1st-Principles Modeling of Sorbent-Based DAC Systems

Advanced PSE+ Stakeholder Summit

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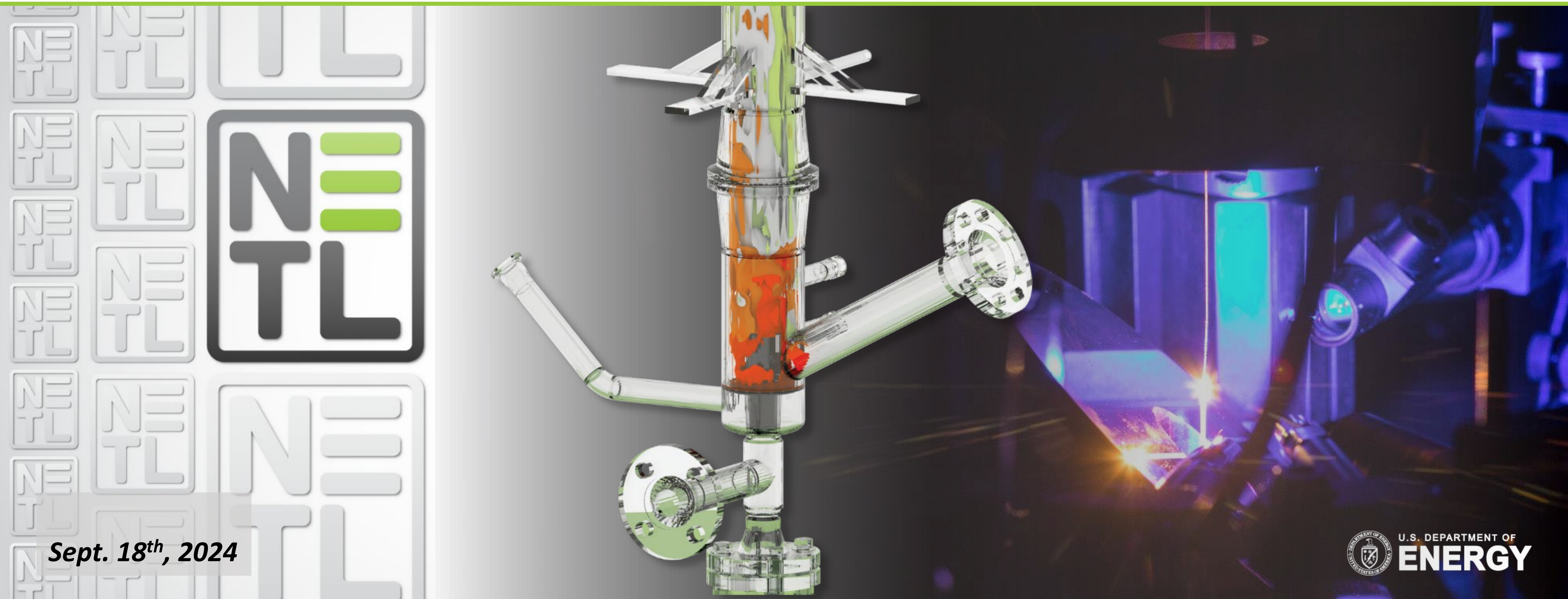


Sept. 18th, 2024

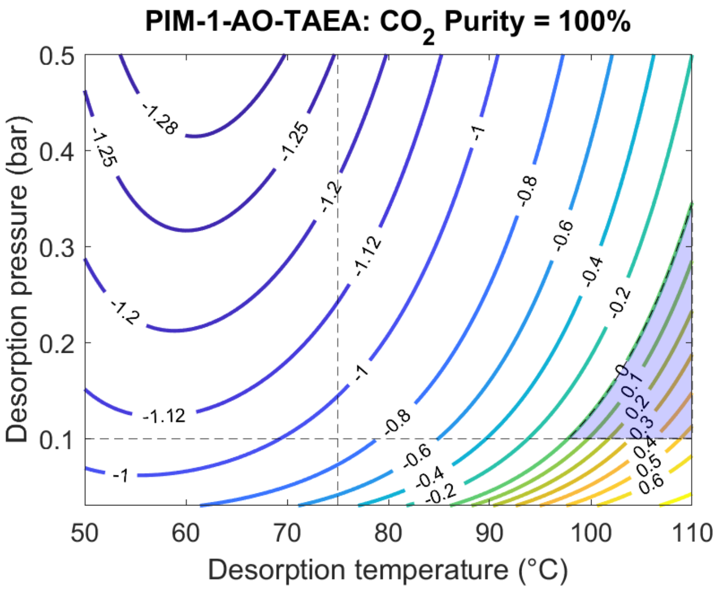
Key Outcome: Support NETL DAC Technology Development

NATIONAL
ENERGY
TECHNOLOGY
LABORATORY

Support process design and scale-up analysis of NETL's novel sorbent

- Guide experiments to reduce modeling uncertainty and reduce technical risk
- Evaluate different regeneration methods (temperature swing, vacuum assisted temperature swing, etc.)
- Characterize sorbent performance

CO_2 Cyclic Working Capacity Analysis



Advanced Modeling tools

CCSI²
Carbon Capture Simulation for Industry Impact

IDAES
Institute for the Design of Advanced Energy Systems

Model libraries

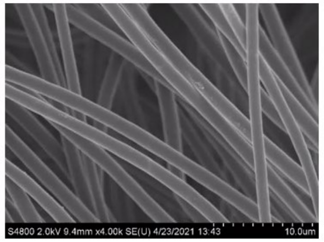
- Large suite of first- principles contactor models
- Adaptable open models for both sorbent and solvent based systems
- Custom models in commercial platforms

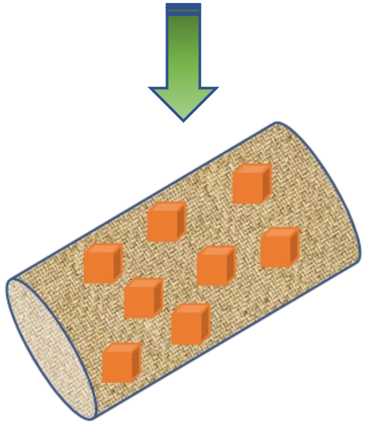
Open Source:
github.com/IDAES/idaes-pse
github.com/CCSI-Toolset

PSE Approach to Support Sorbent Development

Sorbent synthesis and data collection → Property Model Development → Cyclic Working Capacity Analysis → Process Model Development → Advanced Analysis of Process Systems

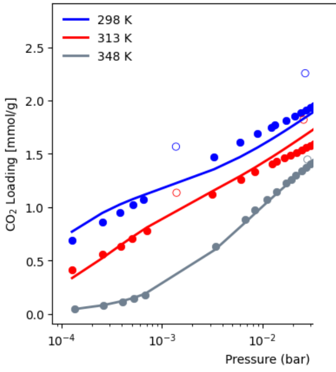
Amidoxime polymer adsorbent



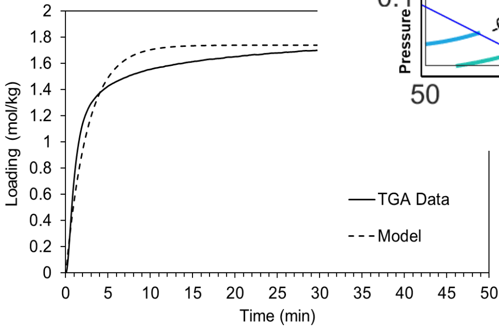


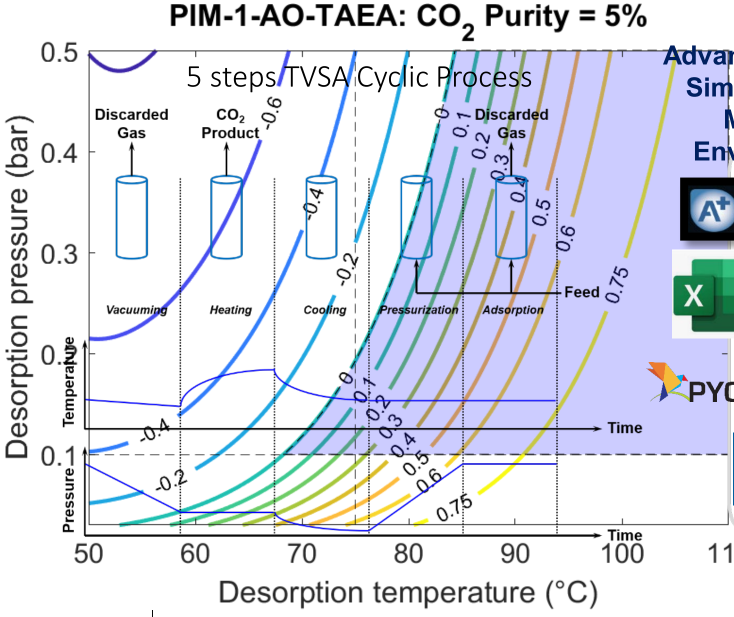
Shapeable microporous functionalized sorbent materials

Isotherm Model



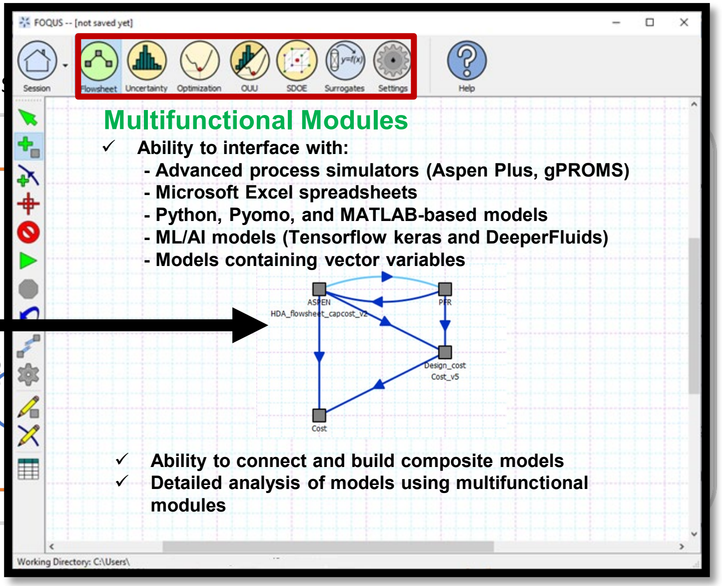
Kinetic Mod





Advanced Process Simulators and Modeling Environments

Core open-source computational tool within the CCSI-Toolset



Multifunctional Modules

- ✓ Ability to interface with:
  - Advanced process simulators (Aspen Plus, gPROMS)
  - Microsoft Excel spreadsheets
  - Python, Pyomo, and MATLAB-based models
  - ML/AI models (Tensorflow keras and DeeperFluids)
  - Models containing vector variables
- ✓ Ability to connect and build composite models
- ✓ Detailed analysis of models using multifunctional modules

How To Support Technology Development For Solid Sorbents?

High Level Cost Estimation **TEA – material performance and ambient conditions** **FEED Studies**

Simplified Model → **Equilibrium-based 0D shortcut model** → **Equilibrium-based 1D model** → **Rate-based 1D model**

Simplified Model
- Separation fixed
- Pressure drop computed
- Cycle times assumed

Equilibrium-based 0D shortcut model
- Cyclical steady-state
- Adsorption is instantaneous
- Ideal gas
- No axial or radial gradients
- Assume cycle steps for adsorbent

Equilibrium-based 1D model
- Include axial variations in state variables
- Adsorption is instantaneous
- Ideal gas
- No radial gradients

Rate-based 1D model
- Add rate equations
- Ideal gas
- No radial gradients

Key Contributions:
- Established a collaboration workflow to support material development and experimental campaigns
- Developed a gas/solid contactor model library
- Capital and operating costs for sorbent systems: leveraged generalized methodology for project & process costing, and fixed and variable O&M [1][2]
- Process design and optimization of Direct Air Capture Technologies

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[1] Direct Air Capture Case Studies: Sorbent System NETL report *(*https://www.osti.gov/biblio/1879535*)*

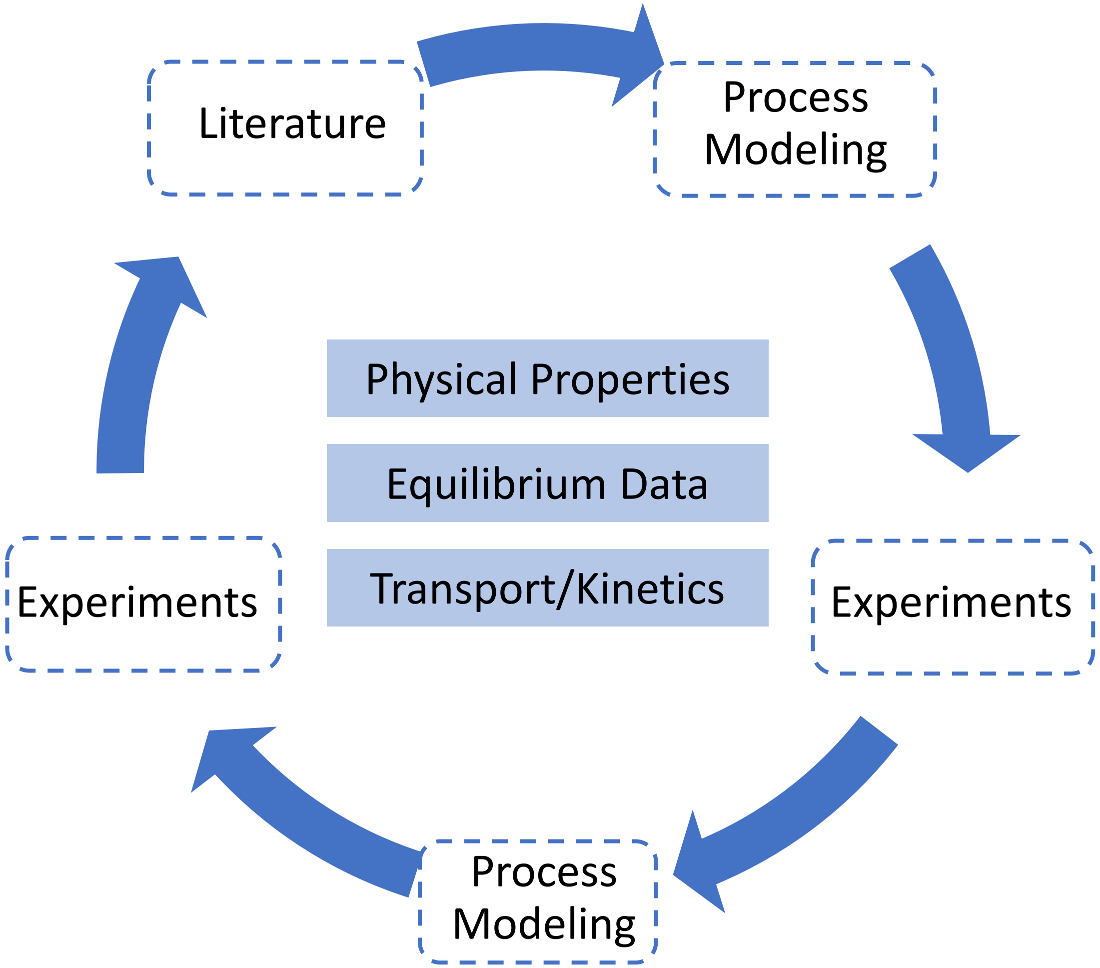
[2] Quality Guidelines for Energy System Studies - Capital Cost Scaling Methodology: Revision 4a NETL Report (https://www.osti.gov/biblio/1893821*)*

From Experiments to Flowsheet Optimization

Guide Experimental collaborators to measure critical data

Measured Data

- Physical properties (sorbent density, heat capacity, size of particles)
- Pure component isotherm of CO_2 at different temperatures
- TGA data of pure CO_2
- TGA data CO_2 under humid conditions



Literature

Process Modeling

Experiments

Process Modeling

Experiments

Physical Properties

Equilibrium Data

Transport/Kinetics

Data Gap

- Pure component isotherm of H_2O
- Cooperative/competitive CO_2+H_2O adsorption data
- Breakthrough data for CO_2 and H_2O
- Breakthrough at different temperatures

Addressing Data Limitations

- Literature data (Pure component isotherm of H_2O, and heat transfer coefficient)
- Model assumptions (Enhancement factor for cooperative CO_2+H_2O adsorption)

Support for NETL DAC Technology Development

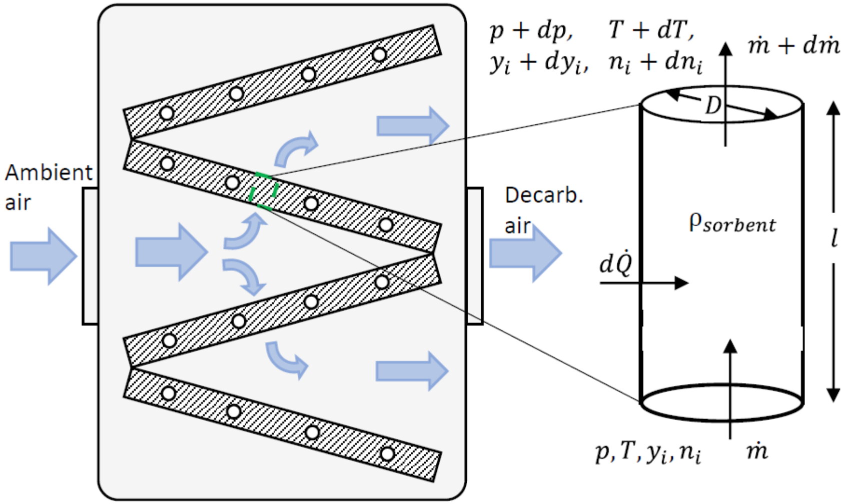
The **goal** is to suspport **NETL’s DAC Test Center** with process system engineering and scale up analysis for their **novel sorbent material** (*PIM-1-AO-TAEA)*.

- Guide experimentalists to measure critical data to inform process models
- Is this sorbent competitive with existing sorbents and MOFs?
- What is the sorbent performance under different ambient conditions?
- How uncertainty affects performance?

Process Modeling of NETL Sorbent Case Study

Modeling Fixed Bed Designs With Low Pressure Drop

- Design of the column to mimic the air contactor presented by Climeworks, which resembles an air ventilation system rather than a conventional adsorber column.



