Integrating working fluid design into the thermo-economic design of ORC processes using PC-SAFT

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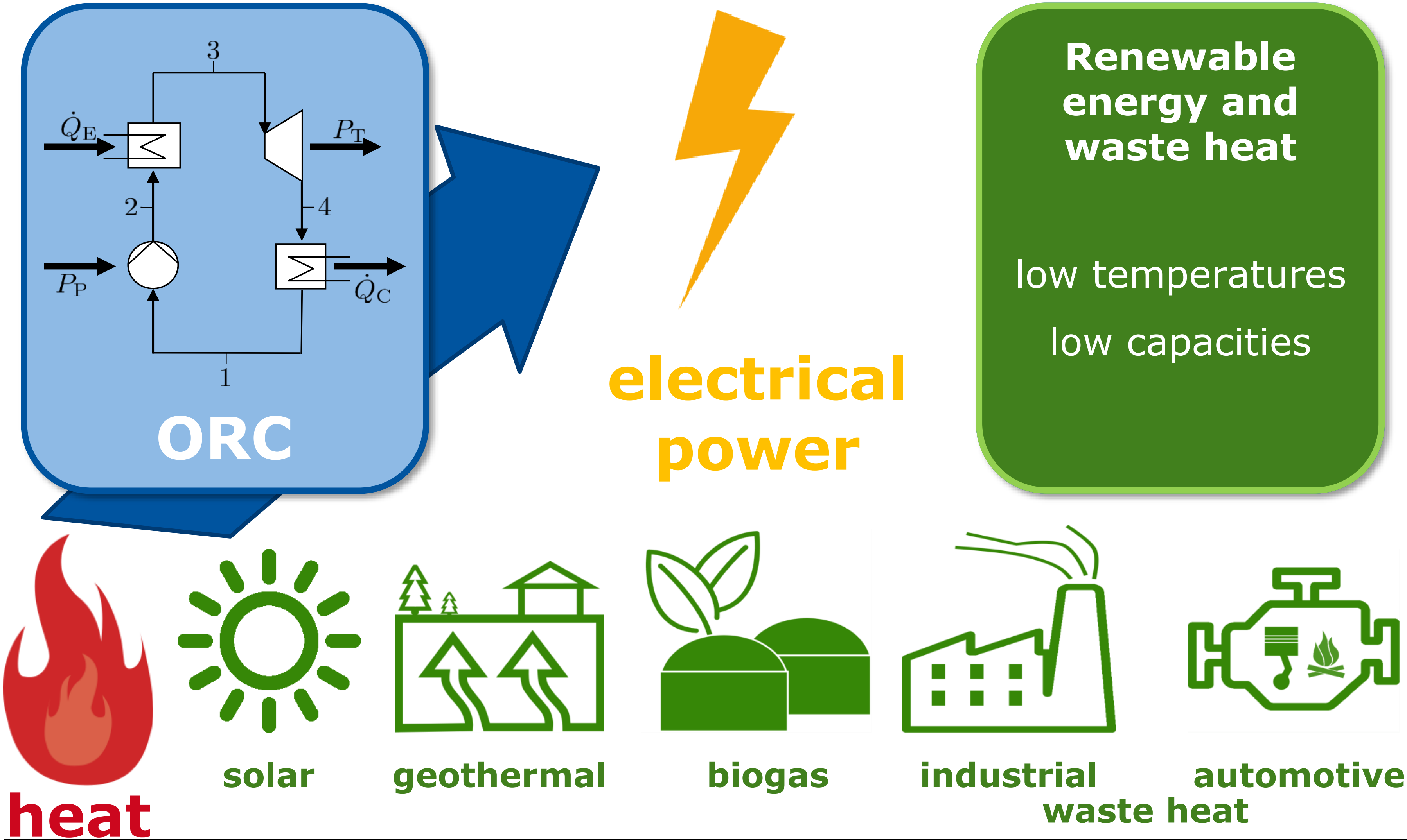
Organic Rankine Cycle (ORC)



Organic Rankine Cycle (ORC)

Working fluid?

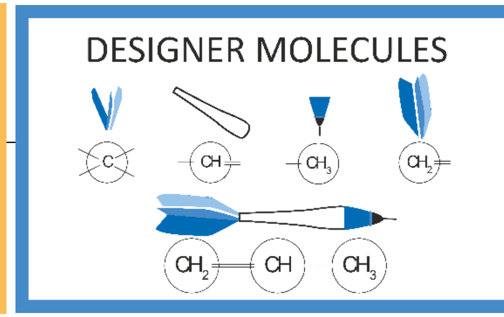
Organic!

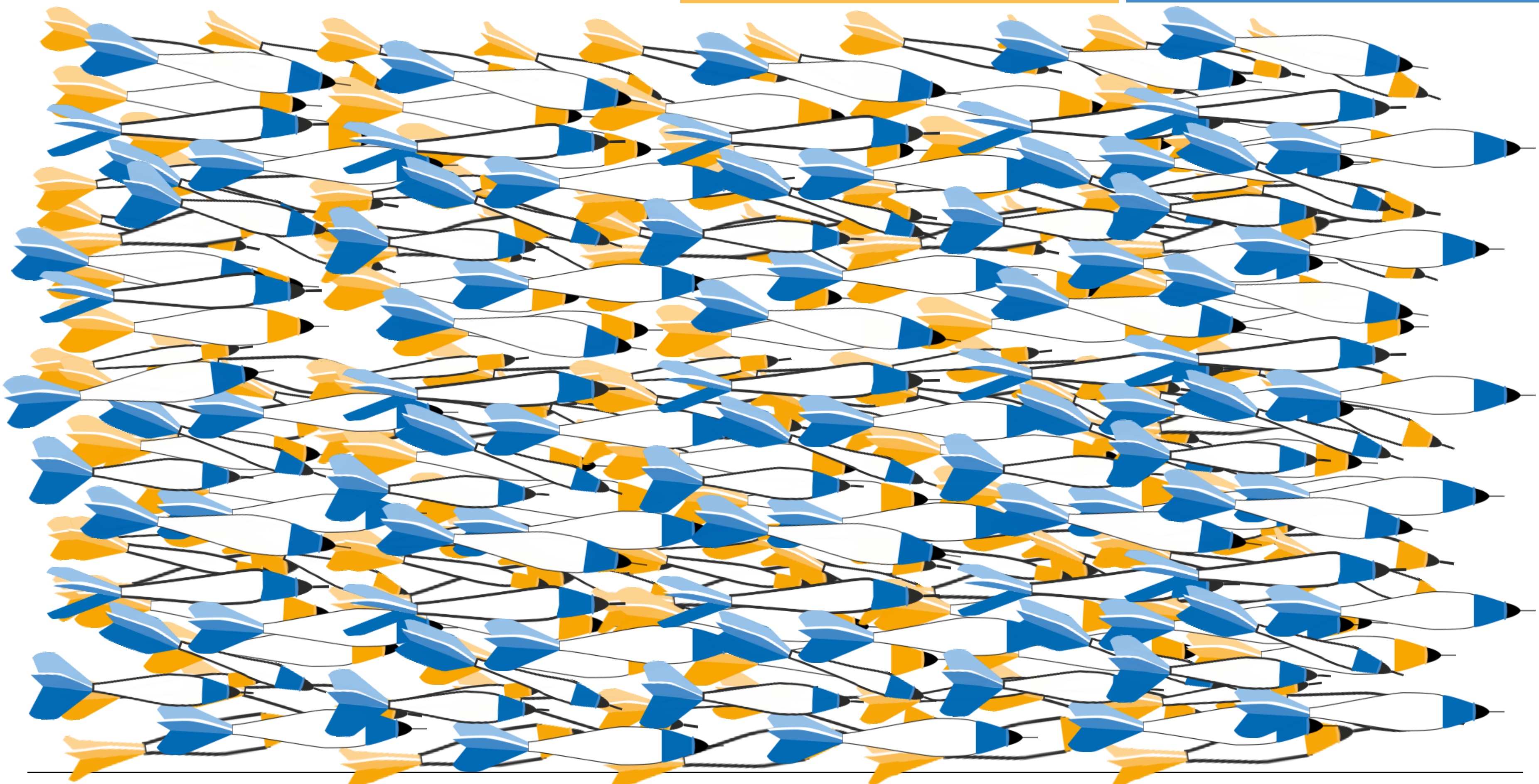
But which?

Working fluids for ORCs

DATABASE

ID	name
1	ethane
2	benzene
3	propane
...	





