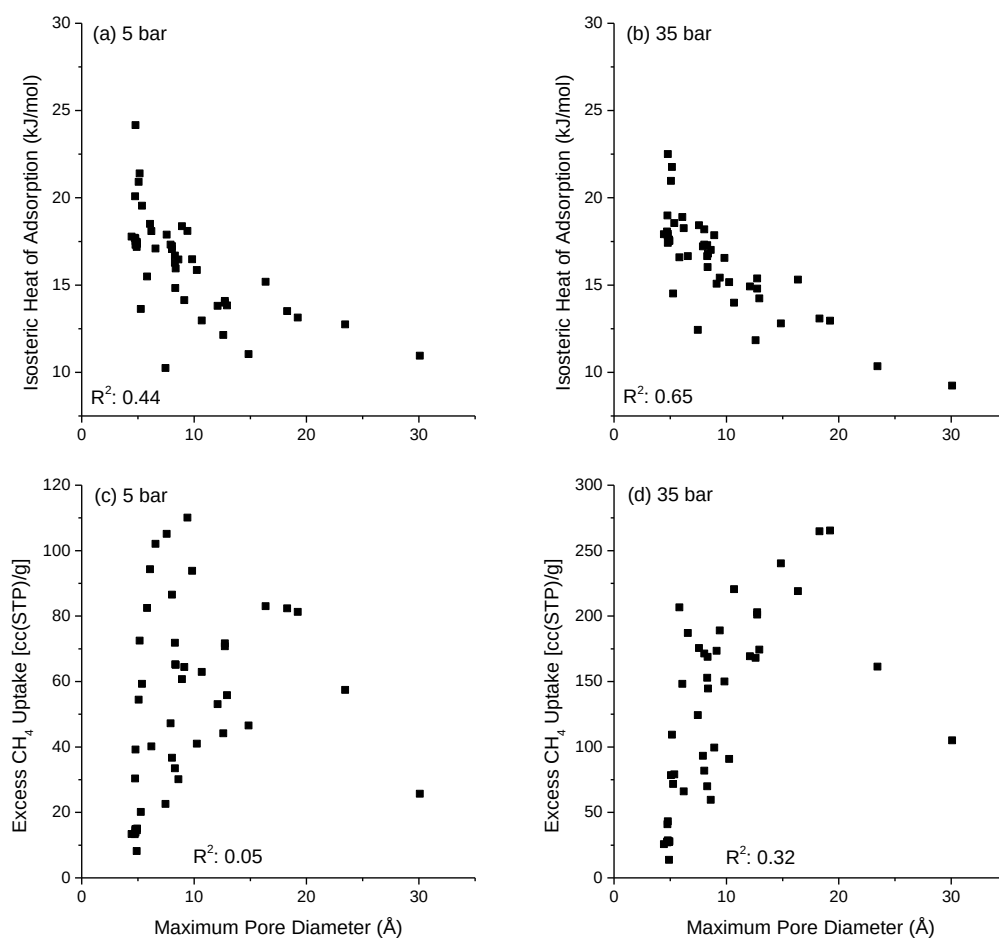
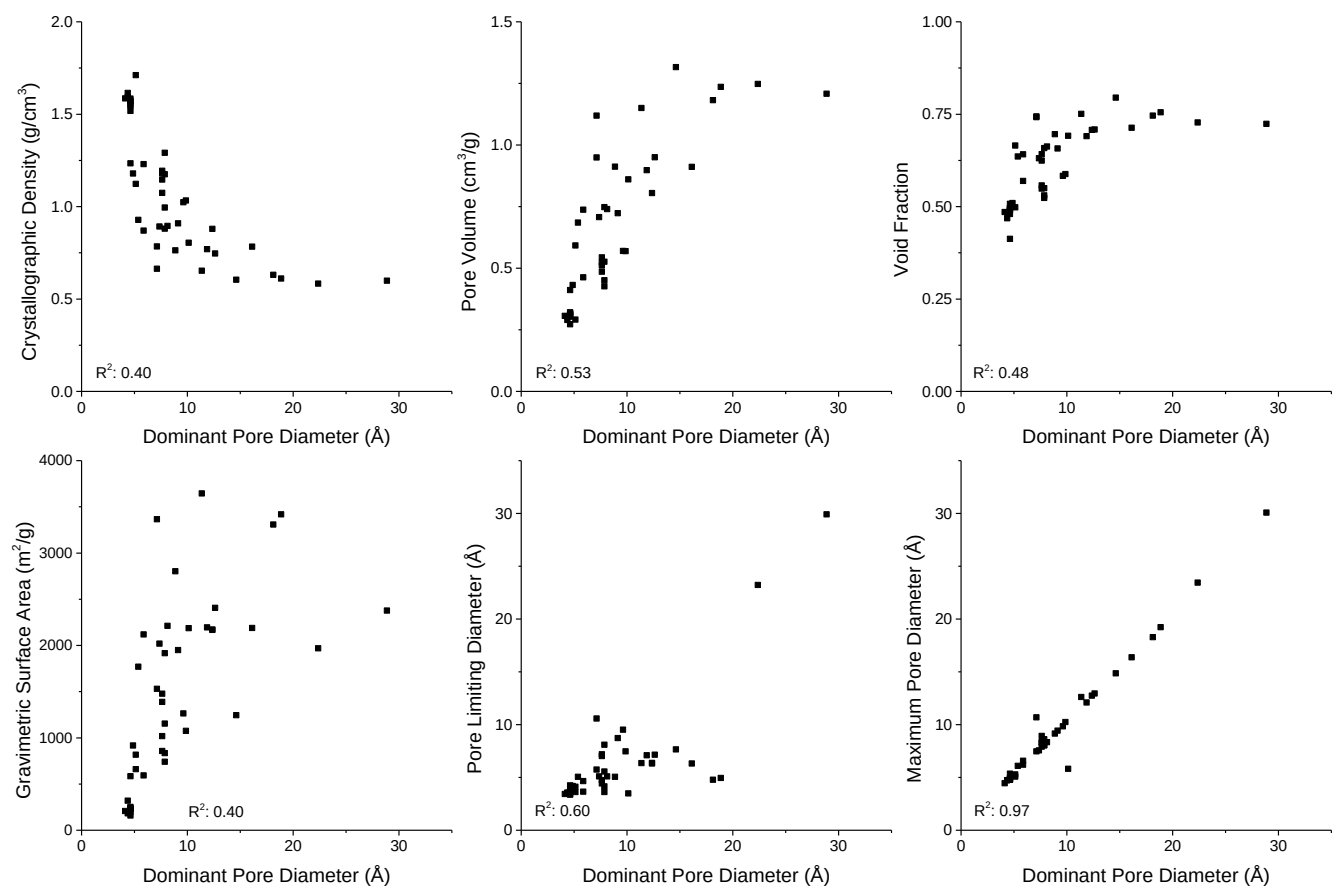


Figure B.27: Binary relations of maximum pore diameter with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.

g. Dominant Pore Diameter (DPD)

