

Integrated design of processes and mixtures using molecule superstructures

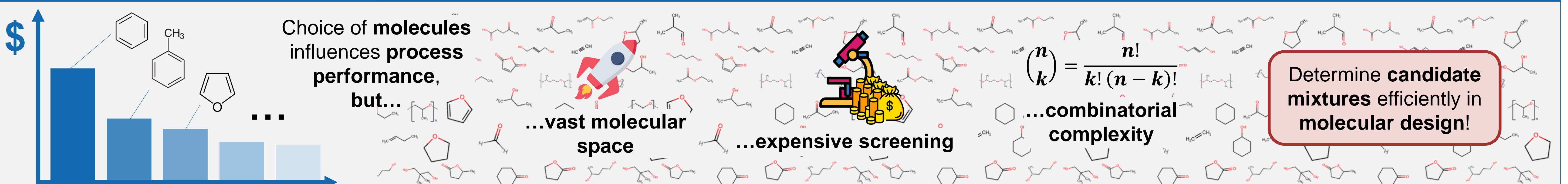
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Motivation



Heterosegmented gc-PC-SAFT¹

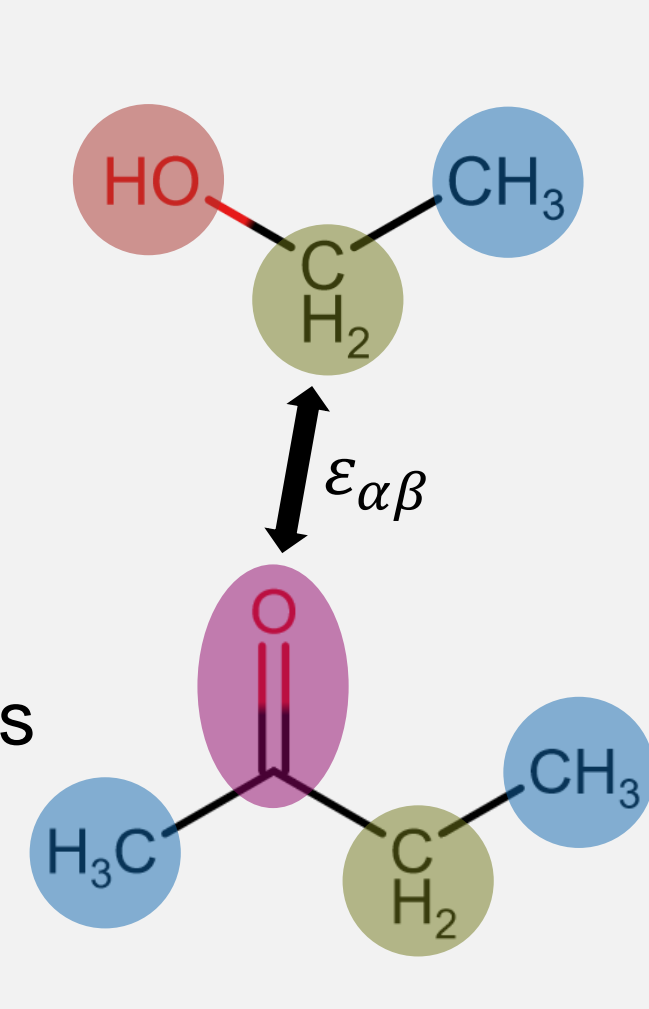
Segments rather than **molecules** as species in the equation of state

group-group interaction²

$$\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_{\alpha}\varepsilon_{\beta}}(1 - k_{\alpha\beta})$$

- ✓ finer resolution of the molecules
- ✓ no (arbitrary) combining rules

✗ higher computational cost



Molecule superstructures³

structural constraints

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 \\ 1 & 1 & 1 & 1 \\ 0 & -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \end{pmatrix} \leq \begin{pmatrix} -1 \\ 0 \\ 3 \\ 0 \end{pmatrix}$$

