CCSI²

Carbon Capture Simulation for Industry Impact

Modeling of LBNL MOF Sorbents

Debangsu Bhattacharyya, Goutham Kotamreddy, Ryan Hughes

West Virginia University

Janine Carney

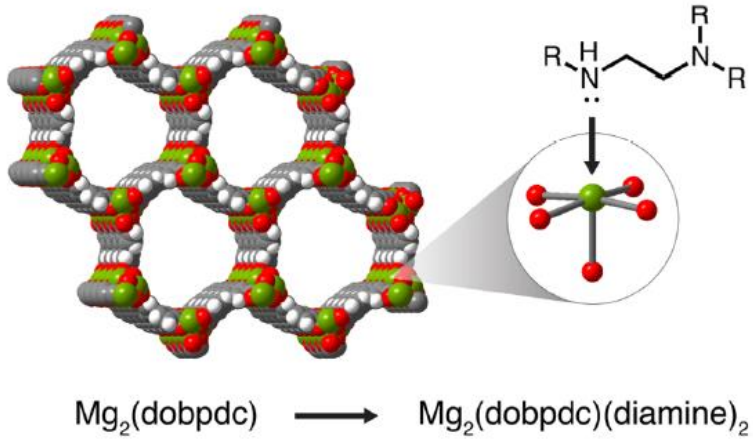
NETL

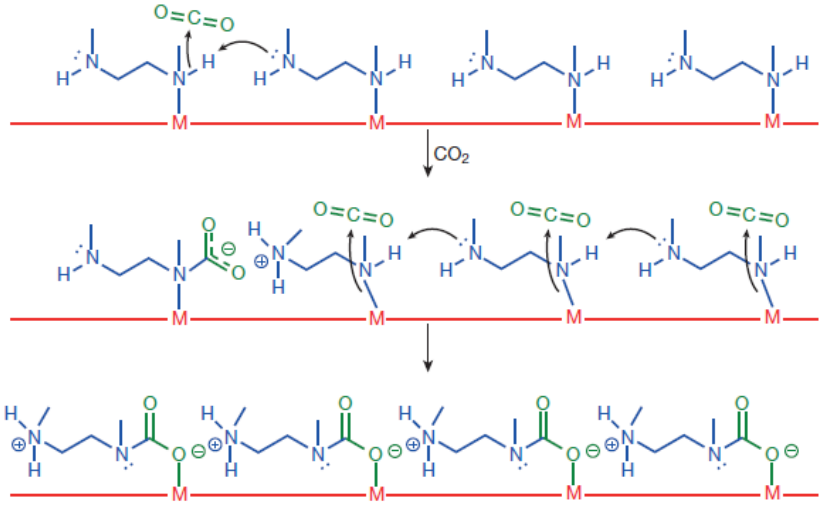
Outline

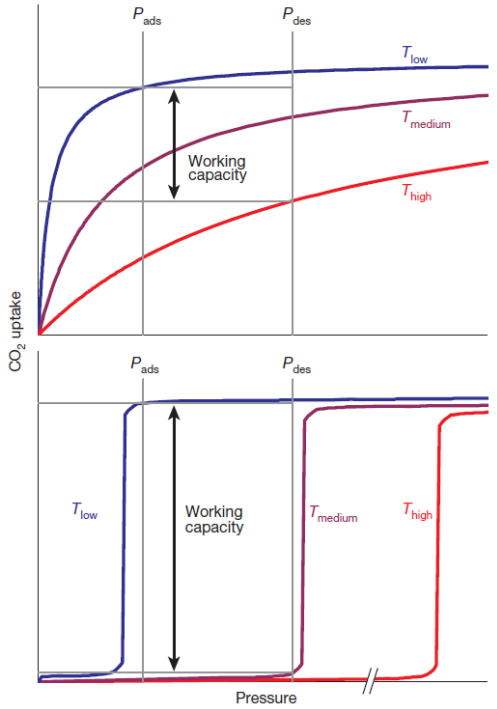
- Diamine-Appended MOF Overview
- Challenges of the Appended MOF
- Isotherm/TGA Modeling
  - Weighted Dual-Site Langmuir
  - Dual-Site Sips
  - TGA Model
- Fixed Bed Modeling
- Future Work

Diamine-Appended MOF Overview

- Being developed by Lawrence Berkeley National Lab
- Currently considering Gen I diamine-appended MOF[1]
- Complicated mechanism forming multiple products- carbamate, carbamic acid, carbamate-carbamic acid chain formation along with physical adsorption







- **dmpn-Mg_2(dobpdc)**

  dmpn=2,2-dimethyl-1,3-diaminopropane

  Dopbdc=4,4′-dioxido-3,3′-biphenyldicarboxylate

1 –Siegelman, R.L., McDonald, T.M., Gonzalez, M.I., Martell, J.D., Milner, P.J., Mason, J.A., Berger, A.H., Bhown, A.S., Long, J.R. Controlling Cooperative Adsorption in Diamine-Appended Mg_2(dobpdc) Metal-Organic Frameworks. Journal of the American Chemical Society. 2017; 139, 10526-10538

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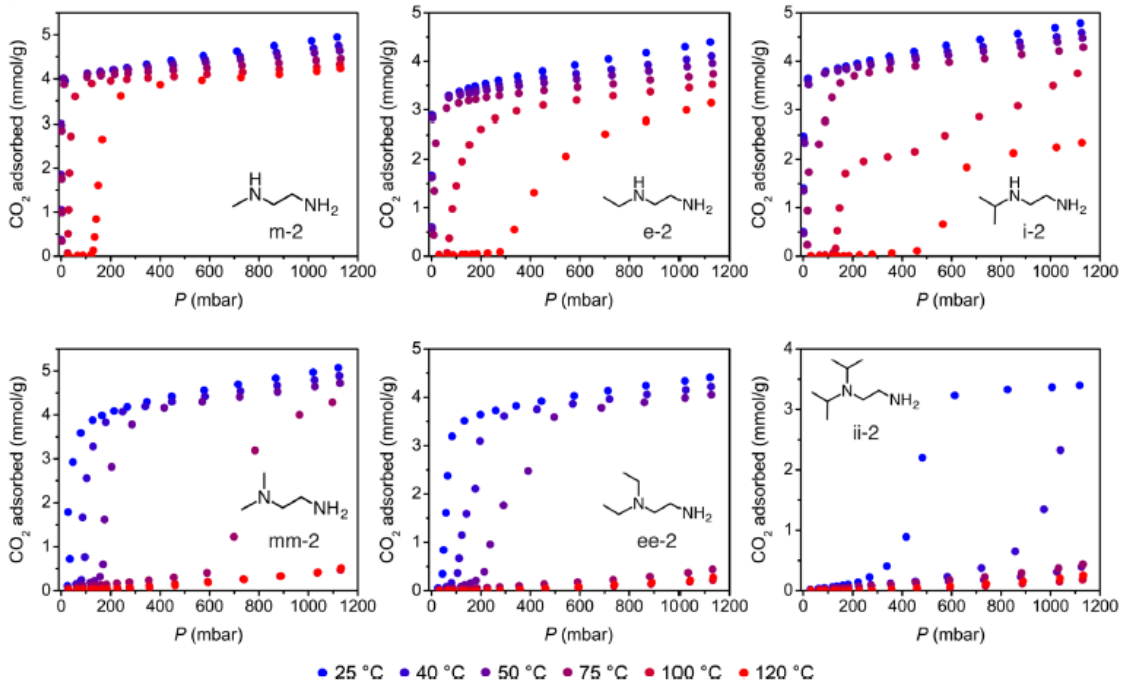
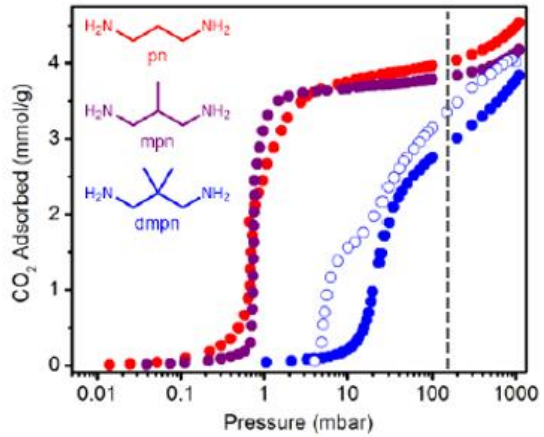
Challenges of the Appended MOFs where Models can Help

- Unusual shapes of the isotherms and strong nonlinearity with temperature
- High driving force, but the limiting mechanisms are mass transfer and heat transfer
- Design and development of efficient thermal management system
- Optimal step location
- Optimal selection and design of the contactor with due consideration of CAPEX and OPEX