**Figure B.28:** Binary relations of dominant pore diameter with other structural parameters.

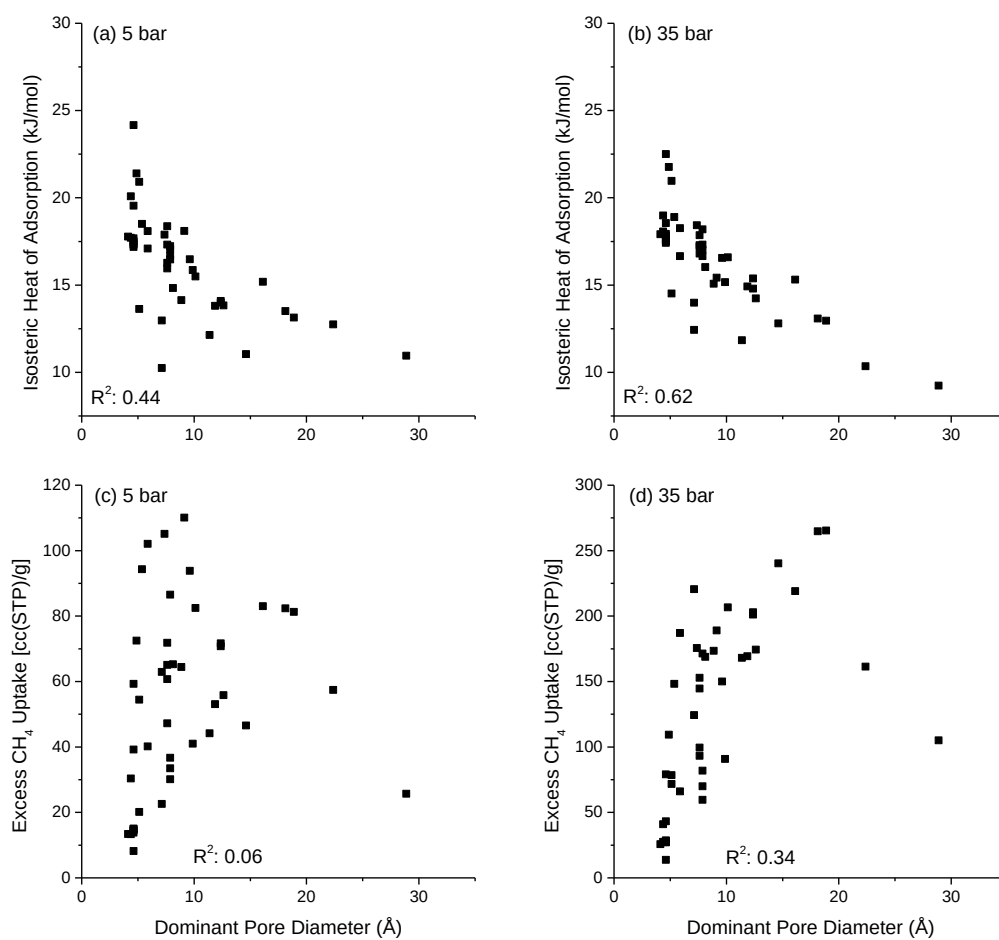
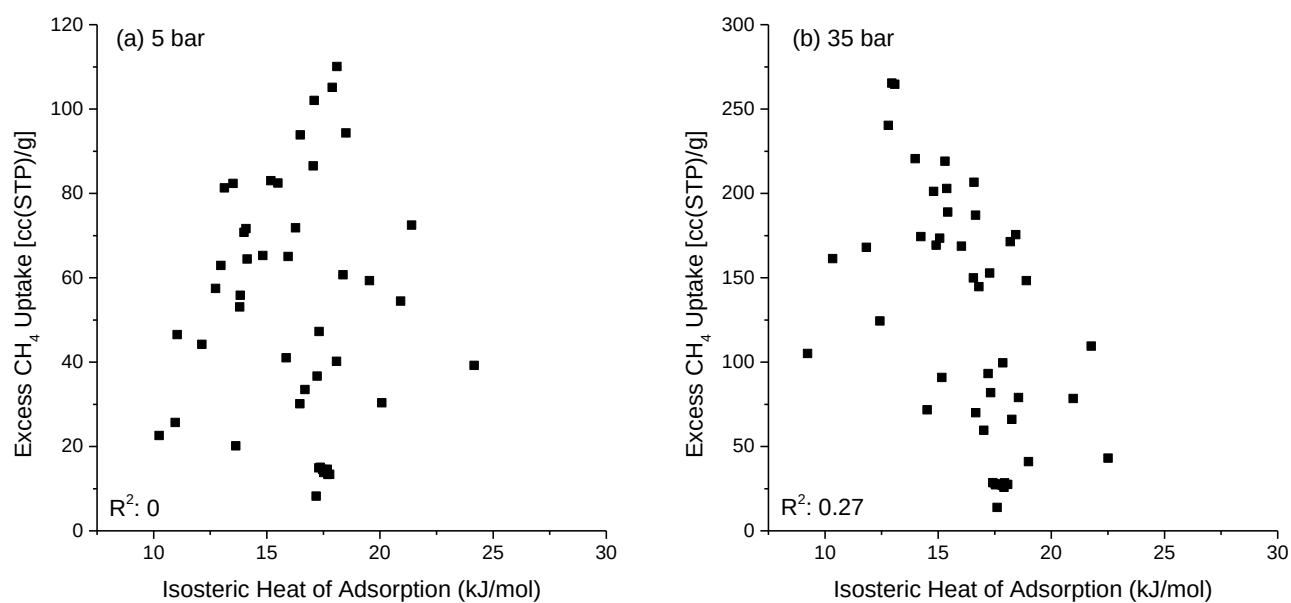


Figure B.29: Binary relations of dominant pore diameter with Q_{st} at (a) 5 bar; (b) 35 bar; and with CH_4 uptake at (c) 5 bar; (d) 35 bar.

h. Relations between Q_{st} and CH_4 uptake (5 & 35 bar)**Figure B.30:** Binary relations between Q_{st} and CH_4 uptake at (a) 5 bar; and (b) 35 bar.

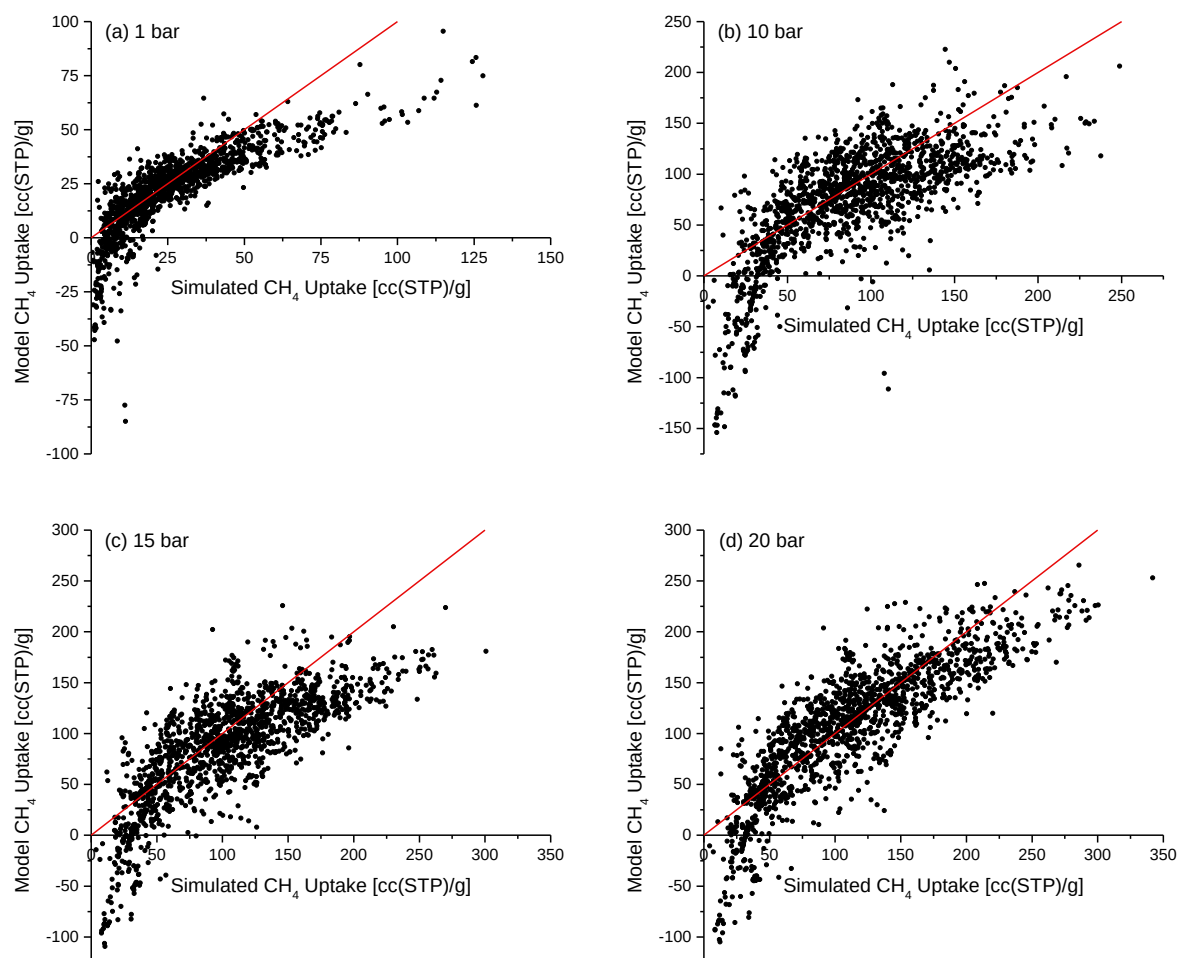
Multivariable Linear Models for Predicting CH₄ Uptake in 1514 MOFs