Assumption of a flat bed[1] to mimic a differential segment of the plates containing the solid sorbent in the Climeworks contactor

Dimension	Value
Bed Diameter (m)	0.1
Bed Height (m)	0.01

Two process models developed for analysis

- Shortcut TVSA model
- Rigorous TVSA model

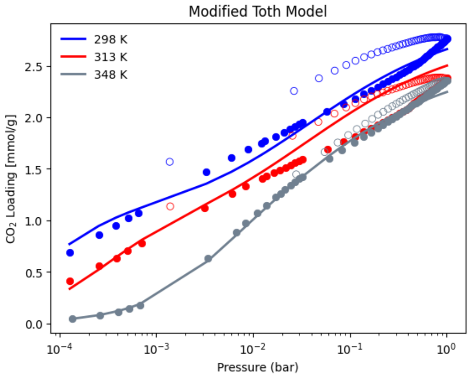
[1] Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, “The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes,” Energy Environ. Sci., (2021), 14(10), 5377-5394

Sorbent Modeling Approaches

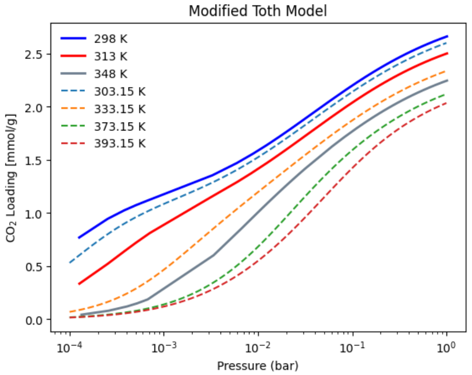
CO_2 Isotherm Model: Modified Toth[1]

$$q^*_{CO_2} = \left[\frac{q^\infty bP}{(1+(bP)^t)^{1/t}}\right]_{chem} + \left[\frac{q^\infty bP}{(1+(bP)^t)^{1/t}}\right]_{phys}$$

Parameter estimation: $\min_{\theta} \left(\frac{q^*_{exp}-q^*_{model}}{q^*_{exp}}\right)' \left(\frac{q^*_{exp}-q^*_{model}}{q^*_{exp}}\right)$



Fit to Experimental Isotherm Data

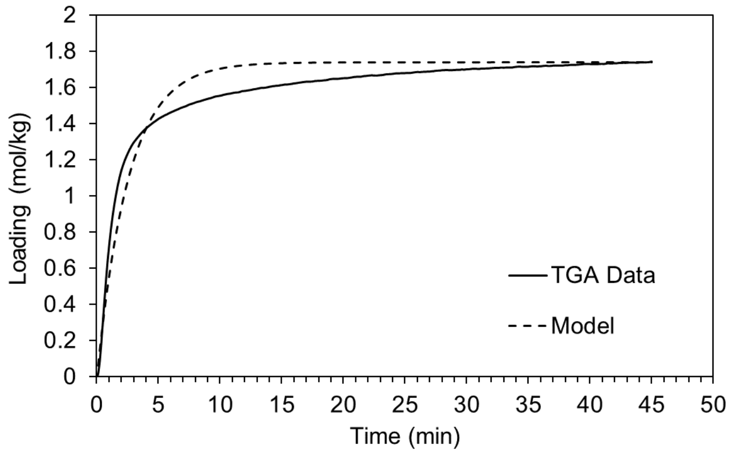


Extrapolation to 100 °C

CO_2 Kinetic Model: Linear Driving Force (LDF) Model

$$\frac{dq_{CO_2}}{dt} = k_{CO_2}\left(q^*_{CO_2} - q_{CO_2}\right)$$

Parameter estimation: $\min_{\theta} \left(q_{exp} - q_{model}\right)' \left(q_{exp} - q_{model}\right)$



Model Fit to experimental TGA data at 25 °C

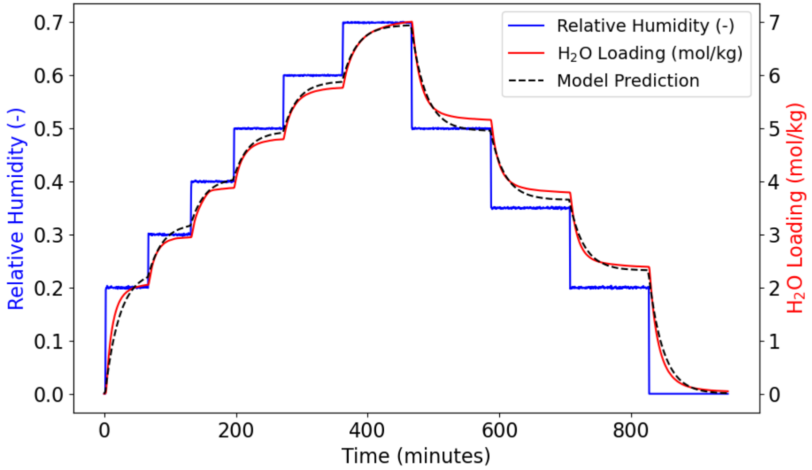
H_2O Isotherm and Kinetic Model

Water Isotherm Model, GAB model[2]:

$$q^*_{H_2O} = q_m \frac{K_{ads}C_G x_{RH}}{(1-K_{ads}x_{RH})(1+(C_G-1)K_{ads}x_{RH})}$$

LDF model: $\frac{dq_{H_2O}}{dt} = k_{H_2O}\left(q^*_{H_2O} - q_{H_2O}\right)$

Parameter estimation: $\min_{\theta} \left(q_{exp} - q_{model}\right)' \left(q_{exp} - q_{model}\right)$



Model Fit to experimental TGA data

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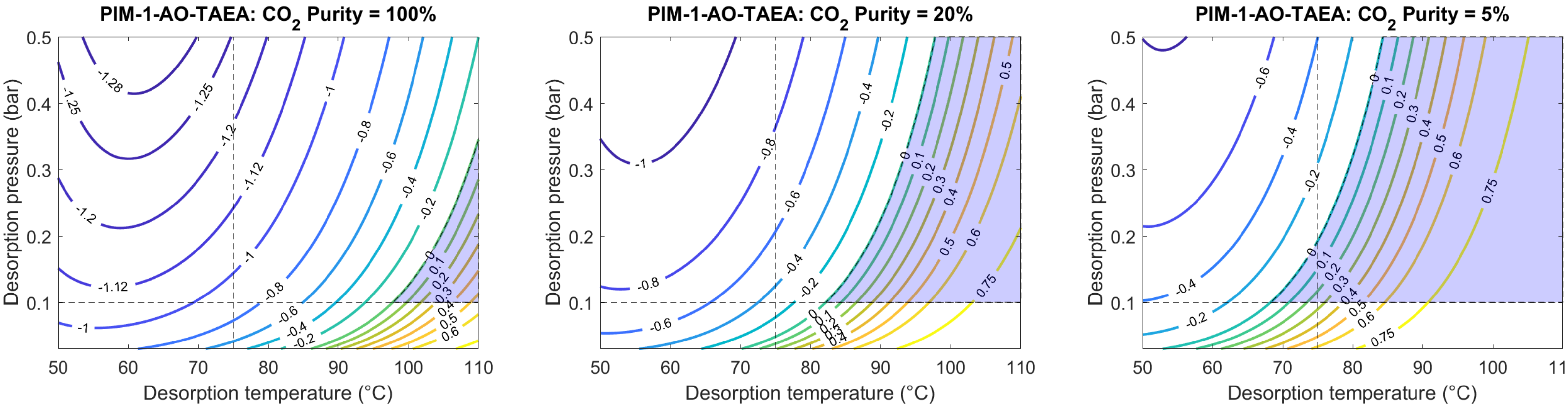
[1] Sabatino, F.; Grimm, A.; Gallucci, F.; van Sint Annaland, M.; Kramer, G. J.; Gazzani, M. A Comparative Energy and Costs Assessment and Optimization for Direct Air Capture Technologies. Joule 2021, 5 (8), 2047–2076. https://doi.org/10.1016/j.joule.2021.05.023.

[2] Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, "The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes," Energy Environ. Sci., (2021), 14(10), 5377-5394

CO_2 Cyclic Working Capacity Analysis



CO_2 cyclic working capacity with varying CO_2 purity

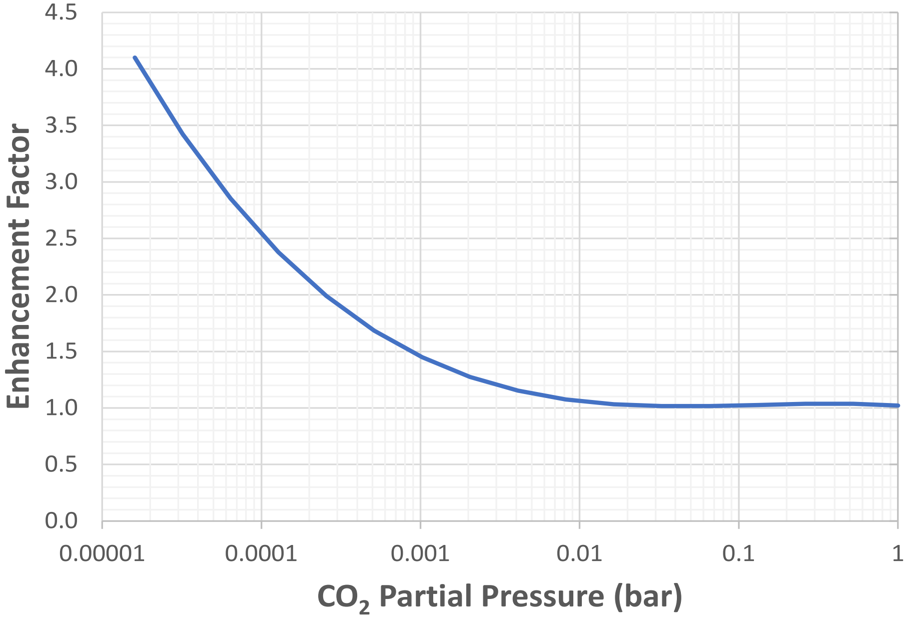
Key Takeaway:

- At mild regeneration conditions, positive working capacity only possible at low CO_2 purities

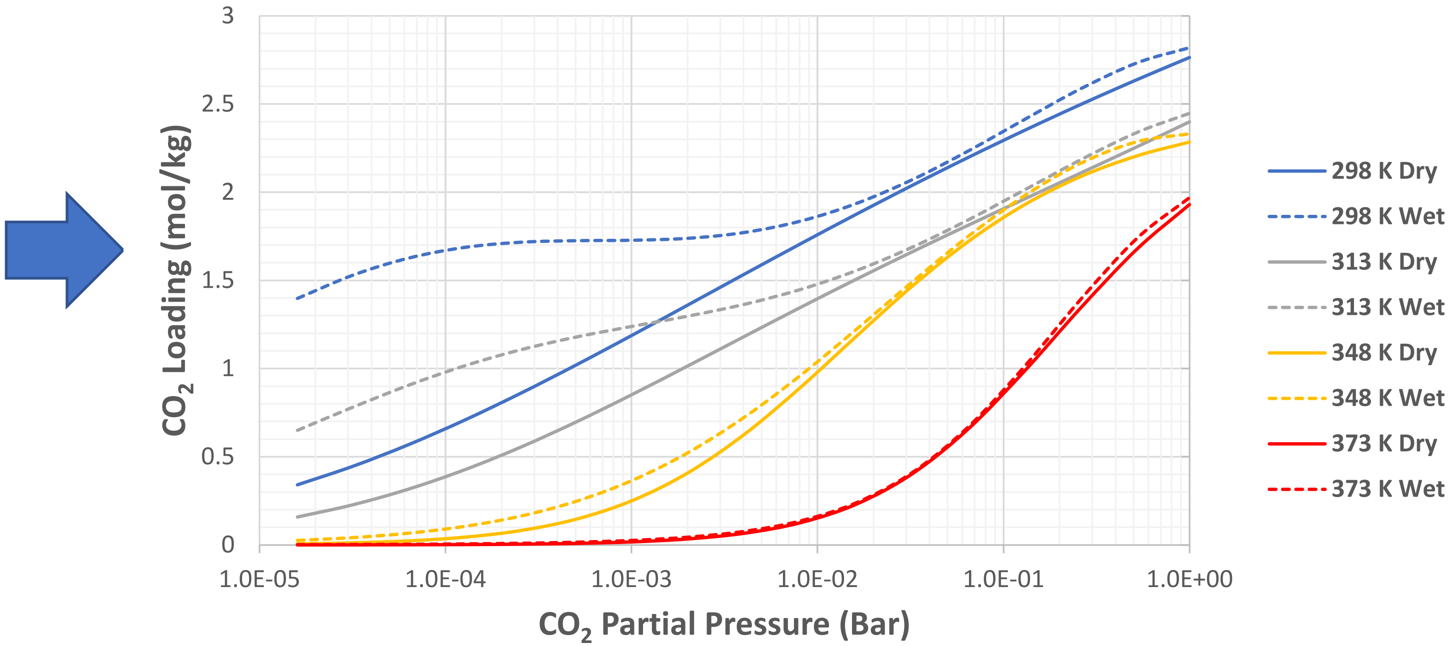
Modeling Water Effects on Sorbent Performance

- Water effects are important, as H_2O in humid air tends to increase CO_2 loading, especially at low CO_2 partial pressure
- Data Gap (humid data): addressed by using an enhancement factor approach for CO_2/H_2O co-adsorption based on comparable sorbent humid data from the literature[1]

Enhancement Factor



Isotherm with/without enhancement factor



[1] Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, "The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes," Energy Environ. Sci., (2021), 14(10), 5377-5394

Case Studies and Sensitivity Studies

Shortcut Model

Cases tested:

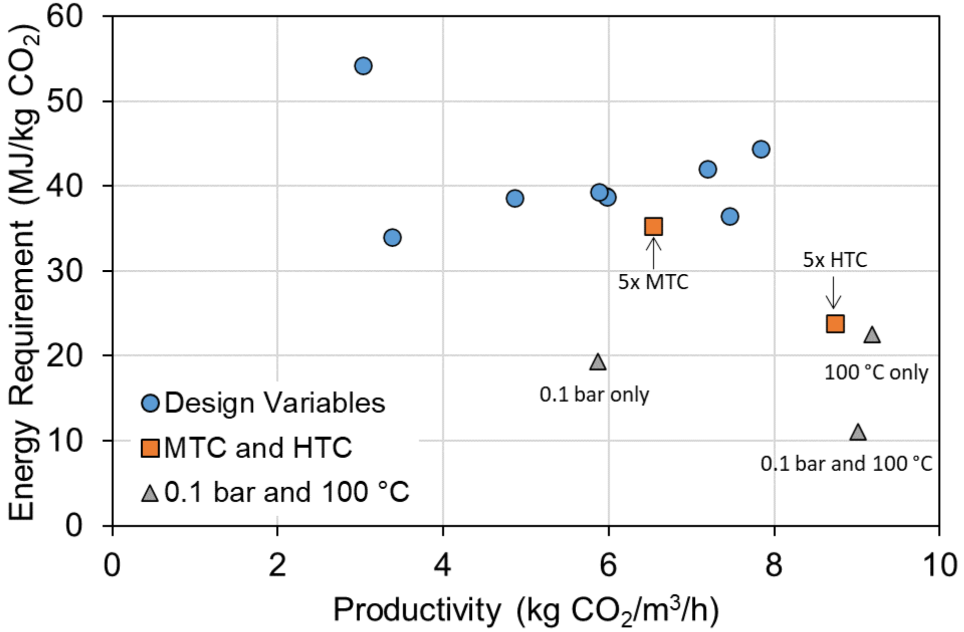
1. 75 °C, humid air, no enhancement factor
2. 100 °C, humid air, no enhancement factor
3. 75 °C, humid air, enhancement factor
4. 100 °C, humid air, enhancement factor

Metric/Cases	1	2	3	4
CO_2 Capture %	0.8	83.2	81.5	99.0
CO_2 Purity %	3.1	12.7	17.7	24.6
CO_2 Purity % (H_2O-free)	10.3	96.2	87.2	98.0
Energy Requirement(MJ/kg)	1707	20.6	33.7	9.3

Rigorous Model

Sensitivity study exploring the tradeoff between energy requirement and productivity

- Design variables adjusted by +/- 50% of their nominal value
- Mass (MTC) and heat (HTC) transfer coefficient increased to 5x their nominal value
- Investigated regeneration conditions of 0.1 bar and 100 °C



Key Takeaways:

- Accounting for water effects will drastically affect performance prediction → Need for H_2O/CO_2 data
- What are the optimal design variables?

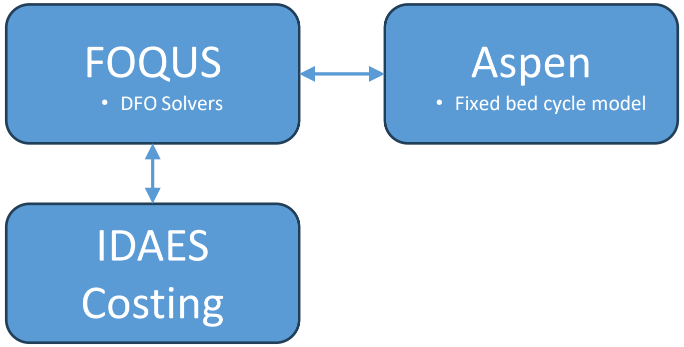
Techno-Economic Optimization

- What are the design and operating variables which minimize the cost of CO_2 capture?
    - Costing model developed using IDAES costing library and NETL Sorbent Case Study[1]
    - Apply the FOQUS toolset to connect the Aspen model, IDAES costing libraries, and optimization algorithms

$\min_{x} \; f(x)$	Cost of Capture ($/tonne)
$s.t.$	
$x^L \leq x \leq x^U$	Decision variable bounds
$h(x) = 0$	Modeling eqs. (mass balances, energy balances, etc.)
$g(x) \leq 0$	Process constraints

Optimization Problem

FOQUS Connection



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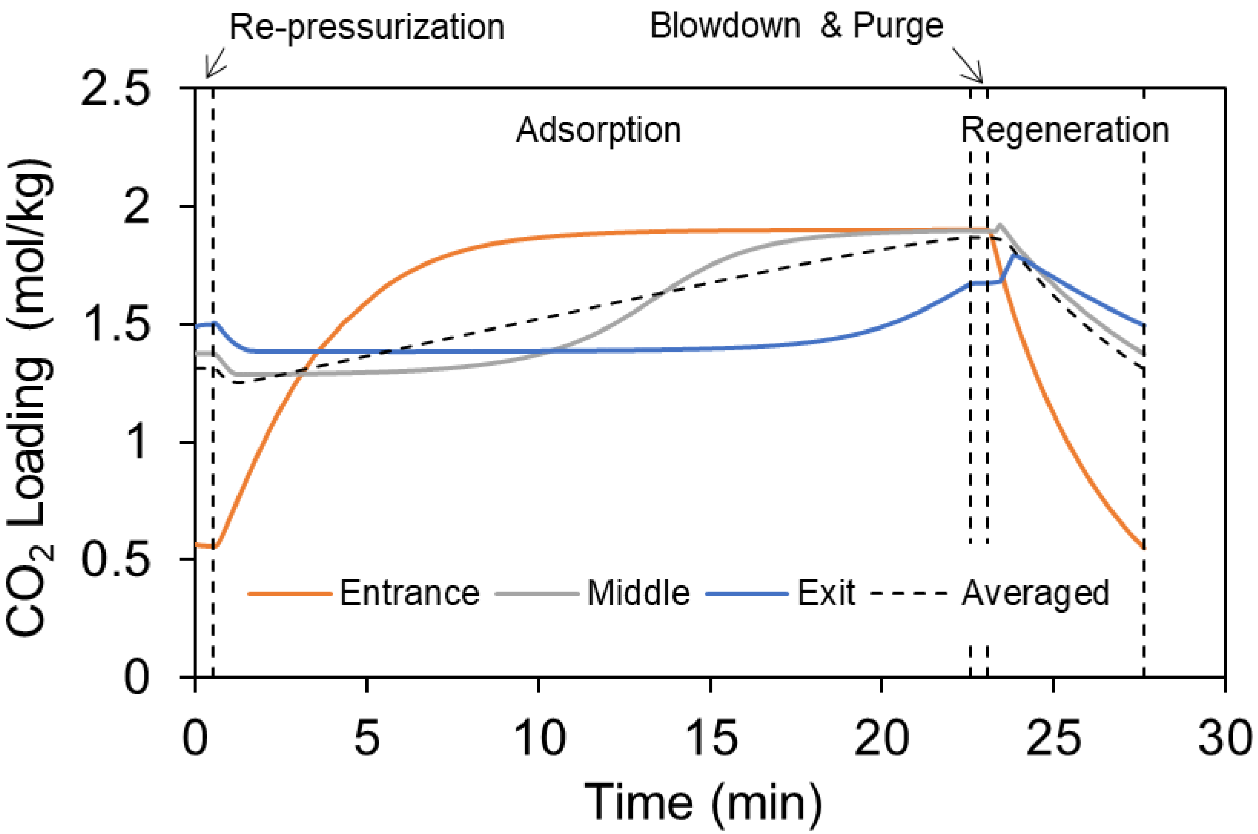
[1] Direct Air Capture Case Studies: Sorbent System NETL report https://www.osti.gov/biblio/1879535

