# Computer-Aided Mixture Design Using Molecule Superstructures

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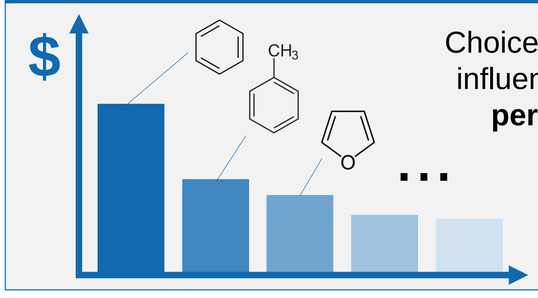
## Motivation




Choice of **molecules** influences **process performance**, **but…**

**…vast molecular space**

**…expensive screening**

$$\binom{n}{k} = \frac{n!}{k!\,(n-k)!}$$

**…for mixtures: combinatorial complexity**

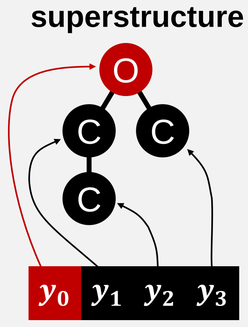
Determine **candidate molecules/mixtures** efficiently in a **molecular design**!

## Optimization problem

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

## Molecule superstructures[1]

**example superstructure**




**structure variables**

**structural constraints**

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

$$A \qquad y \quad \le \quad b$$

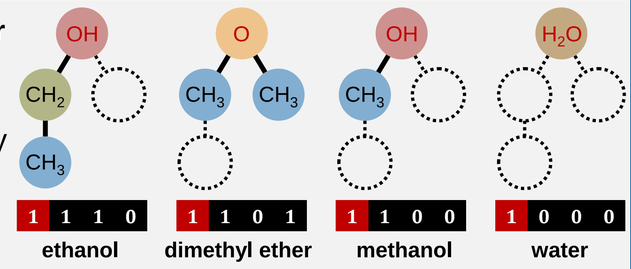
**feature constraints**

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

$$p \quad = \qquad C \qquad y$$

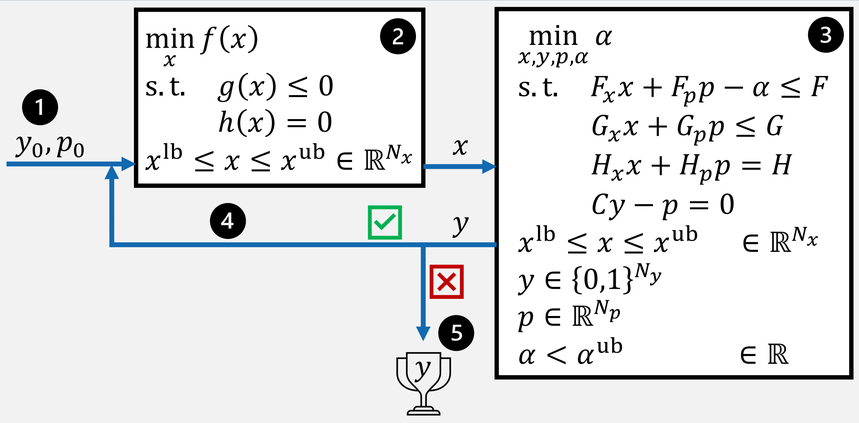
**molecular space**

structurally feasible solutions




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

## Outer approximation algorithm[2,3]



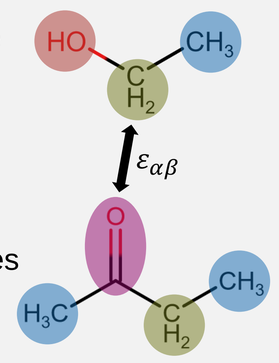

1. initial molecular structure
2. process optimization (NLP)
3. molecular design using linearized process model (MILP)
4. new molecular structure
5. in case of infeasibility: optimal molecule (assuming convexity)