Figure B.31: Comparison of Model-0 and simulations for CH₄ uptake at 298 K and (a) 1; (b) 10; (c) 15; (d) 20 bar.

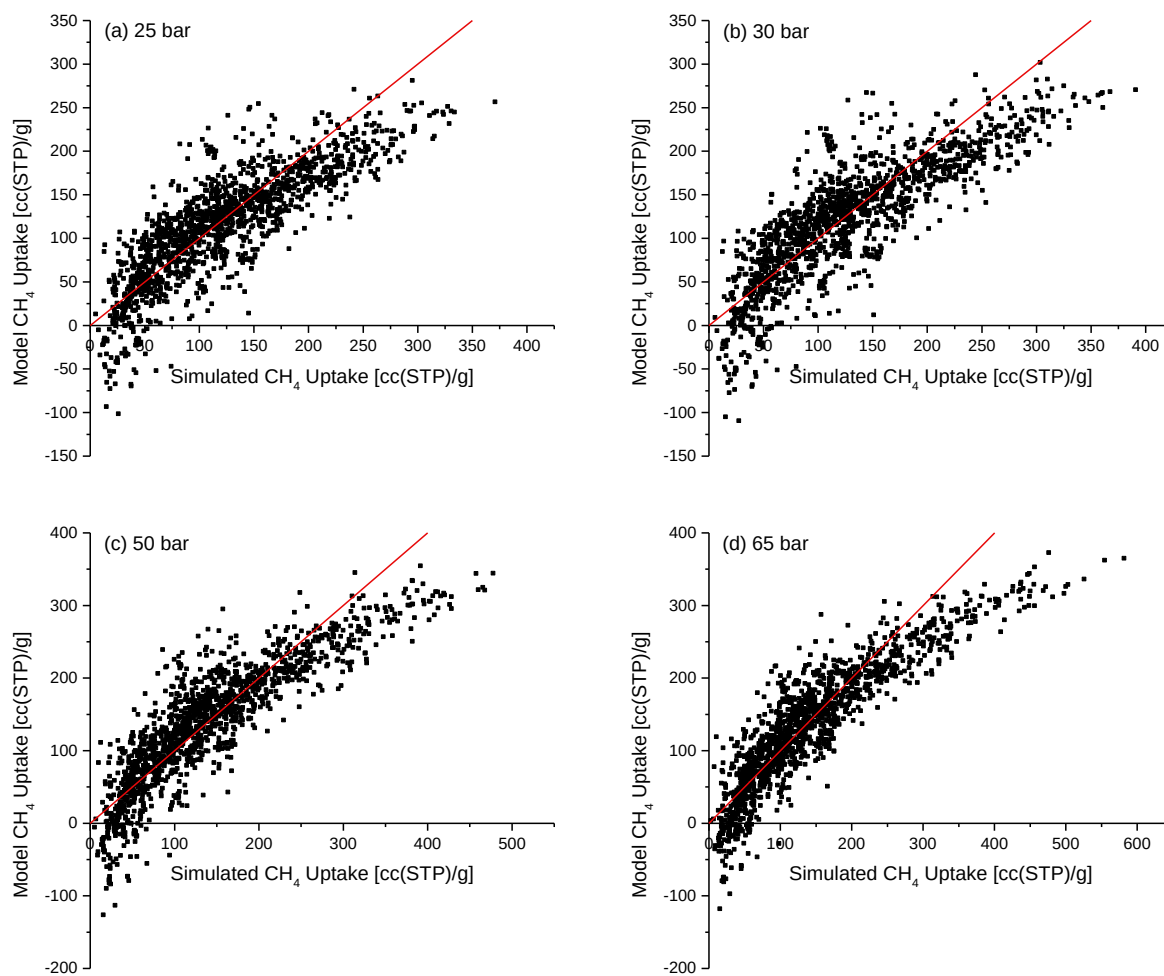


Figure B.32: Comparison of Model-0 and simulations for CH_4 uptake at 298 K and (a) 25; (b) 30; (c) 50; (d) 65 bar.