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Weighted Dual-Site Langmuir I

$$\boldsymbol{n(P,T) = n_L(P,T)\big(1 - w(P,T)\big) + n_U(P,T)w(P,T)}$$

$$n_L = \frac{n_L^{\infty} b_L P}{1 + b_L P}$$

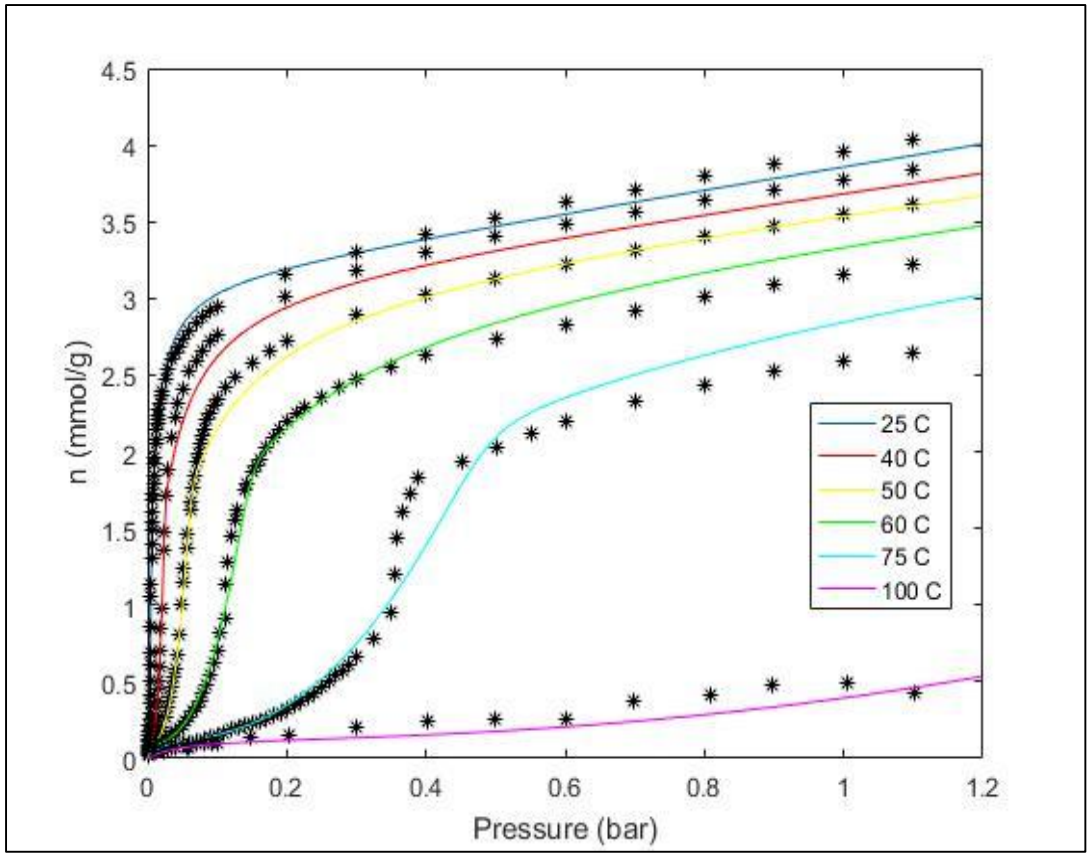
$$n_U = \frac{n_U^{\infty} b_U P}{1 + b_U P} + b_H P$$

$$b_{\propto} = b_{\propto}^{\infty} \exp\left(\frac{E_{\propto}}{RT}\right); \quad \propto = \text{L, U, H}$$

$$w(P,T) = \left(\frac{exp\left(\frac{ln(P) - ln(P_{step}(T))}{\sigma(T)}\right)}{1 + exp\left(\frac{ln(P) - ln(P_{step}(T))}{\sigma(T)}\right)} \right)^{\gamma}$$

$$\sigma(T) = X_1 \exp\left(X_2\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

$$P_{step}(T) = P_{step,0} \exp\left(\frac{-H_{step}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$



Hefti, M., Joss, L, Bjelorbk, Z., Mazzotti, M., Faraday Discussions. 2016; 192, 153-179

Weighted Dual-Site Langmuir II

$$\boldsymbol{n(P,T) = n_L(P,T)\big(1 - w(P,T)\big) + n_U(P,T)w(P,T)}$$

$$n_L = \frac{n_L^{\infty} b_L P}{1 + b_L P} + b_b P$$

$$n_U = \frac{n_U^{\infty} b_U P}{1 + b_U P} + b_H P$$

$$b_{\propto} = b_{\propto}^{\infty} \exp\left(\frac{E_{\propto}}{RT}\right); \quad \propto = \text{L, U, H, b}$$

$$w(P,T) = \left(\frac{exp\left(\frac{ln(P) - ln(P_{step}(T))}{\sigma(T)}\right)}{1 + exp\left(\frac{ln(P) - ln(P_{step}(T))}{\sigma(T)}\right)}\right)^{\gamma}$$

$$\sigma(T) = X_1 \exp\left(X_2\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)$$

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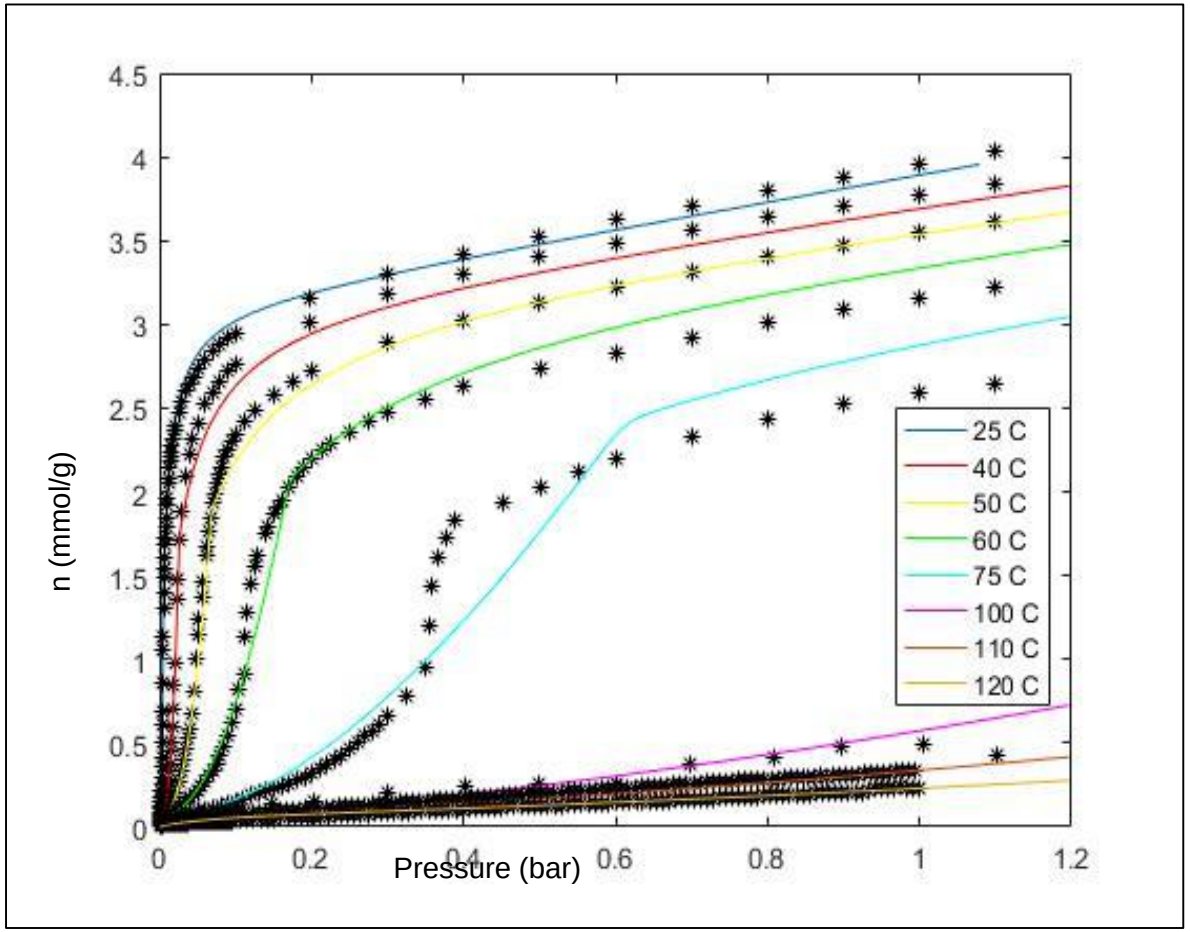
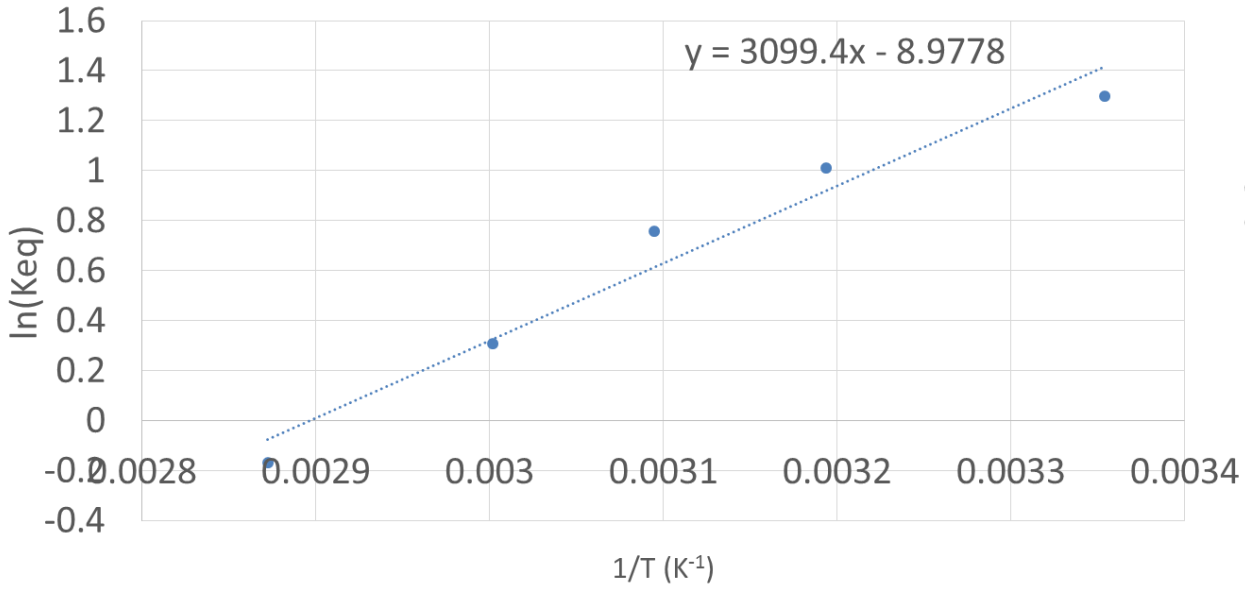