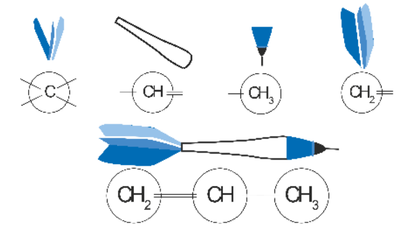
ORC design: heuristics

e.g., normal boiling pressure, enthalpy of evaporation

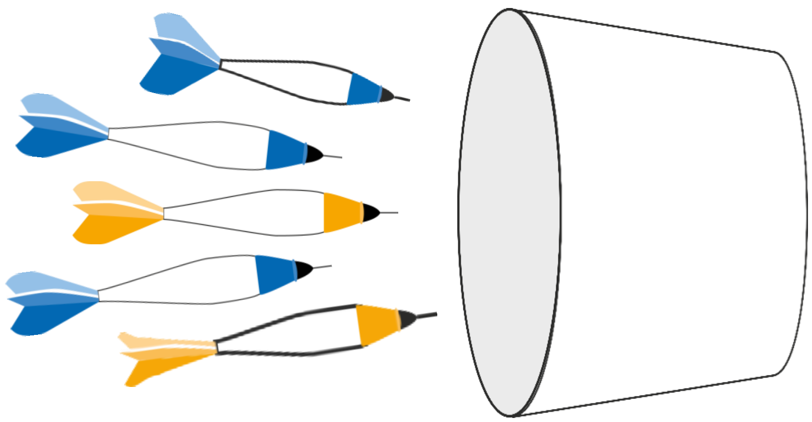
DATABASE

ID	name
1	ethane
2	benzene
3	propane
...	

DESIGNER MOLECULES



thermo-economic performance



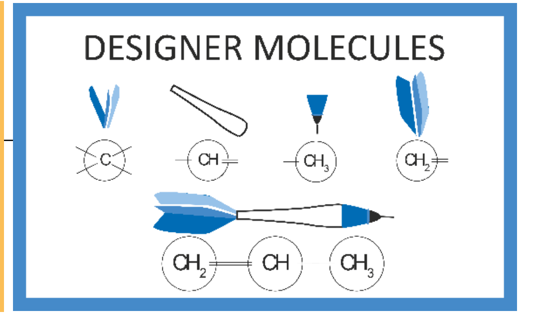
molecule design

ORC design: thermodynamics

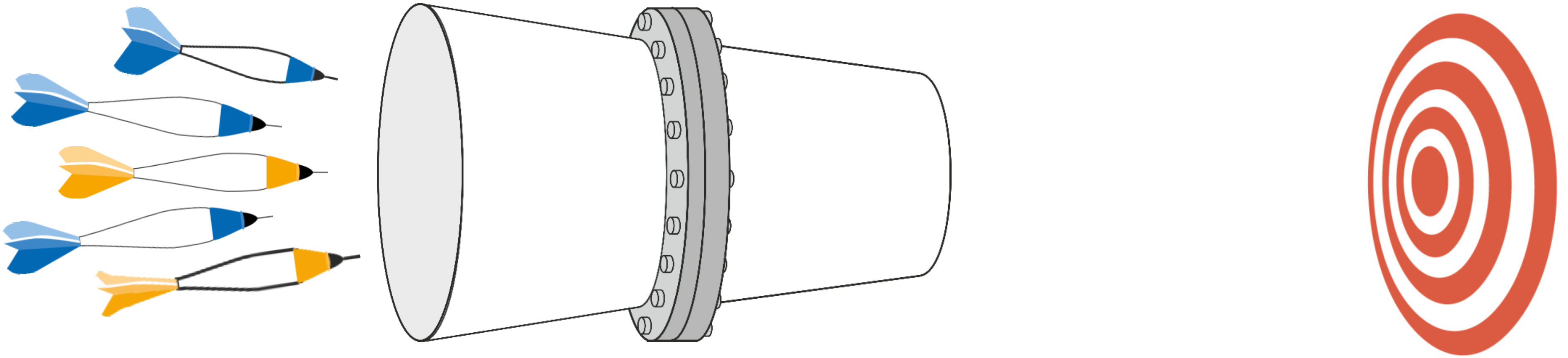
e.g., net power output,
thermal efficiency

DATABASE

ID	name
1	ethane
2	benzene
3	propane
...	



thermo-economic performance



molecule design

process design

model for equilibrium properties

ORC design: economics

e.g., net present value,
specific investment cost

DATABASE

ID	name
1	ethane
2	benzene
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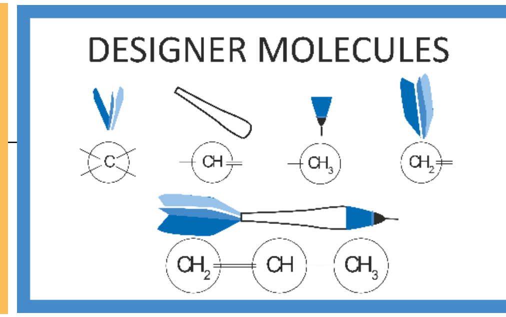
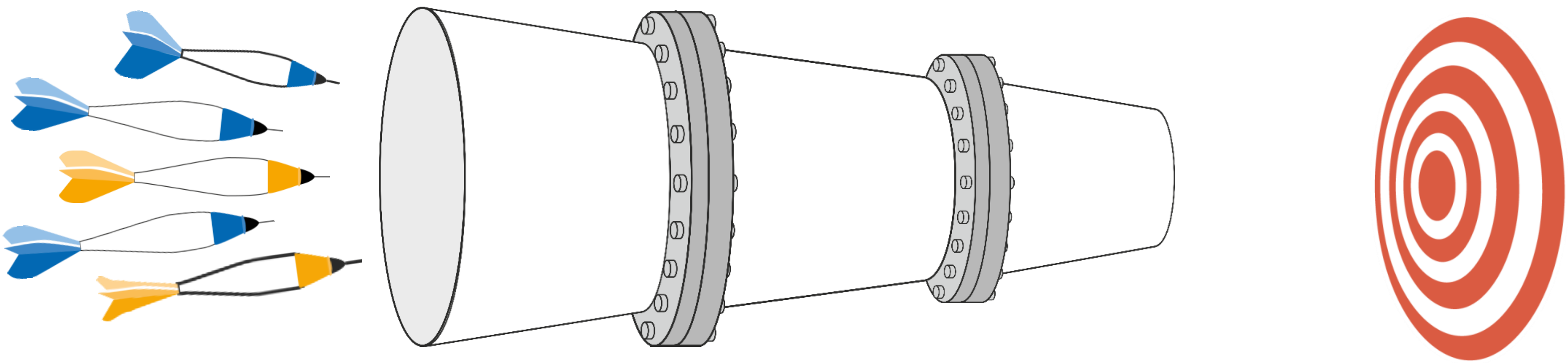
…	