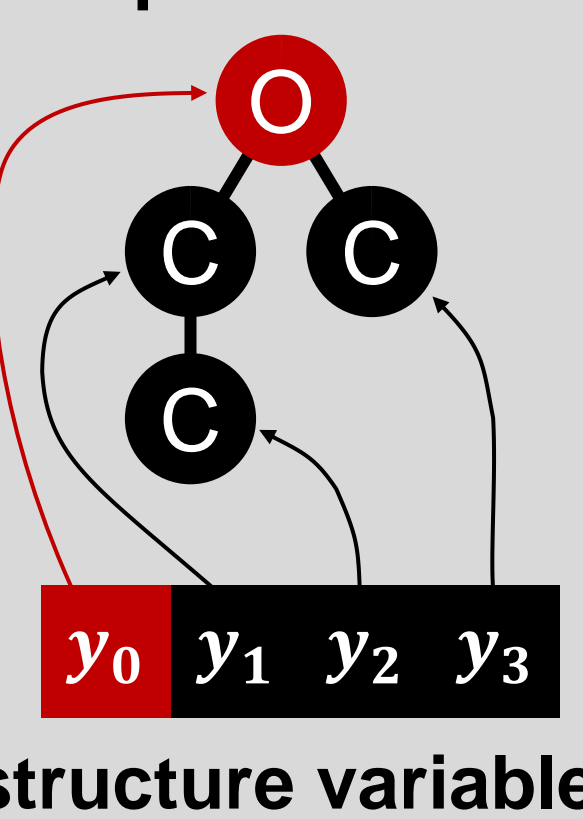
$$A y \leq b$$

feature constraints

$$\begin{pmatrix} n_{CH_2} \\ n_{CH_3} \\ n_O \\ n_{OH} \\ n_{H_2O} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & -1 \\ 1 & -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} y_0 \\ y_1 \\ y_2 \\ y_3 \end{pmatrix}$$