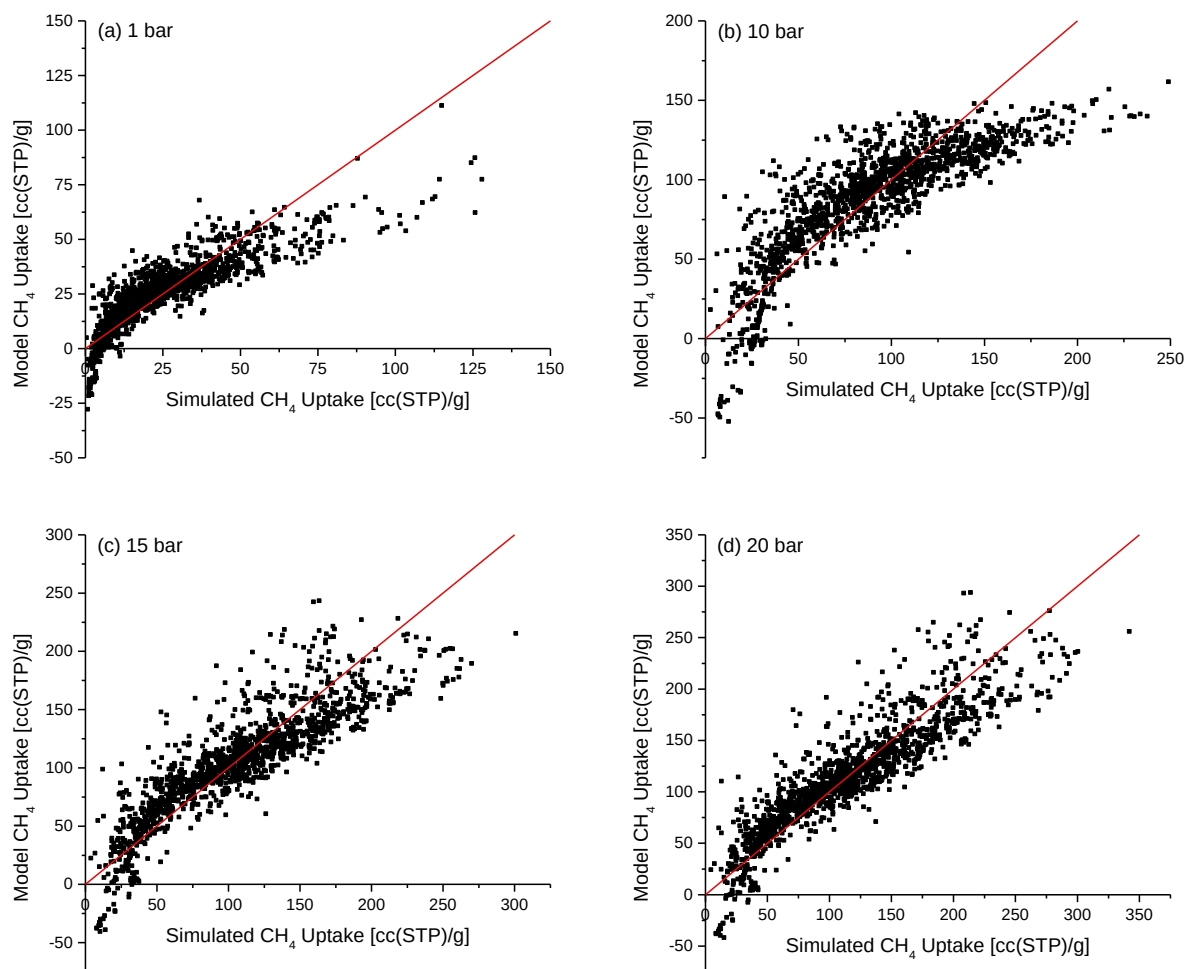


Figure B.33: Comparison of Model-1 and simulations for CH₄ uptake at 298 K and (a) 1; (b) 10; (c) 15; (d) 20 bar.

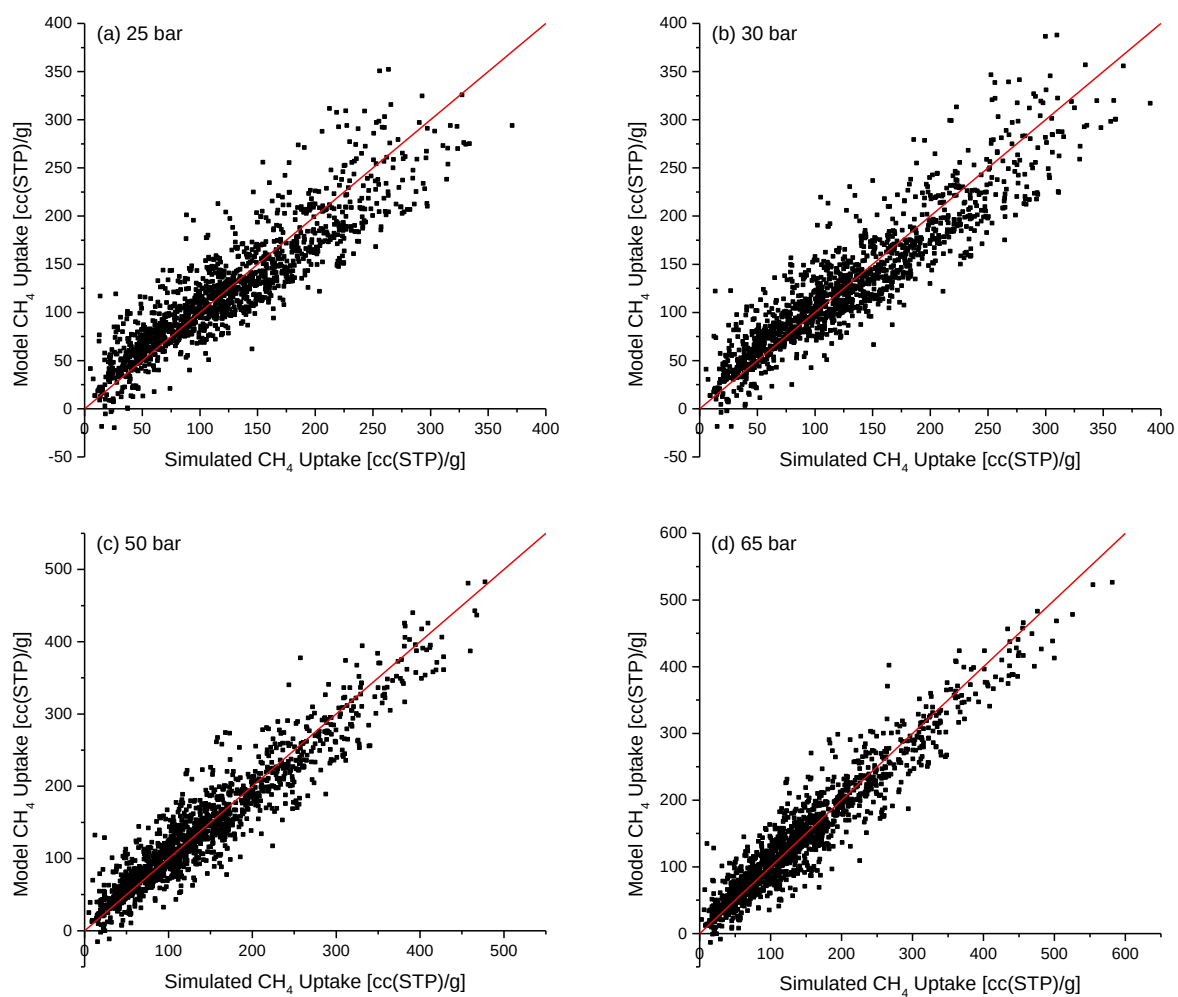


Figure B.34: Comparison of Model-1 and simulations for CH_4 uptake at 298 K and (a) 25; (b) 30; (c) 50; (d) 65 bar.