Optimization Results

Results:

Decision Variable	Optimized Value
Adsorption Time [mins]	21.56
Desorption Time [mins]	4.09
Air pressure drop [bar]	1.63E-6
Steam sweep pressure drop [bar]	4.99E-8
Metric	**Optimized Value**
Recovery	0.73
CO_2 Product Purity	0.09
CO_2 Product Purity (water-free basis)*	0.95
Energy Requirement [MJ/kg CO_2]	14.71
Productivity [kg CO_2/h/m^3]	15.67
Cost of Capture [$/tonne]	268.2

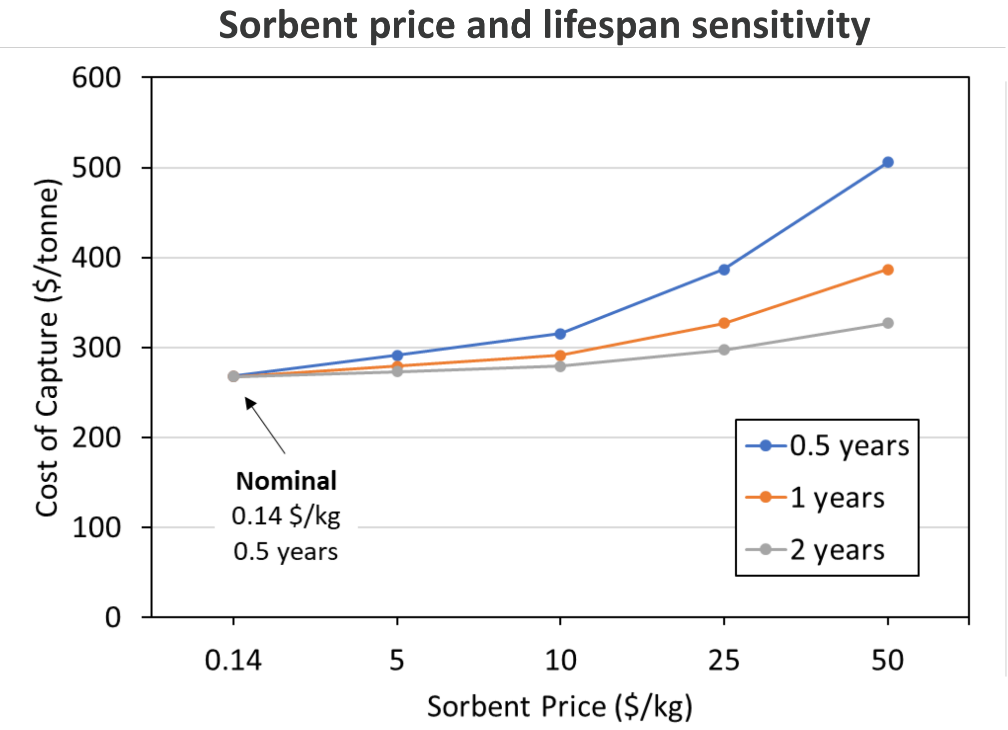
*Cost are preliminary, The cost for removing all water from the product has not yet been included in the costing

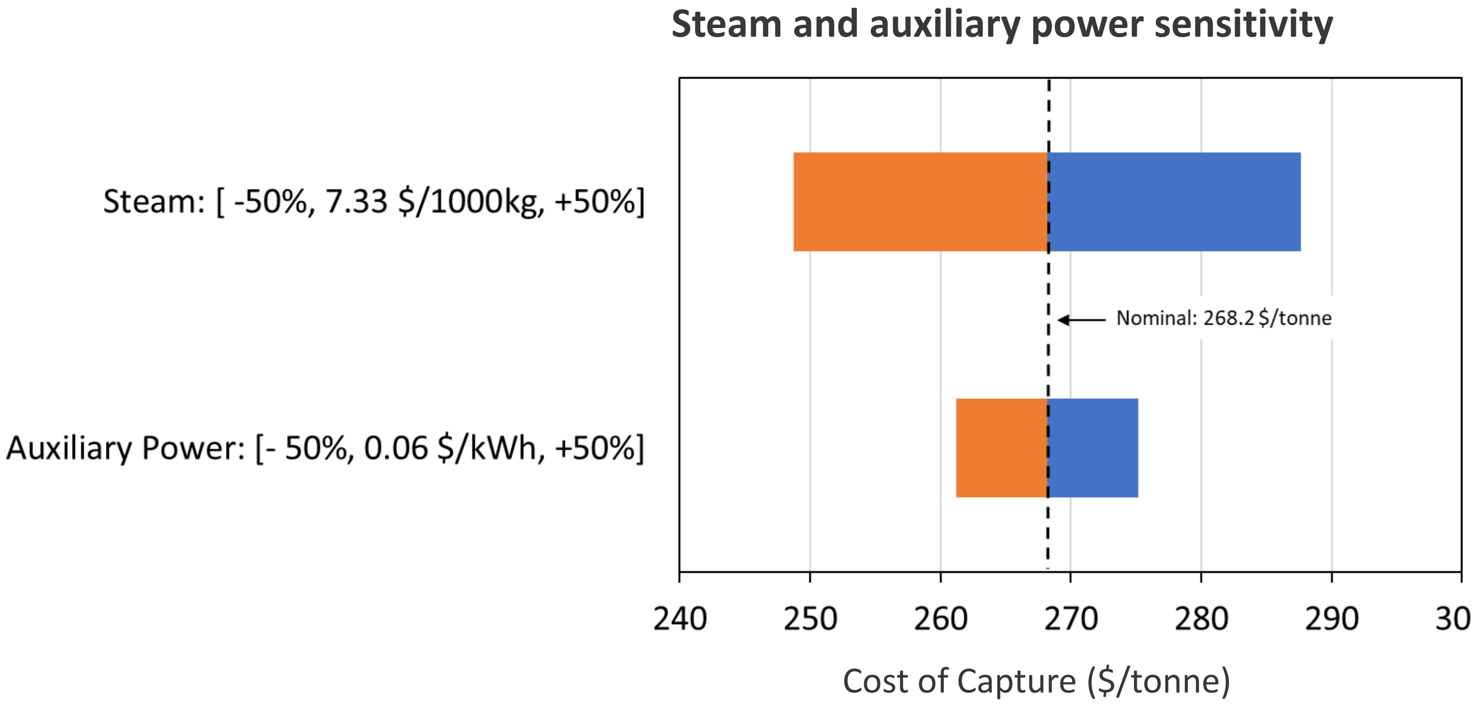


Loading profile for optimized case

Optimization Results

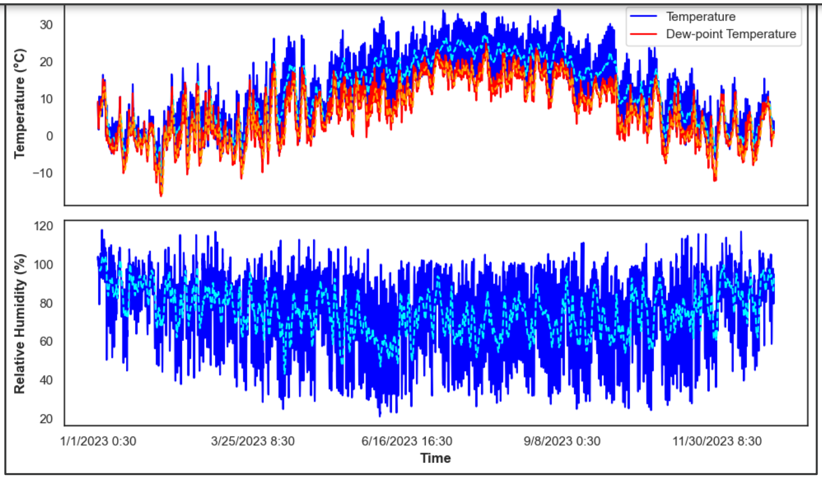
Sensitivity Studies





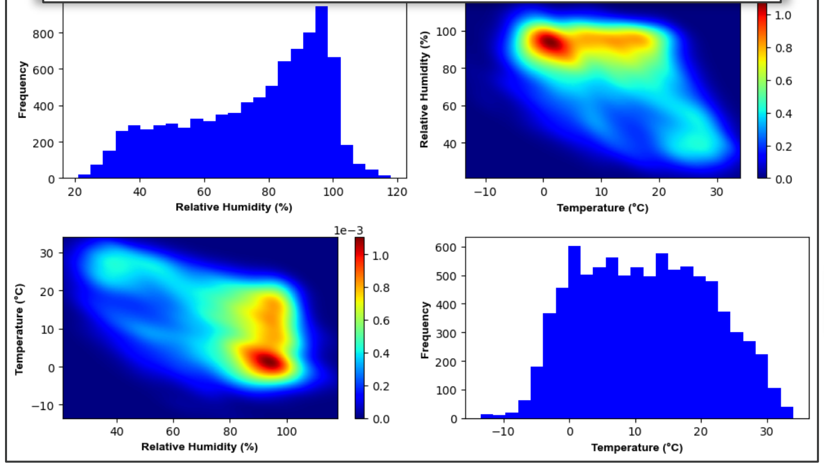
Ambient Conditions Performance Analysis

Time series data for Temperature and Relative Humidity[1]



Statistical Analysis

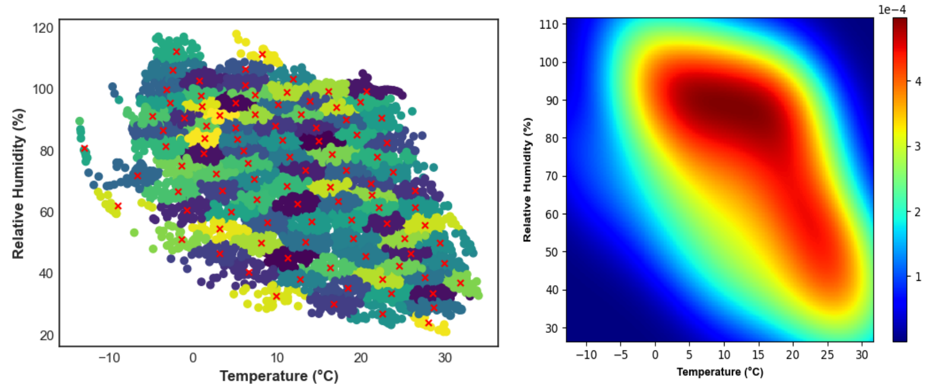
Marginal and joint probability distributions



Sampling

Clustering

Joint probability distribution of sampled data set

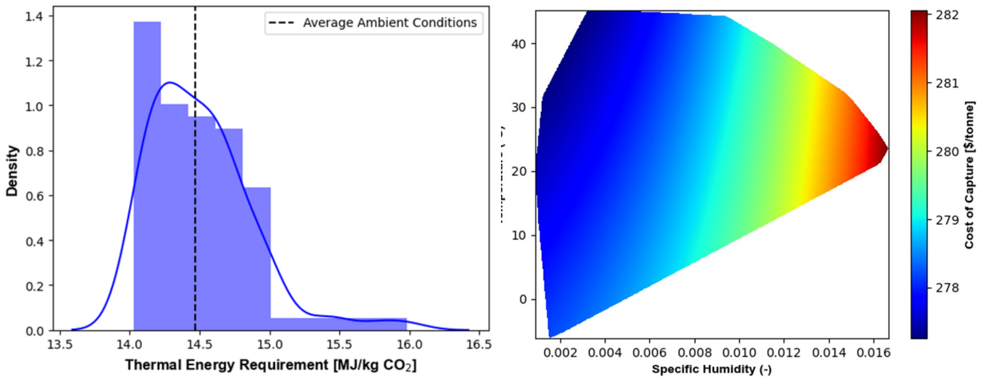


System Performance

- Propagation Through Process Model Using FOQUS

Energy Requirement Distribution

Cost Heatmap

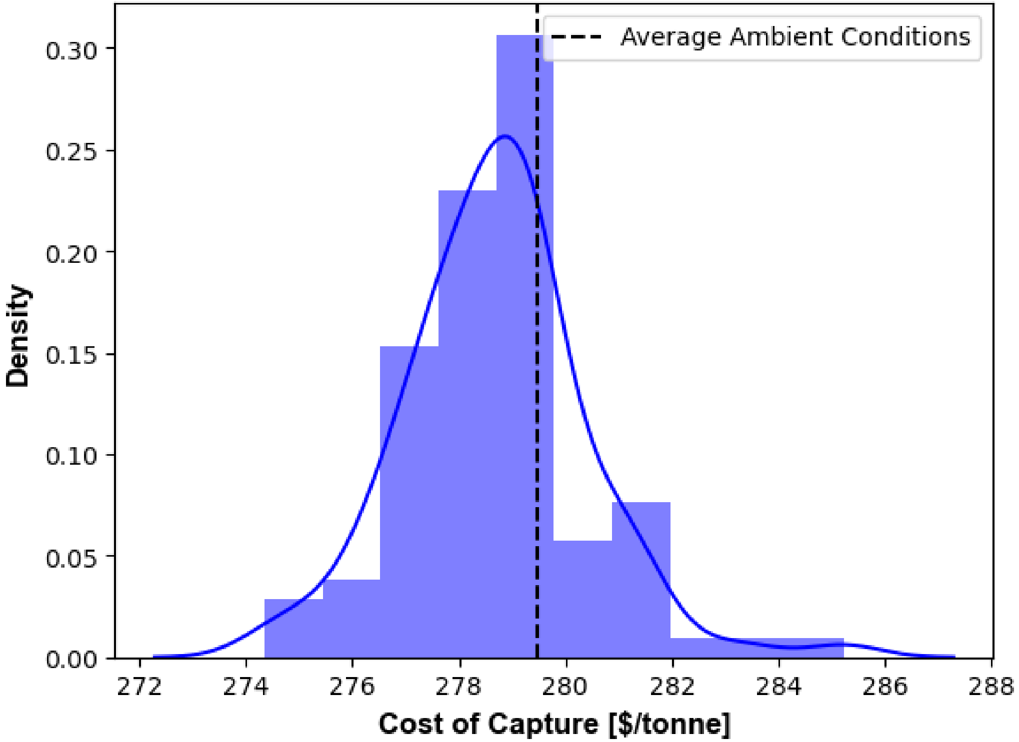


[1] Global Modeling and Assimilation Office (GMAO) (2015), *inst3_3d_asm_Cp: MERRA-2 3D IAU State, Meteorology Instantaneous 3-hourly (p-coord, 0.625x0.5L42), version 5.12.4*, Greenbelt, MD, USA: Goddard Space Flight Center Distributed Active Archive Center (GSFC DAAC), Accessed 3/1/24 at doi: 10.5067/VJAFPLI1CSIV.

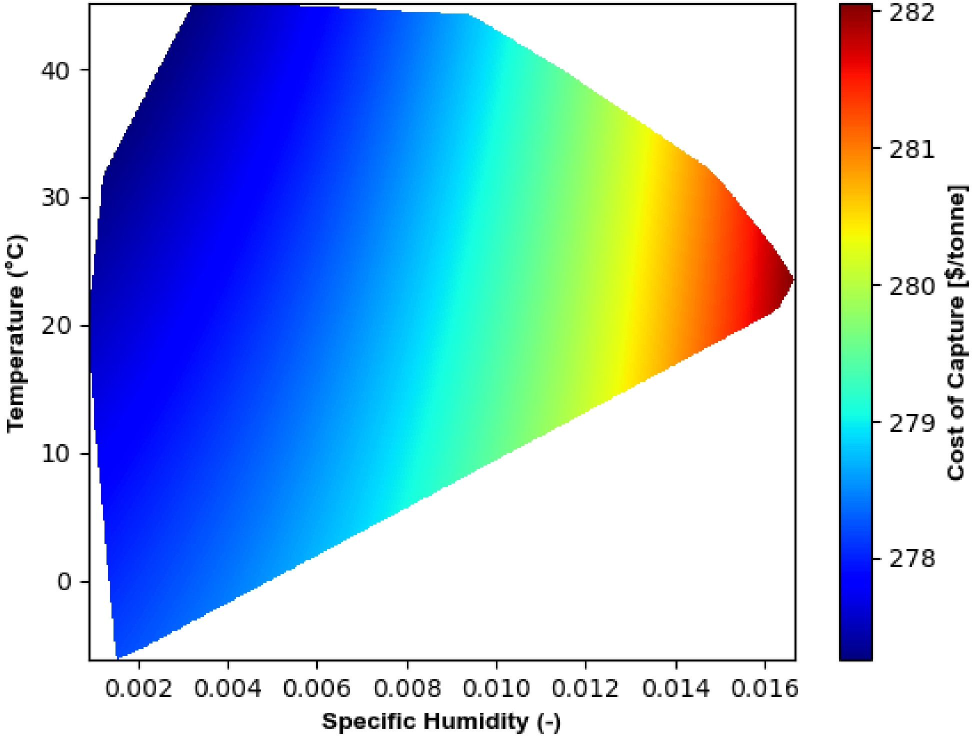
Ambient Conditions Performance Analysis

Analysis of a candidate site (Odessa, TX)

Cost of Capture Probability Distribution



Cost of Capture Heat Map



Poster: "Modeling and Analysis of Climate Variation Effects on Fixed-Bed Direct Air Capture Systems"

