Advanced Modeling and Process-Materials Co-Optimization Strategies for Swing Adsorption Based Gas Separations

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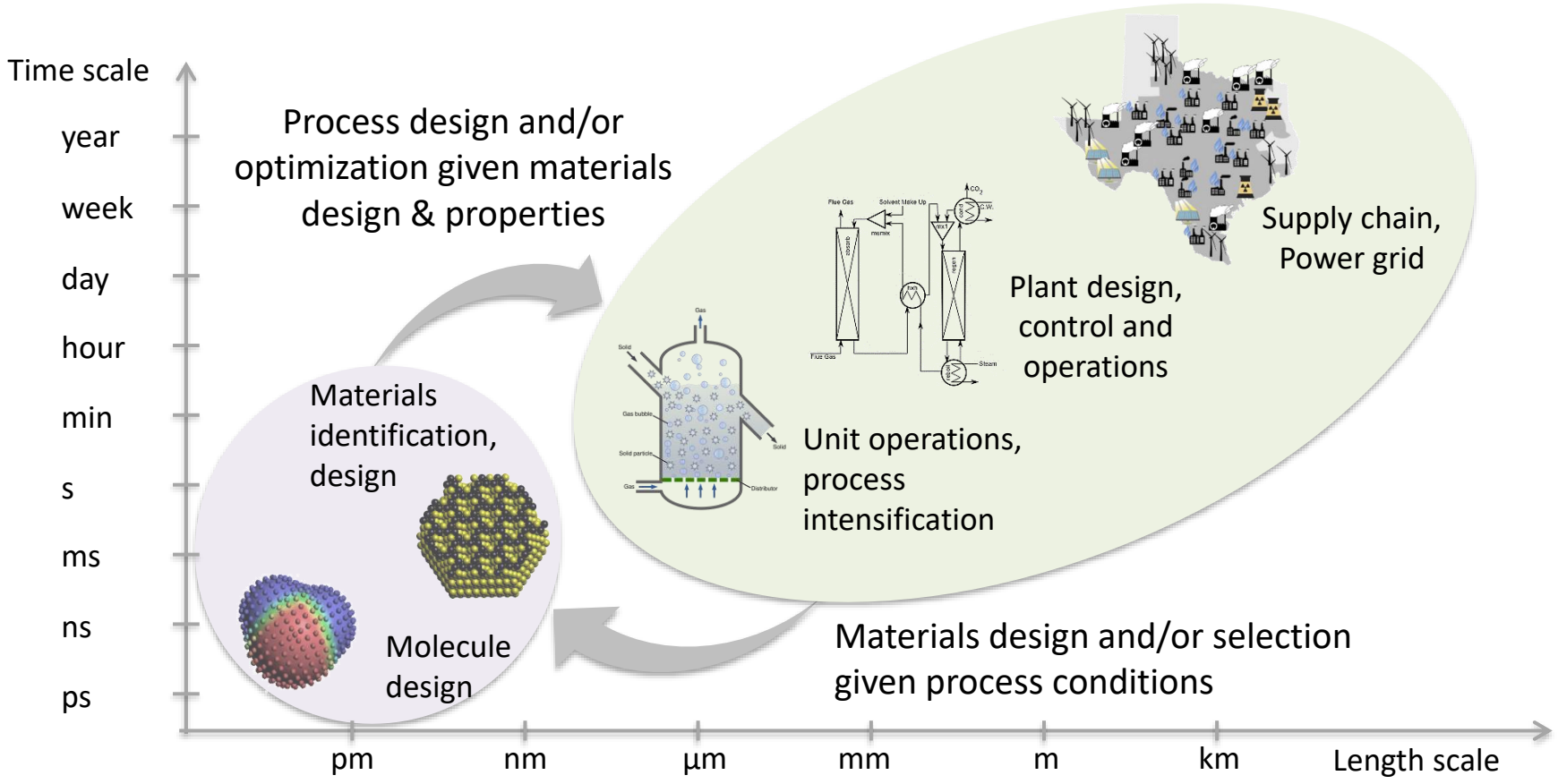
Tuesday, April 23rd, 2024