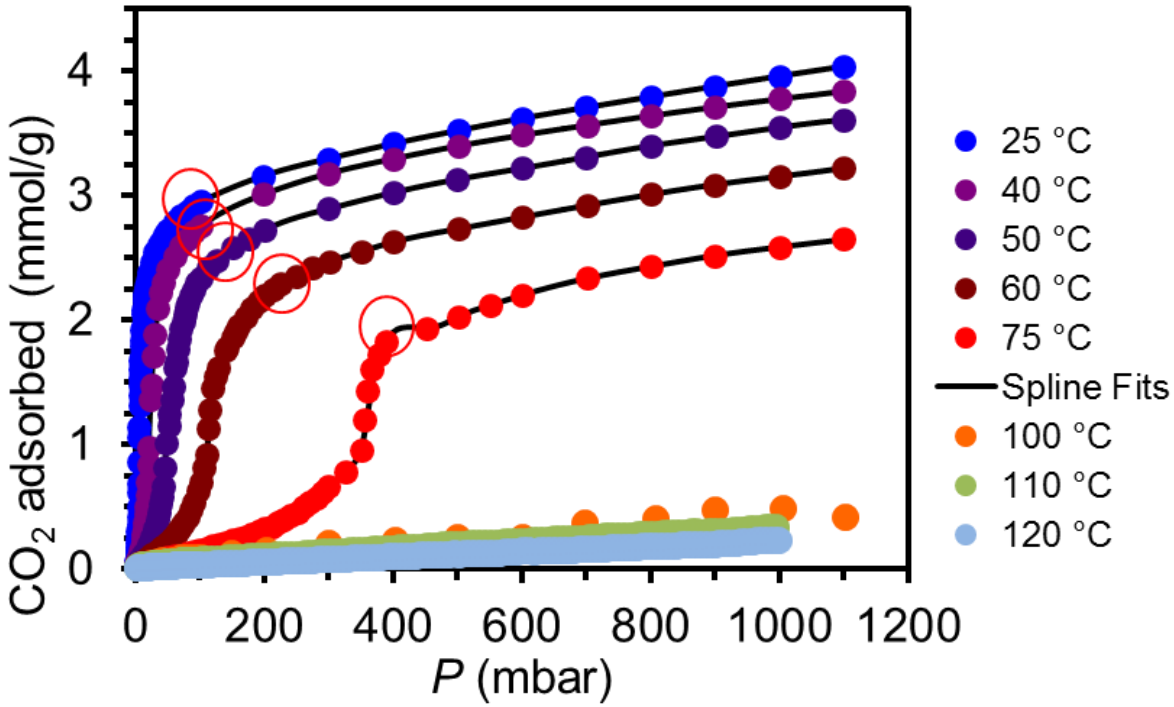
Chemical Equilibrium

$$CO_2 + [N] \leftrightarrow [CO_2\text{–}N]$$

$$K_{eq} = \frac{[CO_2 - N]}{[N]} = \frac{n_{max,c}}{q_{max} - n_{max,c}}$$

$$\ln[K_{eq}] = K_a + \frac{K_b}{T}$$





Dual-Site Sips Isotherm

$$n = n_{max,c}\left[\frac{(b_a P)^{1/n_a}}{1+(b_a P)^{1/n_a}}\right] + n_{max,p}\left[\frac{(b_b P)^{1/n_b}}{1+(b_b P)^{1/n_b}}\right]$$

$$b = b_0 \exp\left[\frac{Q_{st}}{RT_0}\left(\frac{T_0}{T}-1\right)\right]$$

- Previously used to model CO_2 adsorption on MOF's and activated carbons[1,2]

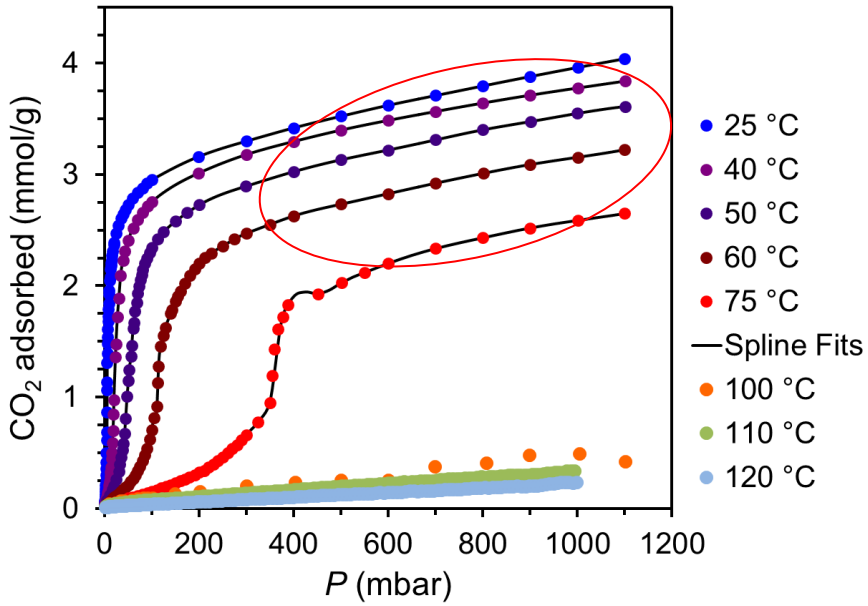
1 - Bao, Z., Yu, L., Ren, Q., Lu, X., Deng, S. Adsorption of CO_2 and CH_4 on a magnesium-based metal organic framework. Journal of Colloid and Interface Science. 2011; 353, 549-556
2 - Tzabar, N., Brake, H. Adsorption isotherm and Sips models of nitrogen, methane, ethane, and propane on commercial activated carbons and polyvinylidene chloride. Adsorption. 2016; 22, 901-914