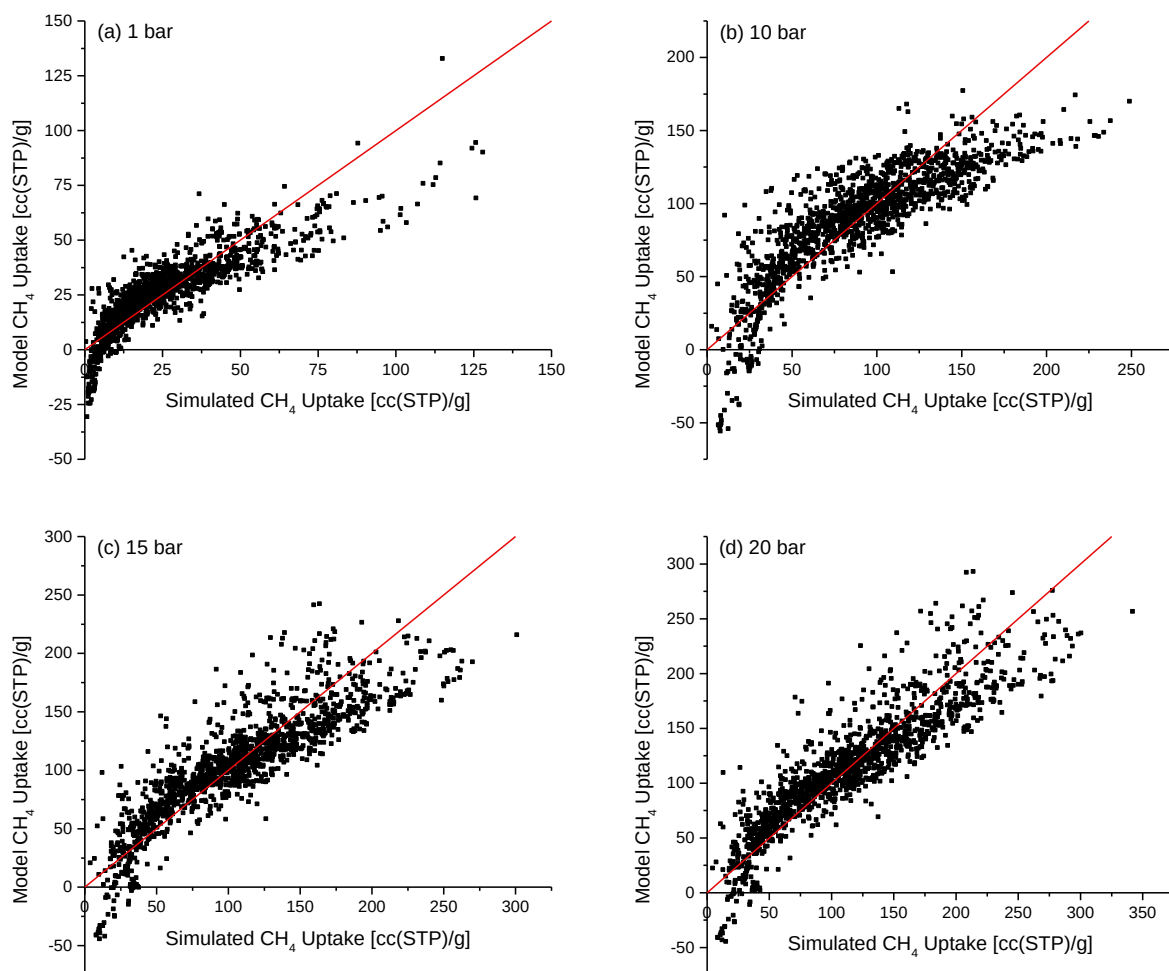


Figure B.35: Comparison of Model-2 and simulations for CH₄ uptake at 298 K and (a) 1; (b) 10; (c) 15; (d) 20 bar.

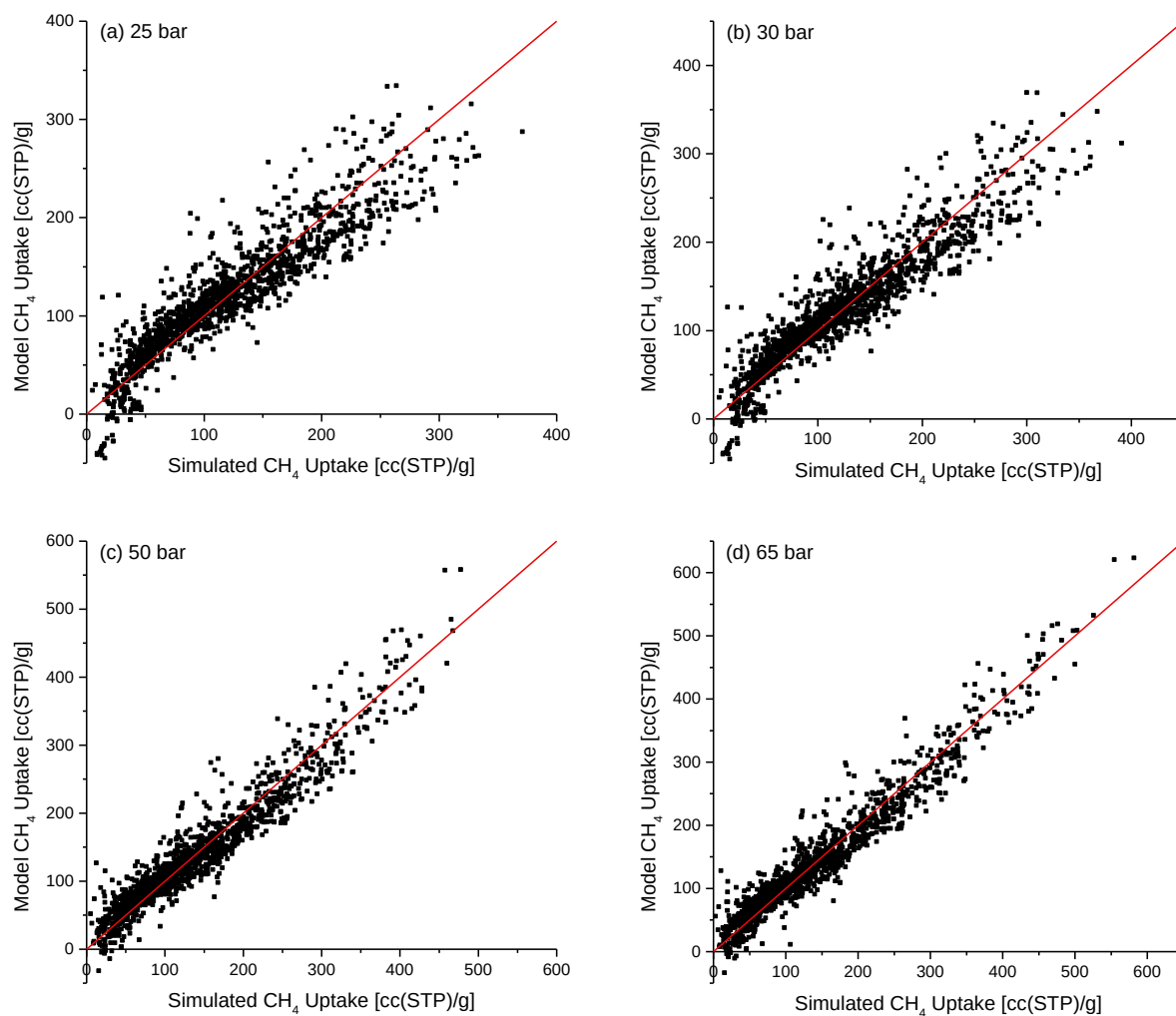
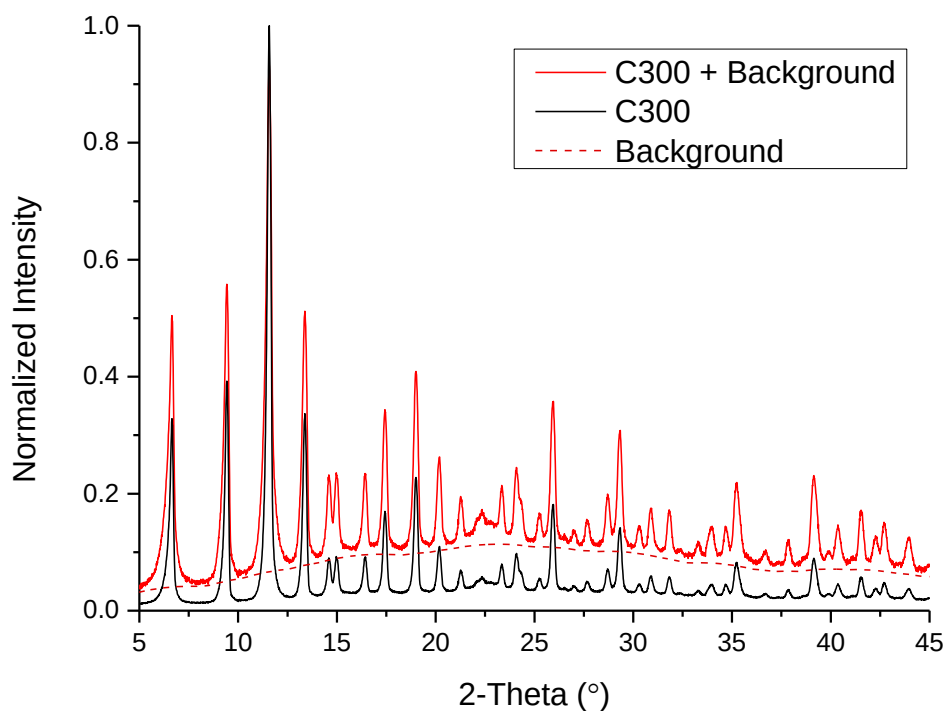
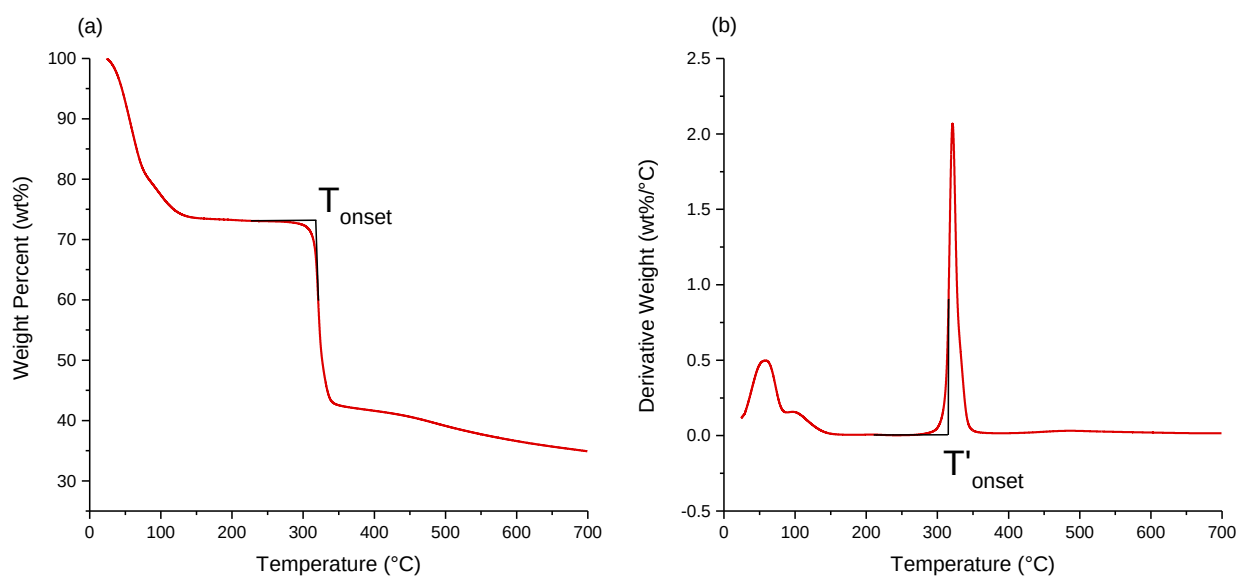