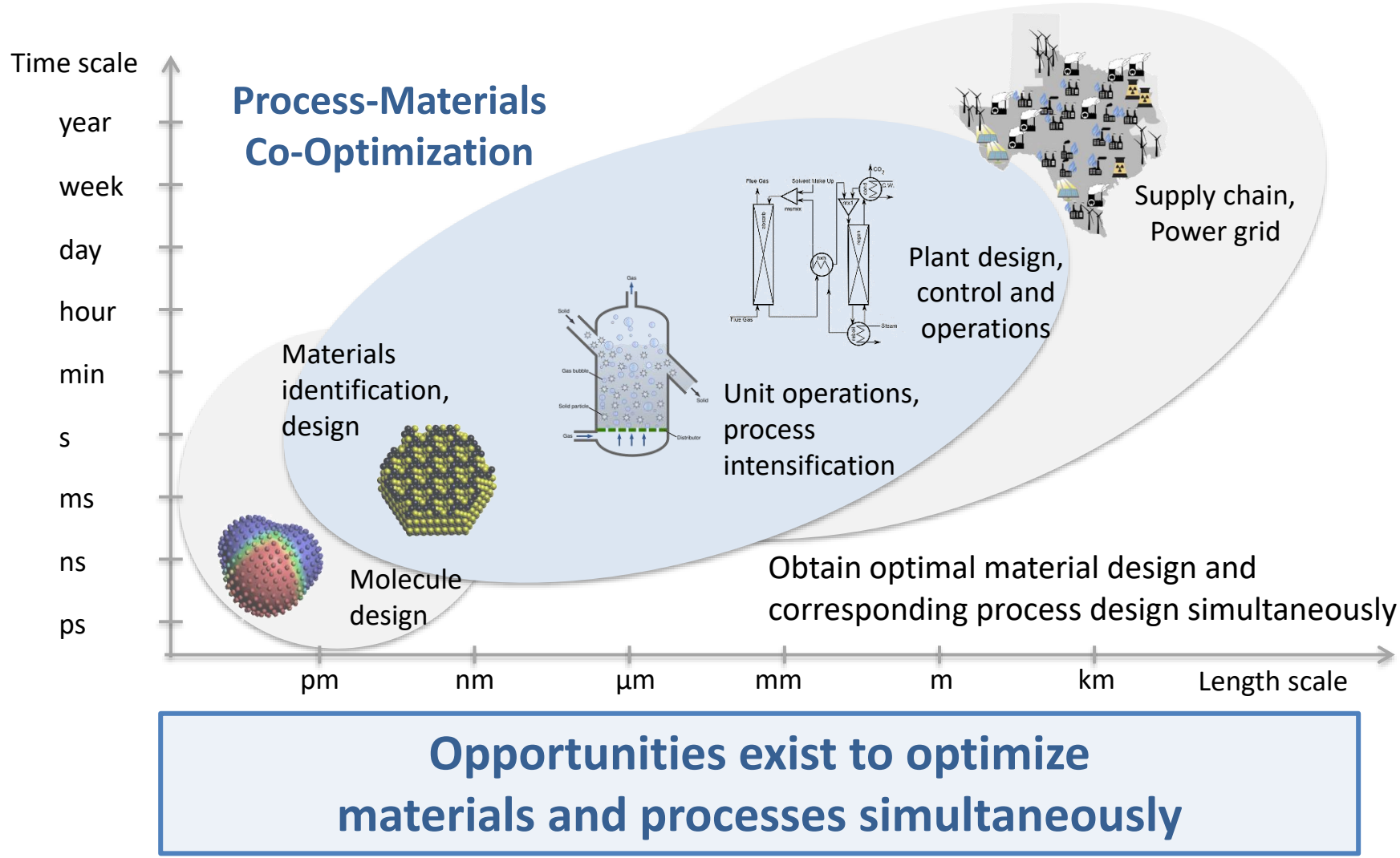
Motivation

- Multi-scale highly integrated energy systems



Motivation

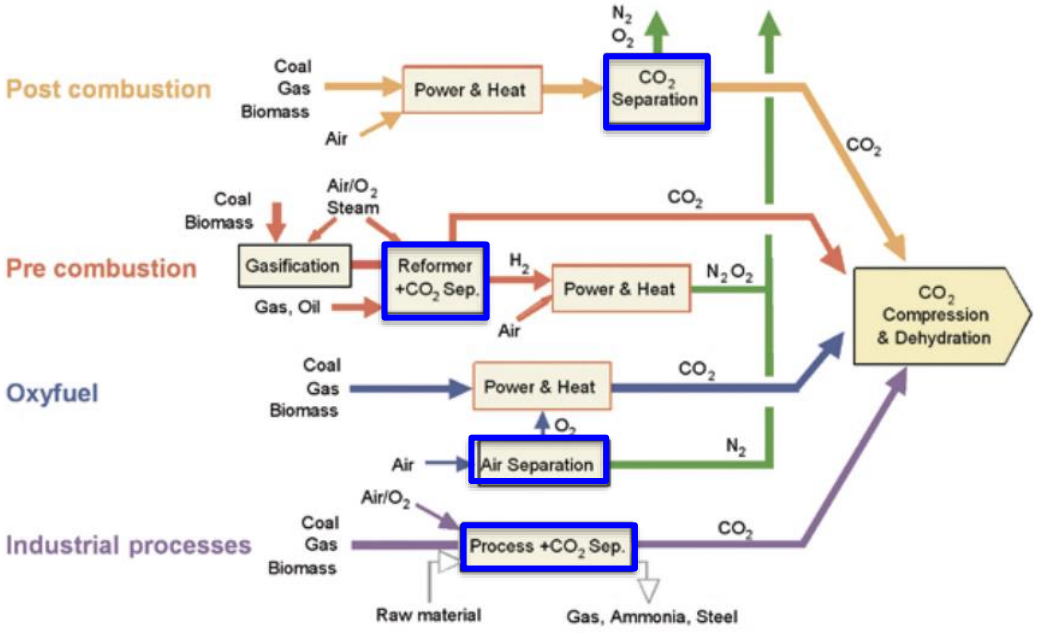
- Multi-scale highly integrated energy systems



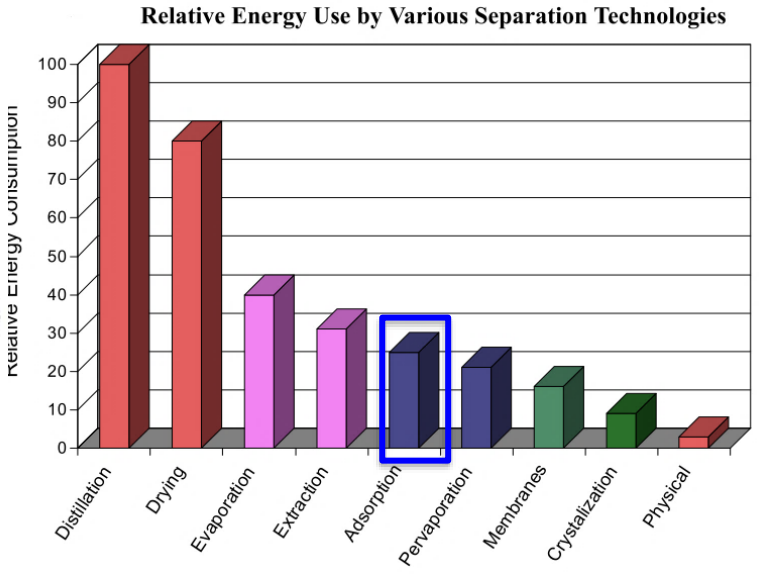
Opportunities exist to optimize materials and processes simultaneously

Adsorption-Based Gas Separation

- Gas separation processes are crucial parts of next-generation energy and environmental technologies
- Adsorption-based separation technologies, such as Pressure Swing Adsorption (PSA), have been intensively investigated for energy-efficiency, low environmental impact etc.



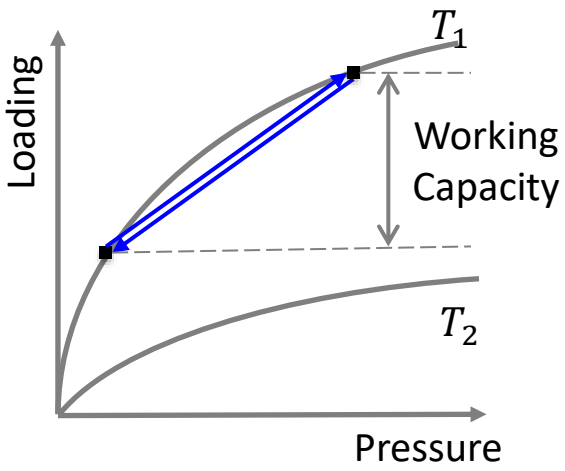
Metz, B., Davidson, O., De Coninck, H.C., Loos, M. and Meyer, L., 2005. IPCC special report on carbon dioxide capture and storage. Cambridge: Cambridge University Press.



Angelini, P., Armstrong, T., Counce, R., Griffith, W., Klasson, T.L., Muralidharan, G., Narula, C., Sikka, V., Closset, G., Keller, G. and Watson, J., 2005. Materials for separation technologies: Energy and emission reduction opportunities. DOE, EERE Office, Washington, DC, 103.

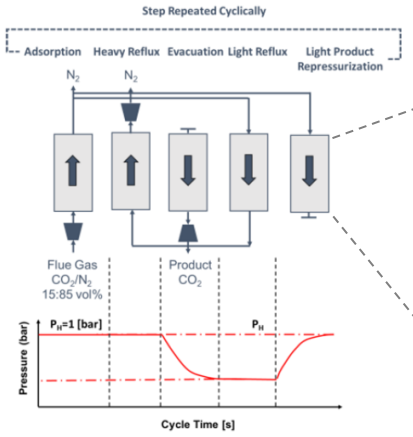
Pressure Swing Adsorption

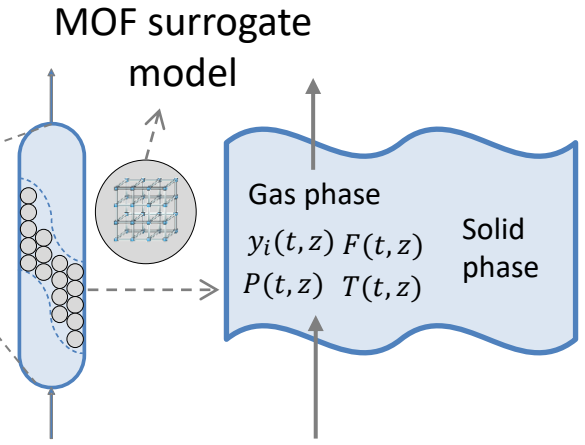
- Pressure difference drives the adsorption
- Continuous adsorption gas separation relies on cyclic operations
- Model columns as 1D dynamic packed-beds
  - No radial gradients → 1D phenomena
  - Rigid adsorbents → fixed solid phase
  - Equilibrium-controlled adsorption → isotherm models