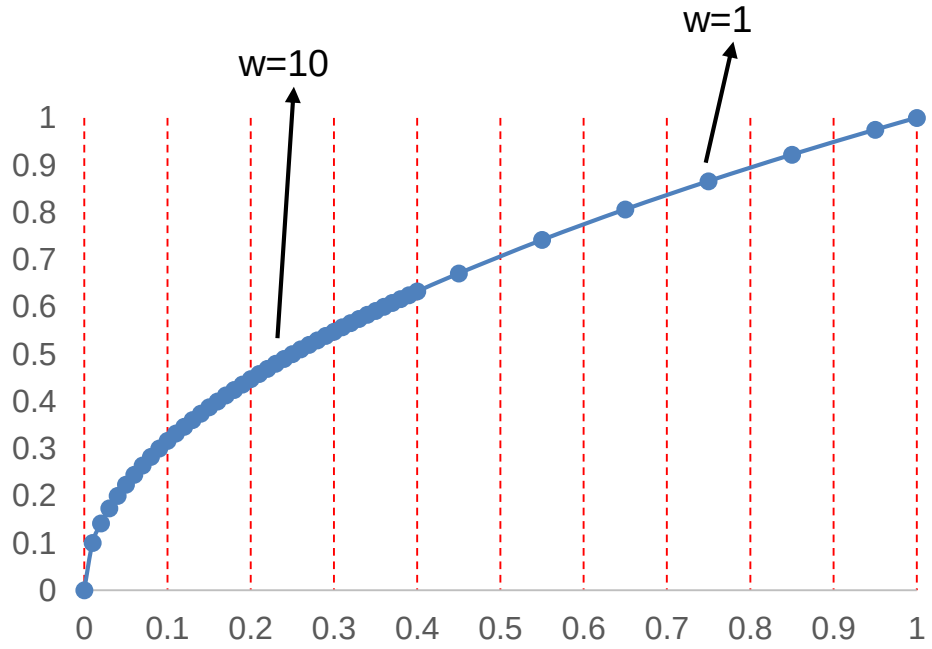
Bin Weighting

- Used to equally represent the data along entire pressure range
- $obj = \varepsilon^T W^{-1} \varepsilon$

$$\varepsilon_i = \frac{q_i - n_i}{q_i}$$

$$\mathbf{1 \leq w \leq 166}$$





Bin Weighting Example

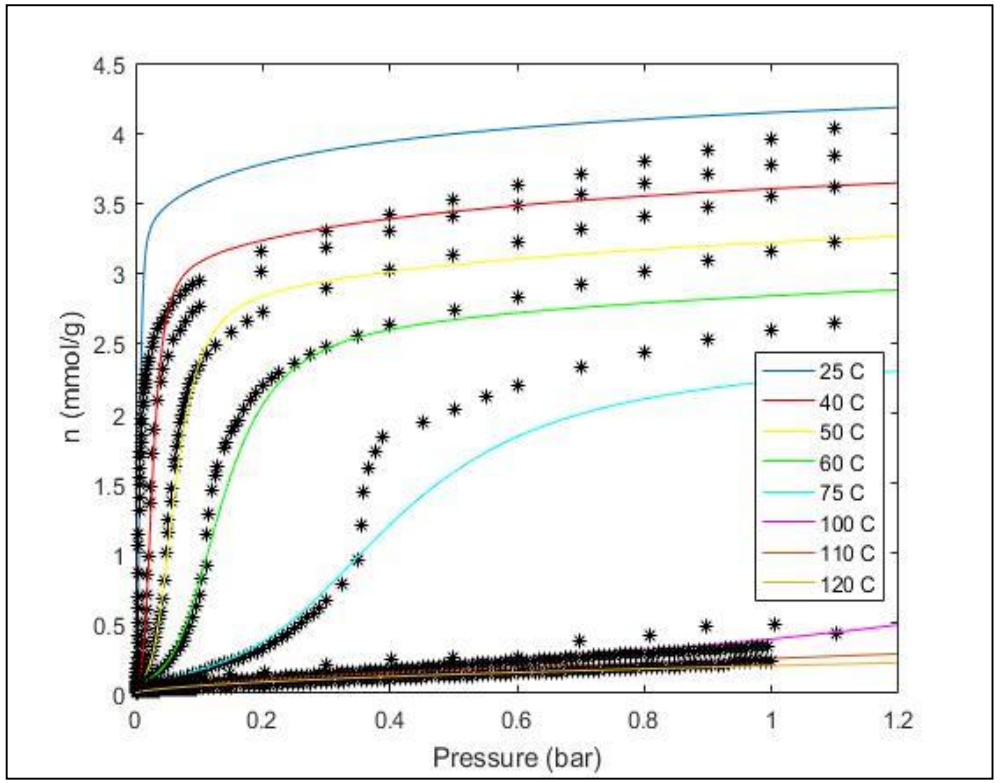
Modified Dual-Site Sips Isotherm

$$\boldsymbol{n = n_{max,c}\left[\frac{(b_a P)^{1/n_a}}{1+(b_a P)^{1/n_a}}\right] + n_{max,p}\left[\frac{(b_b P)^{1/n_b}}{1+(b_b P)^{1/n_b}}\right]}$$

$$n_{max,c} = \frac{n_{max,N} K_{eq,c}}{1 + K_{eq,c}};\ n_{max,N} = 3.82\ mmol/g$$

$$\ln(K_{eq,c}) = K_a + \frac{K_b}{T}$$

$$b = b_0 \exp\left[\frac{Q_{st}}{RT_0}\left(\frac{T_0}{T} - 1\right)\right]$$



Modified Dual-Site Sips Isotherm I

$$\boldsymbol{n = n_{max,c}\left[\frac{(b_a P)^{1/n_a}}{1+(b_a P)^{1/n_a}}\right] + n_{max,p}\left[\frac{(b_b P)^{1/n_b}}{1+(b_b P)^{1/n_b}}\right]}$$

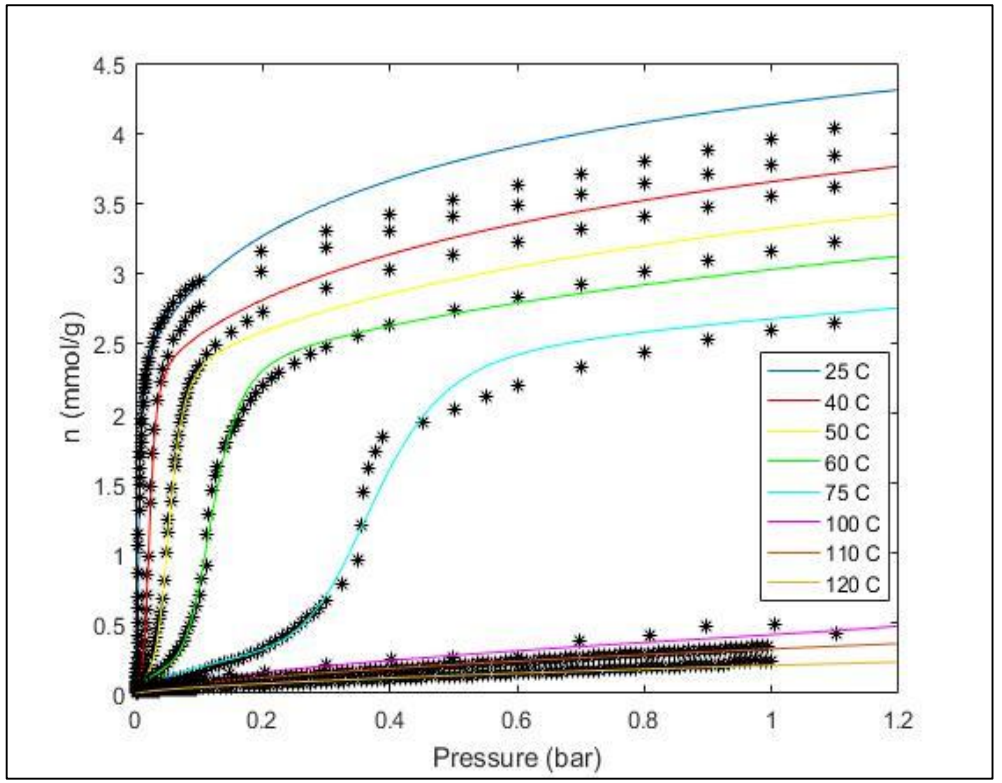
$$n_{max,c} = \frac{n_{max,N} K_{eq,c}}{1+K_{eq,c}};\ n_{max,N} = 3.82\ mmol/g$$

$$\ln(K_{eq,c}) = K_a + \frac{K_b}{T}$$

$$b = b_0 \exp\left[\frac{Q_{st}}{RT_0}\left(\frac{T_0}{T}-1\right)\right]$$

$$n_a = n_{a,1}\exp\left[\frac{E_{na}}{RT_0}\left(\frac{T_0}{T}-1\right)\right];\ T_0 = 318\ K$$

$$n_{max,p} = n_{\max,p,1}\left[\frac{\exp\left(K_c + \frac{K_d}{T}\right)}{1+\exp\left(K_c + \frac{K_d}{T}\right)}\right]$$