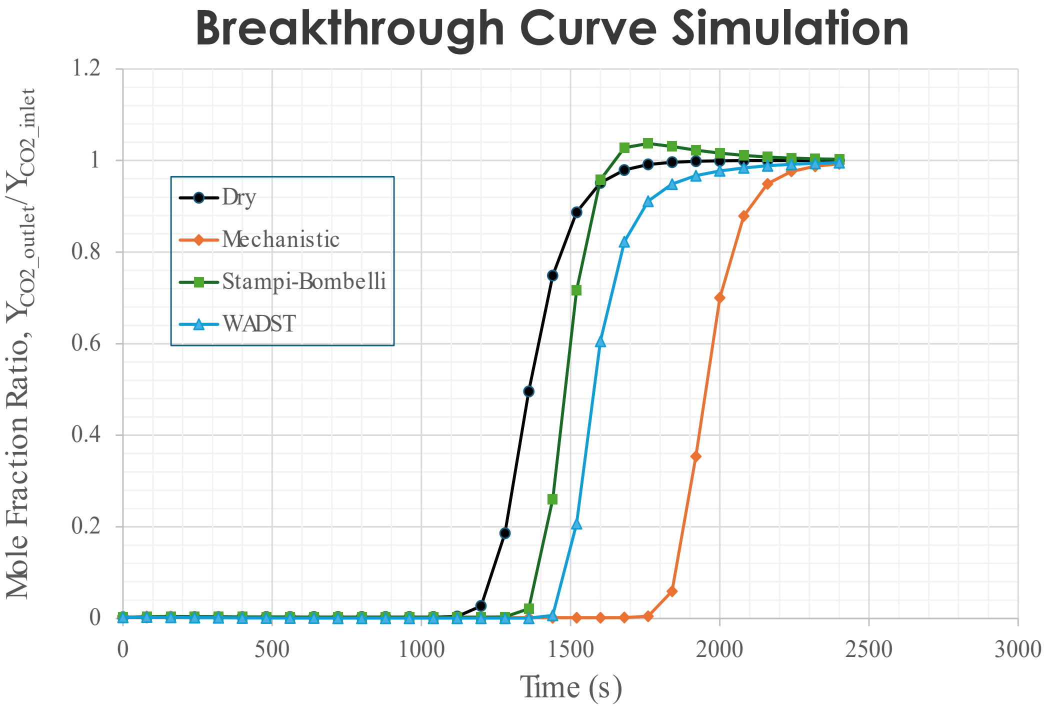
Summary

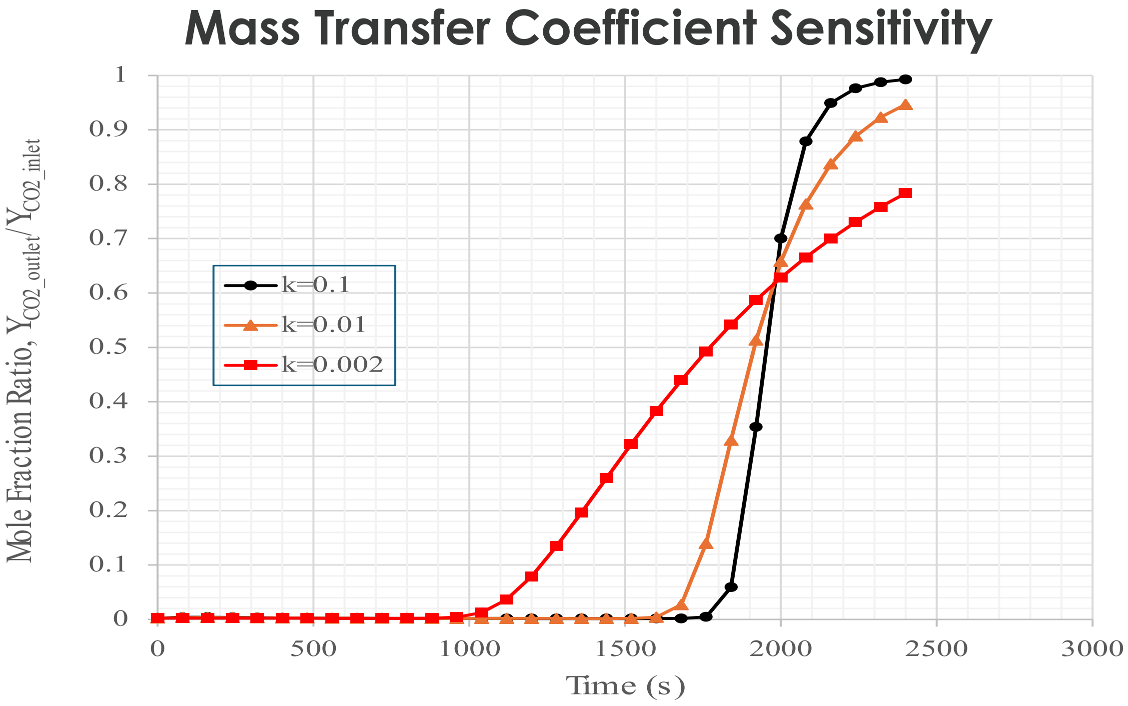
- Provided modeling support to sorbent developers at NETL
- Identified data needs to inform process models and improve fidelity of model predictions
- Used 1st-principles contactor models to identify process configurations and optimal design
- Investigated robustness of process to varying ambient conditions

Future Work: Expand Analysis

Support of NETL DAC Test Center

- Goal is to help develop an experimental testing framework to support technology developers at the NETL DAC Test Center
- Collaboration with Design of Experiments team
  - *"Model-Based Design of Experiments with Pyomo.DOE"*
- Lewatit VP OC 1065[1] as baseline sorbent





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[1] Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, "The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes," Energy Environ. Sci., (2021), 14(10), 5377-5394

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Acknowledgements

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Process System Engineering Team: Benjamin Omell, Jinliang Ma, Anca Ostace

Questions/Comments

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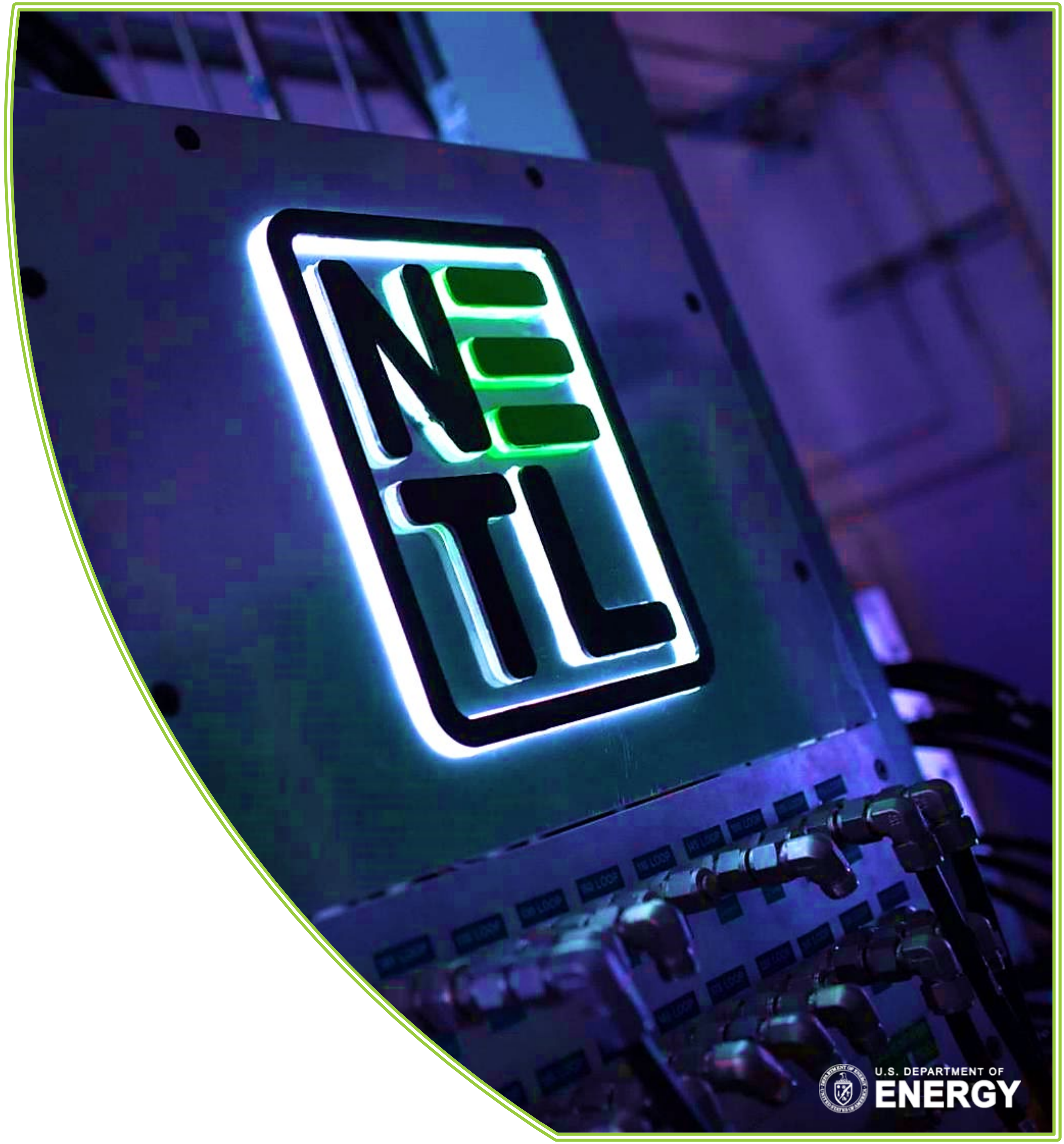

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Extra Slides

NETL's Costing Structure (IDAES Costing Framework)

Data Management

NETL QGESS Reports

FEED Studies

Legacy Models

Public References

Costing Correlations

IDAES Methodology

Excel

Step 1 - Identify/select reference parameters:

- Heat exchanger area, flowrate, heat duty, power, steam flowrate, recirculation flow, etc.

Step 2 - Fit data to expression:

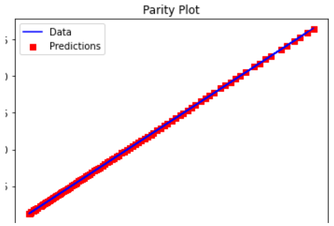
$$SC = RC\left(\frac{SP}{RP}\right)^{EXP}$$

ALAMO a black-box modeling tool

PySMO

Step 3 - Validation:

QGESS Methodology[1]
SC: Scaled Cost
RC: Reference Cost
SP: Scaled Parameter
RP: Reference Parameter



Implementation

Excel

Python Dictionary

IDAES Library

IDAES: General unit model library, power plant library (turbines, heaters, fired boilers, electric boilers, condensers, pumps, compressors, etc.)

WaterTap: desalination and water treatment

PARETO: Produced water desalination and evaporation

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1. QGESS: Capital Cost Scaling Methodology Revision 4
https://github.com/IDAES/idaes-pse/tree/main/idaes/models_extra/power_generation/costing

Data Needs to Inform Process Models

Guide Experimental collaborators to measure critical data

Key Data Requirements

- Physical properties:
  - Sorbent density and heat capacity, particle density and size
- Equilibrium Data:
  - Pure component adsorption isotherms (CO_2 and H_2O), and Cooperative/Competitive CO_2+H_2O adsorption isotherm
- Transport/Kinetic Data:
  - TGA data and breakthrough experiments on binary adsorption of CO_2 and H_2O for mass transfer coefficients.
  - Heating and cooling experiments for heat transfer coefficients

Measured Data

- Physical properties (sorbent density, heat capacity, size of particles)
- Pure component isotherm of CO_2 at different temperatures
- TGA data of pure CO_2 and CO_2 under humid conditions

Missing Data

- Pure component isotherm of H_2O
- Cooperative/competitive CO_2+H_2O adsorption data
- Breakthrough data for CO_2 and H_2O
- Breakthrough at different temperatures

Addressing Data Limitations

- Pure component isotherm of H_2O taken from literature
- Enhancement factor for cooperative CO_2+H_2O adsorption
- Heat transfer coefficient constant and taken from literature

Modeling Equations

IDAES 0-D TVSA Model

1. Heating Step

Mass balance: $\frac{\varepsilon P}{R}\frac{d(y/T)}{dt} + \rho_b \frac{dn_1}{dt} - y\left(\frac{\varepsilon P}{R}\frac{d(1/T)}{dt} + \rho_b \sum_{i=1}^{2} \frac{dn_i}{dt}\right) = 0$

Energy balance: $C_{p,b}\frac{dT}{dt} - \rho_b \sum_{i=1}^{2}(-\Delta H_i)\frac{dn_i}{dt} = US(T_{heat} - T)$

2. Cooling Step

Mass balance: $\frac{\varepsilon}{R}\frac{d(P/T)}{dt} + \rho_b \sum_{i=1}^{2} \frac{dn_i}{dt} = 0$

Energy balance: $C_{p,b}\frac{dT}{dt} - \rho_b \sum_{i=1}^{2}(-\Delta H_i)\frac{dn_i}{dt} = US(T_{cool} - T)$

3. Pressurization Step

Mass balance: $\frac{\rho_b}{\varepsilon}RT\left((n_{1,press}^{end} - n_{1,cool}^{end}) - y_F \sum_{i=1}^{2}(n_{i,press}^{end} - n_{i,cool}^{end})\right) + (y_{press}^{end}P_H - y_{cool}^{end}P_L) - y_F(P_H - P_L) = 0$

Pros:
- Equation-oriented model with CSS automatically satisfied through model constraints
- Suitable for KPI estimation, feasibility studies, and optimization

Cons:
- No axial variation
- No kinetics
- No sweep gas allowed in heating step

Aspen 1-D TVSA Model

Gas phase balances

Mass balance: $\varepsilon_b \frac{\partial C_{g,i}}{\partial t} = -\frac{\partial (v_g C_{g,i})}{\partial z} - (1 - \varepsilon_b)\frac{6k_{f,i}}{d_p}(C_{g,i} - C_{surf,i})$

Energy balance:

$$\varepsilon_b \rho_g C_{v,g}\frac{\partial T_g}{\partial t} = -\rho_g C_{v,g} v_g \frac{\partial T_g}{\partial z} - P\frac{\partial v_g}{\partial z} - (1 - \varepsilon_b)a_p h_f(T_g - T_s) - a_{HX}h_{HX}(T_g - T_t)$$

Solid phase balances

Mass balance: $\frac{dq_{CO_2}}{dt} = k_I(q_{CO_2}^{*} - q_{CO_2})$

Energy balance: $\rho_s C_{p,s}\frac{\partial T_s}{\partial t} = \rho_s(-\Delta H_{CO_2})\frac{dq_{CO_2}}{dt} + a_p h_f(T_g - T_s)$

Momentum Balance (Ergun Equation)

Pros:
- Aspen GUI makes it easy for simulating multiple cycle types
- Suitable for simulation, KPI estimation, and feasibility studies

Cons:
- Satisfying CSS requires successive dynamic simulations
- Increased computational time for advanced analysis (optimization, etc.)

IDAES 1-D TVSA Model

(development ongoing)

Gas phase balances

Mass balance: $\frac{\partial A_g C_i}{\partial t} = -\frac{\partial F_i}{\partial x} - A_s \rho_s \frac{\partial q_i}{\partial t}$

Energy balance:

$$\frac{\partial (A_g \sum C_i U_i)}{\partial t} = -\frac{\partial \sum F_i H_i}{\partial z} - A_s \rho_s \sum H_i \frac{\partial q_i}{\partial t} - \frac{6A_s h_f}{d_p}(T_g - T_s) - \pi D_{w,i} h_{gw}(T_g - T_w)$$

Solid phase balances

Mass balance: $\frac{\partial q_i}{\partial t} = k_f[q_i^{eq}(p_{i,g}, T_s) - q_i]$

Energy balance:

$$\frac{\partial [A_s \rho_s (C_{p,sorb}T_s + \sum q_i H_{i,ads})]}{\partial t} = \frac{6A_s h_f}{d_p}(T_g - T_s) + A_s \rho_s \sum H_i \frac{\partial q_i}{\partial t}$$

Momentum Balance (Ergun Equation)

Pros:
- Equation-oriented model with CSS automatically satisfied through model constraints
- Suitable for optimization

Cons:
- Large model which requires discretization in the spatial and time domains
- Difficult initialization and convergence

Understanding Impacts of Ambient Conditions

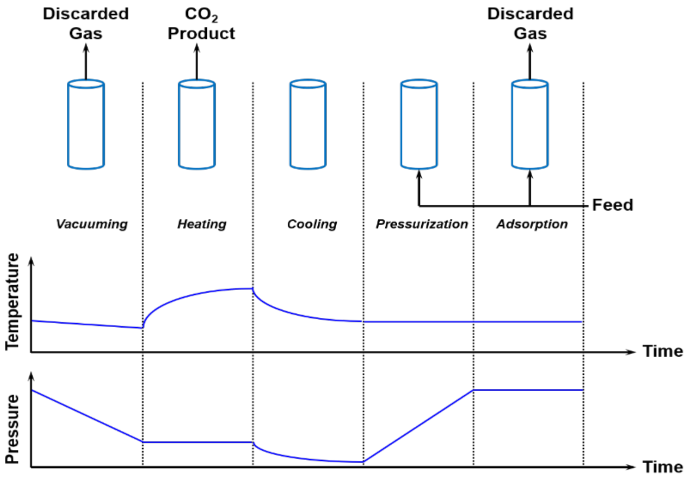
- Direct Air Capture may be significantly impacted by climate and shifting ambient conditions

- Understanding the economic impacts of shifting ambient conditions critical for determining optimal site locations and development of control strategies to minimize negative impacts

- This work demonstrates tool development that can be implemented with first-principal models to better understand these impacts

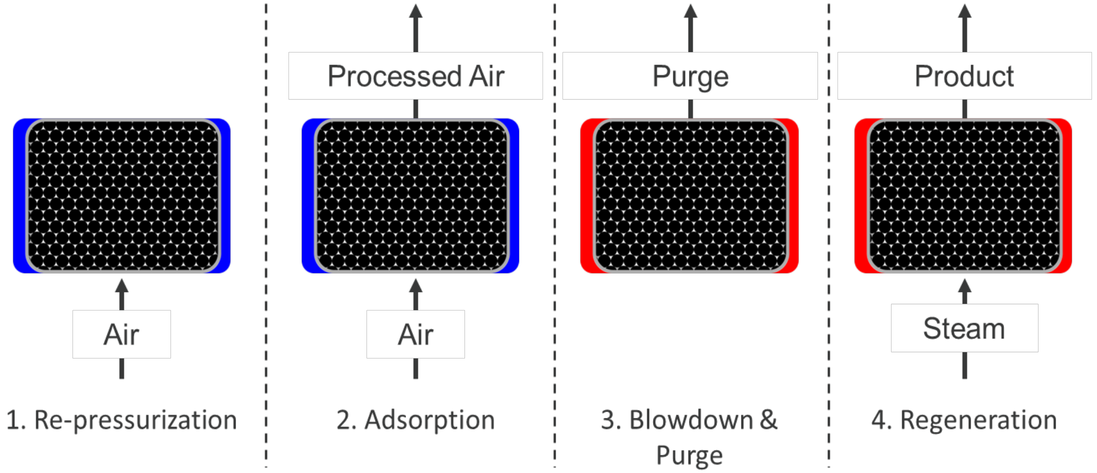
Two Contactor Models Developed

0-D Model Five Step Equilibrium Model



- Model adopted from previous work
- Adsorption assumed isothermal – requiring lengthy cooling step and hence conservative in estimated cycle time
- Adsorption equilibrium presumed
- Quick first pass performance estimate
- May be suitable (preferred) over surrogate for advanced analysis/optimization

Aspen 1-D Four Step Model



- Cooling step and adsorption a single step
- Mass transfer considered (important for pressure drop mass transfer tradeoff when data becomes available)
- Used for rigorous TEA and optimization

Flat bed assumption used for both models[1]

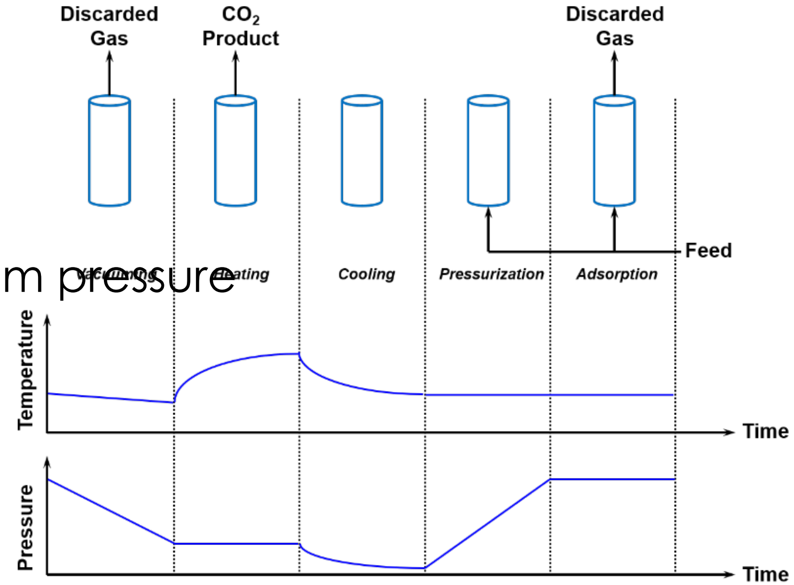
---

[1] Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, “The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes,” Energy Environ. Sci., (2021), 14(10), 5377-5394