https://www.linde-engineering.com/en/images/

5-bed 5-step cycle

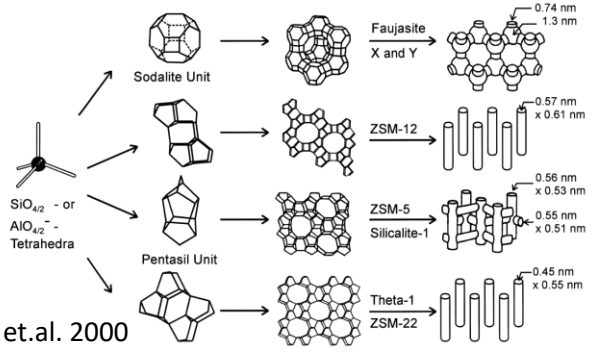




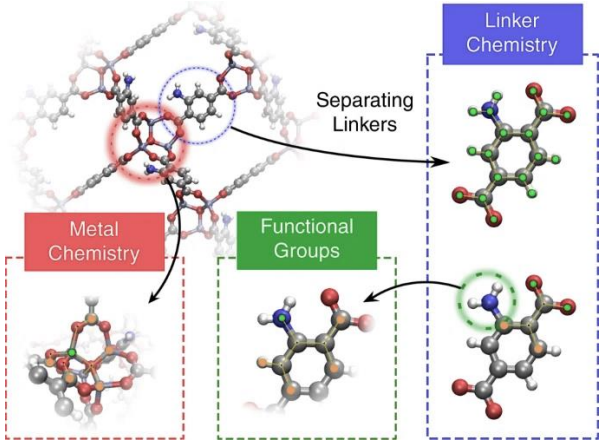
Column conceptual model

Microporous Materials as Adsorbents

- Microporous materials (i.e., MOFs, Zeolites) are promising adsorbents for adsorption-based gas separation processes
- Vast design space of microporous materials calls for systematic computational search method



Weitkamp et.al. 2000



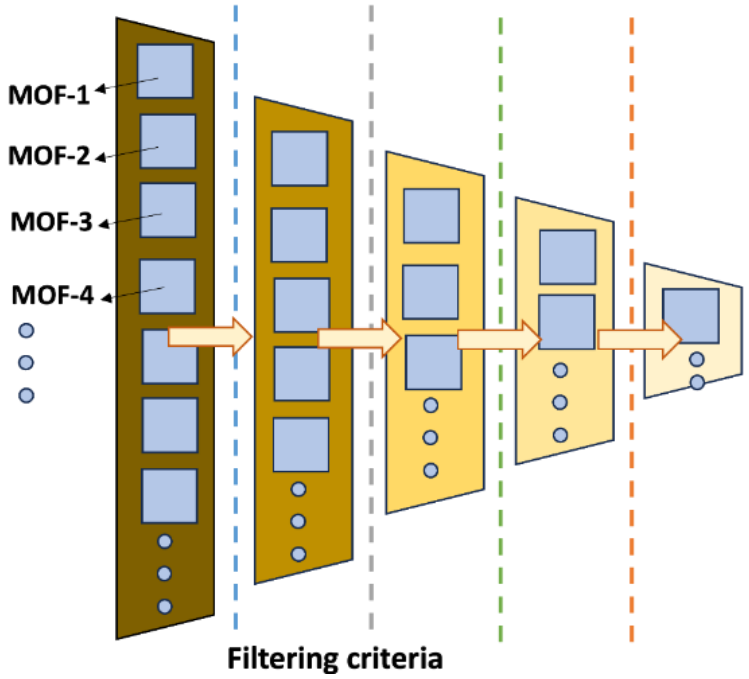
Moosavi et. al. 2016

Database	Number of entries	Origin
CoRE-MOF	14,000+	Experiments
hMOF	137,953	Simulations
ToBaCCo	13,512	Simulations
CSD-MOF	96,000+	Experiments
IZA	252	Experiments
hZeo	2.6M	Simulations
CoRE-COF	449	Experiments
hCOF	69,840	Simulations
CURATED COFs	482	Experiments

247 trillion MOFs (Lee et. al. 2021)

Design of MOFs for PSA Separations

- **Approach 1 : Material screening through process simulation**
  - Screening through all the candidates in a database and filtering them down via certain criteria
  - Limited search space for MOFs
  - Requires a time-consuming process simulation for every MOF to evaluate



Design of MOFs for PSA Separations

- **Approach 2 : Optimize material performance characteristics**
  - Optimizing adsorption isotherm parameters (v) while simulating process
  - Broadest search space, beyond what exists in a structure database
  - Can utilize established numerical optimization solvers for equation-oriented and/or black-box models
  - Does not provide structural information for MOF
    - Optimal adsorption isotherm might not be realizable

$$\begin{aligned} \max_{\nu} \quad & \text{Process Performance} \\ \text{s.t.} \quad & \text{Process Performance} = \text{Adsorption Process}(\nu, p) \\ & \nu \in V \end{aligned}$$

Design of MOFs for PSA Separations

- **Approach 3 : Embedding material surrogate in process model**
  - Optimizing MOF descriptors (d) while simulating process
  - Wide search space, beyond what exists in a structure database, but with explicit guarantees about structural self-consistency
  - Can utilize established numerical optimization solvers for equation-oriented and/or black-box models