Modified Dual-Site Sips Isotherm II

$$n = n_{max,c}\left[\frac{(b_a P)^{1/n_a}}{1+(b_a P)^{1/n_a}}\right] + n_{max,p}\left[\frac{(b_b P)^{1/n_b}}{1+(b_b P)^{1/n_b}}\right] + dP$$

$$d = d_0 \exp\left(\frac{E_d}{RT}\right)$$

$$n_{max,c} = \frac{n_{max,N} K_{eq,c}}{1+K_{eq,c}};\ n_{max,N} = 3.82\ mmol/g$$

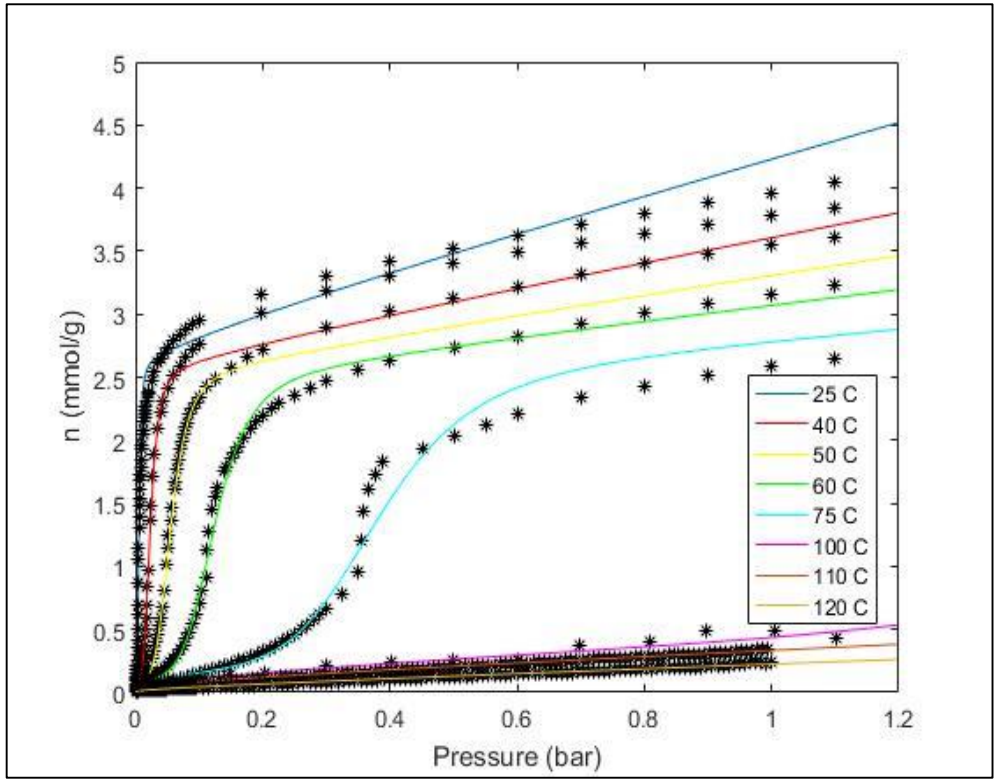
$$\ln(K_{eq,c}) = K_a + \frac{K_b}{T}$$

$$b = b_0 \exp\left[\frac{Q_{st}}{RT_0}\left(\frac{T_0}{T}-1\right)\right]$$

$$n_a = n_{a,1}\exp\left[\frac{E_{na}}{RT_0}\left(\frac{T_0}{T}-1\right)\right];\ T_0 = 318\ K$$

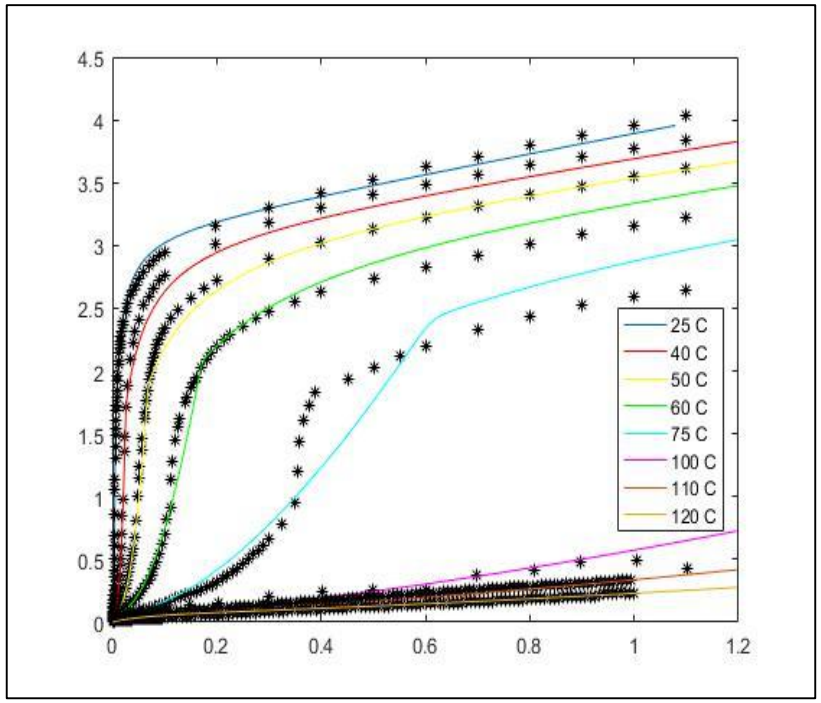
$$n_b = n_{b,1}\exp\left[\frac{E_{nb}}{RT_0}\left(\frac{T_0}{T}-1\right)\right];\ T_0 = 318\ K$$

$$n_{max,p} = n_{\max,p,1}\left[\frac{\exp\left(K_c + \frac{K_d}{T}\right)}{1+\exp\left(K_c + \frac{K_d}{T}\right)}\right]$$