thermo-economic performance



molecule design

process design

equipment design

model for equilibrium properties

model for transport properties

ORC design: economics

e.g., net present value,
specific investment cost

DATABASE

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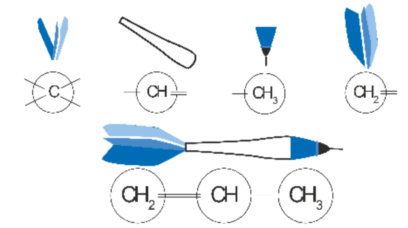
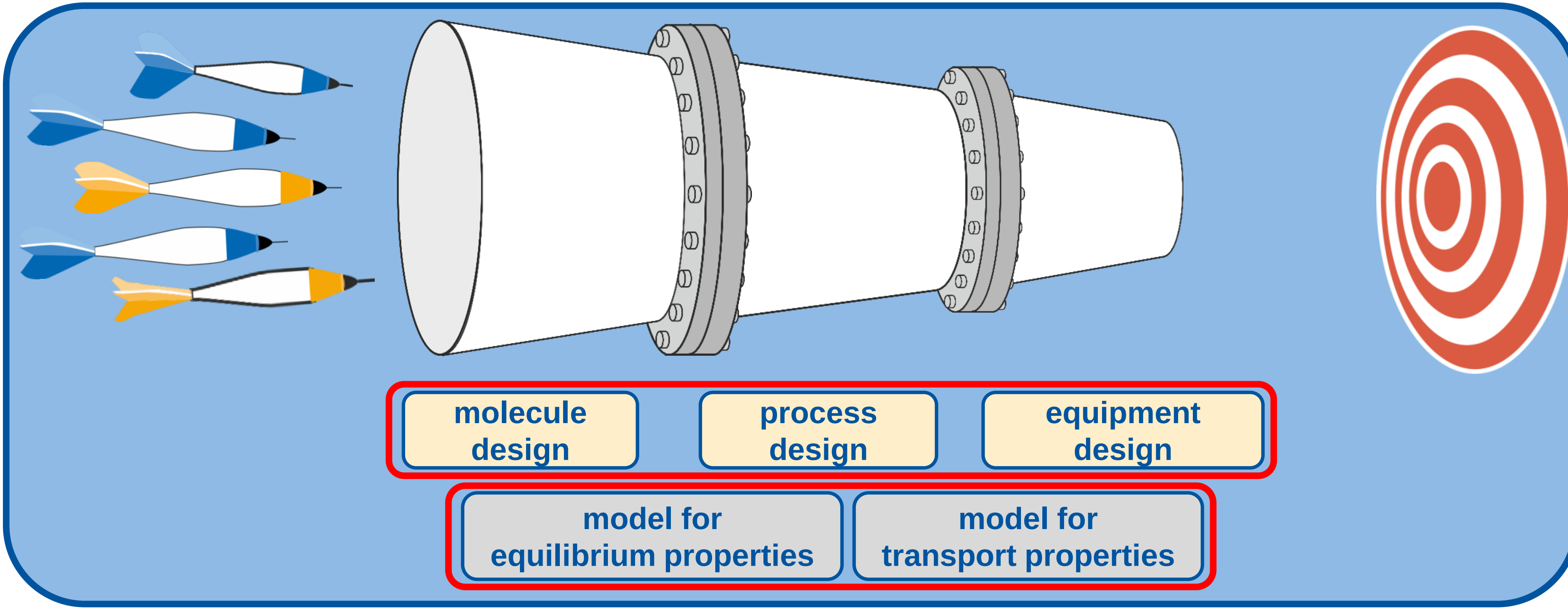
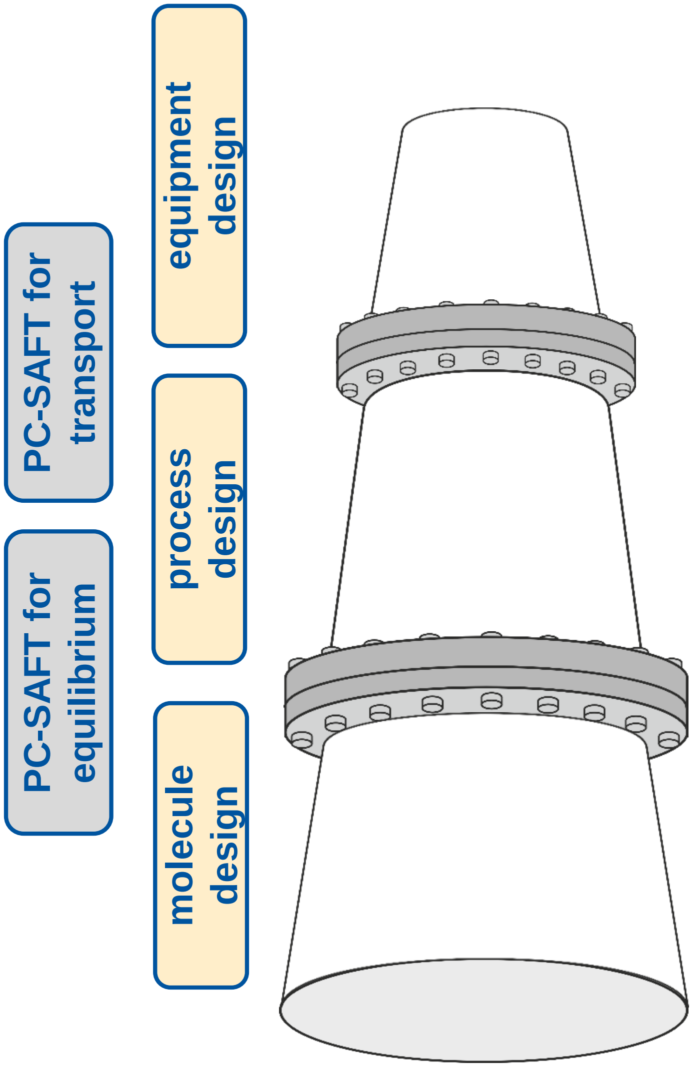
DESIGNER MOLECULES



thermo-economic performance



Integrated thermo-economic Design



$$\min f(x, \Theta, \kappa)$$

e.g., specific investment cost

s.t. $g_1(x, \Theta, \kappa) = 0$ — e.g., heat transfer correlations

$g_2(x, \Theta, \kappa) \leq 0$ — e.g., turbine constraints

$\kappa = k(x, \Theta, z, y^s)$ — PC-SAFT transport properties

$p_1(x, \Theta) = 0$ — e.g., energy balances

$p_2(x, \Theta) \leq 0$ — e.g., min./max. pressure levels

$\Theta = h(x, z, y^s)$ — PC-SAFT equilibrium properties

$z = GC \cdot y^s$
$F_1 \cdot y^s = 0$
$F_2 \cdot y^s \leq 0$

CAMD – feasibility of the molecular structure

$$x_{lb} \leq x \leq x_{ub} \in \mathbb{R}^n$$
$$y^s_{lb} \leq y^s \leq y^s_{ub} \in \mathbb{Z}^l$$

x process degrees of freedom
Θ equilibrium properties
κ transport properties
z pure component parameters
y^s molecular structure

Model for equilibrium properties: PC-SAFT[1-2]

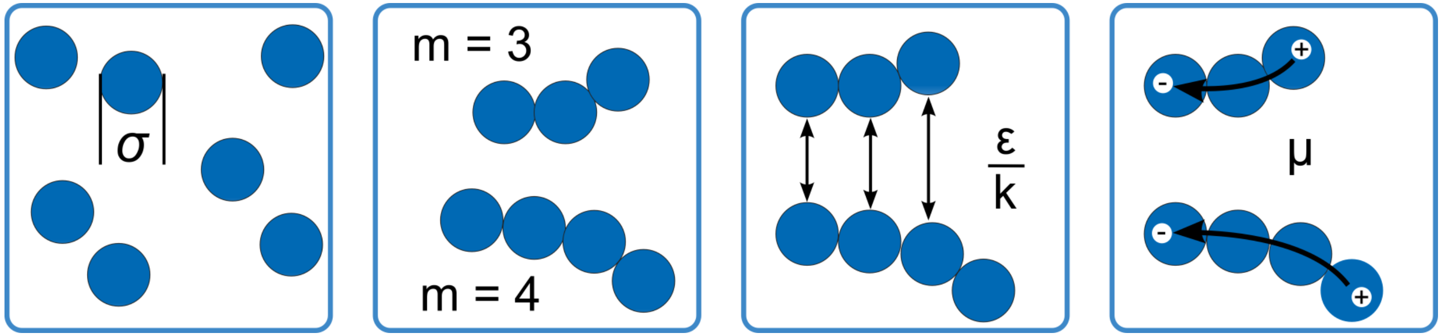
PC-SAFT for transport

PC-SAFT for equilibrium

equipment design

process design

molecule design



$$A^{res} = A^{hs} + A^{chain} + A^{disp} + A^{pol}$$

Pure component parameters:

segment diameter	σ	/	Å
segment number	m	/	-
segment dispersion energy	ε/k	/	K
dipole moment	μ	/	D

$$z = \begin{pmatrix} \sigma \\ m \\ \varepsilon/k \\ \mu \end{pmatrix} \xrightarrow{+\,p,T} \theta = \begin{pmatrix} h \\ s \\ v \\ \dots \end{pmatrix}$$

[1] Gross and Sadowski Ind. Eng. Chem. Res. 2001;40(4):1244–60.
[2] Gross J and Vrabec AIChE J. 2006;52(3):1194–204.