$$\max_{d} \quad \text{Process Performance}$$

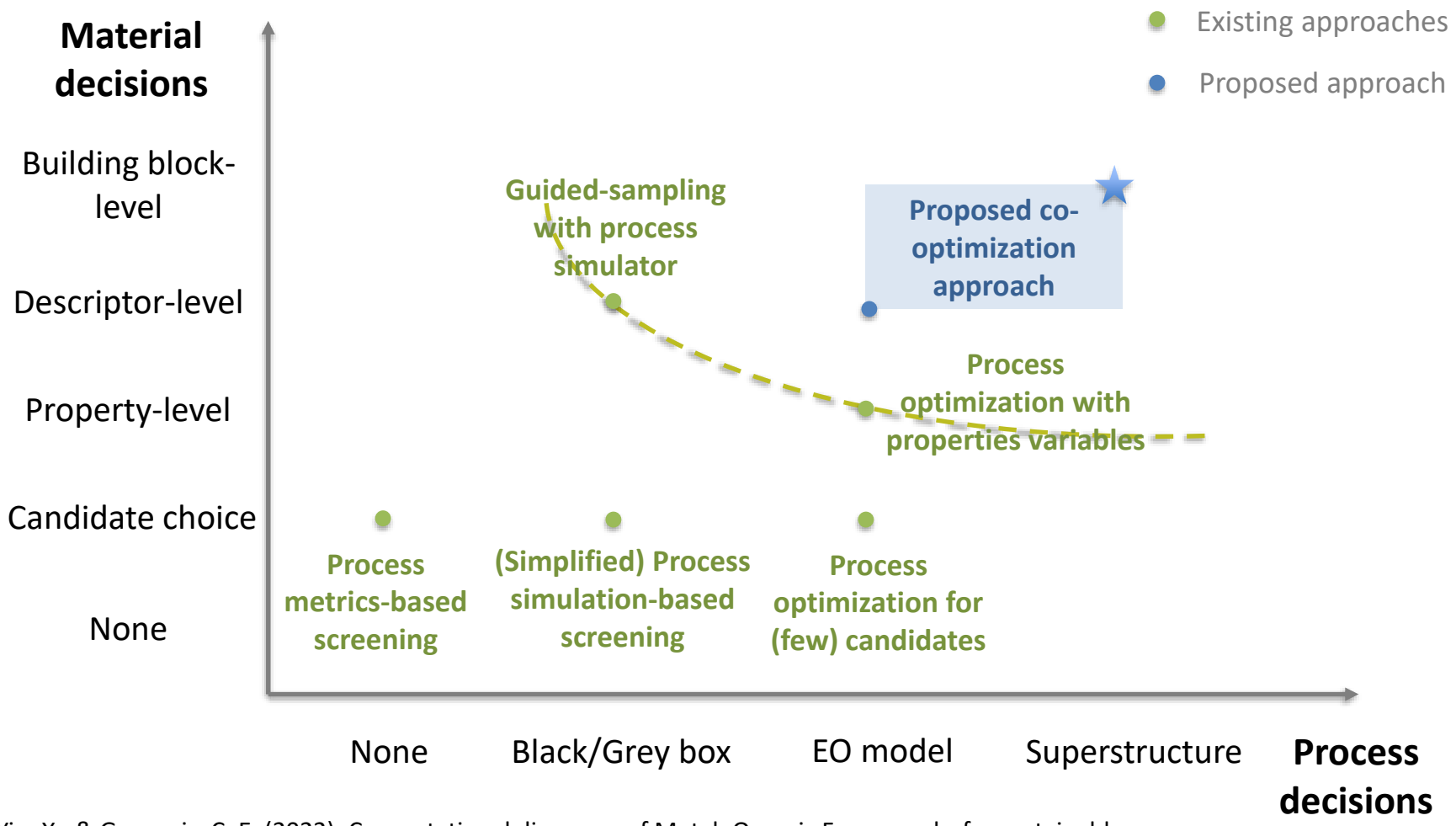
$$\text{s.t.} \quad \nu = \boxed{\text{Adsorption Properties}(d)} \qquad \text{Materials Model}$$