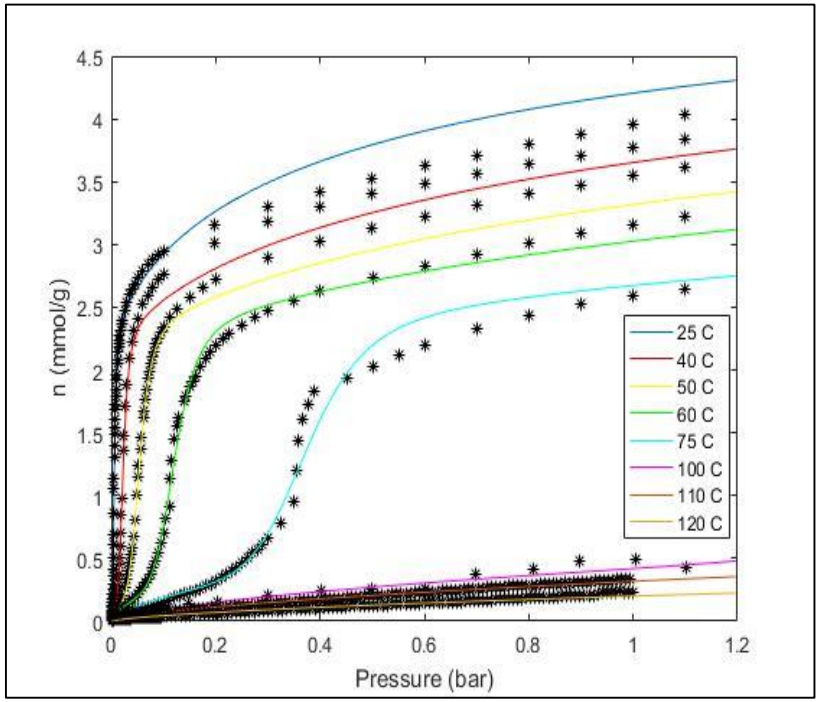
Isotherm Model Comparison

Weighted Dual-Site Langmuir I



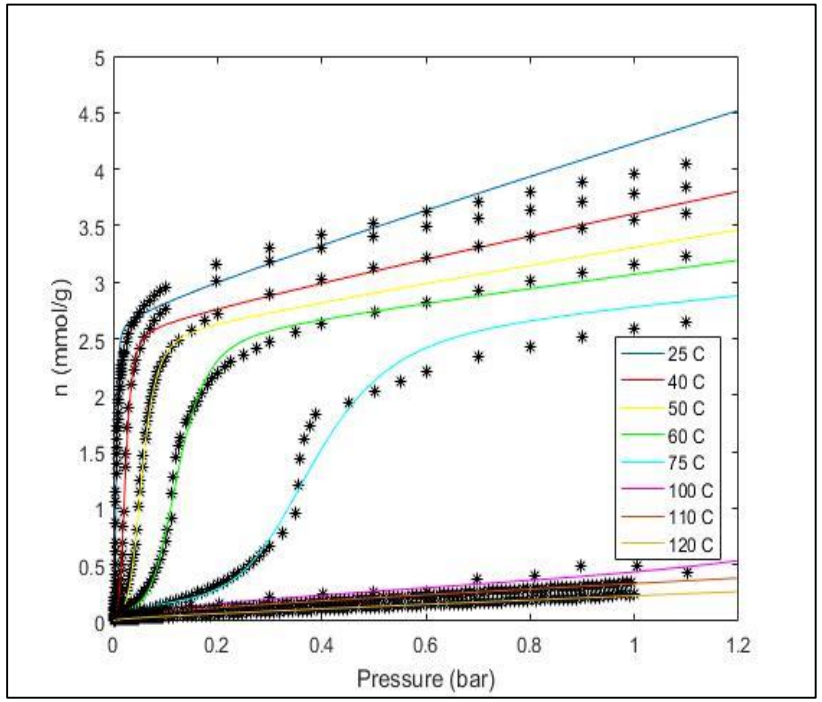
RMSE=0.090

Modified Dual-Site Sips I



RMSE=0.067

Modified Dual-Site Sips II



RMSE=0.083

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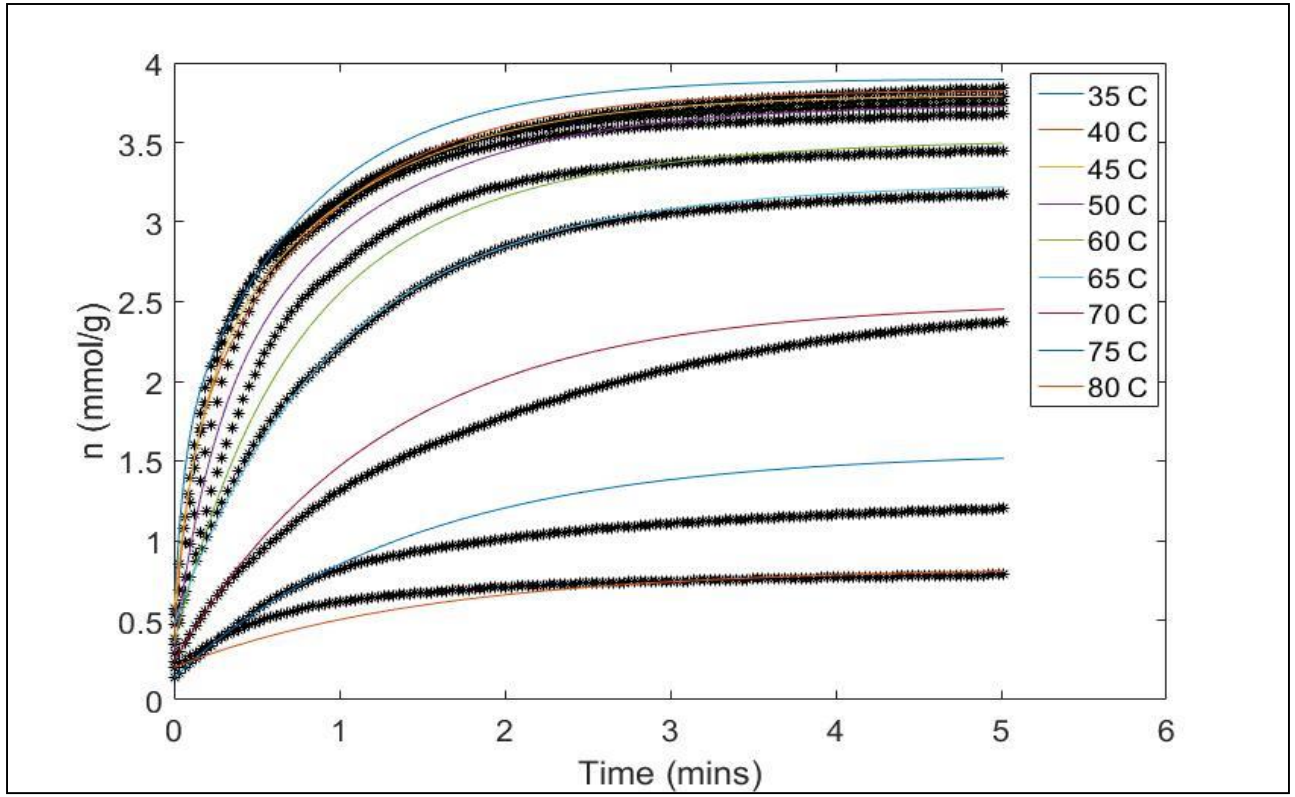
TGA Model Validation

$$\frac{dn}{dt} = \frac{dn_{chem}}{dt} + \frac{dn_{phys}}{dt}$$

$$\frac{dn_{chem}}{dt} = k_{c,0} \exp\left(\frac{-Ec}{RT}\right)\left[n^*_{chem}(P,T) - n_{chem}\right]$$

$$\frac{dn_{phys}}{dt} = k_{p,0} \exp\left(\frac{-Ep}{RT}\right)\left[n^*_{phys}(P,T) - n_{phys}\right]$$



- **Experimental data from LBNL**

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Fixed Bed Modeling

- Dynamic, 1-D, non-isothermal model
- Incorporates external and internal mass transfer resistances
- Model will be updated when the information of the shaped particle is available

Bulk Gas Phase Species Balance

$$\varepsilon \frac{\partial C_{g,i}}{\partial t} = -\frac{\partial \left(v_g C_{g,i}\right)}{\partial z} + \varepsilon \frac{\partial}{\partial z}\left(D_{ax} \frac{\partial C_{g,i}}{\partial z}\right) - (1-\varepsilon)\frac{3k_{f,i}}{a_p}\left(C_{g,i} - C_{p,i}\Big|_{r=r_p}\right)$$

Solid Phase Species Balance:

$$\varepsilon_p \frac{\partial C_{p,i}}{\partial t} = -\left(1-\varepsilon_p\right)\rho_p \frac{dn_i}{dt} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{eff,i}\frac{\partial C_{p,i}}{\partial r}\right)$$

$$\frac{dn_i}{dt} = \frac{dn_{chem,\boldsymbol{i}}}{dt} + \frac{dn_{phys,\boldsymbol{i}}}{dt}$$

$$\frac{dn_{chem,\boldsymbol{i}}}{dt} = k_{c,0}\exp\left(\frac{-Ec}{RT}\right)\left[n^*_{chem,\boldsymbol{i}}(P,T) - n_{chem,\boldsymbol{i}}\right]$$

$$\frac{dn_{phys,\boldsymbol{i}}}{dt} = k_{p,0}\exp\left(\frac{-Ep}{RT}\right)\left[n^*_{phys,\boldsymbol{i}}(P,T) - n_{phys,\boldsymbol{i}}\right]$$

Fixed Bed Modeling

Pressure Drop:

$$-\frac{\partial P_g}{\partial z} = \frac{150\,\mu_g(1-\varepsilon)^2 v_g}{\varepsilon^3\,{d_p}^2} - \frac{1.75(1-\varepsilon)\rho_g|v_g|v_g}{\varepsilon^3\,d_p}$$

Bulk Gas Phase Energy Balance:

$$\varepsilon\rho_g\frac{\partial H_g}{\partial t} = -\rho_g\frac{\partial(v_g H_g)}{\partial z} - (1-\varepsilon)a_p h_f(T_g - T_s) - \frac{4}{D_r}h_w(T_g - T_w)$$

Bulk Solid Energy Balance:

$$\rho_b\frac{\partial H_s}{\partial t} = \rho_b\sum(-\Delta H_i)\frac{dn_i}{dt} + a_p h_f(T_g - T_s)$$