Contactor and Process Modeling

IDAES 0D Model Summary

- 5 steps of TVSA Cycle modeled
  - Vacuum step
    - Inlet closed, outlet open, outlet gas discarded
  - Heating step
    - Inlet closed, outlet open, bed heated externally at vacuum pressure
  - Cooling step
    - Inlet closed, outlet closed, bed cooled externally
  - Pressurization step
    - Inlet open, outlet closed, no heat added
  - Adsorption step
    - Inlet open, outlet open, no heat added, ambient pressure
- External heating and cooling only
  - No sweep gas/steam
- Model Assumptions
  - Equilibrium between solid (adsorbed) and gas phases
    - Extremely fast mass transfer and adsorption/desorption rat



Base Case Design Variable	Value	Units
Length	0.01	m
Diameter	0.1	m
Air Temperature	25	°C
Vacuum Pressure	0.2	bar
Desorption Temperature	75-100	°C
Interstitial Air Inlet Velocity	0.144	m/s
CO_2 in Air	400	ppm

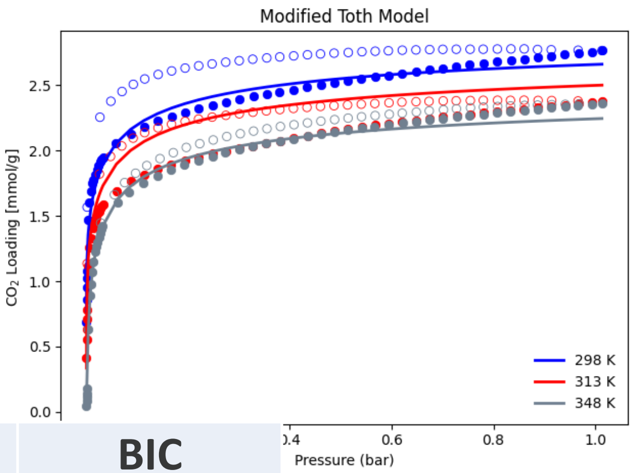
PIM-1-AO-TAEA Submodels

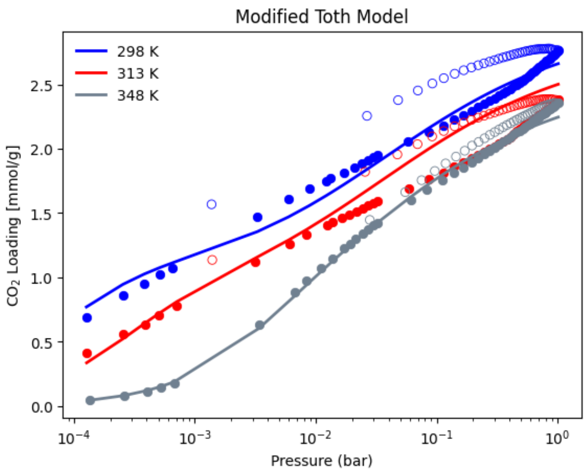
Isotherm Model: Modified Toth (Sabatino et. al., 2021)

- Fit traditional isotherm models along with more complex literature models by performing parameter estimation using available isotherm data
- Pyomo and parmest used to perform parameter estimation for each model
- Evaluate each model by their fit to the data and information criterion take model size into account

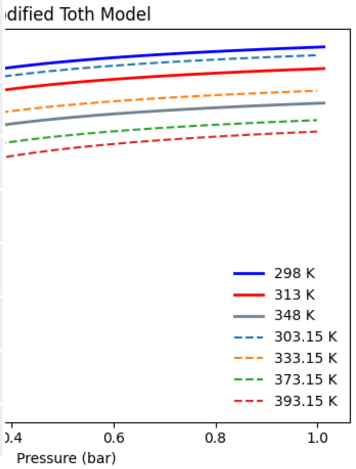
Model Name	RMSE [-]	# parameters	AIC	BIC
Modified Toth	2.65E-03	12	-3.215E+03	-3.171E+03
Dual-Site Sips	4.09E-03	8	-2.987E+03	-2.958E+03
Dual-Site Langmuir	4.33E-03	6	-2.960E+03	-2.938E+03
Toth Model 3	5.14E-03	5	-2.868E+03	-2.849E+03
Toth Model 2	5.41E-03	5	-2.840E+03	-2.822E+03
Langmuir-Freundlich	5.71E-03	5	-2.811E+03	-2.793E+03
Toth Model 1	6.11E-03	4	-2.775E+03	-2.761E+03
Langmuir Model 2	8.92E-03	4	-2.569E+03	-2.555E+03
Langmuir Model 1	9.14E-03	3	-2.558E+03	-2.547E+03
Freundlich Model	1.11E-02	4	-2.449E+03	-2.434E+03

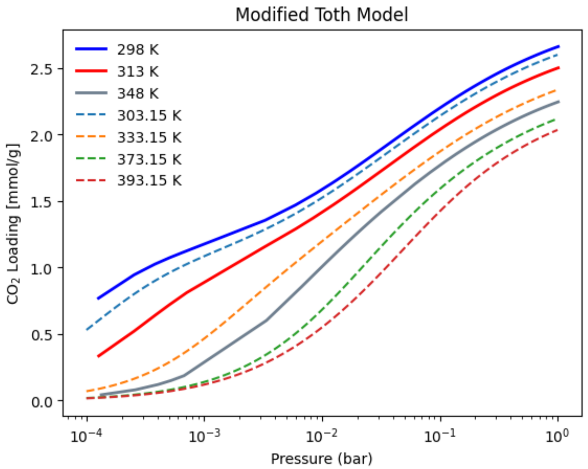
Fit to Experimental Data





ion to 100 °C





Sabatino, F.; Grimm, A.; Gallucci, F.; van Sint Annaland, M.; Kramer, G. J.; Gazzani, M. A Comparative Energy and Costs Assessment and Optimization for Direct Air Capture Technologies. Joule 2021, 5 (8), 2047–2076. https://doi.org/10.1016/j.joule.2021.05.023.

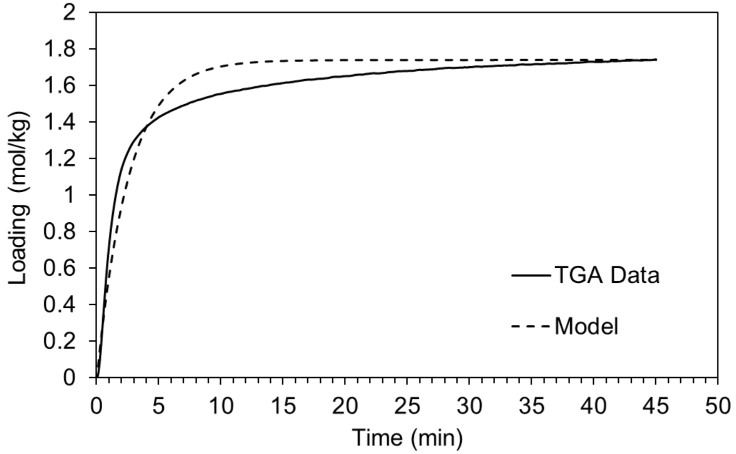
PIM-1-AO-TAEA Submodels

CO_2 Kinetic Model

- Fit a linear driving force model to available TGA adsorption data

Linear driving force (LDF) model: $\frac{dq}{dt} = k(q^* - q)$

Parameter estimation: $\min\limits_{\theta} \ (q_{exp} - q_{model})' \, (q_{exp} - q_{model})$



Model Fit to experimental TGA data at 25 °C

H_2O Isotherm and Kinetic Model

- Fit isotherm and kinetic parameters to pure H_2O TGA data with varying humidity

Water Isotherm Model, GAB model (Young et. al., 2021):

$$q^*_{H_2O} = q_m \frac{K_{ads} C_G x_{RH}}{(1 - K_{ads} x_{RH})(1 + (C_G - 1) K_{ads} x_{RH})}$$

LDF model: $\frac{dq_{H_2O}}{dt} = k_{H_2O}\left(q^*_{H_2O} - q_{H_2O}\right)$

Parameter estimation: $\min\limits_{\theta} \ (q_{exp} - q_{model})' \, (q_{exp} - q_{model})$

$$\min_{\theta} \left(q_{exp} - q_{model}\right)' \left(q_{exp} - q_{model}\right)$$

Model Fit to experimental TGA data

PIM-1-AO-TAEA Submodels

Kinetic Model

- Fit a linear driving force model to available TGA adsorption data

Linear driving force model:

$$\frac{dq}{dt} = k(q^* - q)$$

Assuming k and q^* are constant, analytical solution can be obtained:

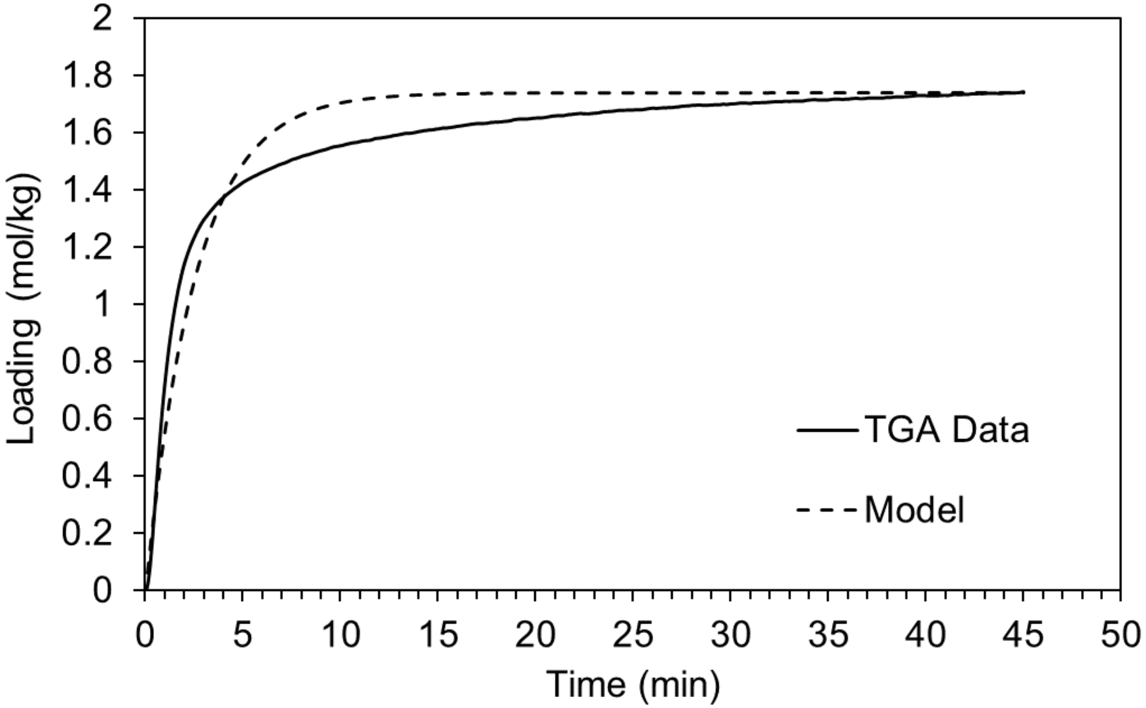
$$q = q^*\left(1 - exp(-kt)\right)$$

Parameter estimation:

$$\min_{\theta} \left(q_{exp} - q_{model}\right)' \left(q_{exp} - q_{model}\right)$$

Results:

RMSE = 0.90E-2 [mol/kg]   k=0.0065 s^{-1}



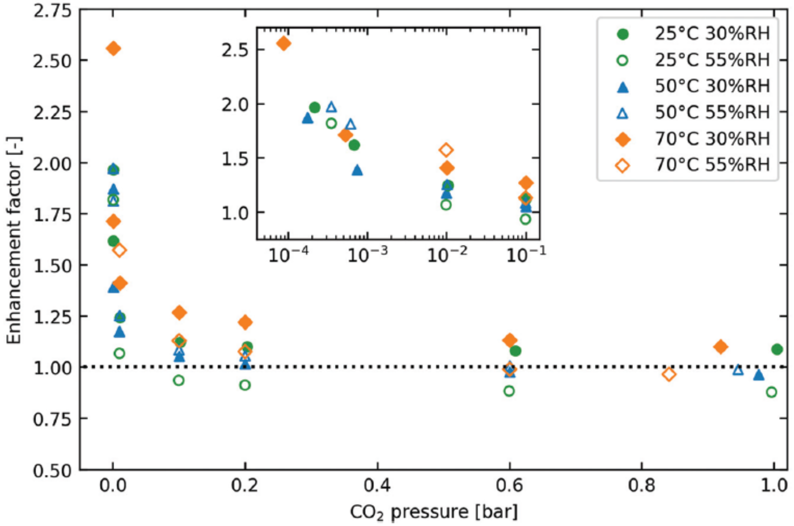
Model Fit to experimental TGA data at 25 °C

PIM-1-AO-TAEA Submodels

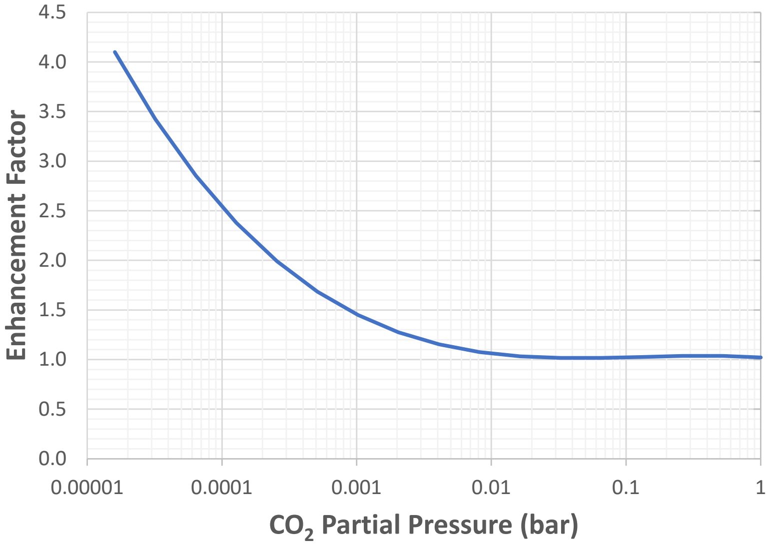
Water Effects

- **Assumption**: We cope with the limited availability of data by combining the sorbent *PIM-1-AO-TAEA* CO_2 isotherm with available H_2O isotherm for other materials (Lewatit VP OC 1065 [Young et. at., 2021])

Effect of H_2O on CO_2 Isotherm for Lewatit VP OC 1065



Enhancement Factor of Lewatit VP OC 1065



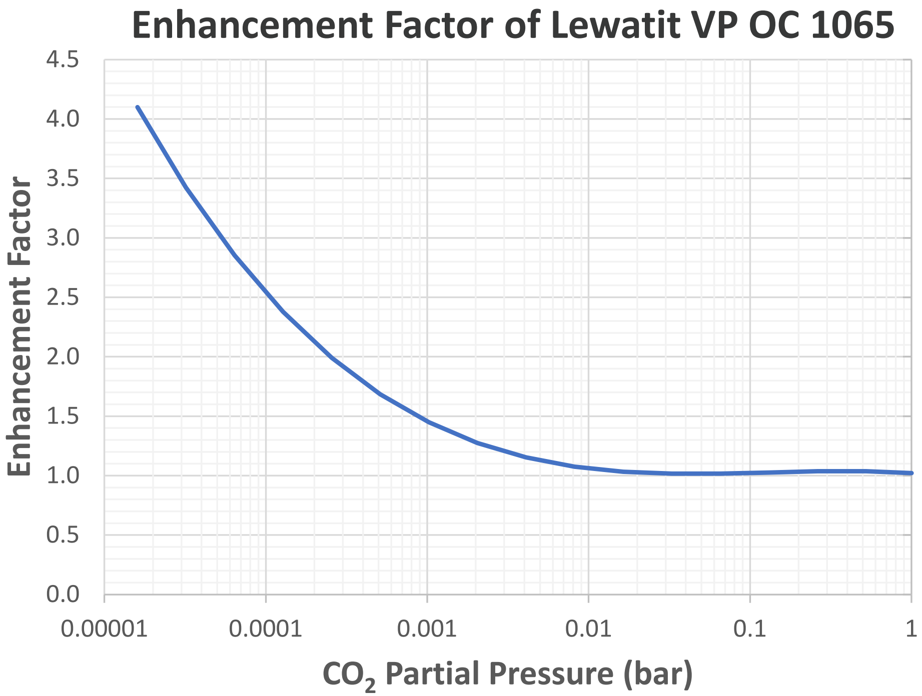
- **Usually, CO_2 does not affect H_2O loading**
- **H_2O in humid air tends to increase the CO_2 loading**
  - Esp. at low CO_2 partial pressure
  - Enhancement factor as high as 2.5
- **Higher enhancement factor at lower CO_2 partial pressures**

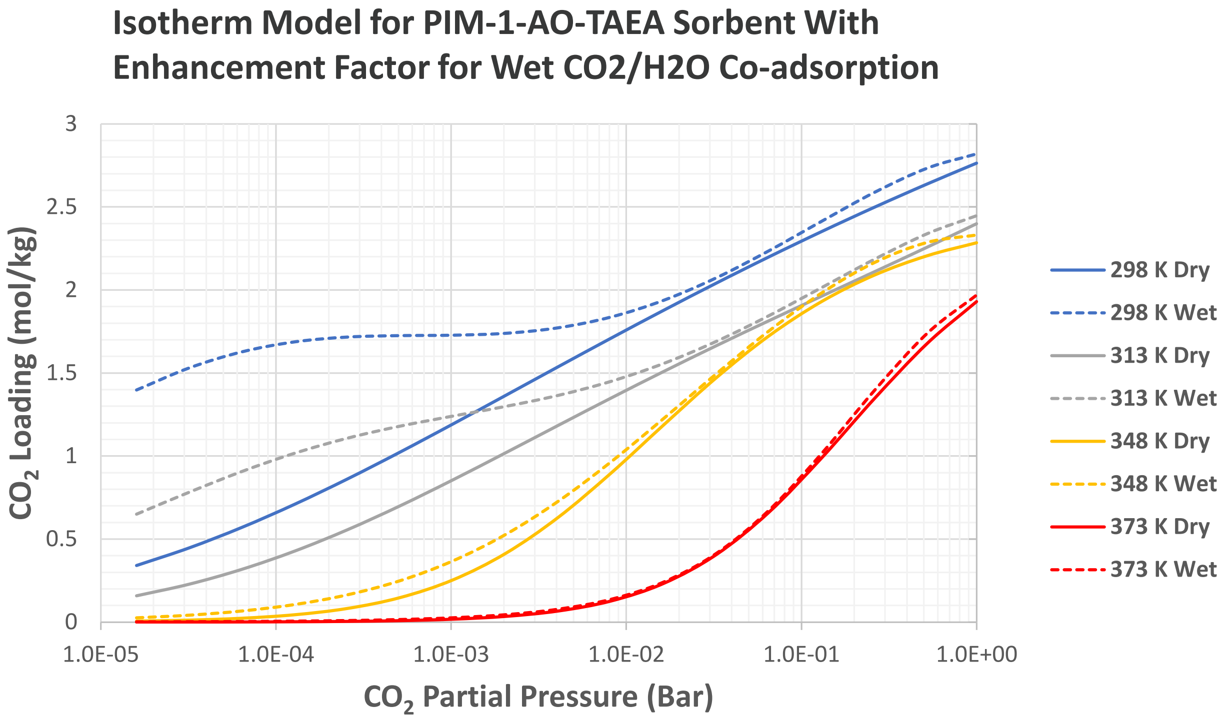
Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, "The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes," Energy Environ. Sci., (2021), 14(10), 5377-5394