Model for transport properties: PC-SAFT[1-3]

PC-SAFT for transport

PC-SAFT for equilibrium

equipment design

process design

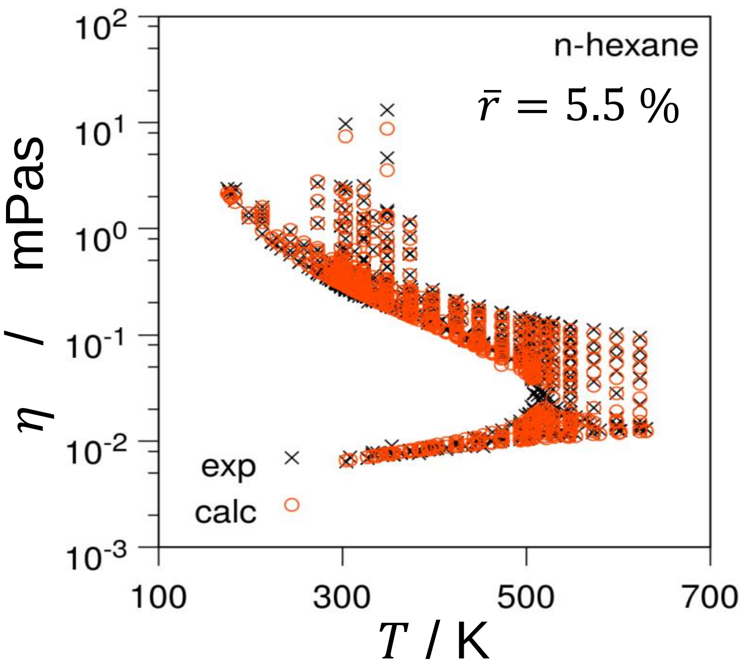
molecule design

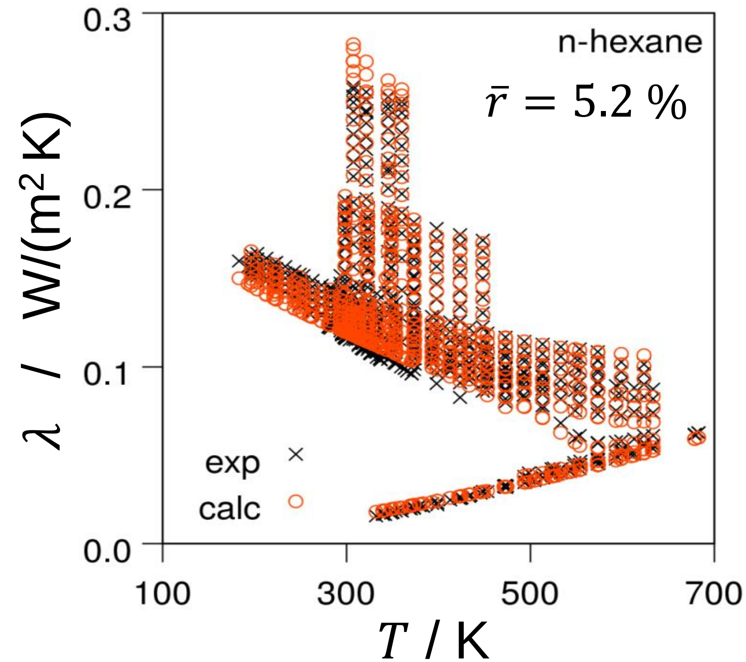
Based on Rosenfeld's entropy scaling:

$$\kappa = \binom{\eta}{\lambda} = \kappa_{\mathrm{ref}} \cdot \kappa^*$$

$$\kappa_{\mathrm{ref}} = f(CE)$$

$$\ln(\kappa^*) = A_\kappa + B_\kappa \hat{s} + C_\kappa \hat{s}^2 + D_\kappa \hat{s}^3$$





[1] Lötgering-Lin and Gross, *Ind. Eng. Chem. Res.*, 2015, 54 (32), 7942-7952
[2] Hopp and Gross, *Ind. Eng. Chem. Res.*, 2017, 56 (15), 4527–4538
[3] Hopp and Gross, PPEPPD, 22-26 May 2016, Granja – Portugal

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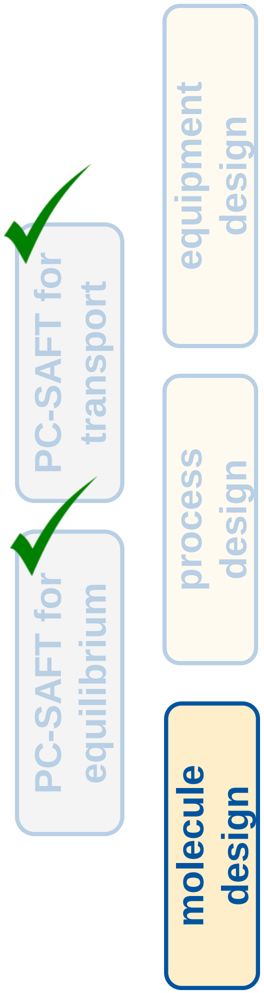
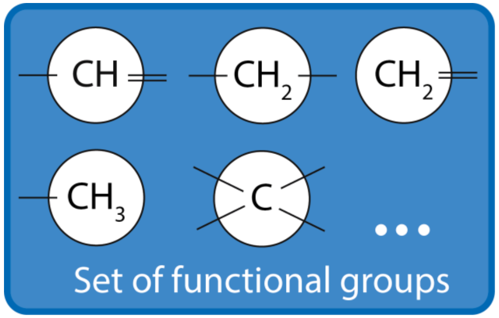
Computer-aided Molecular Design

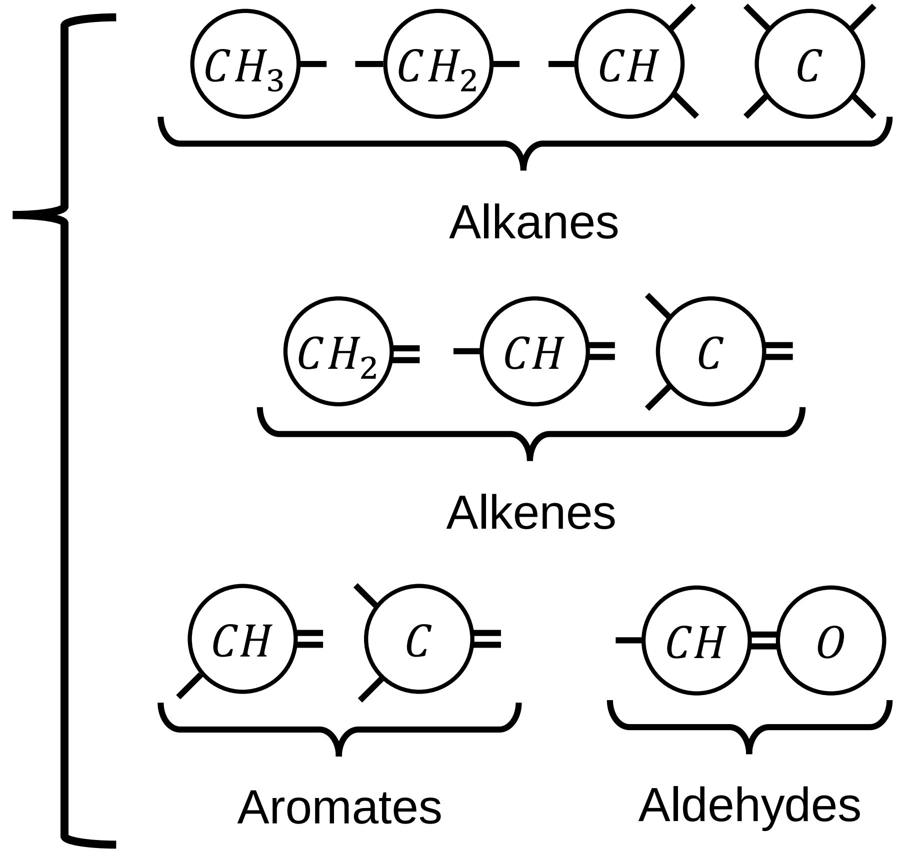


Groups for:



$$y^S = \begin{pmatrix} n_{\mathrm{CH_3}} \\ n_{\mathrm{CH_2}} \\ n_{\mathrm{CH}} \\ \cdots \end{pmatrix}$$

Constraints to ensure structural feasibility



Computer-aided Molecular Design

equipment design

PC-SAFT for transport ✓

process design

PC-SAFT for equilibrium ✓

molecule design

Group contribution methods for:

$$y^S = \begin{pmatrix} n_{\mathrm{CH_3}} \\ n_{\mathrm{CH_2}} \\ n_{\mathrm{CH}} \\ \cdots \end{pmatrix}$$

$$z = \begin{pmatrix} \sigma \\ m \\ \varepsilon/k \\ \mu \end{pmatrix}$$

Pure component parameters of PC-SAFT[1]

$$t = \begin{pmatrix} A_\kappa \\ B_\kappa \\ C_\kappa \\ D_\kappa \end{pmatrix}$$

Factors for the reduced transport properties[2,3]

$$c_p^{ig}$$

Heat capacity of the ideal gas[4]

[1] Sauer, Stavrou and Gross Ind. Eng. Chem. Res. 2014;53(38):14854-64.
[2] Lötgering-Lin and Gross Ind. Eng. Chem. Res. 2015, 54 (32), 7942-7952
[3] Hopp and Gross, PPEPPD, 22-26 May 2016, Granja – Portugal
[4] Joback and Reid, *Chem. Eng. Commun.*, 1987, **57**, 233–243.