$$\text{Process Performance} = \text{Adsorption Process}(\nu, p)$$

$$\boxed{d \in D} \qquad \text{Descriptor Domain}$$

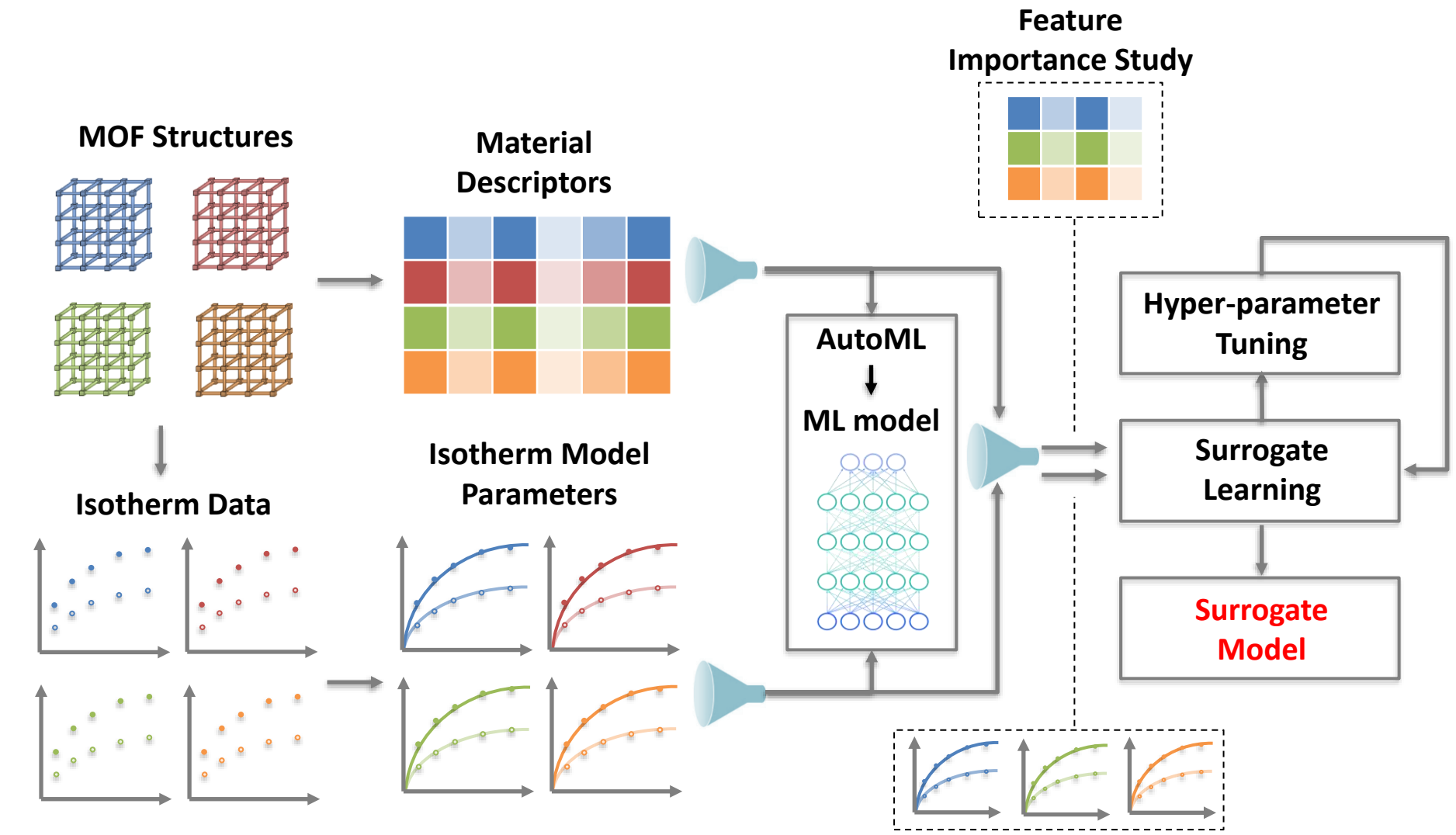
(Co-)Optimization Approaches Landscape

- **Goal:** Push Pareto front of material-process decision fidelity

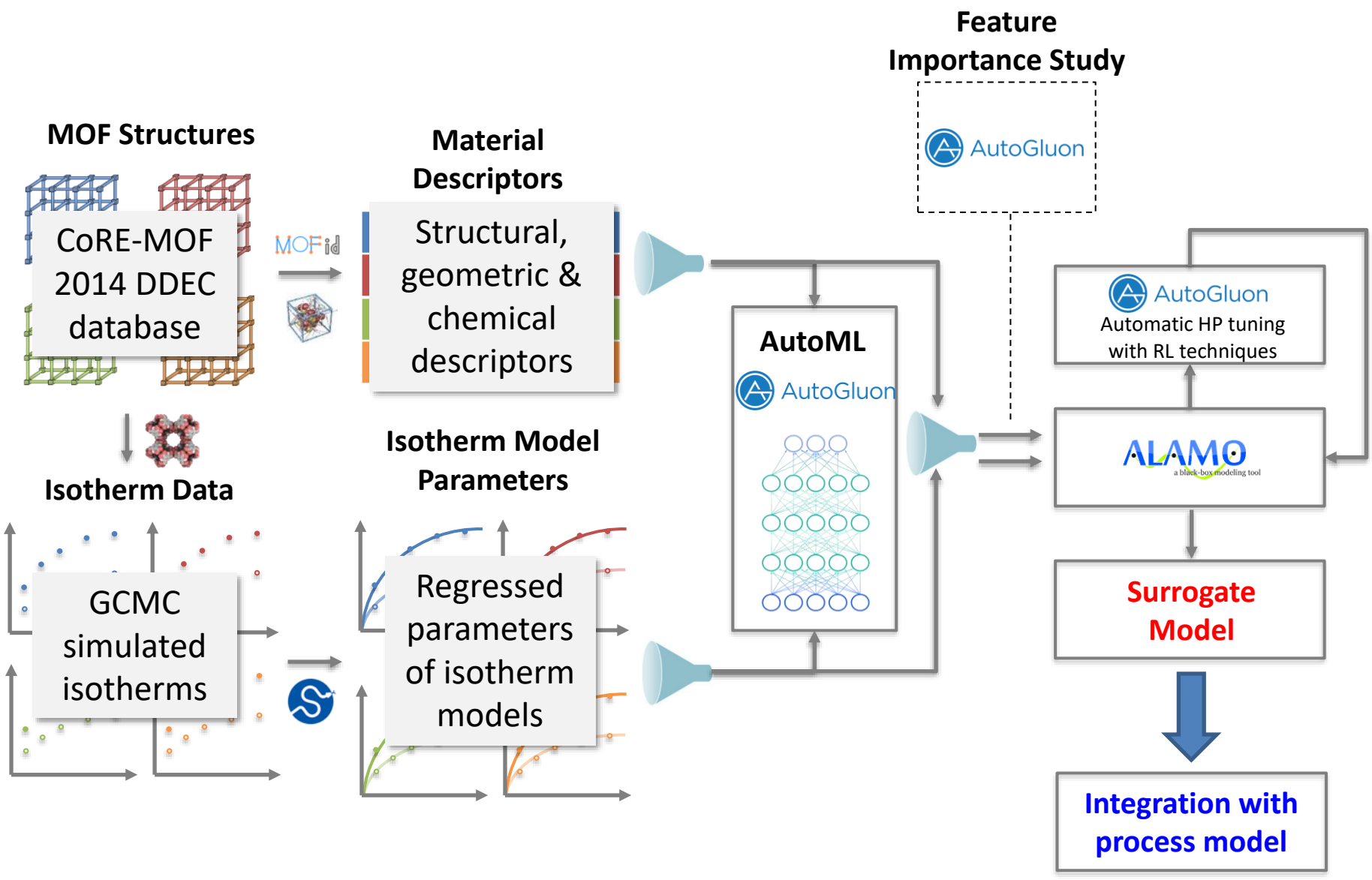


Yin, X., & Gounaris, C. E. (2022). Computational discovery of Metal–Organic Frameworks for sustainable energy systems: Open challenges. Computers & Chemical Engineering, 167, 108022.

Optimizable Adsorption Isotherm Surrogate Model Construction

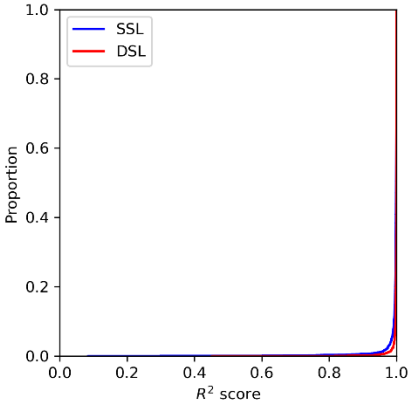


Optimizable Adsorption Isotherm Surrogate Model Construction

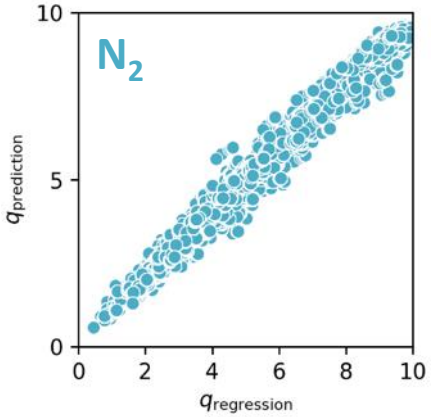


Isotherm Model Predictive Performance

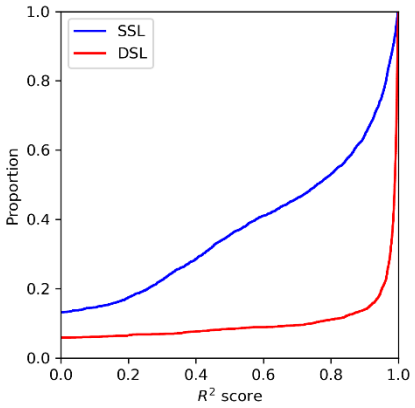
- ML model regression quality (CoRE-MOF 2014 database):



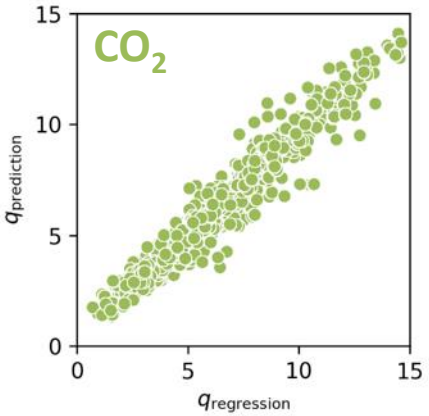
Cumulative distribution of regression R^2 scores



Simulated and ML-predicted loading parity plots



Cumulative distribution of regression R^2 scores



Simulated and ML-predicted loading parity plots

- Isotherm model parameter prediction via surrogate model (ALAMO):

N_2 (SSL) *(3 params)*

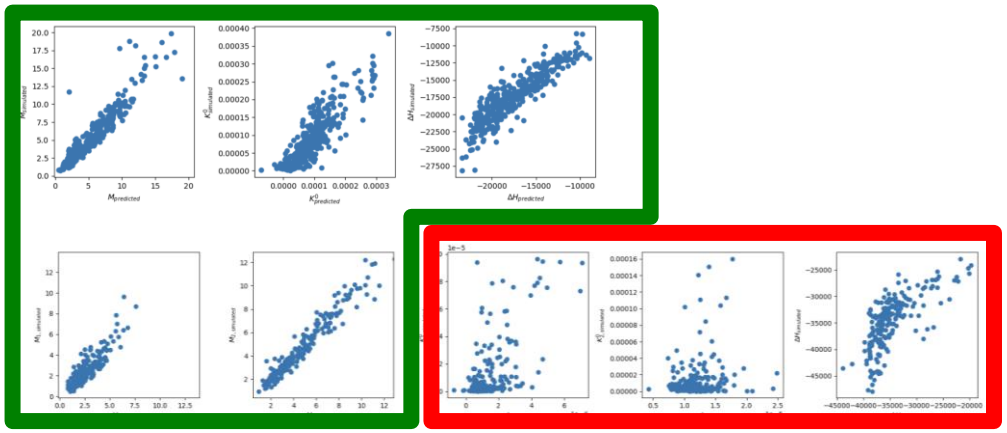
$$n^*_{N_2} = M_{N_2} \frac{K_{N_2} P}{1 + K_{N_2} P}$$