Figure B.36: Comparison of Model-2 and simulations for CH_4 uptake at 298 K and (a) 25; (b) 30; (c) 50; (d) 65 bar.

APPENDIX C: Supplementary Experimental Results

**Figure C.1:** XRD results for Basolite C300 with background signal.**Figure C.2:** Determination of T_{onset} and T'_{onset} values on a representative TGA data obtained for Basolite C300.

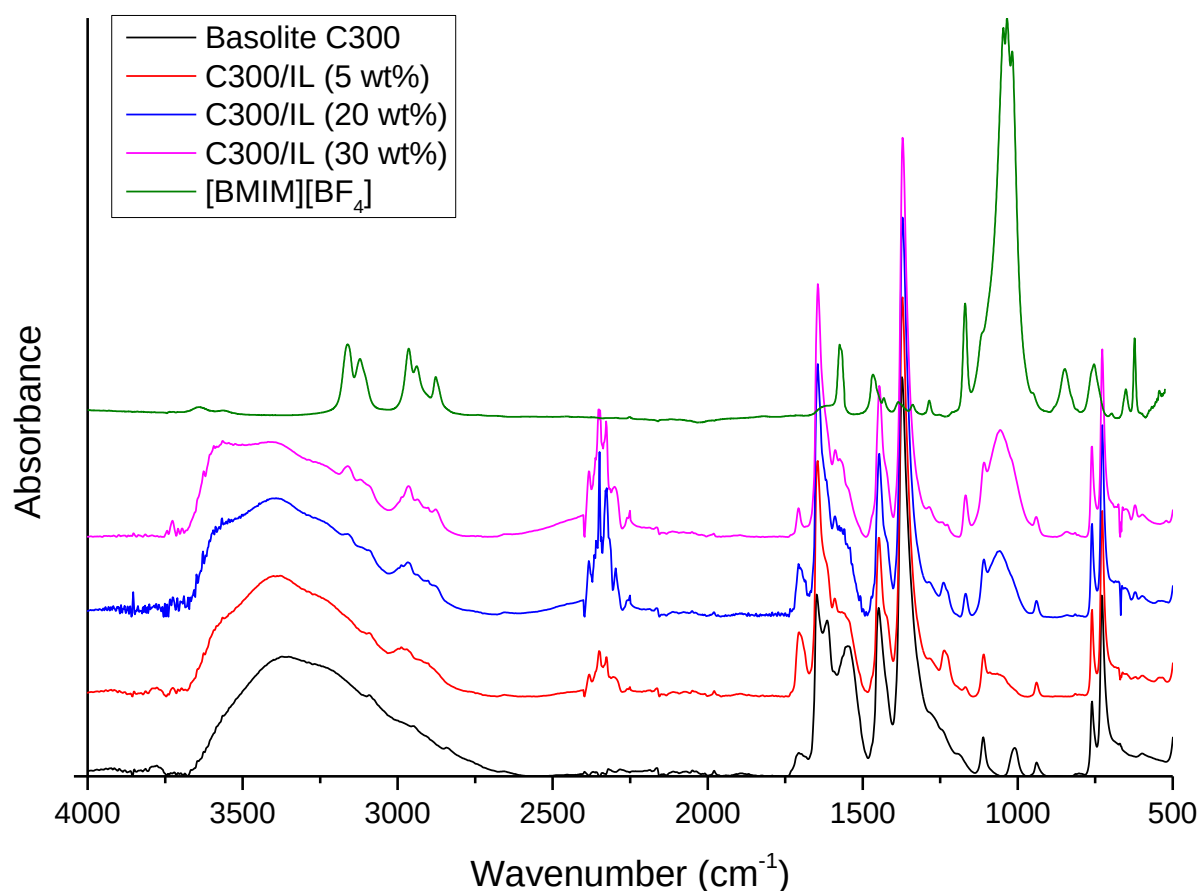


Figure C.3: Full range (4000-500 cm^{-1}) IR spectra for all samples.