## Heterosegmented gc-PC-SAFT[4]

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

**group-group interaction[5]**

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

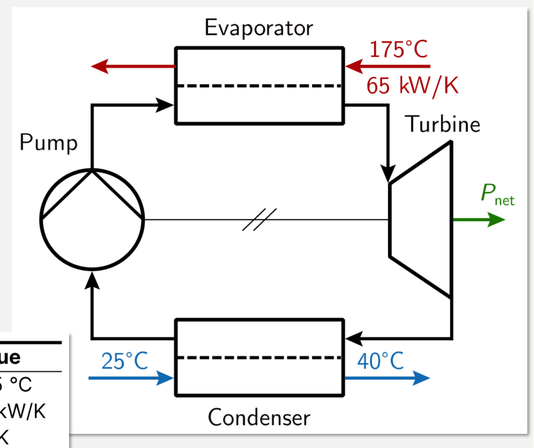



- ✓ finer resolution of the molecules
- ✓ no (arbitrary) combining rules
- x higher computational cost

## Organic Rankine cycle case study

**Organic Rankine cycle[6]**

converts waste heat to power



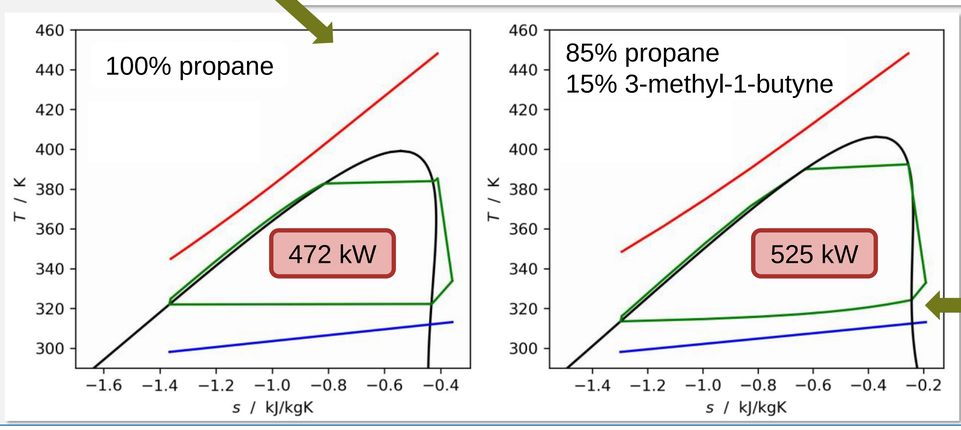

| Component | Parameter | Value |
|---|---|---|
| Heat source | Inlet temperature | 175 °C |
| | Heat capacity rate | 65 kW/K |
| | Min. approach temp. | 20 K |
| Turbine | Isentropic efficiency | 0.65 |
| | Min. vapor quality (outlet) | 1 |
| Pump | Isentropic efficiency | 0.8 |
| Condenser | Min. absolute pressure | 1 bar |
| | Min. relative pressure | 1e-3 |
| Evaporator | Max. absolute pressure | 50 bar |
| | Max. relative pressure | 0.8 |
| Cooling | Inlet temperature | 25 °C |
| | Outlet temperature | 40 °C |
| | Min. approach temp. | 10 K |

Optimal working fluid mixture?

## Case study results

| # | Component 1 SMILES | Component 1 Name | Component 2 SMILES | Component 2 Name | Molar composition | Net power [kW] |
|---|---|---|---|---|---|---|
| 1 | CCC | propane | C#CC(C)C | 3-methyl-1-butyne | 85% / 15% | 525 |
| 2 | CCC | propane | CC(C)(C)C | neopentane | 92% / 8% | 524 |
| 3 | CCC | propane | C#CCC | 1-butyne | 65% / 35% | 522 |
| 4 | CCC | propane | CCC(C)C | isopentane | 94% / 6% | 519 |
| 5 | C=CC | propene | CCCC | butane | 83% / 17% | 519 |
| 6 | C=CC | propene | CCC(C)C | Isopentane | 93% / 7% | 518 |
| 7 | CCC | propane | C=C(C)CC | 2-methyl-1-butene | 95% / 5% | 518 |
| 8 | CCC | propane | CCCCC | pentane | 97% / 3% | 515 |
| 9 | CCC | propane | CCCOC | 1-methoxypropane | 96% / 4% | 514 |
| 10 | CCC | propane | COC(C)C | 2-methoxypropane | 95% / 5% | 512 |

Mixed working fluid increases power output by 11%




Efficient calculation of rankings of candidate mixtures

Molecular design aligns the temperature glides in the condenser

## 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 fluid[7]

**Code based on $FeO_s$ framework[8] and published open-source**

crates.io/crates/feos-campd

github.com/feos-org/feos-campd

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### References

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