$$K_{N_2} = K^0_{N_2} \exp\left(\frac{\Delta H_{N_2}}{RT}\right)$$

CO_2 (DSL) *(5 params)*

$$n^*_{CO_2} = \sum_{j=1}^{2} \left[M_{j,CO_2} \frac{K_{j,CO_2} P}{1 + K_{j,CO_2} P} \right]$$

$$K_{j,CO_2} = K^0_{j,CO_2} \exp\left(\frac{\Delta H_{CO_2}}{RT}\right)$$



Algebraic Surrogate Model

- Nitrogen adsorption (SSL)

$$n^*_{N_2} = M_{N_2} \frac{K_{N_2} P}{1 + K_{N_2} P}$$

$$K_{N_2} = K^0_{N_2} \exp\left(\frac{\Delta H_{N_2}}{RT}\right)$$

$$M = 0.501198 \times \text{void fraction} + 0.180014 \times \text{density} + 0.564126 \times \text{pssd} - 2.119656 \times \text{psd}_3 - 3.070411 \times \text{psd}_1 + 0.282018 \times \text{pssd}^2 - 0.101757e^{-6} \times \text{surface area}^2 + 1.787132 \times \text{psd}_3^2 - 5.230239 \times \text{void fraction} \times \text{pssd} + 0.239656e^{-2} \times \text{void fraction} \times \text{surface area} - 0.112717e^{-3} \times \text{void fraction} \times \text{pssd} \times \text{surface area} + 15.675051 \times \text{void fraction/density} \quad +\varepsilon_{\mathbf{M}}$$

$$K^0 = 0.435066e^{-3} \times \text{void fraction} - 0.208241e^{-4} \times M - 0.163226e^{-3} \times \text{psd}_2 + 0.181835e^{-4} \times \text{lcd} - 0.458682e^{-4} \times \text{density} - 0.674073e^{-3} \times \text{void fraction}^2 + 0.566632e^{-6} \times M^2 + 0.195776e^{-3} \times \text{psd}_2^2 - 0.128304e^{-5} \times \text{lcd}^2 + 0.939266e^{-3} \times \text{void fraction}^3 + 0.279167e^{-4} \times \text{void fraction} \times \text{lcd} + 0.117142e^{-4} \times \text{lcd}/M \quad +\varepsilon_{\mathbf{K}}$$

$$\Delta H = 36310662.568495 \times K^0 + 21849.163143 \times \text{void fraction} - 381.468363 \times M + 19649.357880 \times \text{density} - 407.611611 \times \text{psd}_3 + 7478.069611 \times \text{void fraction}^2 + 88.653985 \times M^2 - 8326.098874 \times \text{density}^2 - 51381.053022 \times \text{void fraction}^3 - 2.573389 \times M^3 + 1055.017163 \times \text{density}^3 - 40247.766670 \quad +\varepsilon_{\mathbf{\Delta H}}$$

Yin, X., et al., *Inverse Design of Metal-Organic Frameworks for Adsorption Processes: Learning Surrogate Models of Isotherm Parameters.* Forthcoming, 2024.

Evaluation of MOF Performance via Process Simulation

- PSA process simulation using open-source code (Yancy-Caballero *et al.,* 2020) to evaluate process performance of material with given isotherm behavior
  - MATLAB implementation
  - Input:
    - Sorbent isotherm parameters (v)
    - Process parameters (p)
    - Process configuration, feed
      - 5-step Skarstrom cycle, ~5kmol/sec 15/85% (CO_2/N_2) stream
  - Output:
    - Four process performance metrics

$$\text{Purity} = \frac{\text{Moles of } CO_2 \text{ in the product}}{\text{Total moles in the product}} \times 100\%$$

$$\text{Productivity}\left[\frac{\text{mol } CO_2}{\text{kg s}}\right] = \frac{\text{Moles of } CO_2 \text{ in the product}}{\text{Mass of adsorbent} \times \text{cycle time}}$$

$$\text{Recovery} = \frac{\text{Moles of } CO_2 \text{ in the product}}{\text{Moles of } CO_2 \text{ fed into the cycle}} \times 100\%$$

$$\text{Energy Req.}\left[\frac{\text{kW h}}{\text{ton } CO_2}\right] = \frac{\text{Energy required for all steps}}{\text{mass of } CO_2 \text{ collected in the product per cycle}}$$

Yancy-Caballero, D., et al., *Process-level modelling and optimization to evaluate metal–organic frameworks for post-combustion capture of CO2.* Molecular Systems Design & Engineering, 2020. **5**(7): p. 1205-1218

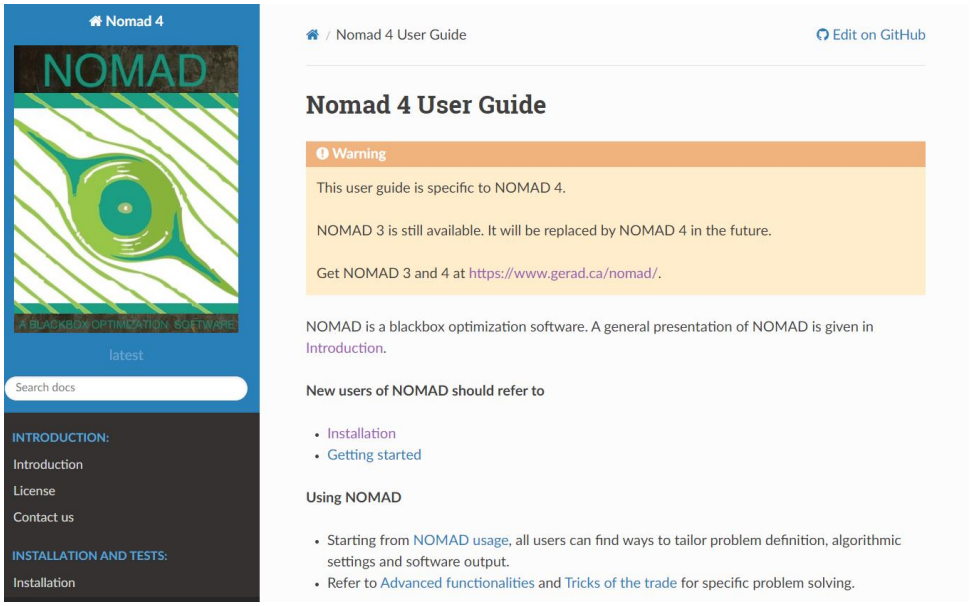
Co-Optimization of MOF Structure and Process Parameters

- PSA process simulation using open-source code (Yancy-Caballero *et al.,* 2020) to evaluate process performance of material with given isotherm behavior
- Our own equation-oriented surrogate to explicitly link MOF structure (descriptors d) with isotherm model

$$
\begin{aligned}
\max_{p,d} \quad & \text{Productivity} \\
\text{s.t.} \quad & \nu = \boxed{\text{Adsorption Properties}(d)} \qquad \text{Isotherm Surrogate} \\
& \text{Purity, Recovery, Productivity, Energy Requirement} = \boxed{\text{Adsorption Process}(\nu, p)} \qquad \text{PSA Process Simulator} \\
& \text{Recovery} \geq 0.9 \\
& \text{Purity} \geq 0.9 \\
& p \in P \quad d \in D \quad \nu \in \boxed{T} \qquad \text{Isotherm Trust Region}
\end{aligned}
$$