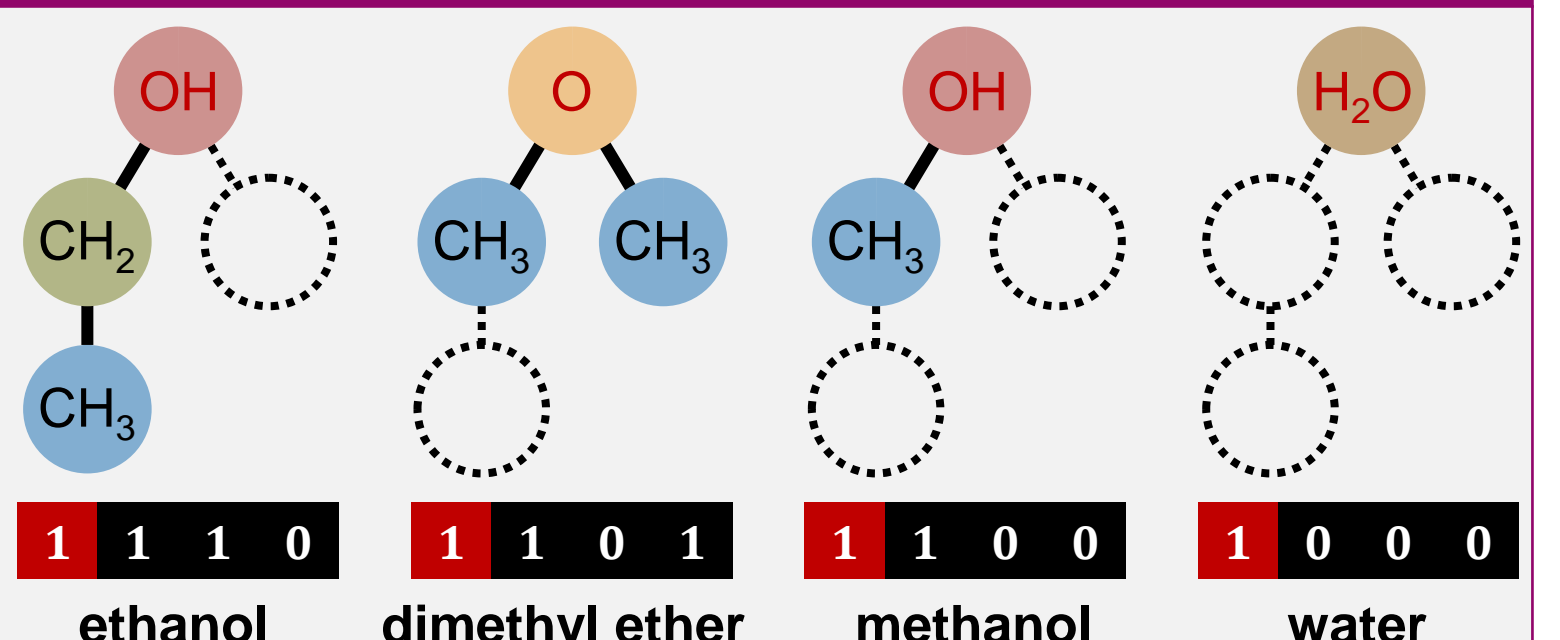
$$p = C y$$

example superstructure



molecular space

structurally feasible solutions

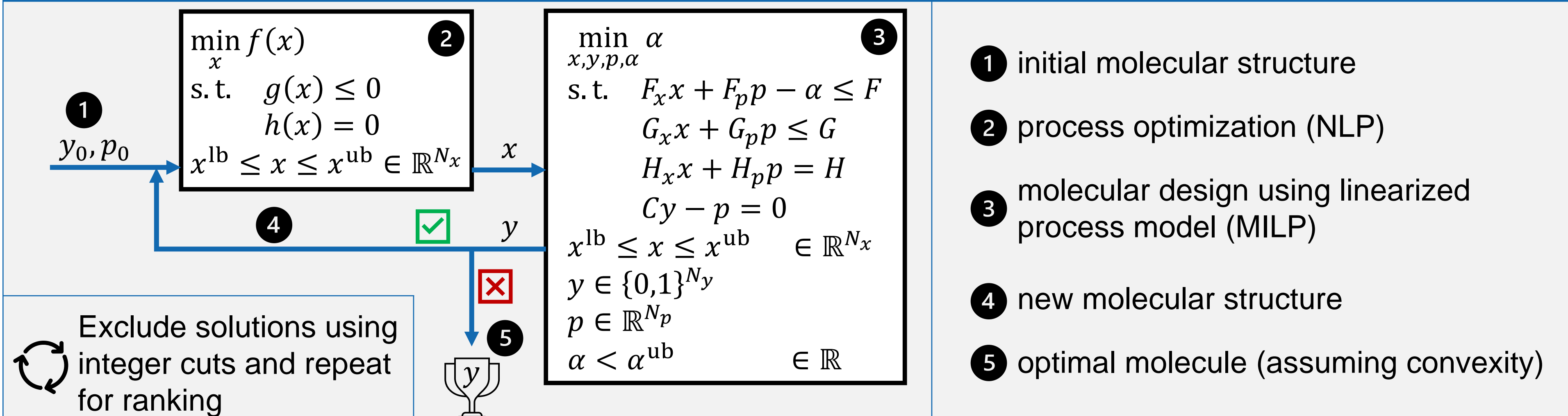


- Generalizable for **more complex superstructures** and **larger molecular spaces**
- Simultaneous optimization of superstructures using **disjunctive programming** and **convex hull relaxation**