Computer-aided Molecular Design

PC-SAFT for transport

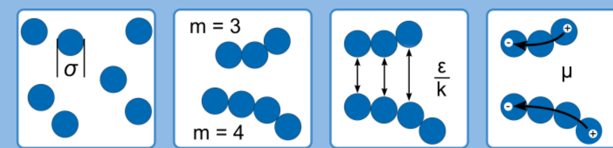
PC-SAFT for equilibrium

Heat capacity of the ideal gas

$$\underbrace{c_{\mathrm{p}}^{\mathrm{ig}}(y^{\mathrm{S}}, T)}_{\text{Joback}}$$

+

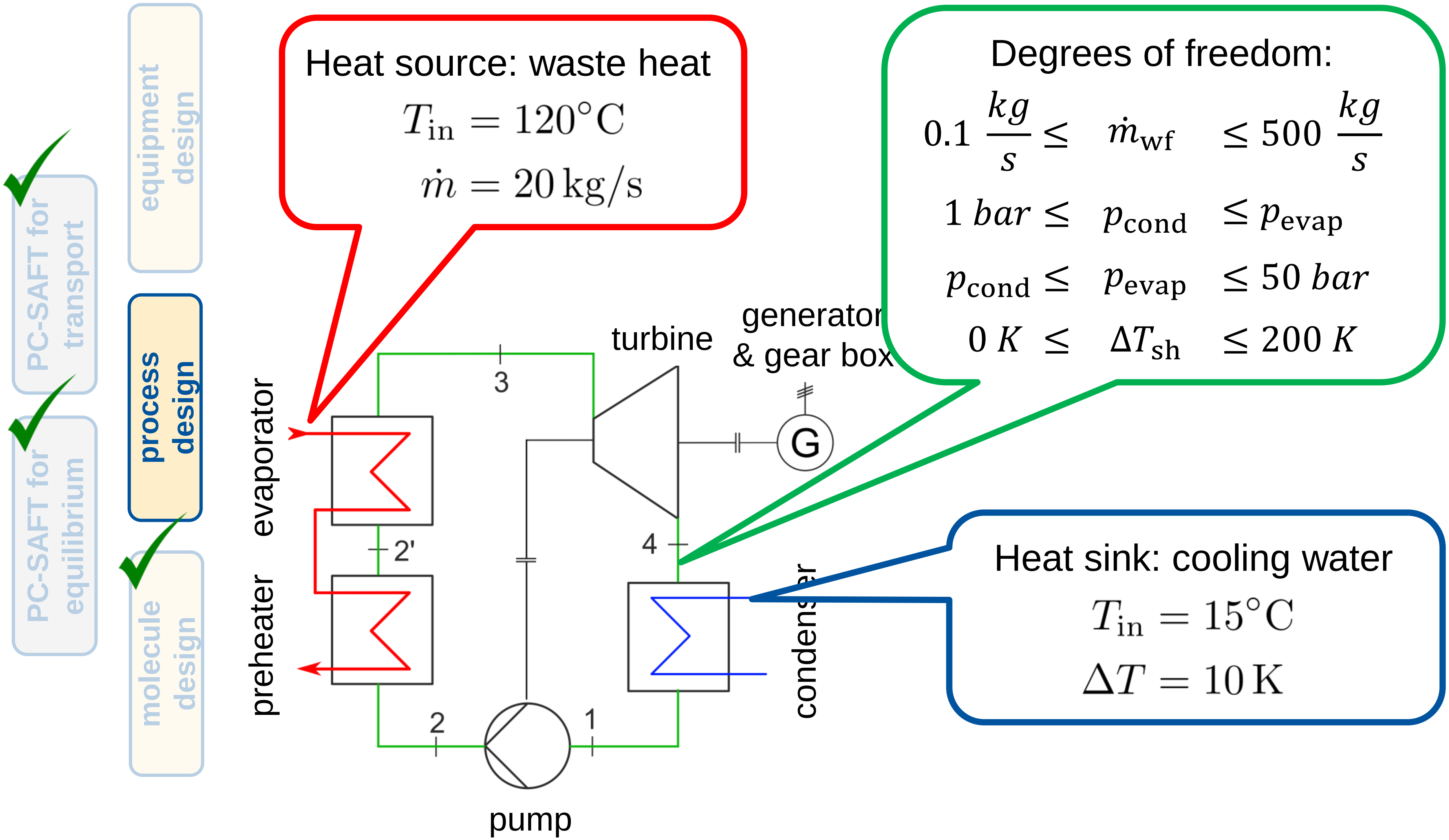
PC-SAFT equation of state



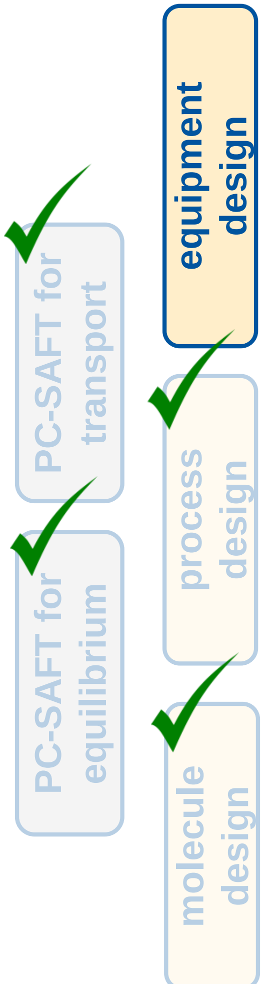
Model of Helmholtz energy A

$\Rightarrow$ **consistent thermodynamic model for equilibrium and transport properties**

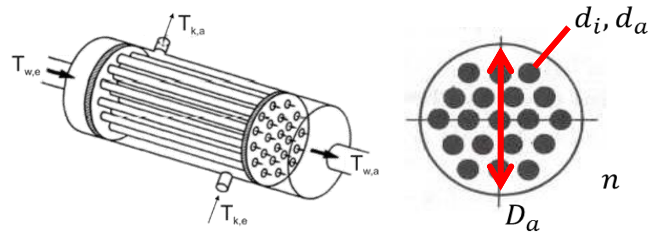
ORC for waste heat recovery as case study

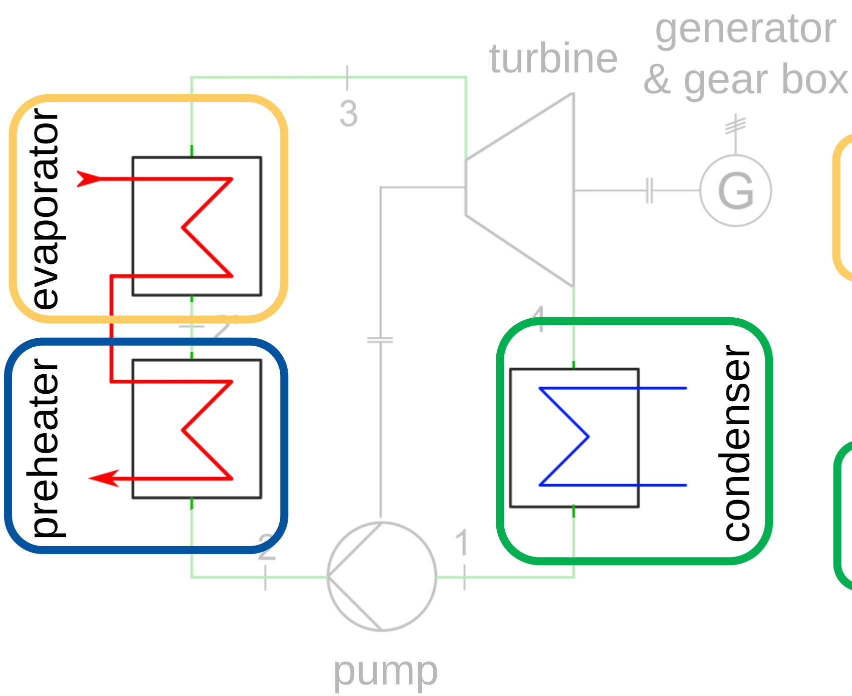


Equipment 1: Heat exchanger



Shell and tube heat exchanger





Detailed design correlations:

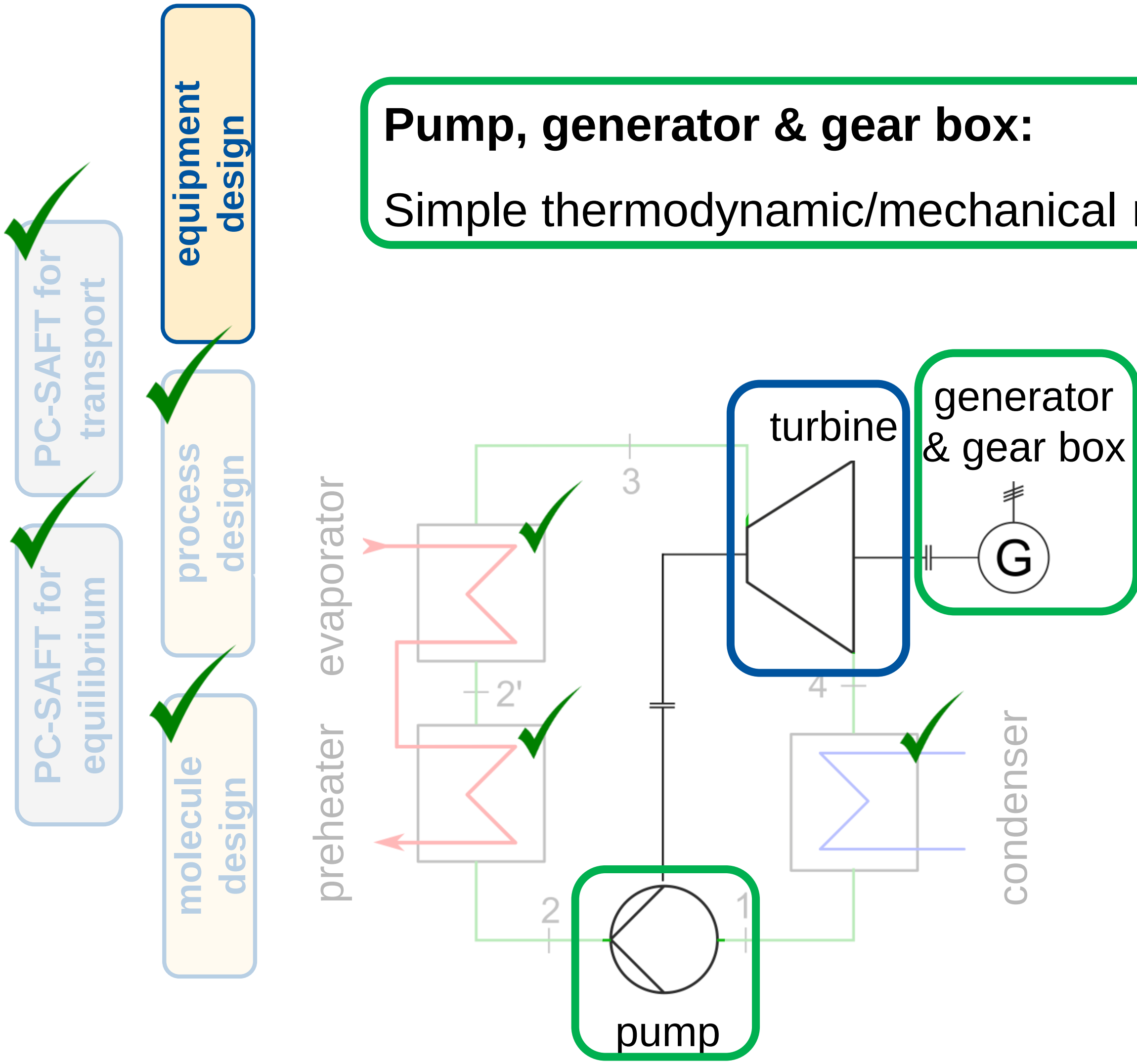
Single phase, forced convection[1]

Superposition of forced convection and bulk boiling[2]

Filmwise condensation of pure vapors[3]

[1] Gnielinski, *NASA STI/Recon Technical Report A*, 1975, 8–16
[2] Gungor and Winterton, *Int. J. Heat Mass Transfer*, 1986, **29**, 351–358.
[3] *VDI-Wärmeatlas*, Springer Vieweg, Berlin, 11th edn., 2013.

Equipment 2: Rotating equipment



Pump, generator & gear box:

Simple thermodynamic/mechanical model

Turbine: axial turbine[1]:

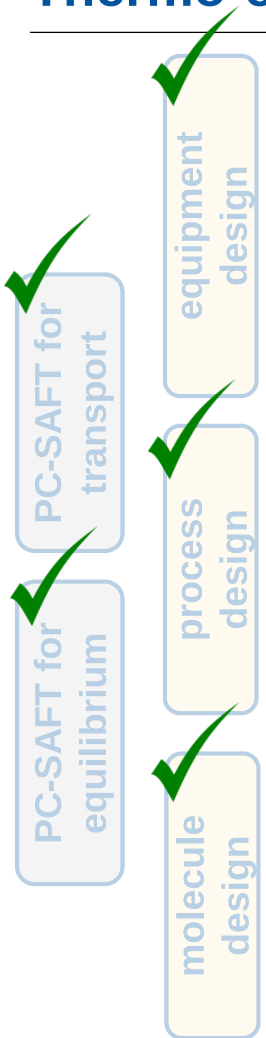
$$V_{\mathrm{V,Stages}} = \left(V_{\mathrm{V,T}}\right)^{\frac{1}{n_{\mathrm{Stages}}}} \leq 4$$

$$\Delta h_{\mathrm{is,Stages}} = \frac{\Delta h_{\mathrm{is,T}}}{n_{\mathrm{Stages}}} \leq 65 \, \frac{kJ}{kg}$$

→ Degree of freedom: Number of stages n_{Stages}

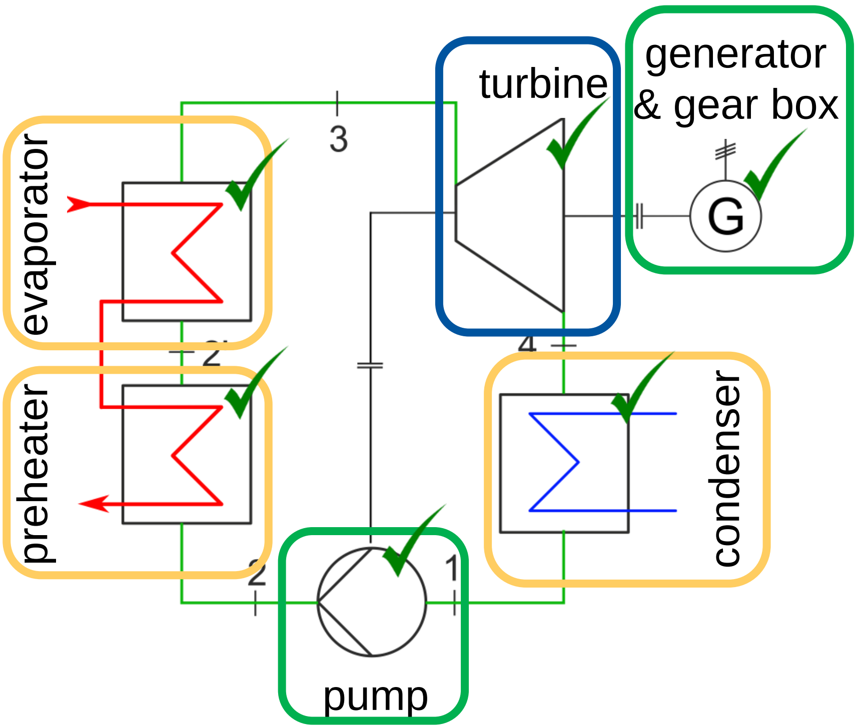
[1] Astolfi, Romano, Bombarda and Macchi, *Energy*, 2014, **66**, 435–446.