Solving via Derivative-Free Optimizer

- Derivative-Free Optimization (DFO) tool *NOMAD* (Audet *et al.*, 2022) to solve formulation
  - Mesh Adaptive Direct Search (MADS) algorithm
  - Python interface

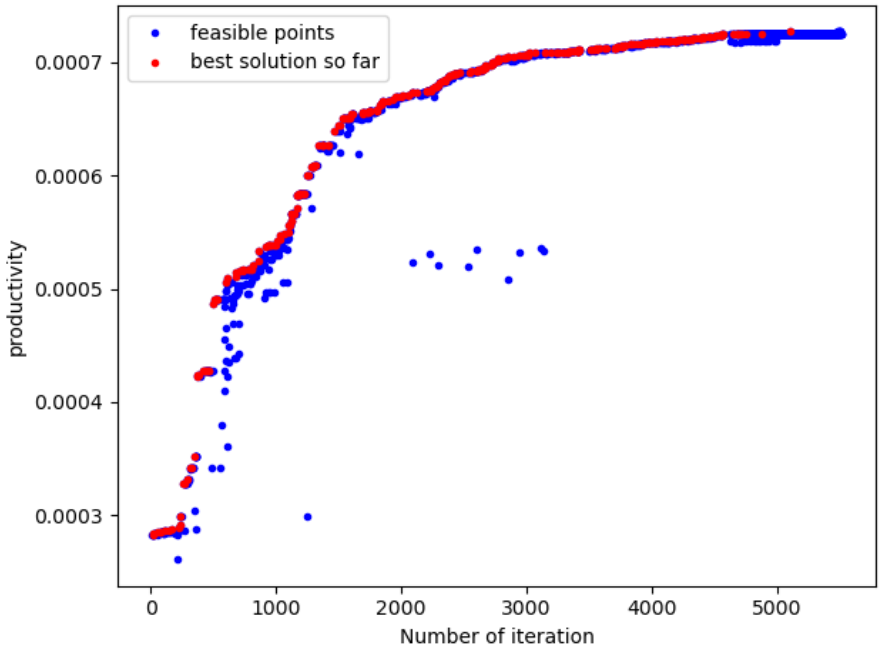


Nomad 4 User Guide — Nomad 4 documentation. https://nomad-4-user-guide.readthedocs.io/en/latest/index.html

Audet, C., et al., *NOMAD version 4: Nonlinear optimization with the MADS algorithm*. ACM Transactions on Mathematical Software, 2022. **48**(3), 35:1-35:22.

Material Optimization Results (for fixed process parameters)

- Productivity objective gradually improved through the DFO iterations
- Converged at approximately 5500 iterations (~1600 feasible solutions)
  - ~22 hrs CPU time
- Improvement compared to the baseline MOF structure in all process performance metrics

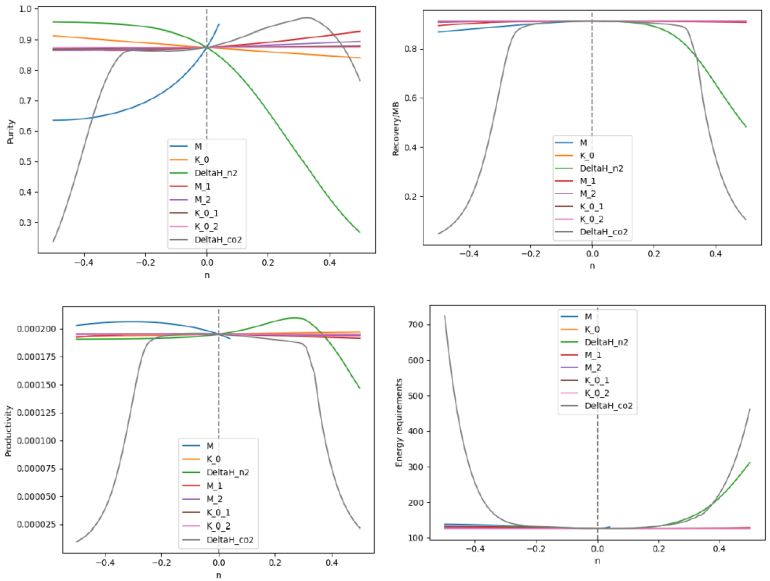


MOF	Productivity (objective)	Energy Requirement	Purity	Recovery
UTSA-16 (Baseline)	0.37×10^{-3}	134	0.90	0.90
Optimized	0.73×10^{-3}	131	0.96	0.90

—preliminary results—

Solution Robustness to Prediction Errors from Surrogate Model

- *Since the MOF was optimized based on a "predicted" isotherm (surrogate model) as opposed to its "true" isotherm, is it robustly good?*
- Step 1: Identify isotherm parameters that more strongly impact metrics
  - Perturb isotherm parameters one at a time, and re-evaluate optimal MOF's process performance

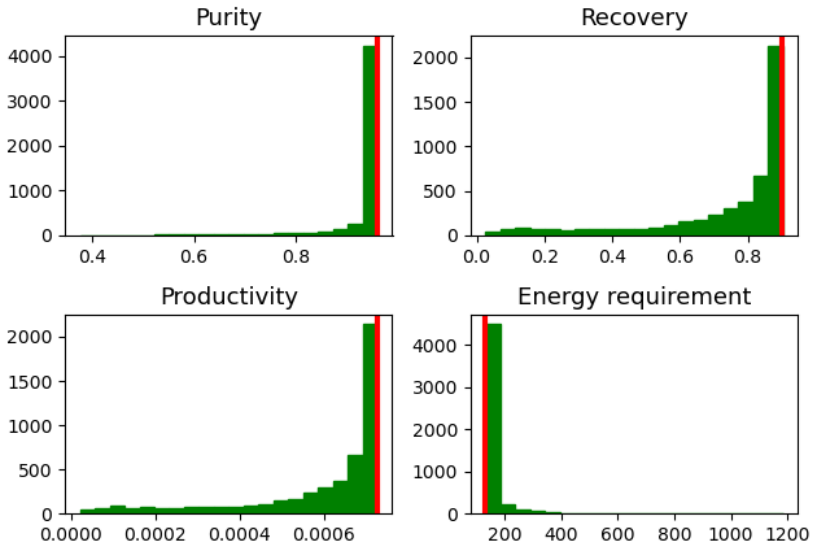


- A total of 4 parameters were found to be critical:
  - nitrogen max capacity (M_{N_2}) and energy of adsorption (ΔH_{N_2})
  - CO_2 max capacity for site #2 (M_{2,CO_2}) and energy of adsorption (ΔH_{CO_2})

—preliminary results—

Solution Robustness to Prediction Errors from Surrogate Model

- *Since the MOF was optimized based on a "predicted" isotherm (surrogate model) as opposed to its "true" isotherm, is it robustly good?*
- Step 2: Process performance spread across multiple isotherm samples
  - Sample 5000 isotherm perturbations (4d-ellipsoid), and re-evaluate optimal MOF's process performance