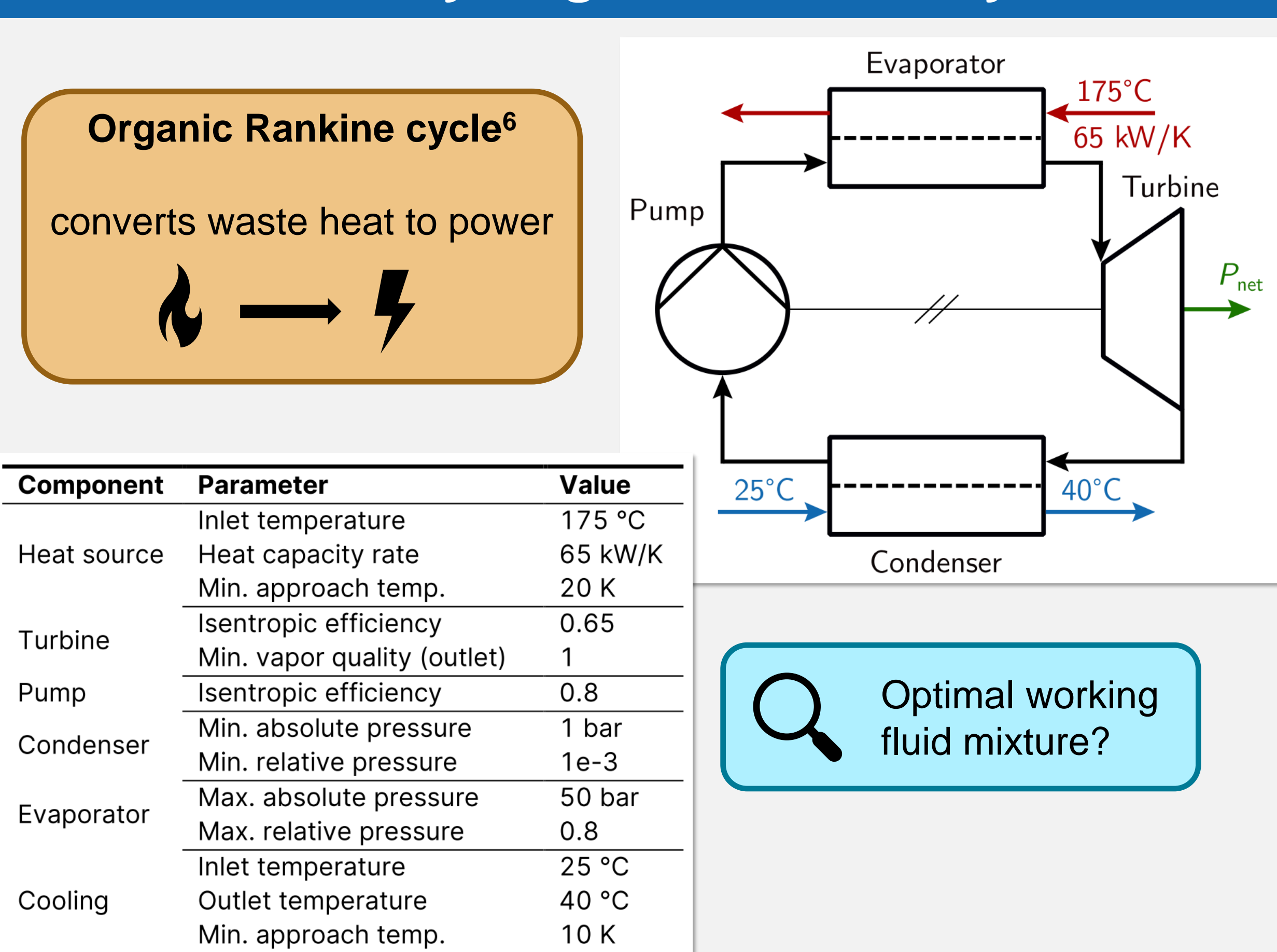
Optimization Problem

$$\begin{aligned} \min_{x,y,p} \quad & f(x,p) && \text{process target} \\ \text{s.t.} \quad & g(x,p) \leq 0 && \text{process model and constraints} \\ & h(x,p) = 0 && \\ & Ay \leq b && \text{structural constraints} \\ & Cy - p = 0 && \text{feature constraints} \\ & x^{lb} \leq x \leq x^{ub} \in \mathbb{R}^{N_x} && \text{process degrees of freedom} \\ & y \in \{0,1\}^{N_y} && \text{structure variables} \\ & p \in \mathbb{R}^{N_p} && \text{molecular features} \end{aligned}$$