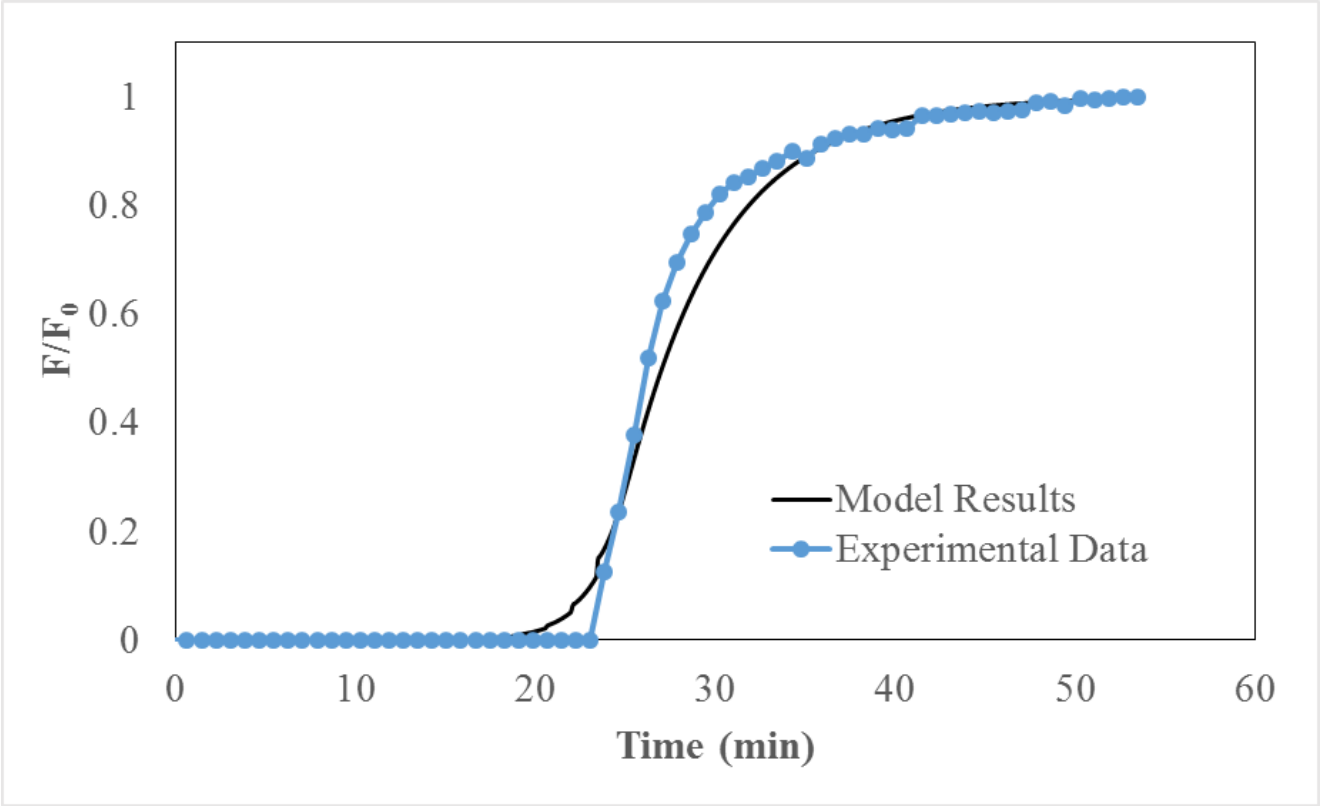
Wall Energy Balance:

$$\rho_w C_{p,w}\frac{\partial T_w}{\partial t} = a_w h_w(T_g - T_w) - a_{w1}U_0(T_w - T_\infty)$$

Model Validation

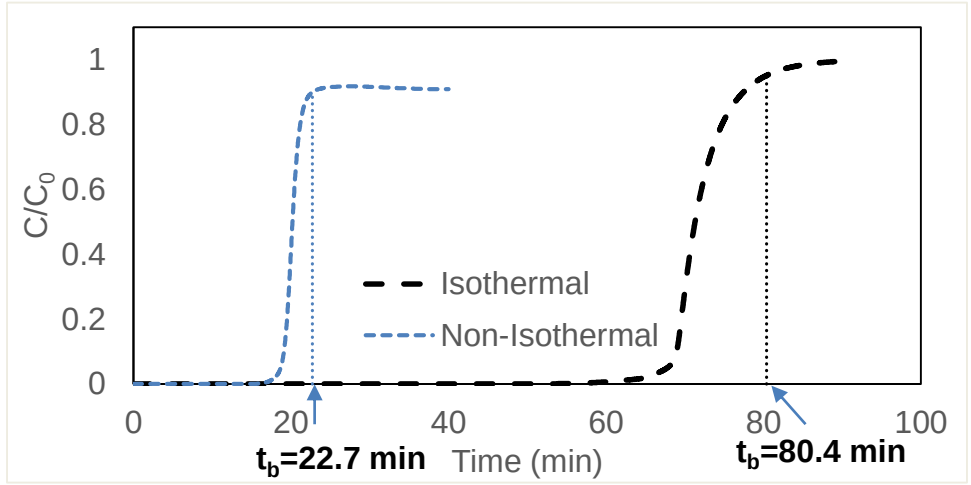
- **Model Validation**
  - PDAEs solved using Aspen Custom Modeler using method of lines
  - Experimental data from LBNL for the powdered material

Model Constants	
Heat of Adsorption (kJ/mol)	-65
Heat Capacity (J/g/^{o}C)	1.457
Thermal Conductivity (W/m/K)	0.075
Heat Transfer Coefficient (W/m^2/K)	50



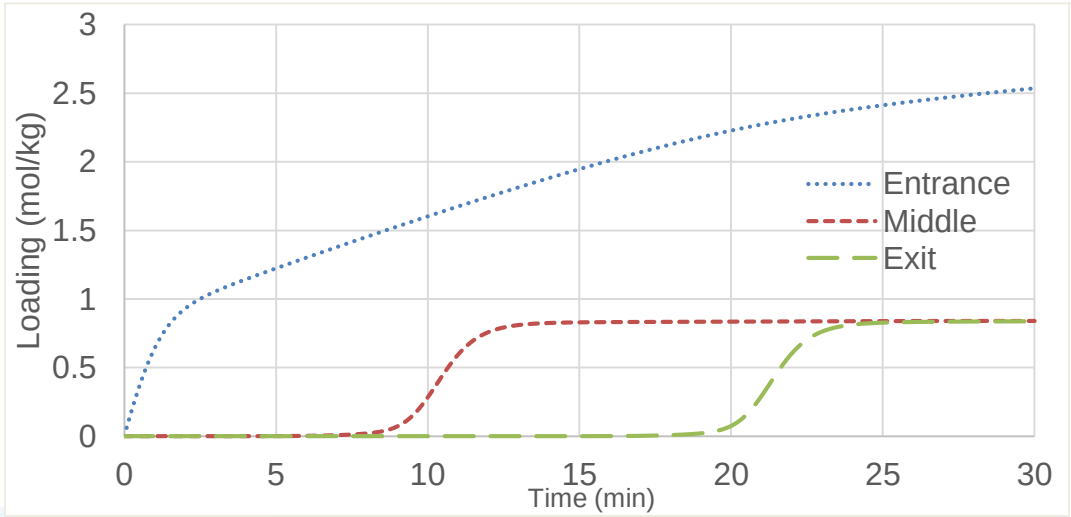
Base Case

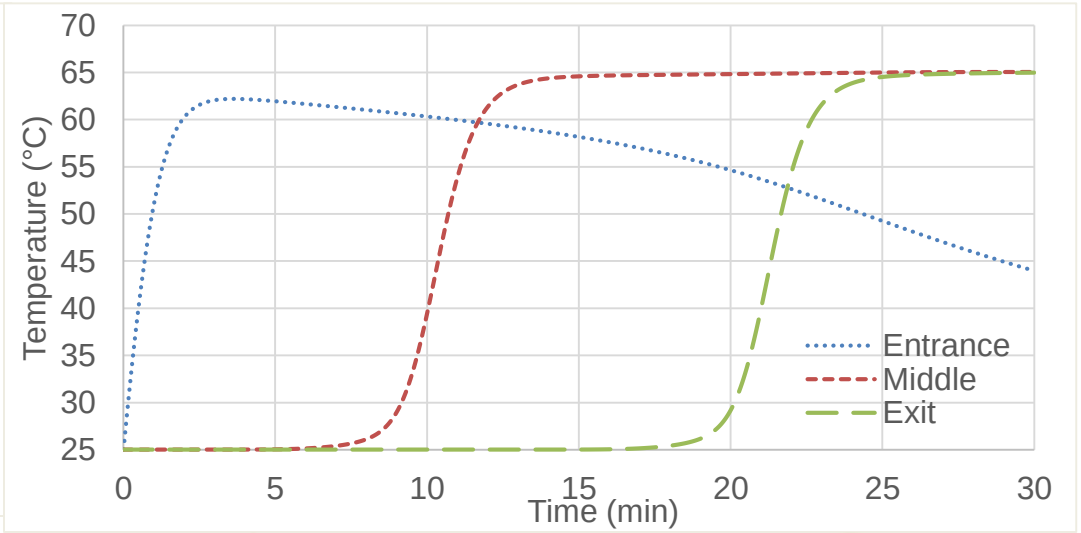
Operating Conditions	
Pressure (bar)	1.1
Temperature (°C)	25
Flow rate (mol/s)	120
y_{CO2}	0.132
y_{H2O}	0.055
y_{N2}	0.813
Bed Length (m)	10
Bed Diameter (m)	3