PIM-1-AO-TAEA Submodels

Water Effects

- **Assumption**: Enhancement Factor of Lewatit VP OC 1065 applied to *PIM-1-AO-TAEA* CO_2 isotherm (Lewatit VP OC 1065 [Young et. at., 2021])


Enhancement Factor of Lewatit VP OC 1065


Isotherm Model for PIM-1-AO-TAEA Sorbent With Enhancement Factor for Wet CO2/H2O Co-adsorption

Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, "The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes," Energy Environ. Sci., (2021), 14(10), 5377-5394

PIM-1-AO-TAEA Submodels

CO_2 Cyclic Working Capacity Analysis

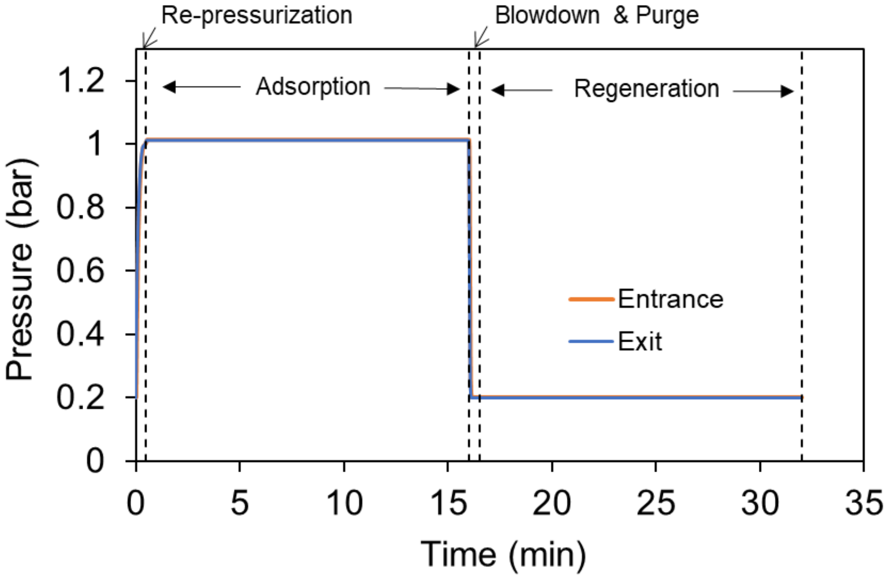
Difference between the equilibrium CO2 loading at adsorption and at desorption conditions

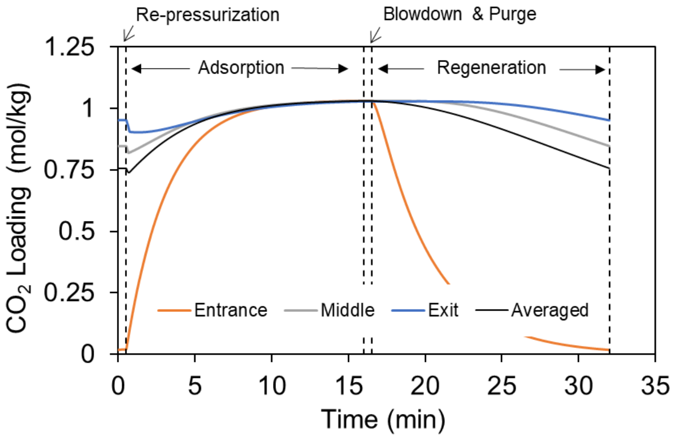
$$\Delta q_{CO_2} = q_{ads} - q_{des}$$

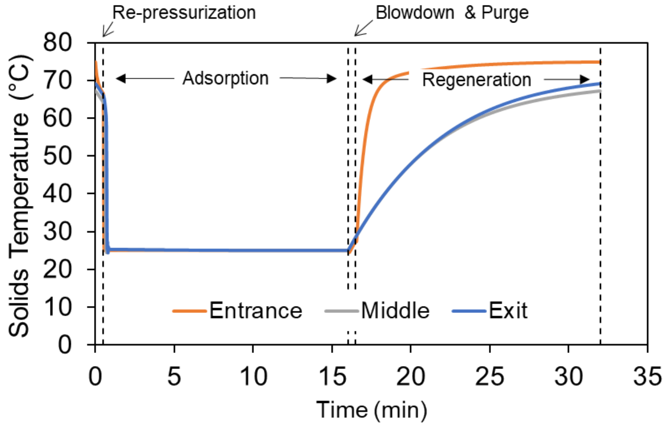
Adsorption conditions	Desorption conditions
T = 25 °C	T = 50-110 °C
P = 1 bar	P = 0.00001-0.5 bar
y_{CO_2} = 400 ppm	y_{CO_2} = 0.02-1 → purity = 2-100%

Aspen 1D Model: Base Case Results

Variable	Value	Units
CO_2 Capture Fraction	0.133	-
CO_2 Product Purity	2.35E-02	-
CO2 Product Purity (Water-free basis)	0.878	-
Cycle Time	32	Mins
Energy Requirement	38.84	MJ/kg CO_2
Productivity	5.96	kg CO_2/h/m^3
Inlet Air Velocity	0.871	m/s
Inlet Steam Velocity	0.00437	m/s







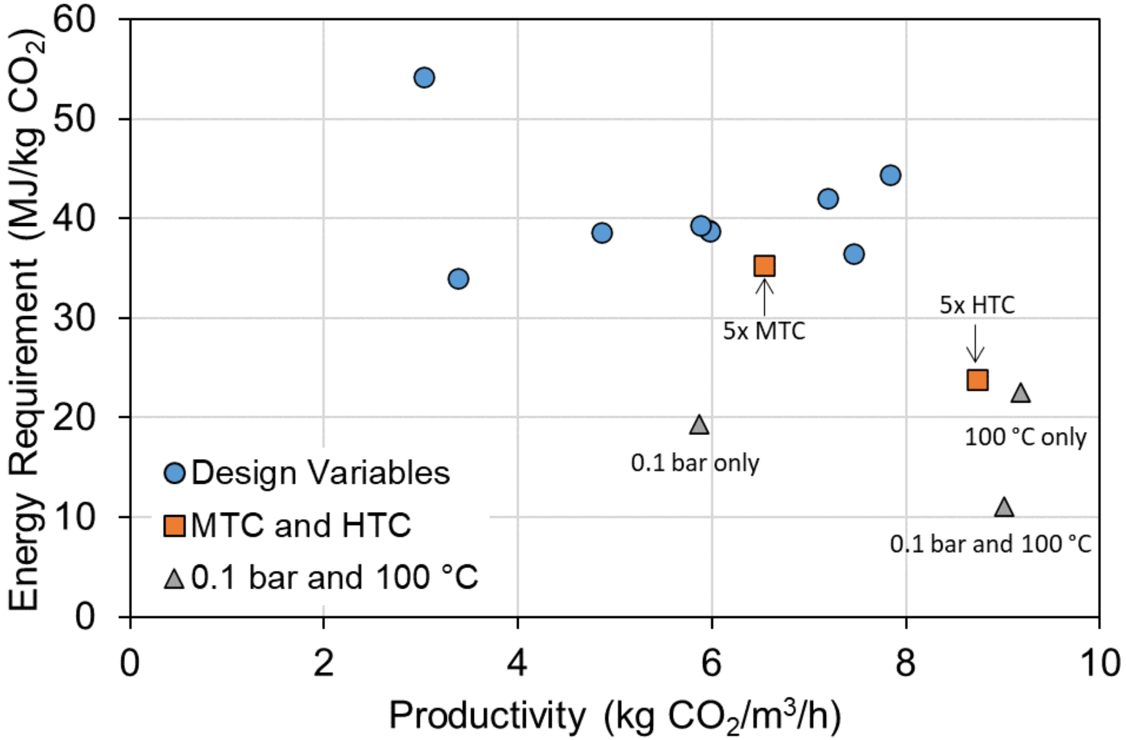
Notes:

- Energy requirement consists of only thermal energy: heating energy and energy required to generate the steam feed
- Steam generation energy calculated assuming ΔH_{vap}=2257 kJ/kg (saturated steam at 1 bar)

Aspen 1D Model: Sensitivity Study

Exploring the tradeoff between energy requirement and productivity

- Design variables adjusted by +/- 50% of their nominal value
- Mass (MTC) and heat (HTC) transfer coefficient increased to 5x their nominal value
- Investigated regeneration conditions of 0.1 bar and 100 °C



Comparison to Sabatino et. al., 2021:

- Productivity Range: 4-11 kg CO_2/h/m^3
- Energy Requirement Range: 4.9-13.3 MJ/kg CO_2
- Include a lower regeneration pressure (0.01 bar) and higher temperature (120 °C) in optimization space

Sabatino, F.; Grimm, A.; Gallucci, F.; van Sint Annaland, M.; Kramer, G. J.; Gazzani, M. A Comparative Energy and Costs Assessment and Optimization for Direct Air Capture Technologies. Joule 2021, 5 (8), 2047–2076. https://doi.org/10.1016/j.joule.2021.05.023.

Optimization Results

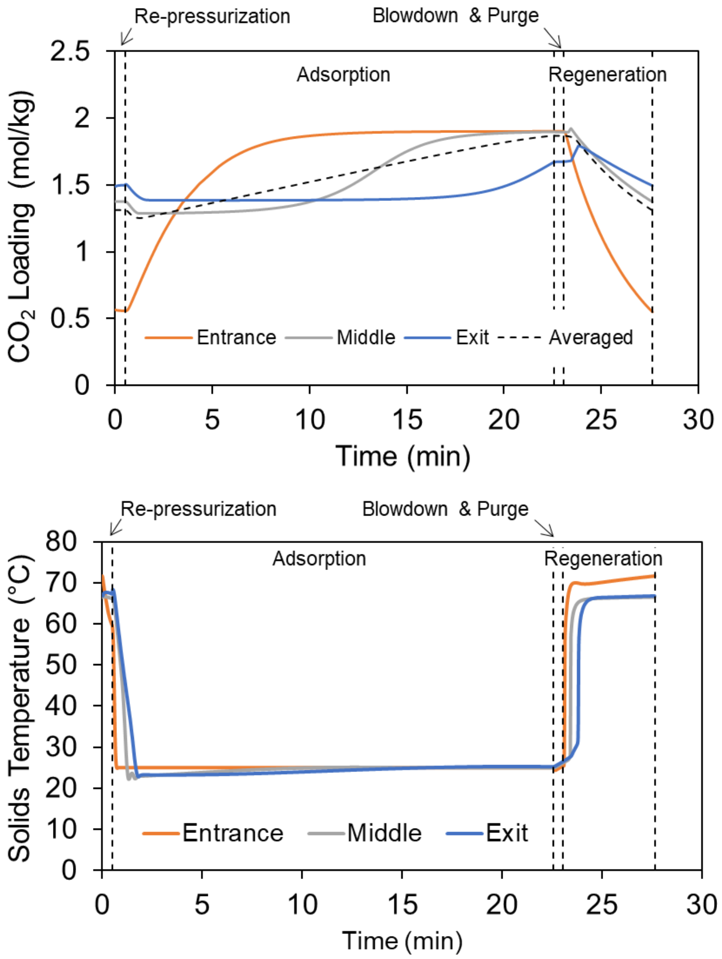
Results:

Decision Variable	**Optimized Value**
Adsorption Time [mins]	21.56
Desorption Time [mins]	4.09
Air pressure drop [bar]	1.63E-6
Steam sweep pressure drop [bar]	4.99E-8
Metric	**Optimized Value**
Recovery	0.73
CO_2 Product Purity	0.09
CO_2 Product Purity (water-free basis)*	0.95
Energy Requirement [MJ/kg CO_2]	14.71
Productivity [kg CO_2/h/m^3]	15.67
Cost of Capture [$/tonne]	268.2

*Cost are preliminary, DO NOT CITE

* The cost for removing all water from the product has not yet been included in the costing

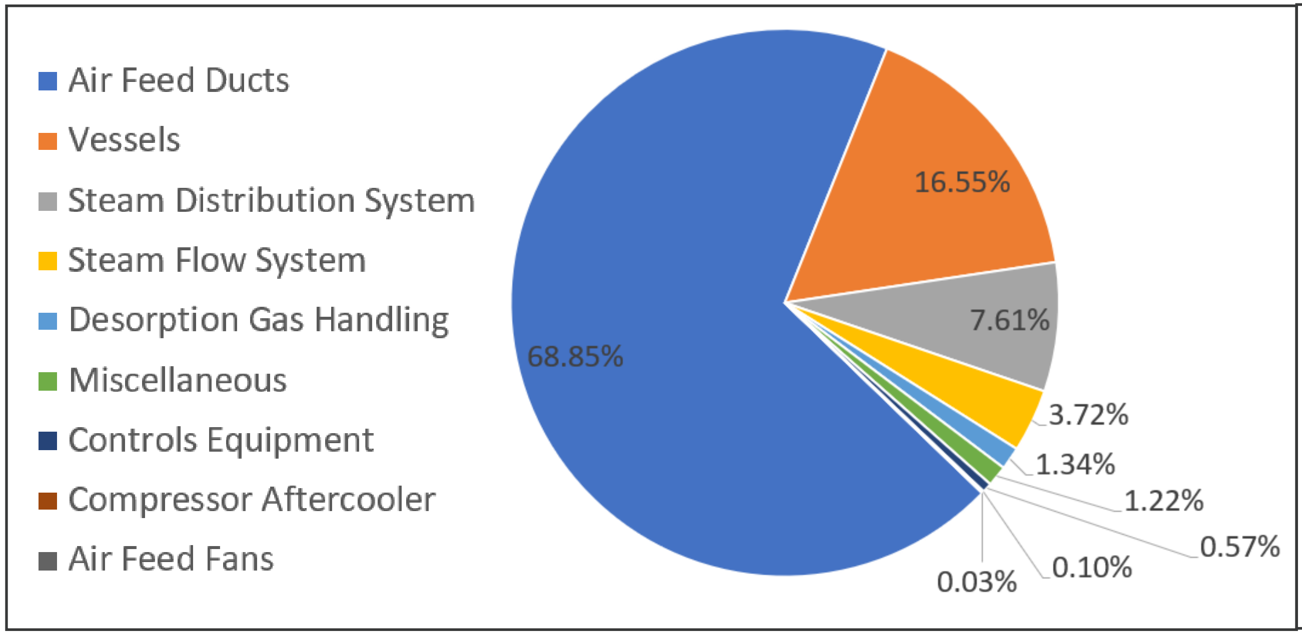
Profiles for optimized case



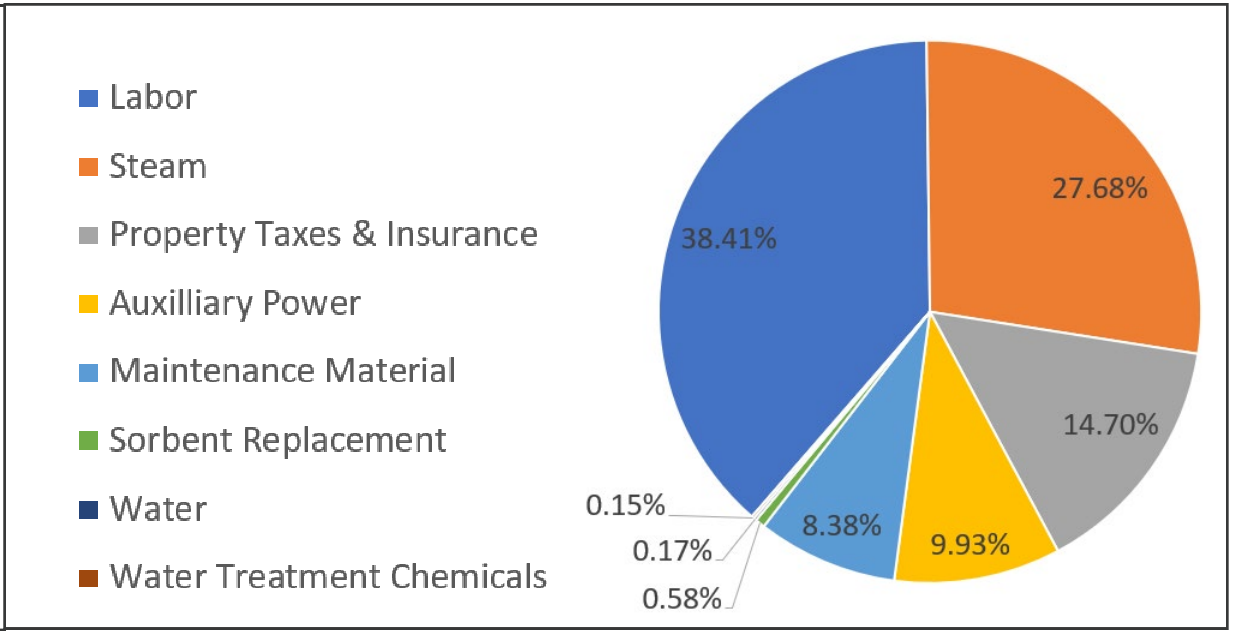
1. Direct Air Capture Case Studies: Sorbent System NETL report https://www.osti.gov/biblio/1879535

Optimization Results

TPC Breakdown



Operating Cost Breakdown



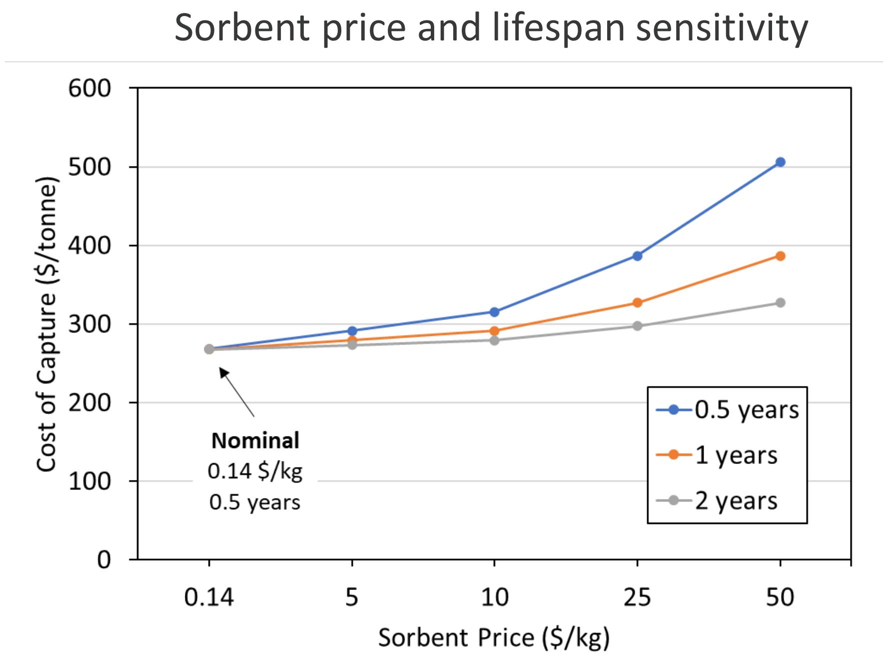
Costing Issues/Concerns:

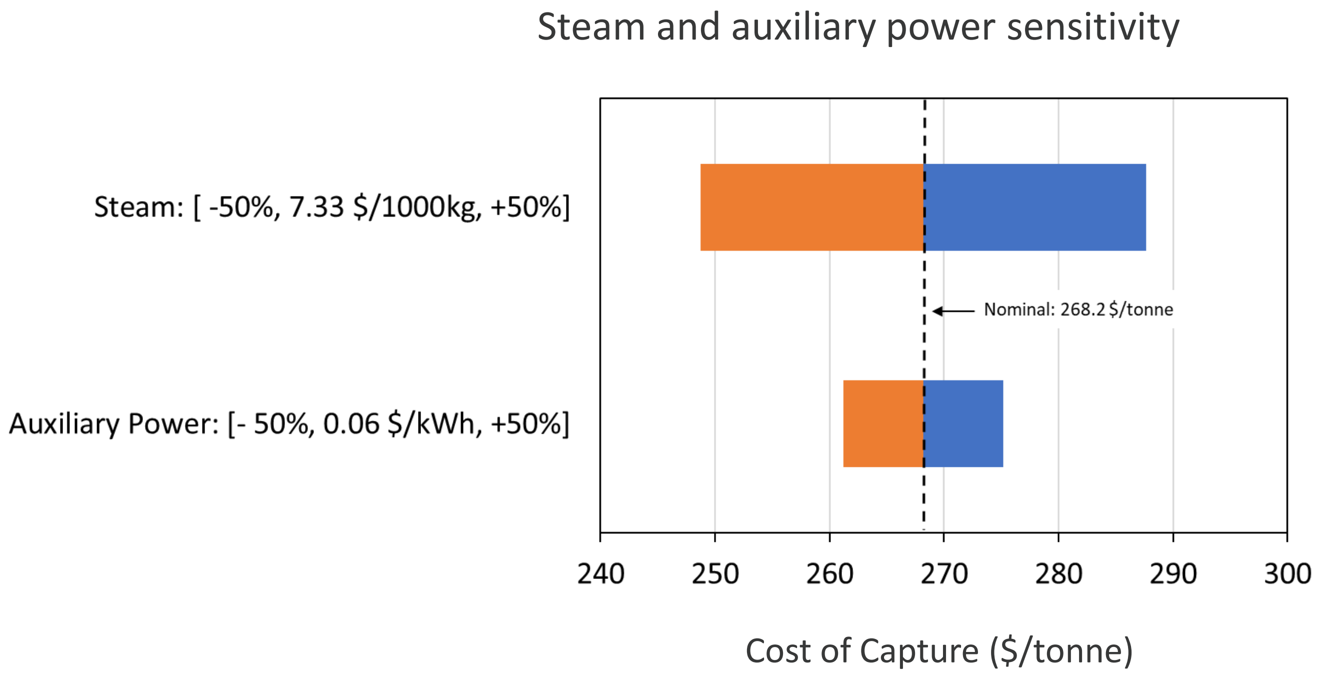
- Low pressure drop outside of feed fans scaling bounds. At minimum ΔP value: 363.3 $/tonne, 35% increase
- Steam extraction vs. use of low-quality/waste steam
- Water removal before CO_2 product compression
- Gross removal vs. Net removal. Accounting for emissions of energy sources

1. Direct Air Capture Case Studies: Sorbent System NETL report https://www.osti.gov/biblio/1879535

Optimization Results

Sensitivity Studies

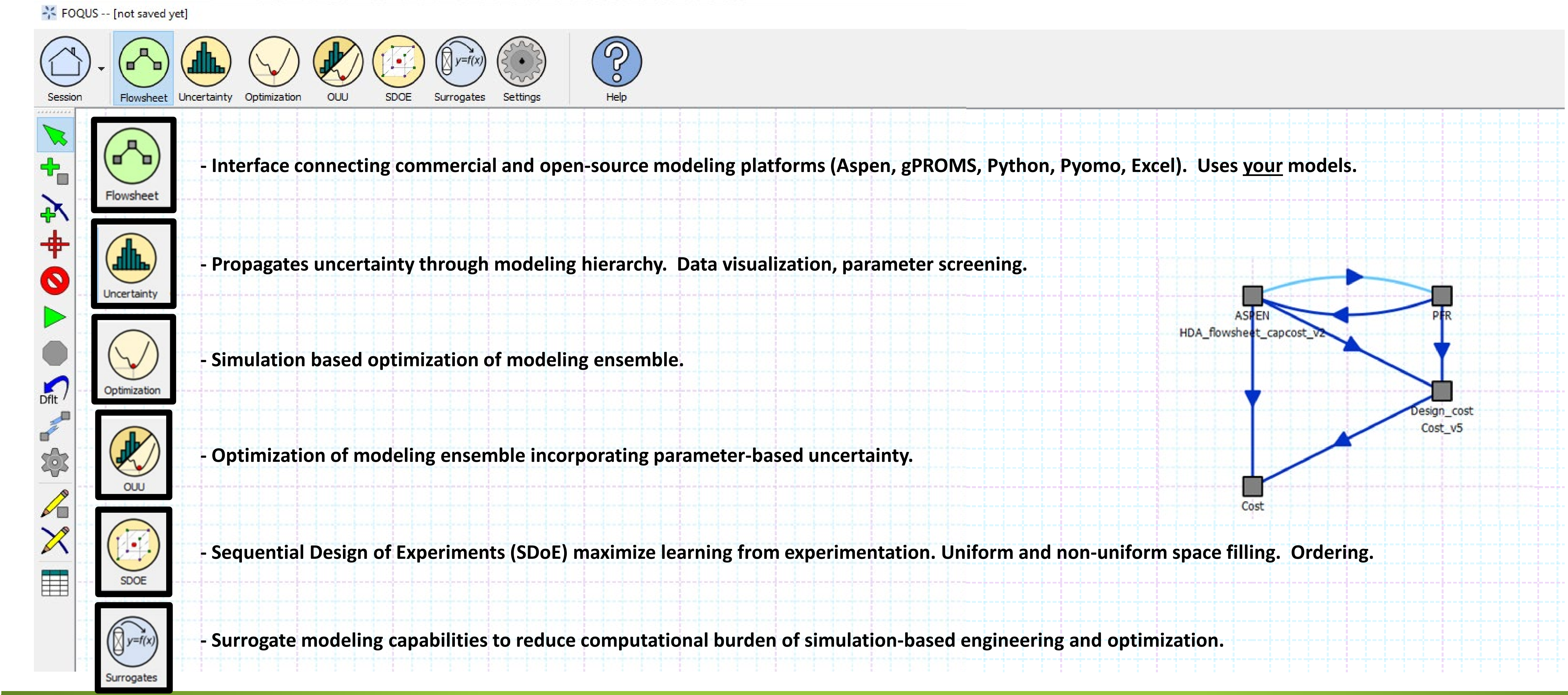




1. Direct Air Capture Case Studies: Sorbent System NETL report https://www.osti.gov/biblio/1879535

FOQUS Tool – Central Framework for CCSI^2 Analysis

Framework for Optimization, Quantification of Uncertainty, and Surrogates



- Interface connecting commercial and open-source modeling platforms (Aspen, gPROMS, Python, Pyomo, Excel). Uses your models.
- Propagates uncertainty through modeling hierarchy. Data visualization, parameter screening.
- Simulation based optimization of modeling ensemble.
- Optimization of modeling ensemble incorporating parameter-based uncertainty.
- Sequential Design of Experiments (SDoE) maximize learning from experimentation. Uniform and non-uniform space filling. Ordering.
- Surrogate modeling capabilities to reduce computational burden of simulation-based engineering and optimization.

PIM-1-AO-TAEA Submodels

Isotherm Models

- Fit traditional isotherm models along with more complex literature models by performing parameter estimation using available isotherm data
- Pyomo and parmest used to perform parameter estimation for each model
- Evaluate each model by their fit to the data and information criterion take model size into account

Parameter Estimation:

$$\min_{\theta} \; obj = \left(\frac{q_{exp}^{*} - q_{model}^{*}}{q_{exp}^{*}}\right)' \left(\frac{q_{exp}^{*} - q_{model}^{*}}{q_{exp}^{*}}\right)$$

RMSE [dimensionless]: $\sqrt{\frac{obj}{N}}$

AIC: $2p + N ln\left(\frac{obj}{N}\right)$

BIC: $\ln(N)p + N ln\left(\frac{obj}{N}\right)$

N = # of data points
p = # of parameters

Model Name	RMSE [-]	# parameters	AIC	BIC
Modified Toth	2.65E-03	12	-3.215E+03	-3.171E+03
Dual-Site Sips	4.09E-03	8	-2.987E+03	-2.958E+03
Dual-Site Langmuir	4.33E-03	6	-2.960E+03	-2.938E+03
Toth Model 3	5.14E-03	5	-2.868E+03	-2.849E+03
Toth Model 2	5.41E-03	5	-2.840E+03	-2.822E+03
Langmuir-Freundlich	5.71E-03	5	-2.811E+03	-2.793E+03
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Langmuir Model 1	9.14E-03	3	-2.558E+03	-2.547E+03
Freundlich Model	1.11E-02	4	-2.449E+03	-2.434E+03

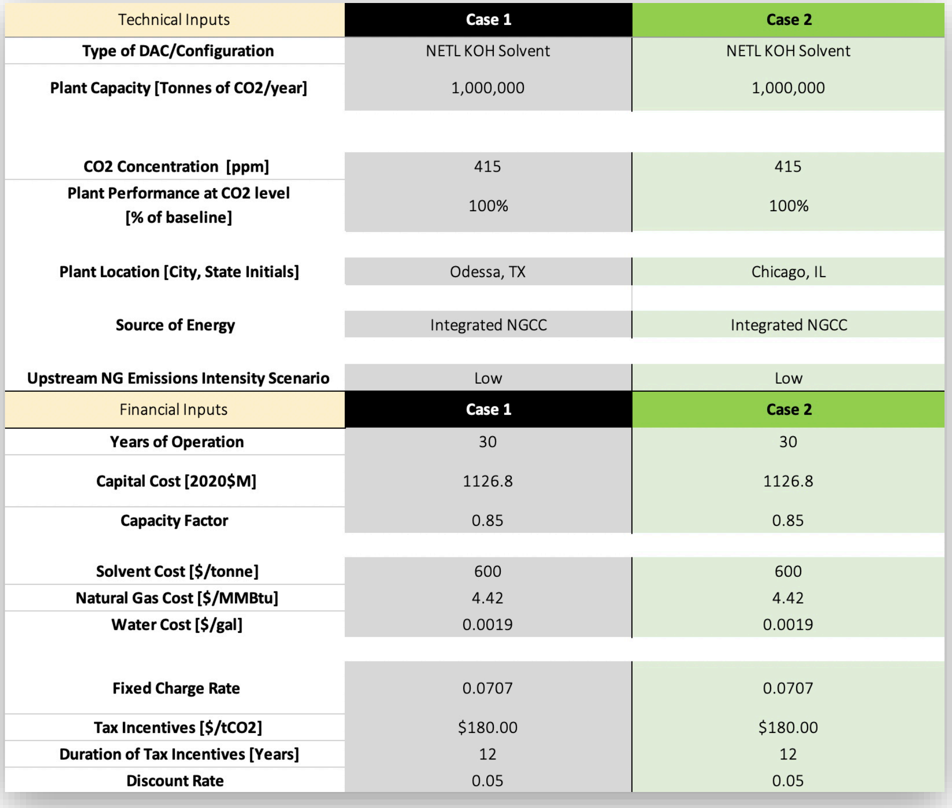
- Modified Toth gives best RMSE, AIC, and BIC

DAC siting tool

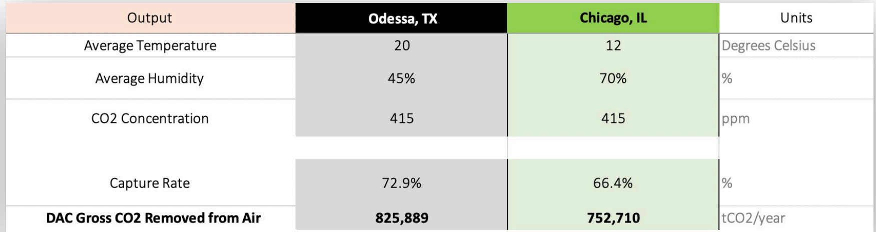
NATIONAL ENERGY TECHNOLOGY LABORATORY

Exercise to visualize DAC favorability in different regions

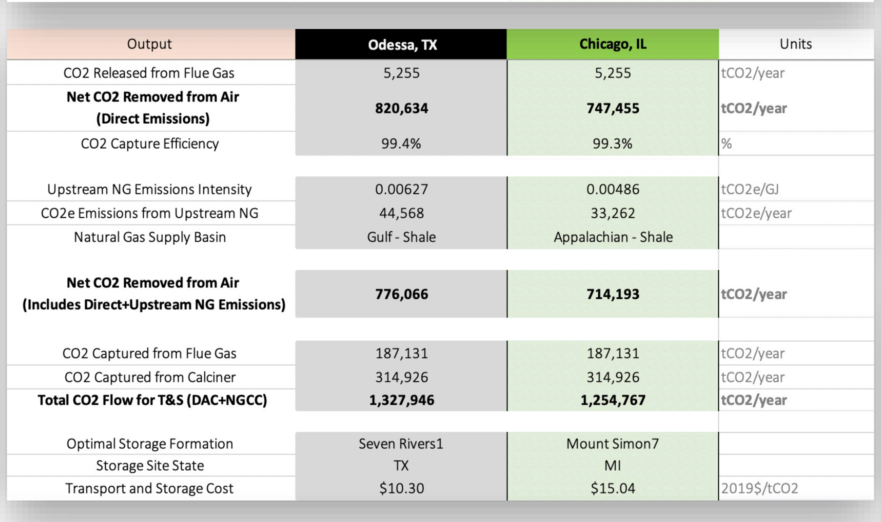
Excel-based tool which accounts for annualized temperature and humidity & proximity to storage to map and calculate costs for comparative sites



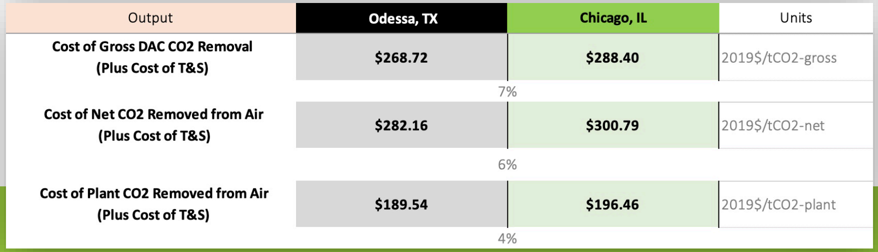
Technical Inputs	Case 1	Case 2
Type of DAC/Configuration	NETL KOH Solvent	NETL KOH Solvent
Plant Capacity [Tonnes of CO2/year]	1,000,000	1,000,000
CO2 Concentration [ppm]	415	415
Plant Performance at CO2 level [% of baseline]	100%	100%
Plant Location [City, State Initials]	Odessa, TX	Chicago, IL
Source of Energy	Integrated NGCC	Integrated NGCC
Upstream NG Emissions Intensity Scenario	Low	Low
Financial Inputs	**Case 1**	**Case 2**
Years of Operation	30	30
Capital Cost [2020$M]	1126.8	1126.8
Capacity Factor	0.85	0.85
Solvent Cost [$/tonne]	600	600
Natural Gas Cost [$/MMBtu]	4.42	4.42
Water Cost [$/gal]	0.0019	0.0019
Fixed Charge Rate	0.0707	0.0707
Tax Incentives [$/tCO2]	$180.00	$180.00
Duration of Tax Incentives [Years]	12	12
Discount Rate	0.05	0.05



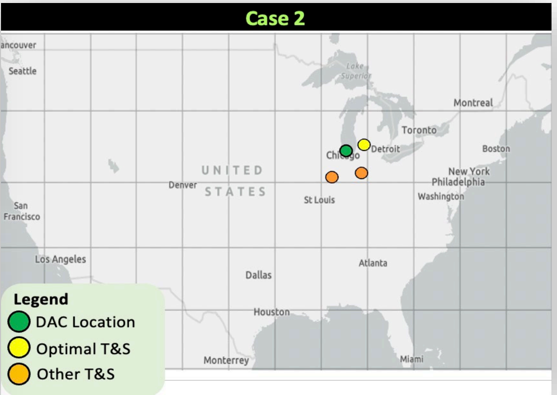
Output	Odessa, TX	Chicago, IL	Units
Average Temperature	20	12	Degrees Celsius
Average Humidity	45%	70%	%
CO2 Concentration	415	415	ppm
Capture Rate	72.9%	66.4%	%
DAC Gross CO2 Removed from Air	**825,889**	**752,710**	tCO2/year



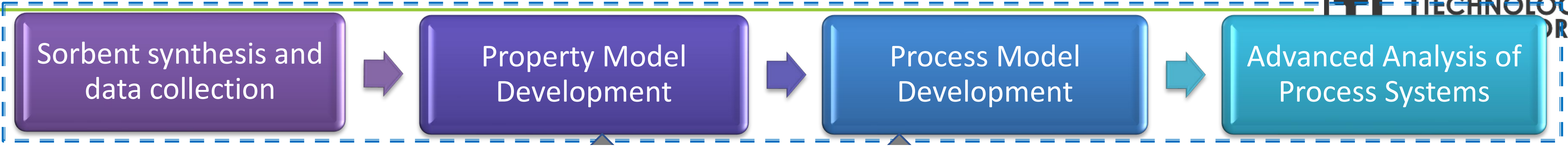
Output	Odessa, TX	Chicago, IL	Units
CO2 Released from Flue Gas	5,255	5,255	tCO2/year
Net CO2 Removed from Air (Direct Emissions)	**820,634**	**747,455**	**tCO2/year**
CO2 Capture Efficiency	99.4%	99.3%	%
Upstream NG Emissions Intensity	0.00627	0.00486	tCO2e/GJ
CO2e Emissions from Upstream NG	44,568	33,262	tCO2e/year
Natural Gas Supply Basin	Gulf - Shale	Appalachian - Shale	
Net CO2 Removed from Air (Includes Direct+Upstream NG Emissions)	**776,066**	**714,193**	**tCO2/year**
CO2 Captured from Flue Gas	187,131	187,131	tCO2/year
CO2 Captured from Calciner	314,926	314,926	tCO2/year
Total CO2 Flow for T&S (DAC+NGCC)	**1,327,946**	**1,254,767**	**tCO2/year**
Optimal Storage Formation	Seven Rivers1	Mount Simon7	
Storage Site State	TX	MI	
Transport and Storage Cost	$10.30	$15.04	2019$/tCO2



Output	Odessa, TX	Chicago, IL	Units
Cost of Gross DAC CO2 Removal (Plus Cost of T&S)	**$268.72**	**$288.40**	2019$/tCO2-gross
	7%		
Cost of Net CO2 Removed from Air (Plus Cost of T&S)	**$282.16**	**$300.79**	2019$/tCO2-net
	6%		
Cost of Plant CO2 Removed from Air (Plus Cost of T&S)	**$189.54**	**$196.46**	2019$/tCO2-plant
	4%		



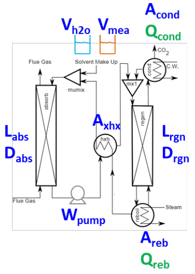
Applying Advanced Computational Tools To Support DAC Test Center