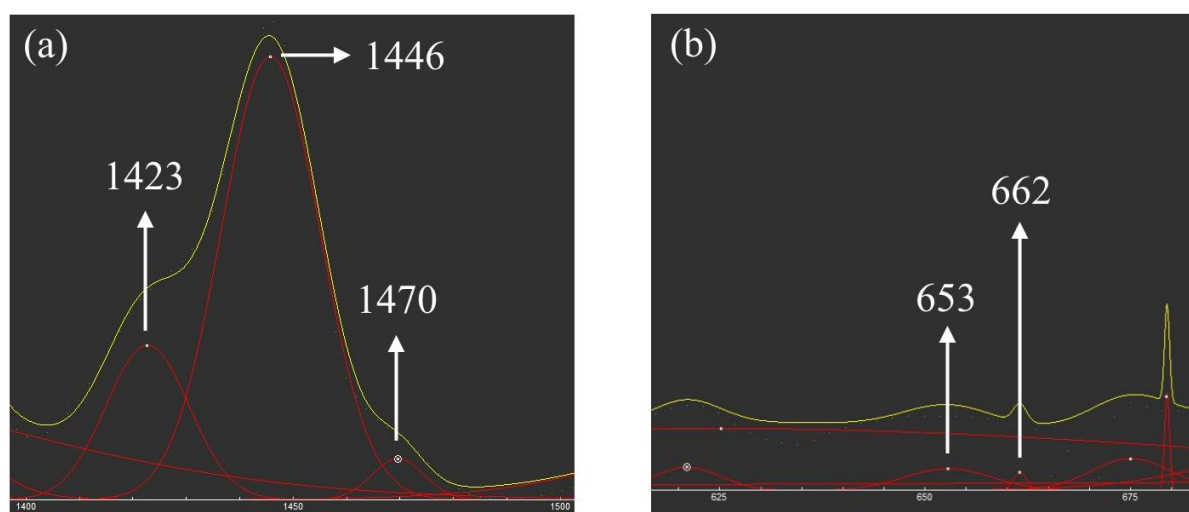


Figure C.4: Deconvolution of IR spectra for 30 wt% IL-incorporated Basolite C300 sample between (a) 1400-1500 cm^{-1} ; (b) 625-675 cm^{-1} .

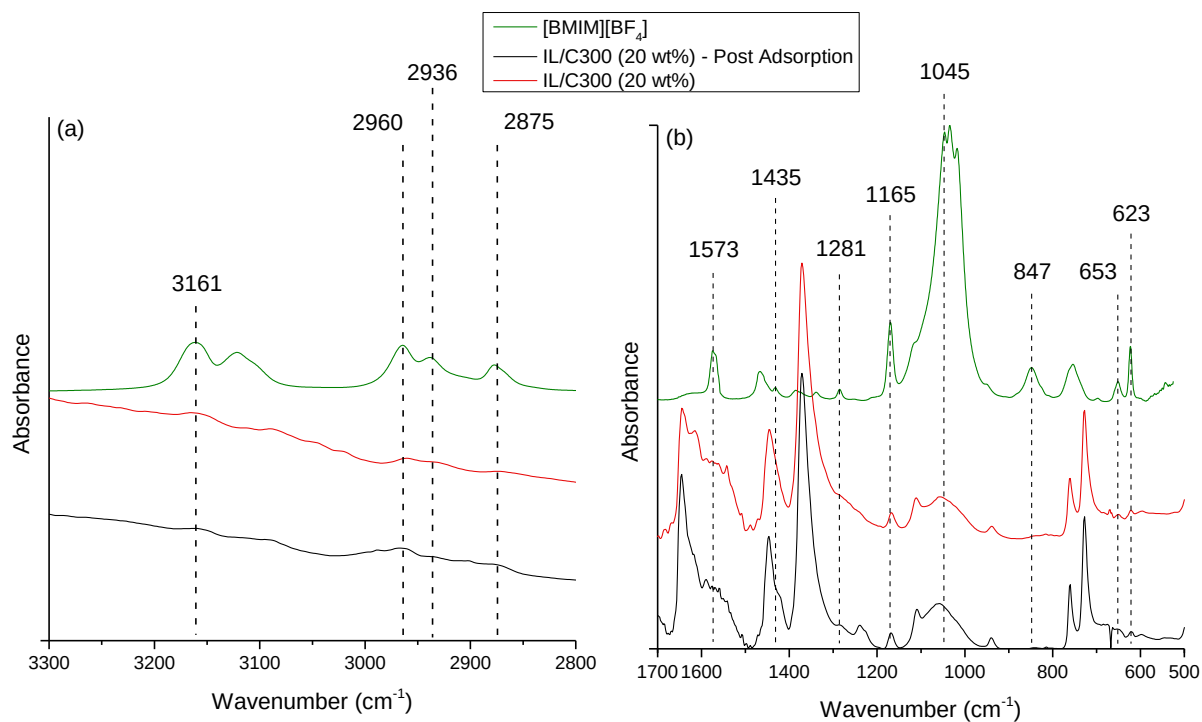


Figure C.5: IR spectra of 20 wt% IL-incorporated Basolite C300 before (black) and after (red) adsorption measurements.

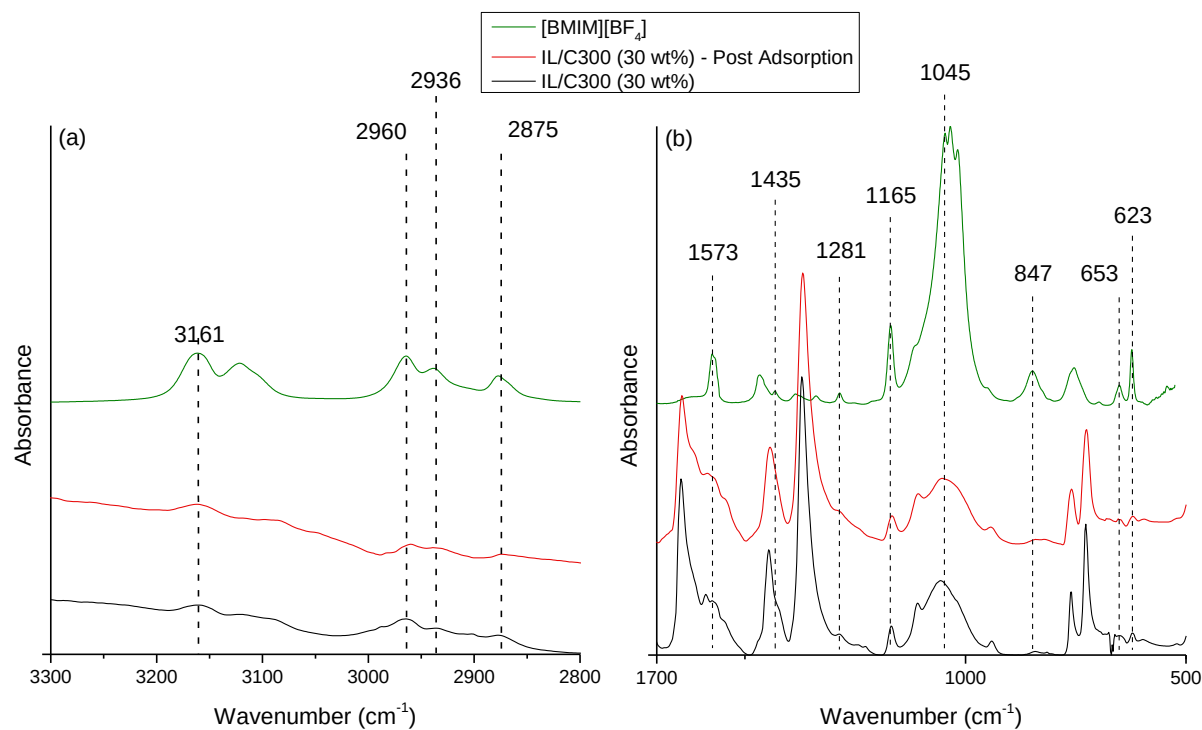


Figure C.6: IR spectra of 30 wt% IL-incorporated Basolite C300 before (black) and after (red) adsorption measurements.