Red line:
Nominal performance
Green distribution:
Perturbed performance

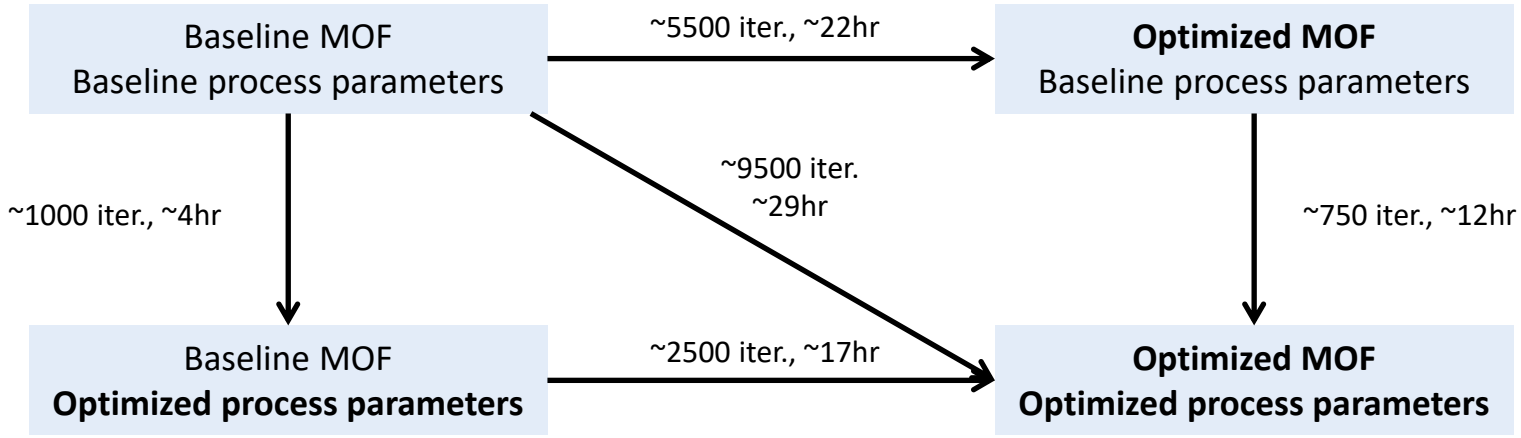
- This analysis suggests that any potential errors in the surrogate model predictions do not noticeably affect the process performance of the optimal MOF

—preliminary results—

Co-Optimizing Process and Material

Perf. Metric	Value
Purity	0.90
Recovery	0.90
Productivity (objective)	0.37 $\left[\times 10^{-3}\ \frac{\text{mol } CO_2}{\text{kg s}}\right]$
Energy Requirement	134 $\left[\frac{\text{kW h}}{\text{ton } CO_2}\right]$

Perf. Metric	Value
Purity ↑	0.96
Recovery →	0.90
Productivity (objective) ↑	0.73
Energy Requirement ↓	131



Perf. Metric	Value
Purity →	0.90
Recovery ↑	0.99
Productivity (objective) ↑	0.52
Energy Requirement ↑	205

Perf. Metric	Value
Purity ↑	0.93
Recovery ↓	0.90
Productivity (objective) ↑	0.96
Energy Requirement ↑	214

Perf. Metric	Value
Purity ↑	0.93
Recovery ↑	0.98
Productivity (objective) ↑	2.01
Energy Requirement ↑	190

Perf. Metric	Value
Purity ↓	0.92
Recovery ↑	0.99
Productivity (objective) ↑	1.01
Energy Requirement ↑	193

—preliminary results—

Co-Optimizing Process and Material

Perf. Metric	Value
Purity	0.90
Recovery	0.90
Productivity (objective)	0.37 $\left[\times 10^{-3}\ \frac{\text{mol } CO_2}{\text{kg s}}\right]$
Energy Requirement	134 $\left[\frac{\text{kW h}}{\text{ton } CO_2}\right]$

Restrict energy use/increase:

$$\max_{p,d} \text{ Productivity}$$

$$\text{s.t. } \nu = \text{Adsorption Properties}(d)$$

$$\text{Purity, Recovery, Productivity, Energy Req.} = \text{Adsorption Process}(\nu, p)$$

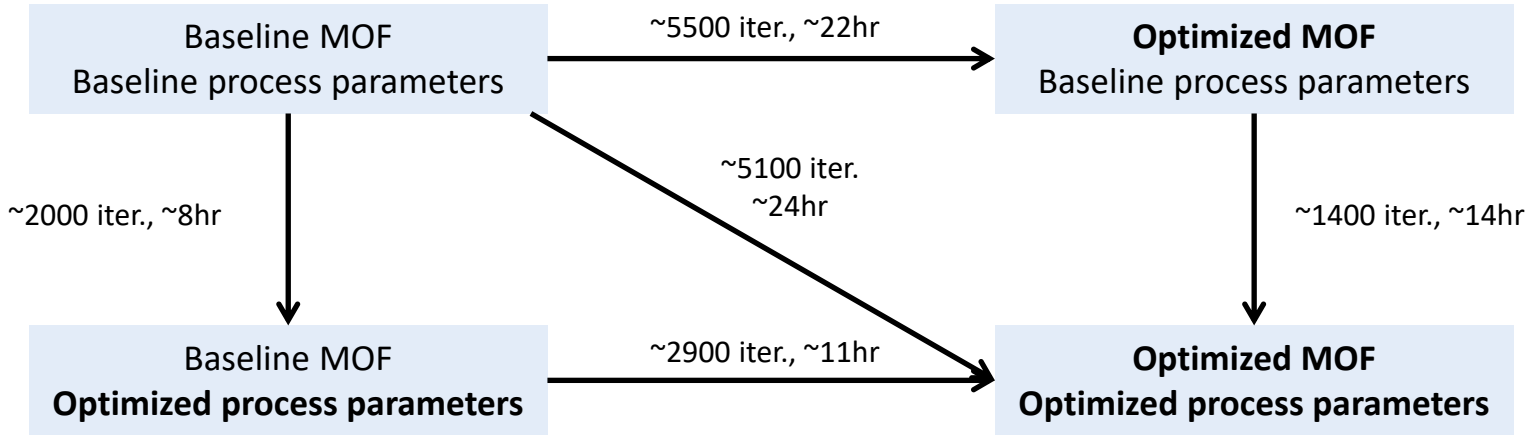
$$\text{Recovery} \geq 0.9$$

$$\text{Purity} \geq 0.9$$

$$\text{Energy Req.} \leq 150$$

$$p \in P \quad d \in D \quad \nu \in T$$

Perf. Metric	Value
Purity ↑	0.96
Recovery →	0.90
Productivity (objective) ↑	0.73
Energy Requirement ↓	131



Perf. Metric	Value
Purity →	0.90
Recovery ↑	0.92
Productivity (objective) ↑	0.48
Energy Requirement ↑	150

Perf. Metric	Value
Purity ↑	0.95
Recovery ↓	0.90
Productivity (objective) ↑	0.87
Energy Requirement ↓	148

Perf. Metric	Value
Purity ↑	0.91
Recovery ↑	0.94
Productivity (objective) ↑	1.62
Energy Requirement ↑	150

Perf. Metric	Value
Purity ↓	0.94
Recovery ↑	0.97
Productivity (objective) ↑	0.97
Energy Requirement ↑	150

—preliminary results—

Conclusions

- Opportunities exist in incorporating **materials** design with **process** design/operation in a **co-optimization framework**
- A **PSA process with MOF adsorbents co-optimization** model was formulated and solved with the NOMAD DFO tool
  - **Optimizable MOF adsorption isotherm models** were learned via a custom-built ML-assisted surrogate learning workflow
  - **An open-source PSA simulator** was utilized as a black-box process model, allowing us to optimize productivity subject to purity, recovery, and energy requirement constraints

Acknowledgment: "This material is based upon work supported by the Department of Energy under Award Number DE-FE0032069."

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