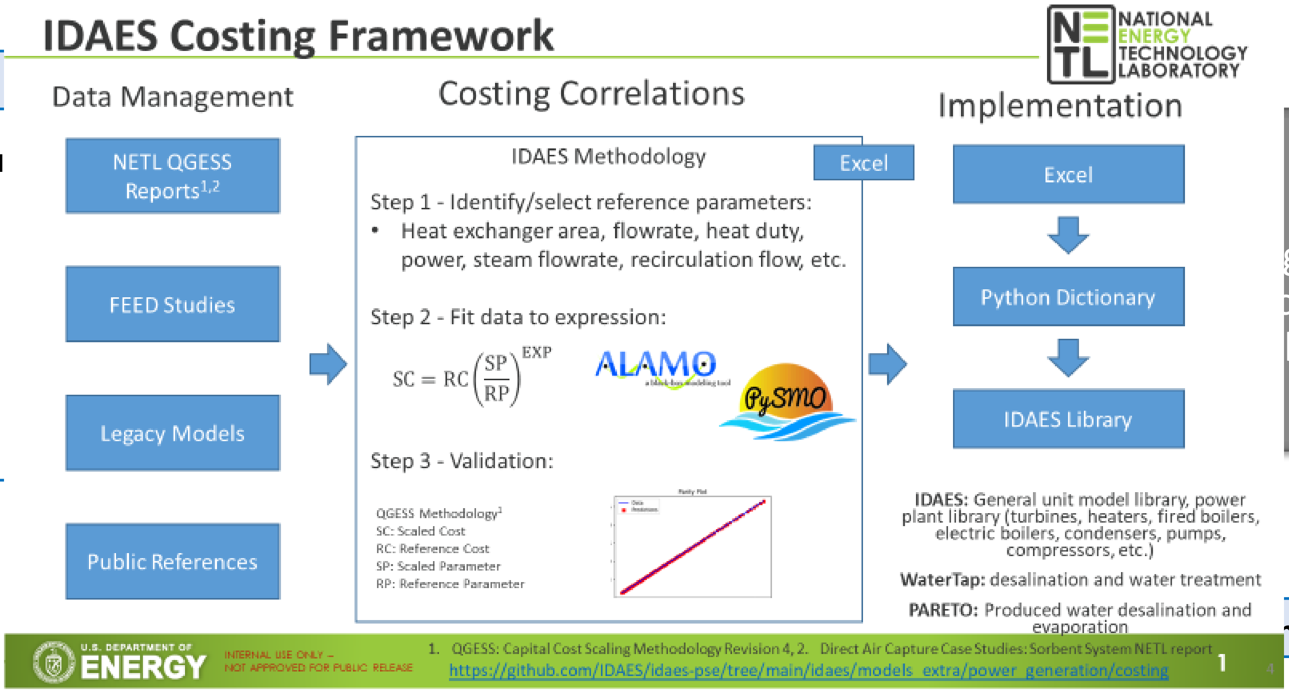


Sorbent synthesis and data collection → Property Model Development → Process Model Development → Advanced Analysis of Process Systems

Rigorous

High Fidelity Process Model





IDAES Costing Framework

Data Management

- NETL QGESS Reports[1,2]
- FEED Studies
- Legacy Models
- Public References

Costing Correlations

IDAES Methodology

Excel

Step 1 - Identify/select reference parameters:

- Heat exchanger area, flowrate, heat duty, power, steam flowrate, recirculation flow, etc.

Step 2 - Fit data to expression:

$$SC = RC\left(\frac{SP}{RP}\right)^{EXP}$$

ALAMO

PySMO

Step 3 - Validation:

QGESS Methodology[1]
SC: Scaled Cost
RC: Reference Cost
SP: Scaled Parameter
RP: Reference Parameter

Implementation

Excel → Python Dictionary → IDAES Library

IDAES: General unit model library, power plant library (turbines, heaters, fired boilers, electric boilers, condensers, pumps, compressors, etc.)

WaterTap: desalination and water treatment

PARETO: Produced water desalination and evaporation

[1] QGESS: Capital Cost Scaling Methodology Revision 4, 2. Direct Air Capture Case Studies: Sorbent System NETL report

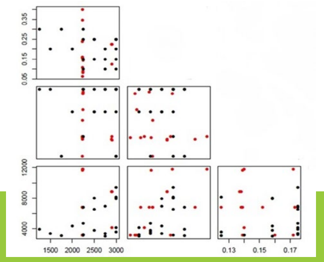
https://github.com/IDAES/idaes-pse/tree/main/idaes/models_extra/power_generation/costing

INTERNAL USE ONLY – NOT APPROVED FOR PUBLIC RELEASE

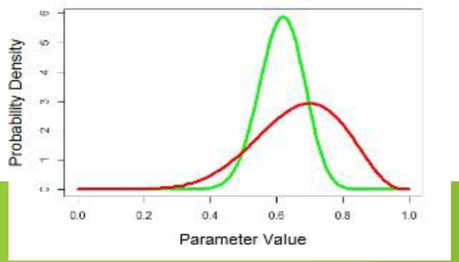
Bench and Pilot
g – Reducing time
chnical risk in
logy scale-up

mize Data Value, Maximize Learning

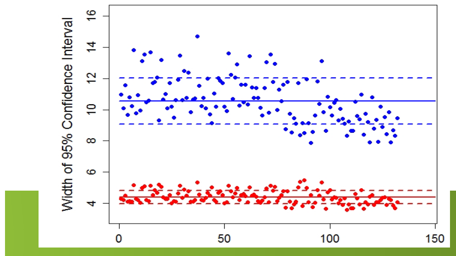
Optimize Experimental Design



Refine Model Parameters



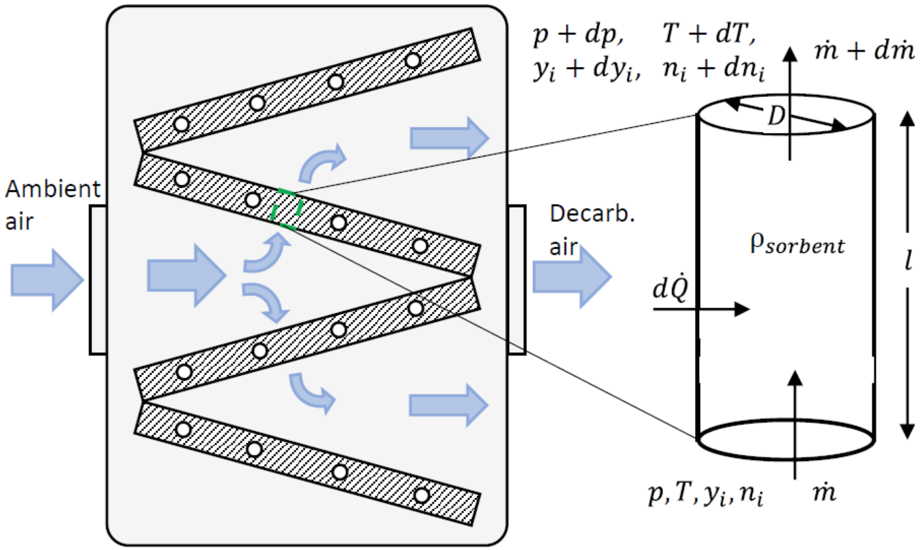
Maximizing Learning



Contactor and Process Modeling

Modeling a Fixed Bed Design With Low Pressure Drop

- Design of the column to mimic the air contactor presented by Climeworks, which resembles an air ventilation system rather than a conventional adsorber column.



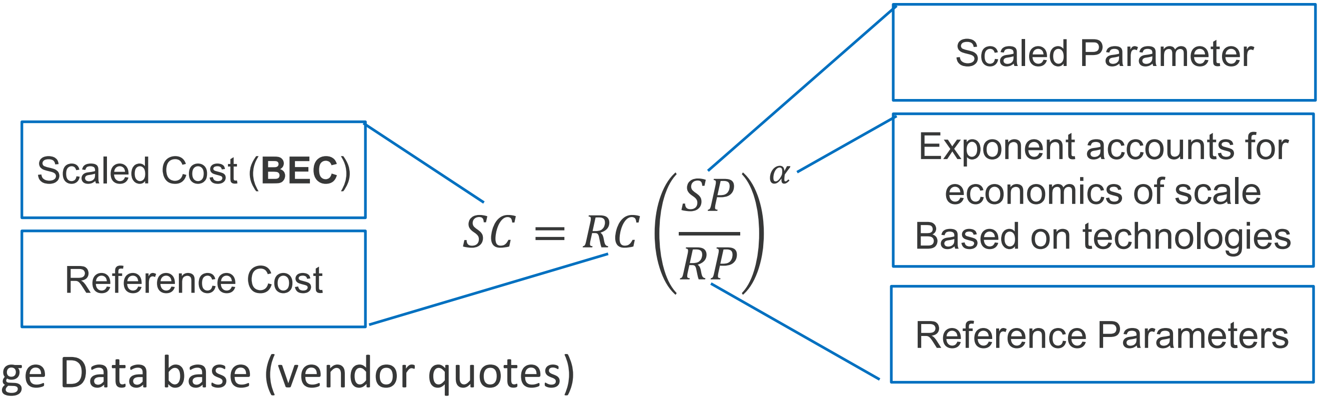
Assumption of a flat bed (Young et. al., 2021) to mimic a differential segment of the plates containing the solid sorbent in the Climeworks contactor

Dimension	IDAES Model
Bed Diameter (m)	0.1
Bed Height (m)	0.01

Young, John and García-Díez, Enrique and Garcia, Susana and van der Spek, Mijndert, "The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes," Energy Environ. Sci., (2021), 14(10), 5377-5394

Costing Implementation for DAC systems

Cost Scaling



Scaled Cost (**BEC**)

Reference Cost

$$SC = RC\left(\frac{SP}{RP}\right)^{\alpha}$$

Scaled Parameter

Exponent accounts for economics of scale Based on technologies

Reference Parameters

Large Data base (vendor quotes)

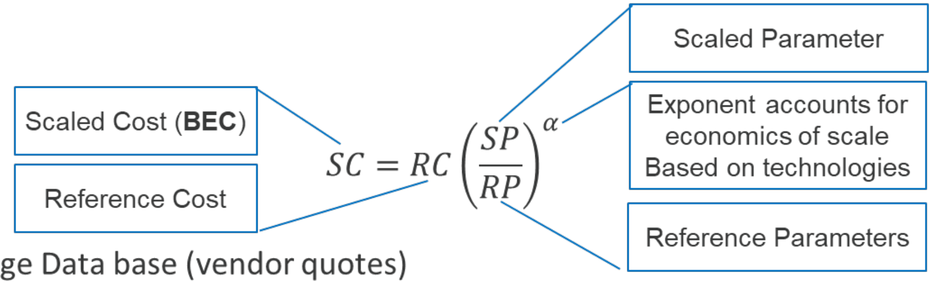
Account Number	Item Description	Parameter
15	**Direct Air Capture System**	
15.1	DAC Adsorption/Desorption Vessels[A]	Vessel Internal Diameter, ft
15.2	DAC CO_2 Compression & Drying	Compressor Auxiliary Load, kW
15.3	DAC CO_2 Compressor Aftercooler	Heat Exchanger Duty, MMBtu/hr
15.4	DAC System Air Handling Duct and Dampers	Inlet Air Flow, lb/hr
15.5	DAC System Air Handling Fans[A]	Pressure Drop, in. H_2O (differential)
15.6	DAC Desorption Process Gas Handling System	DAC CO_2 Product Flow Rate, lb/hr
15.7	DAC Steam Distribution System	DAC Steam Flow Rate, lb/hr
15.8	DAC System Controls Equipment	Total DAC Auxiliary Load, kW

1. Direct Air Capture Case Studies: Sorbent System NETL report https://www.osti.gov/biblio/1879535

NETL’s Costing Structure (IDAES Costing Framework)

- Annualized costing methodology based on established NETL guidelines[1]

Quality Guidelines for Energy System Studies: Capital Cost Scaling Methodology (DOE/NETL-2013/341)



Scaled Cost (**BEC**)

Reference Cost

$$SC = RC\left(\frac{SP}{RP}\right)^{\alpha}$$

Scaled Parameter

Exponent accounts for economics of scale Based on technologies

Reference Parameters

Large Data base (vendor quotes)

α, RP, RC, SP

- Subcritical, Supercritical, and ultra-supercritical
- NGCC, IGCC, etc.
- SOFC/SOEC
- Air Separation Unit
- Carbon Capture System

Variable	Definition	Expression	Units
BMC	Bare Module Cost	$BMC = F_{BM} * \frac{CEPCI_{2019}}{CEPCI_{2013}} * C_E$	\$MM
TPC	Total Plant Cost	$TPC = TBMC + engineering\ fee + process/project\ contingencies$	\$MM
TOC	Total Overnight Cost	$TOC\ = TPC + Owner's\ cost$	\$MM
TASC	Total As Spent Cost	$TASC = TOC\ * 1.093$	\$MM
Annualized capital cost	Annualized cost	$Annualized\ Cost\ = 0.0707\ * TASC$	\$MM/y

[1] J. Theis, "Quality Guidelines for Energy Systems Studies: Cost Estimation Methodology for NETL Assessments of Power Plant Performance - Feb 2021" , NETL-PUB-22580, United States, 2021. https://doi.org/10.2172/1567736

NETL's Costing Structure (IDAES Costing Framework)

- Fixed O&M Costs:
  - $Annual\ Operating\ Labor = \#\ Operators * Labor\ Rate * (1 + Op.Labor\ Burden) = 8 * 38.50 \left[\frac{\$}{hr}\right] 8760 \left[\frac{hr}{y}\right] * (1 + 0.3)$
  - $Maintenance\ Labor = 0.4 * 0.019 * TPC$
  - $Administration\ \&\ Support\ Labor = 0.25 * (Annual\ Op.Labor + Maint.Labor)$
  - $Property\ Taxes\ \&\ Insurance = 0.02 * TPC$

- Variable O&M Costs:
  - $Maintenance\ Material\ Cost = TPC * 0.6 * 0.019/0.85 * Capacity\ Factor$
  - $Auxilliary\ Power = \$0.06/kWh$
  - $Cooling\ Water = \$0.354/GJ$
  - $Steam = \$7.33/1000kg$
  - $Sorbent = \$0.5/kg$

$$\boxed{Total\ Annualized\ Cost\ [\$MM/y] = Annualized\ Capital\ Cost + Fixed\ O\&M + Variable\ O\&M}$$

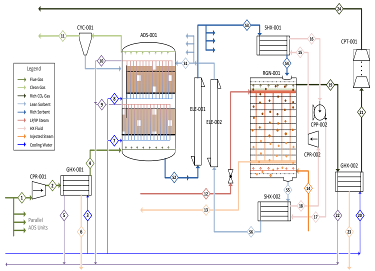
CCSI^2 – Modeling, Optimization and Technical Risk Reduction

CCSI^2
Carbon Capture Simulation for Industry Impact

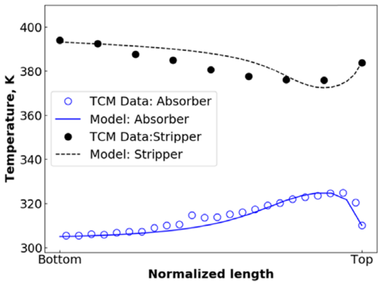
Multi-lab modeling initiative to support carbon capture technology development

NATIONAL ENERGY TECHNOLOGY LABORATORY
BERKELEY LAB
Lawrence Livermore National Laboratory
Los Alamos NATIONAL LABORATORY EST.1943
Pacific Northwest NATIONAL LABORATORY
OAK RIDGE National Laboratory
Carnegie Mellon
West Virginia University
UNIVERSITY OF NOTRE DAME
THE UNIVERSITY OF TEXAS AT AUSTIN
UT
UNIVERSITY OF PITTSBURGH

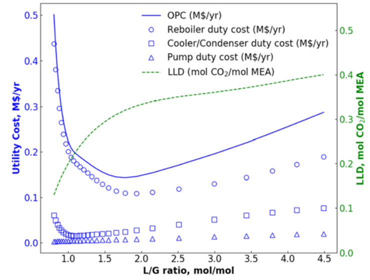
High Fidelity Process Modeling



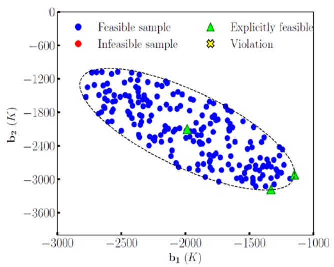
Model Validation



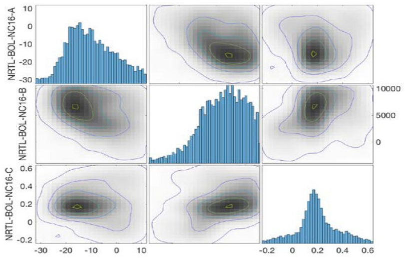
Process Optimization



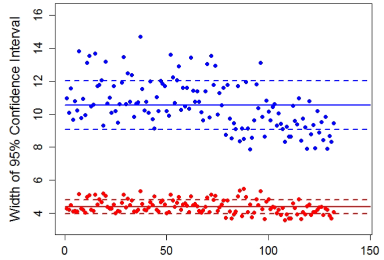
Robust Design

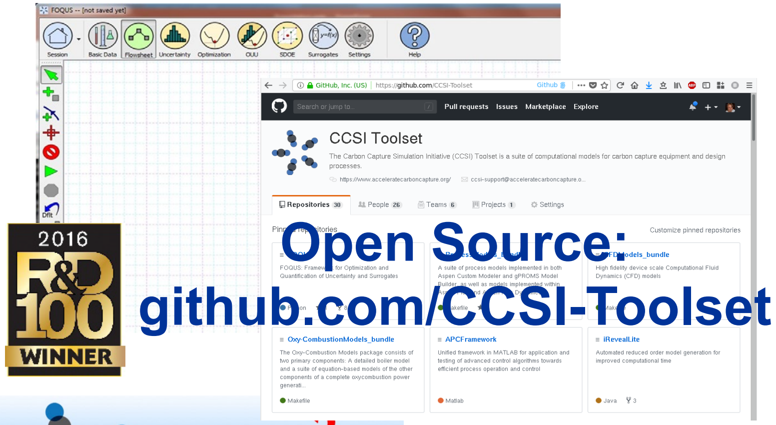


Uncertainty Quantification



Maximizing Learning





CCSI Toolset

The Carbon Capture Simulation Initiative (CCSI) Toolset is a suite of computational models for carbon capture equipment and design processes.

https://www.acceleratecarboncapture.org/ ccsi-support@acceleratecarboncapture.o...

FOQUS: Framework for Optimization and Quantification of Uncertainty and Surrogates

A suite of process models implemented in both Aspen Custom Modeler and gPROMS Model Builder, as well as models implemented within

CFDModels_bundle
High fidelity device scale Computational Fluid Dynamics (CFD) models

Oxy-CombustionModels_bundle
The Oxy-Combustion Models package consists of two primary components: A detailed boiler model and a suite of equation-based models of the other components of a complete oxycombustion power generati...
Makefile

APCFramework
Unified framework in MATLAB for application and testing of advanced control algorithms towards efficient process operation and control
Matlab

iRevealLite
Automated reduced order model generation for improved computational time
Java 3

2016 R&D 100 WINNER

Open Source: github.com/CCSI-Toolset

CCSI^2
Carbon Capture Simulation for Industry Impact

IDAES
Institute for the Design of Advanced Energy Systems

Open Source: github.com/IDAES/idaes-pse