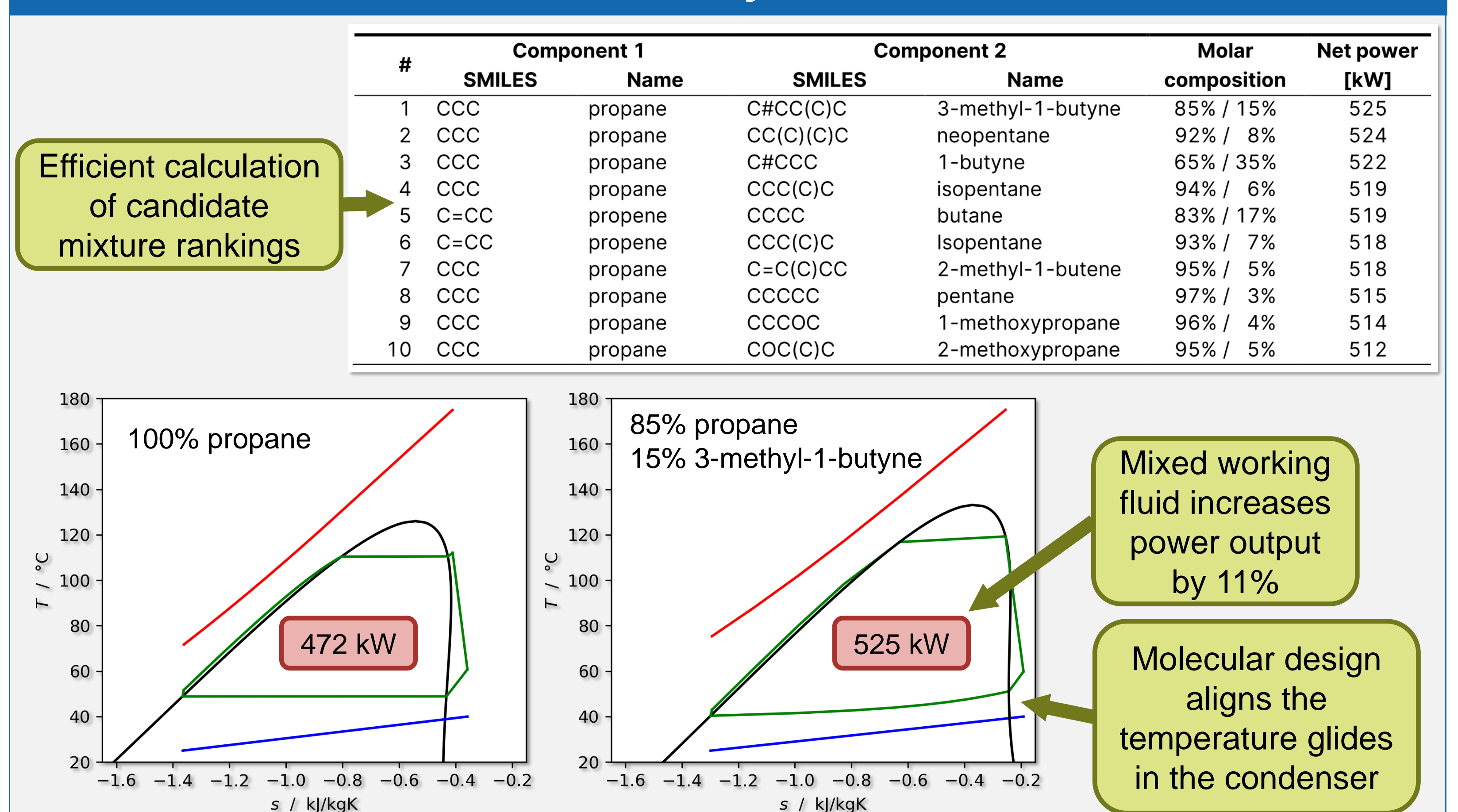
Outer approximation algorithm^{4,5}



Case study: organic Rankine cycle



Case study results



Conclusion & Outlook

- ✓ Integrated molecular and process design of pure components and mixtures
- ✓ **Process target function** to assess performance beyond molecular heuristics
- ✓ **Molecule superstructures** unlock **high-fidelity property predictions** with gc-PC-SAFT
- ✓ Tailored **outer approximation algorithm** for efficient calculation of **candidate rankings**



Extend method to include **economic and environmental** performance of working fluid⁷

Code based on FeO_s framework⁸ and published open-source

crates.io/crates/feos-campd

github.com/feos-org/feos-campd



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2. Rehner, Bardow and Gross (2023), *Int. J. Thermophys.*, 44, 179
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