Thermo-economic objective function



Objective function:
specific investment cost

$$f = SIC = \frac{TCI}{P_{\text{net}}}$$



Heat exchanger[1]

$$Invest = f(A_i)$$

Pump, generator & gear box[2]

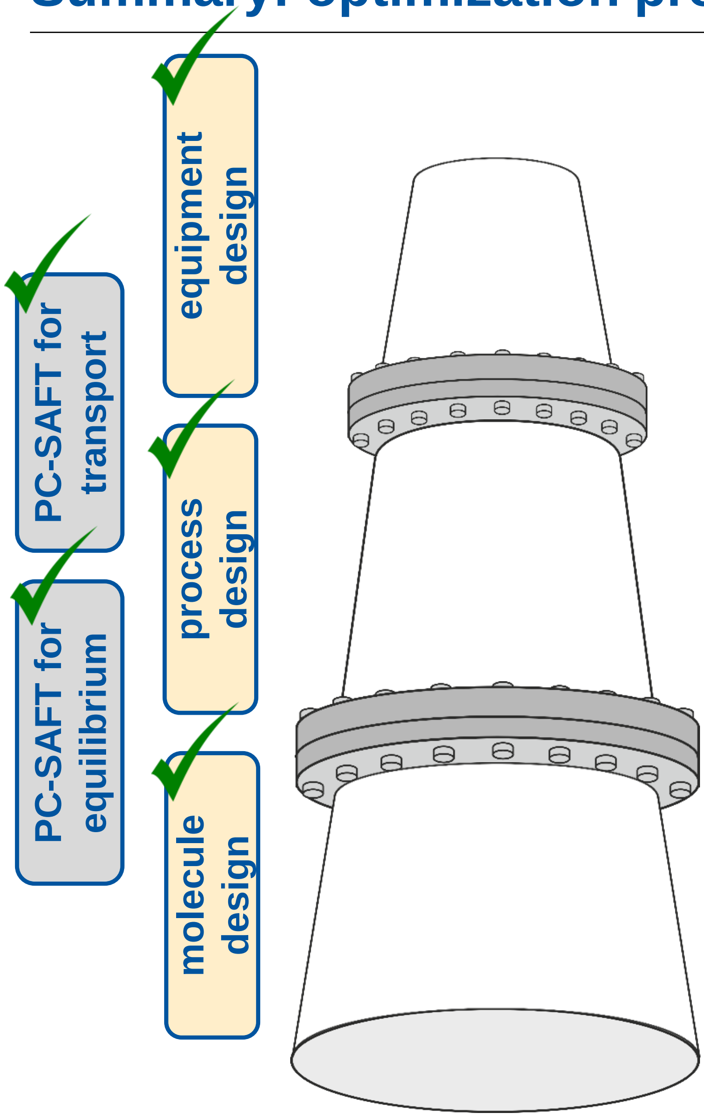
$$Invest = f(P_i)$$

Turbine[2]

$$Invest = f\left(n_{\text{Stages}}, \dot{V}, \Delta h_{\text{is,Stage}}\right)$$

[1] Hall, Ahmad, and Smith, *Comput. Chem. Eng.*, 1990, **14**, 319-335
[2] Astolfi, Romano, Bombarda and Macchi, *Energy*, 2014, **66**, 435–446.

Summary: optimization problem



$$\min_{x,y^s} f(x,\Theta,\kappa)$$

s.t.

$$g_1(x,\Theta,\kappa) = 0$$
$$g_2(x,\Theta,\kappa) \leq 0$$

$$\kappa = k(x,z,\Theta,y^s)$$

$$p_1(x,\Theta) = 0$$
$$p_2(x,\Theta) \leq 0$$

$$\Theta = h(x,z,y^s)$$

$$z = GC \cdot y^s$$
$$F_1 \cdot y^s = 0$$
$$F_2 \cdot y^s \leq 0$$
$$n(y^s) \leq 0$$

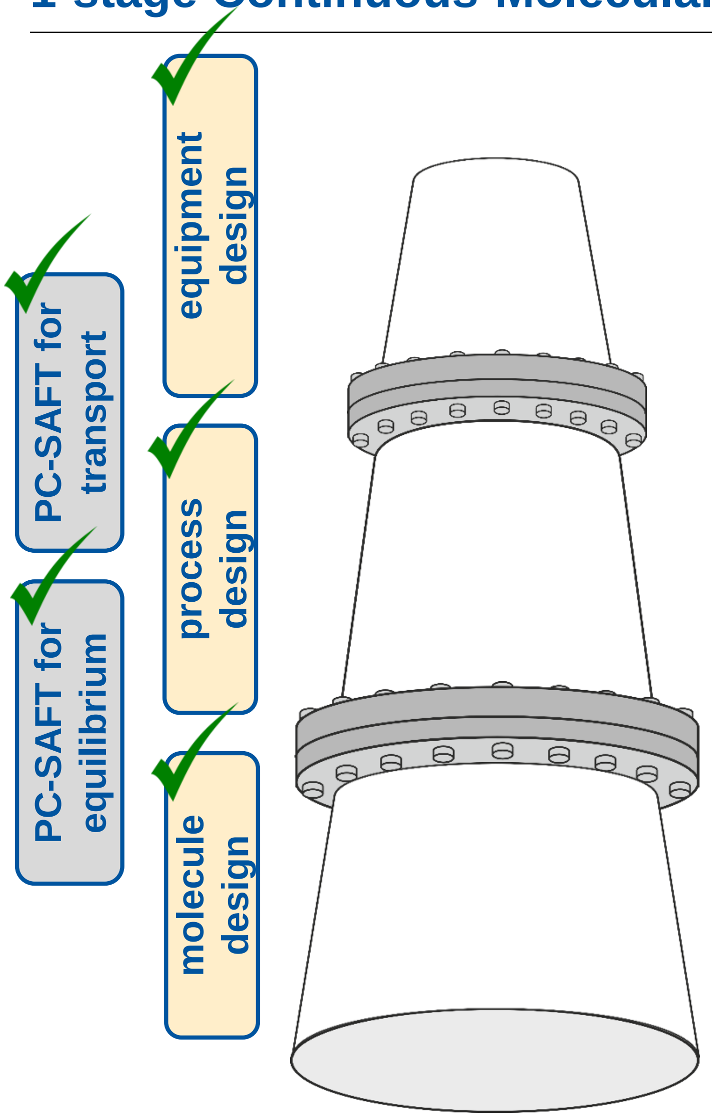
$$x_{lb} \leq x \leq x_{ub} \in \mathbb{R}^n$$
$$y^s_{lb} \leq y^s \leq y^s_{ub} \in \mathbb{Z}^l$$

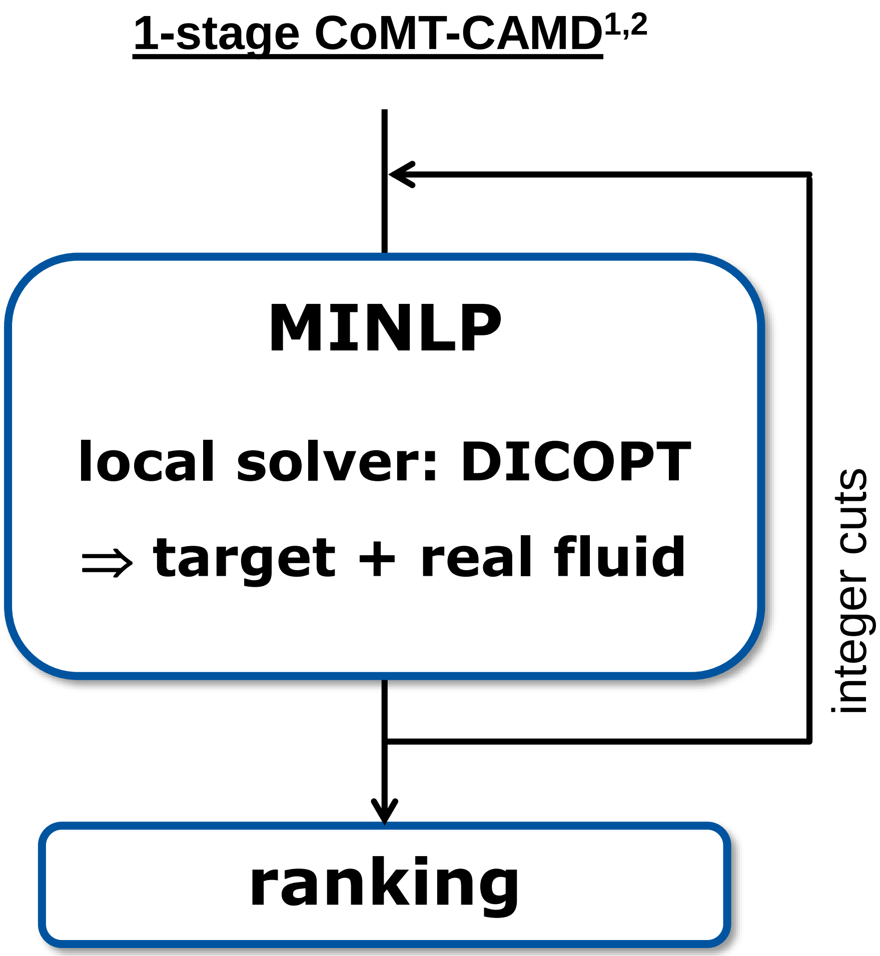
external functions

↓

stable optimization

1-stage Continuous-Molecular Targeting – Computer-Aided Molecular Design[1,2]