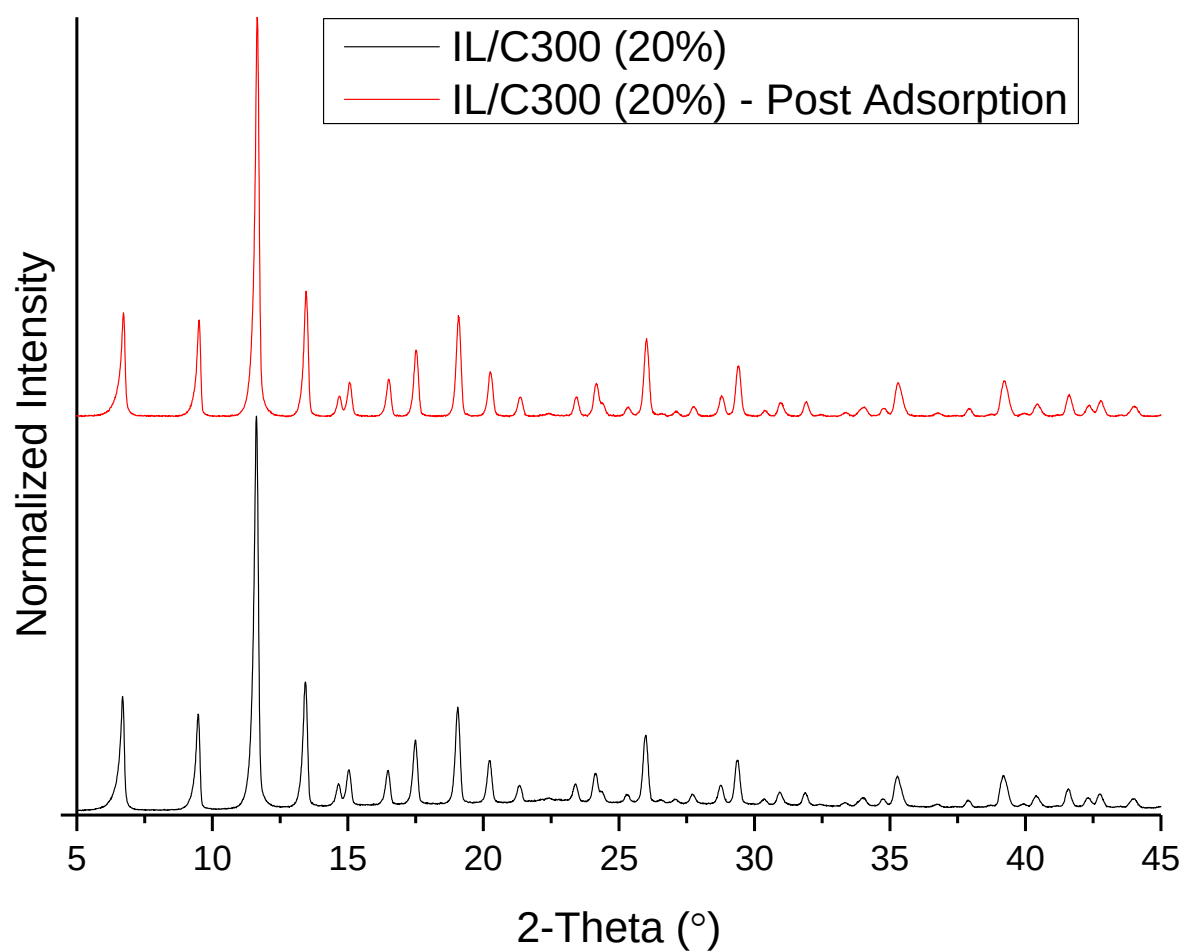


Figure C.7: XRD results of 20 wt% IL-incorporated Basolite C300 before (black) and after (red) adsorption measurements.

APPENDIX D: Full names of Ionic Liquids**Table D.1:** Full names of ionic liquids mentioned in this thesis.

IL Abbreviations	IL Full Name
[BMIM][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[HMIM][Tf ₂ N]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[EMIM][DEP]	1-ethyl-3-methylimidazolium diethyl phosphate
[THTDP][PHOS]	trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate
[THTDP][DCA]	trihexyltetradecylphosphonium dicyanamide
[AMIM][DCA]	1-allyl-3-methylimidazolium dicyanamide
[BMPYRR][DCA]	1-butyl-1-methylpyrrolidinium dicyanamide
[CPROP][DCA]	1,2,3-tris(diethylamino)cyclopropenylium dicyanamide
[CPROP][Tf ₂ N]	1,2,3-tris(diethylamino)cyclopropenylium bis(trifluoromethylsulfonyl)imide
[BMPIP][Tf ₂ N]	1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide
[TES][Tf ₂ N]	triethylsulfonium bis(trifluoromethylsulfonyl)imide
[TOA][Tf ₂ N]	methyltrioctylammonium bis(trifluoromethylsulfonyl)imide
[BMIM][Tf ₂ N]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM][PF ₆]	1-butyl-3- methylimidazolium hexafluorophosphate
[EMIM][SCN]	1-ethyl-3-methylimidazolium thiocyanate
[EMIM][DCN]	1-ethyl-3-methylimidazolium dicyanamide
[EMIM][TCB]	1-ethyl-3- methylimidazolium tetracyanoborate
[OMIM][Tf ₂ N]	1-octyl-3- methylimidazolium bis(trifluoromethylsulfonyl)amide
[OMIM][PF ₆]	1-methyl-3-octylimidazolium hexafluorophosphate
[EMIM][Tf ₂ N]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₂ OHMIM][Tf ₂ N]	1(2-hydroxyethyl)3-methylimidazolium bis(trifluoromethane-sulfonyl) imide
[BMIM][Cl]	1-butyl-3-methylimidazolium chloride
[BMIM][MeSO ₄]	1-butyl-3-methylimidazolium methyl sulfate
[EMIM][EtSO ₄]	1-ethyl-3-methylimidazolium ethyl sulfate
[EMIM][PF ₆]	1-ethyl-3-methylimidazolium hexafluorophosphate
[HMIM][PF ₆]	1-hexyl-3-methylimidazolium hexafluorophosphate
[BMIM][Ac]	1-butyl-3-methylimidazolium acetyl
[EMIM][Ac]	1-ethyl-3-methylimidazolium acetyl
[BMIM][DCA]	1-butyl-3-methylimidazolium dicyanamide
[EMIM][DCA]	1-ethyl-3-methylimidazolium dicyanamide
[EMIM][BF ₄]	1-ethyl-3-methylimidazolium tetrafluoroborate
[HMIM][BF ₄]	1-hexyl-3-methylimidazolium tetrafluoroborate
[BMIM][TfO]	1-butyl-3-methylimidazolium trifluoromethane sulfonate

[EMIM][TfO]	1-ethyl-3-methylimidazolium trifluoromethane sulfonate
[HMIM][TfO]	1-hexyl-3-methylimidazolium trifluoromethane sulfonate
[doc]	1,4-bis(2-ethylhexyloxy)2 1,4-dioxobutane-2-sulfonate
[N ₄₄₄₄]	tetrabutylammonium
[b ₂ Nic]	1-butyl-nicotinic acid butyl ester
[FEP]	fluorinated ethylene propylene
[C ₆ H ₄ F ₉ mim]	1-methyl-3-(3, 3,4,4,5,5,6,6,6-nonafluorohexyl) imidazolium