- Large temperature spikes due to high heat of adsorption and poor heat removal from the system
  - Thermal management can considerably increase performance as seen by comparing isothermal with non-isothermal cases for same inlet conditions
    - $t_{b,\ isothermal}$ = 80.4 min
    - $t_{b,\ non\text{-}isothermal}$ = 22.7 min

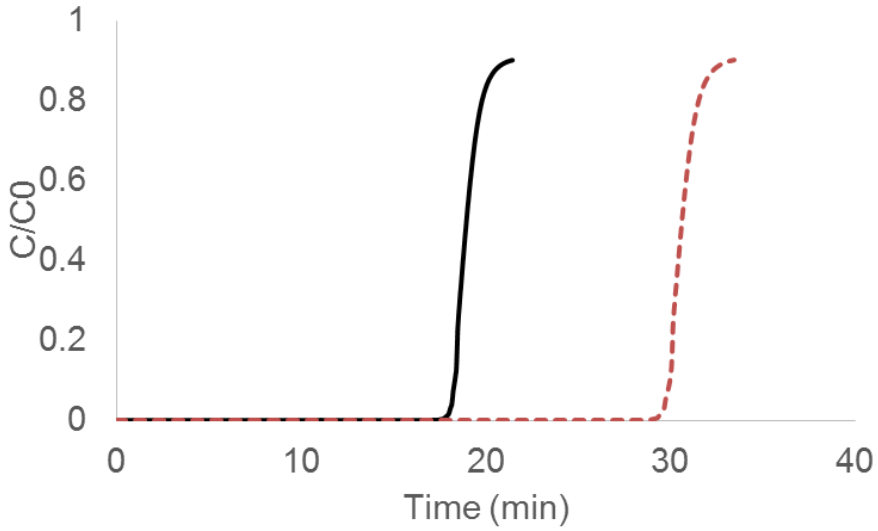
Breakthrough time: $\left[F_{in} z_{CO_2,in} * 0.1 * t_b = \sum_{i=1}^{n} F_{out,i}\, z_{CO_2,out,i} \Delta t\right]$

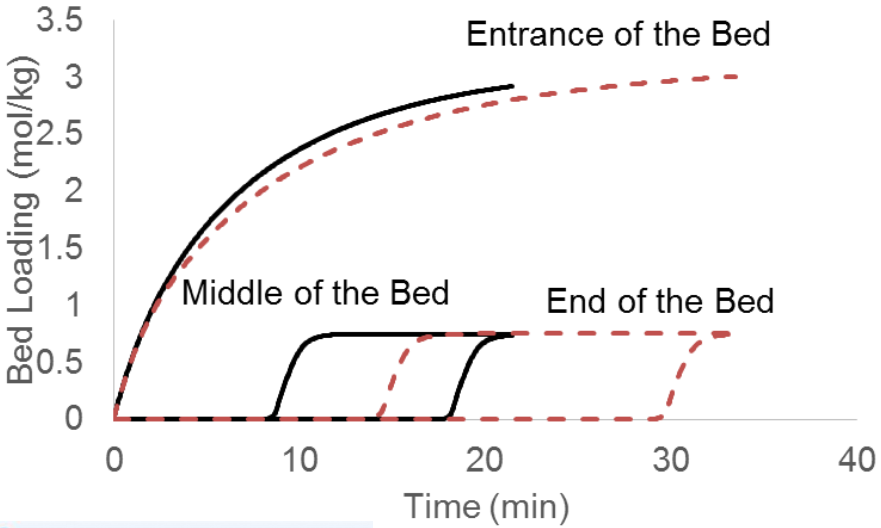




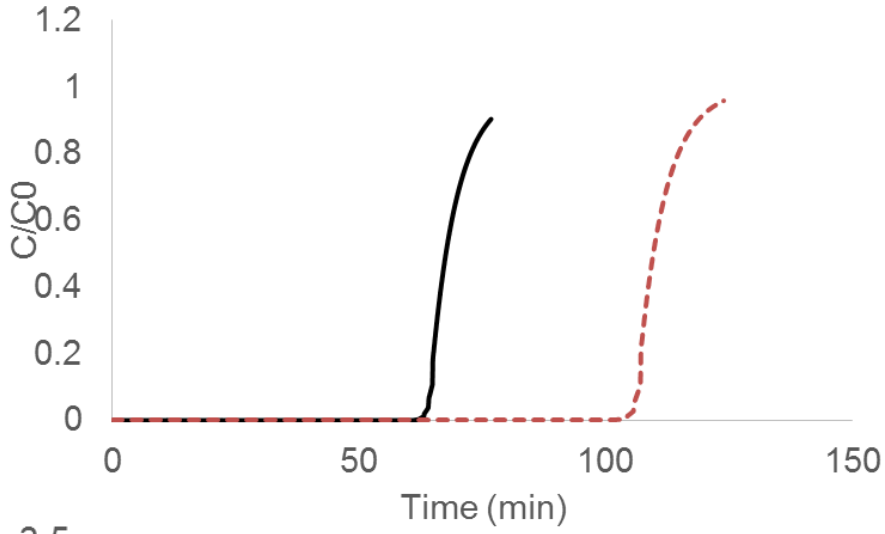
Impact of Residence Time (superficial velocity)

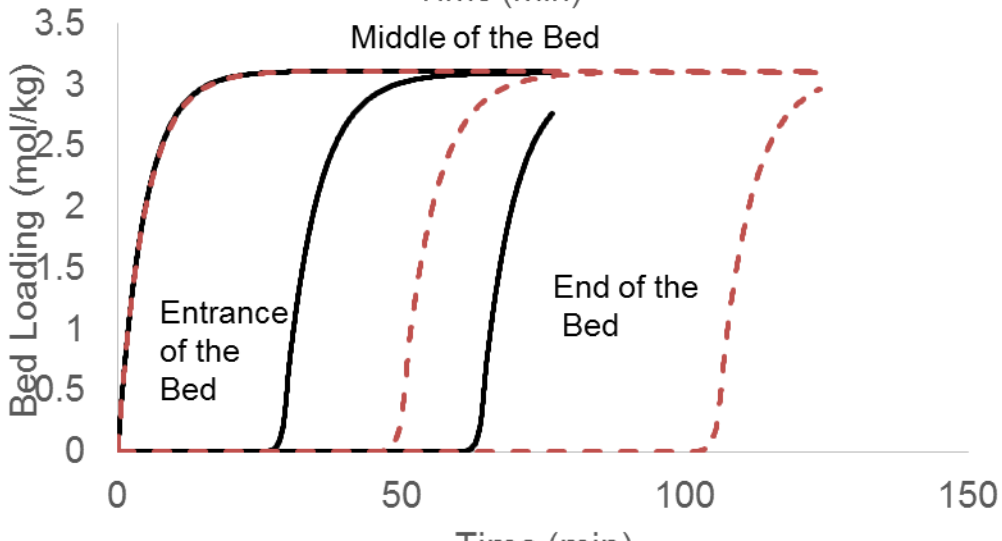
Nonisothermal





Isothermal





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Future Work

- LBNL is setting up fixed bed experiments where the temperature measurements at three different locations in a fixed bed system will be available. The process model will be validated with that data. The process model will be used to predict the temperature at other locations where there are no sensors.
- Adsorption Chemistry Modeling
  - Physically meaningful isotherm model
  - Multicomponent isotherm model with due consideration of presence of water
- Modeling mass transfer and heat transfer for the final shaped particle
- Determination of optimal step location
- Develop efficient thermal management strategies
- Optimal fixed bed design
- Process modeling and optimization of a rotary packed bed
- Process modeling and optimization of a moving bed
- Development of a CFD model for the fluidized bed contactor

Acknowledgements

- LBNL and UC, Berkley(Jeffrey Long, Stephanie Didas, Rebecca Siegelman, Surya Parker, Alex Forse, Jeff Martell) for the experimental data and support

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Carbon Capture Simulation for Industry Impact

For more information
https://www.acceleratecarboncapture.org/

Debangsu Bhattacharyya
West Virginia University
Debangsu.Bhattacharyya@mail.wvu.edu

Janine Carney
NETL
Janine.Craney@netl.doe.gov