[1] Schilling et al., *Mol. Syst. Des. Eng.*, 2017, **2**, 301–320
[2] Schilling et al., *Chem. Eng. Sci.*, 2017, **159**, 217-230

Case study: resulting ranking and validation

Heat source: waste heat

$$T_{\text{in}} = 120^\circ\text{C}$$

$$\dot{m} = 20\,\text{kg/s}$$

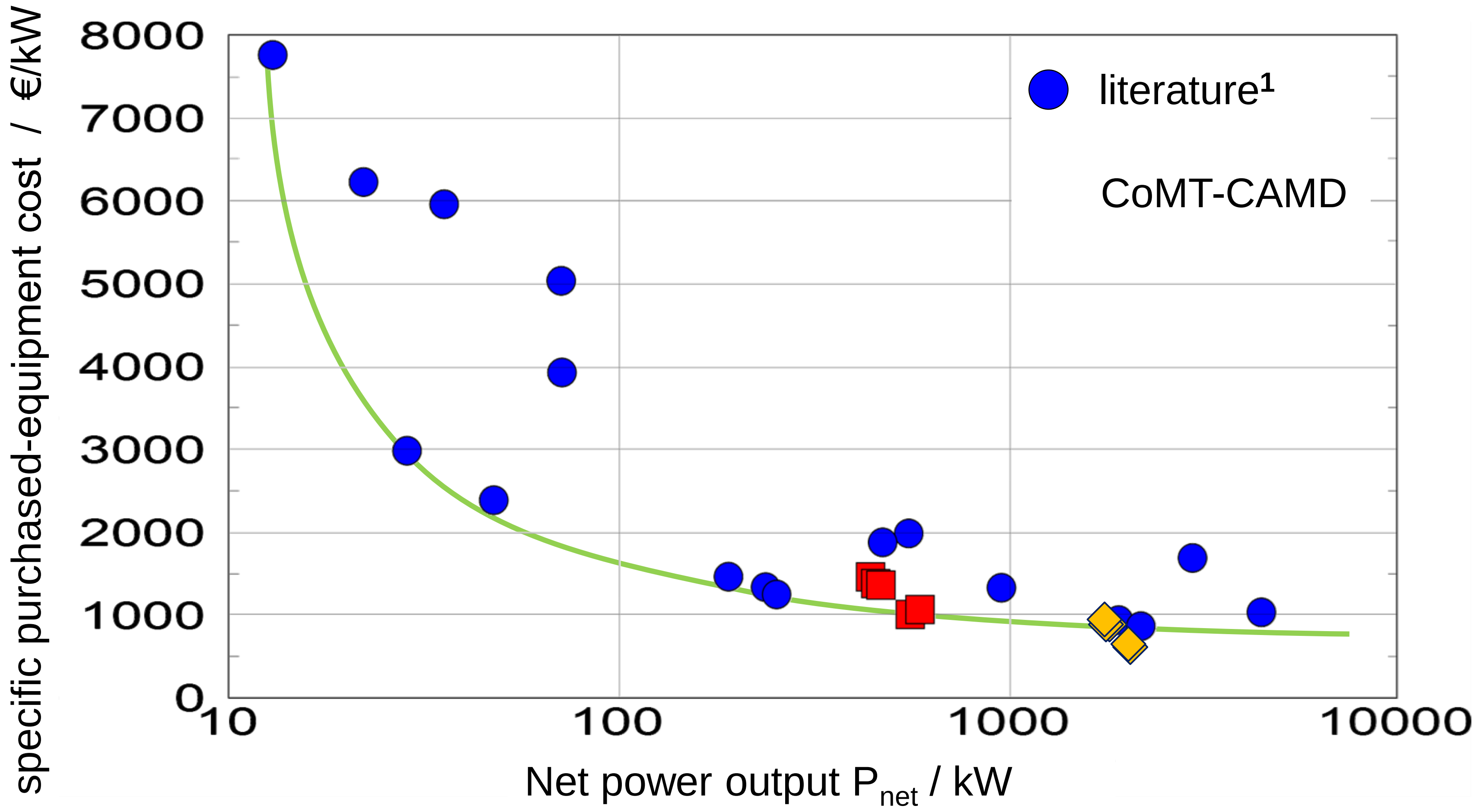
Heat sink: cooling water

$$T_{\text{in}} = 15^\circ\text{C}$$

$$\Delta T = 10\,\text{K}$$

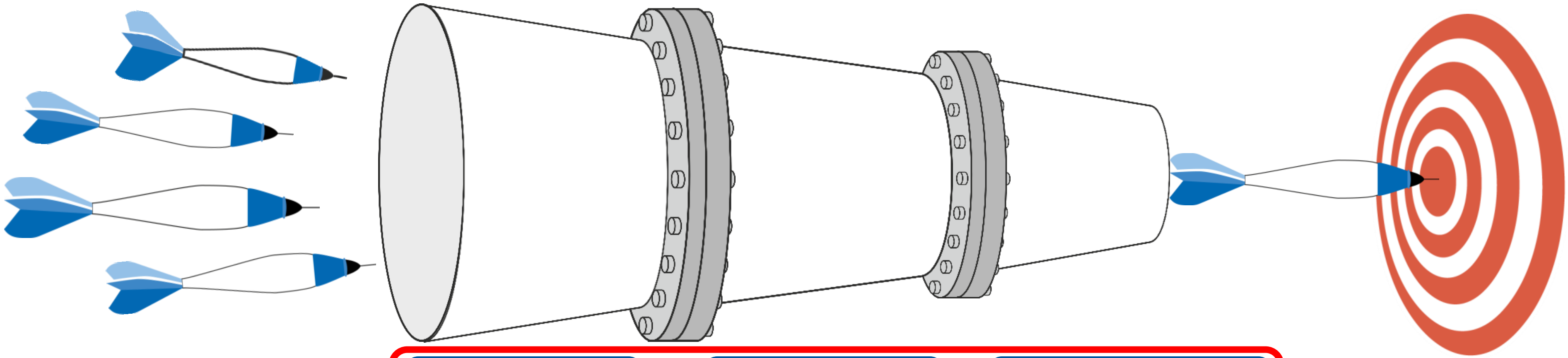
Rank	Name	SIC / €/kW	P_{net} / kW	TCI / 10^6 €
-	Target	2915	456	1.33
1	Propene	3303	417	1.38
2	Propane	3474	411	1.43
3	But-1-ene	4546	389	1.77
4	Isobutane	4573	387	1.77
5	n-Butane	4874	378	1.84

Results: specific purchased-equipment cost



[1] Quoilin, van Broek, Declaye, Dewallef and Lemort, *Renew. Sust. Energ. Rev.*, 2013, **22**, 168–186.

Conclusions



molecule design | process design | equipment design

PC-SAFT for equilibrium | PC-SAFT for transport

Integrated design of molecule, process and equipment

PC-SAFT: consistent thermodynamic model

Efficient identification of the best working fluid

Good accordance to applications from literature

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Thank you for your attention

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References on CoMT-CAMD:

- Schilling, J., Tillmanns, D., Lampe, M., Hopp, M., Gross, J., Bardow, A., 2017. From molecules to dollars: integrating molecular design into thermo-economic process design using consistent thermodynamic modeling. *Mol. Syst. Des. Eng.* 2, 301-320.

- Schilling, J., Lampe, M., Gross, J., Bardow, A., 2017. 1-stage CoMT-CAMD: An approach for integrated design of ORC process and working fluid using PC-SAFT. *Chem. Eng. Sci.* 159, 217-230.

- Lampe, M., Stavrou, M., Schilling, J., Sauer, E., Gross, J., Bardow, A., 2015. Computer-aided molecular design in the continuous-molecular targeting framework using group-contribution PC-SAFT. *Comput. Chem. Eng.* 81, 278–287.

- Stavrou, M., Lampe, M., Bardow, A., Gross, J., 2014. Continuous molecular targeting-computer-aided molecular design (CoMT-CAMD) for simultaneous process and solvent design for CO2 capture. *Ind. Eng. Chem. Res.* 53 (46), 18029–18041.

- Lampe, M., Stavrou, M., Bücker, H. M., Gross, J., Bardow, A., 2014. Simultaneous optimization of working fluid and process for organic Rankine cycles using PC- SAFT. *Ind. Eng. Chem. Res.* 53 (21), 8821–8830.

- Bardow, A., Steur, K., Gross, J., 2010. Continuous-molecular targeting for integrated solvent and process design. *Ind. Eng. Chem. Res.* 49 (6), 2834–2840.