1-stage CoMT-CAMD: An approach for integrated design of ORC process and working fluid using PC-SAFT

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Abstract

Organic Rankine Cycles (ORC) transform low-temperature heat into electrical power. To exploit the full potential of a low-temperature heat source, the ORC system is tailored to the specific application. Tailoring an ORC system is challenging, since both process and working fluid have to be optimized simultaneously. We present an approach for integrated design of ORC process and working fluid that enables tailoring an ORC process and the working fluid in a single optimization problem. This approach builds upon the continuous-molecular targeting - computer-aided molecular design (CoMT-CAMD) approach presented by Lampe et al. [1]. Here, a detailed process model is combined with a modern model of the working fluid, the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state. A group contribution approach for PC-SAFT is integrated to allow the computer-aided molecular design (CAMD) of novel fluids within the optimization. In this work, we formulate the corresponding mixed integer nonlinear program (MINLP) problem and solve it in one stage by deterministic optimization combining CoMT and outer-approximation. We therefore call the approach 1-stage CoMT-CAMD. 1-stage CoMT-CAMD problems can

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be solved efficiently using commercial solvers enabling both single-objective and multi-objective optimization of process and working fluid. The presented approach is employed in two ORC case studies. The first case study outlines the applicability for single-objective and multi-objective optimization for combined heat and power generation. In the second case study, a detailed turbine model is considered within the optimization showing the possibility of modelling the process components in a more detailed manner. The 1-stage CoMT-CAMD approach thus efficiently solves complex integrated design problems based on a consistent thermodynamic picture.

Keywords: Integrated process and fluid design, Computer-aided Molecular Design, Continuous-Molecular Targeting, PC-SAFT, Organic Rankine Cycle

1. Introduction

Integrating computer-aided molecular design (CAMD) into product and process design is an important and emerging problem in engineering: The problem of integrated design of molecules and process arises, e.g., for design of
 5 solvents [2, 3, 4, 5, 6, 7], refrigerants [8, 9] and the design of adsorption materials [10].

In particular, integrated fluid and process design is a crucial challenge in the design of Organic Rankine Cycles (ORC) as recently reviewed by Linke et al. [11]. Power generation from renewable sources is a key need for sustainable
 10 societies. ORCs enable power generation from low-temperature heat [12]. Low-temperature heat can be captured from various renewable heat sources, e.g., solar heat [13], geothermal heat [14], biomass [15], or waste heat from industrial [16] as well as automotive applications [17]. To exploit the full potential of a heat source, the ORC has to be tailored to the specific application. In order to
 15 tailor an ORC, process and working fluid have to be optimized simultaneously as pointed out in several recent reviews [11, 18].

Today, fluid selection and process optimization are carried out separately following a two-stage approach [13, 15, 19]: In a first stage, promising working

fluid candidates are preselected based on experience and heuristic guidelines
 20 defining favorable fluid properties. In a second stage, an individual process
 optimization is performed for each preselected working fluid candidate. For the
 first preselection stage, a variety of heuristic criteria have been proposed. Bao
 and Zhao [18] reviewed shortcomings in common heuristics for preselection. If
 the preselection fails, the two-stage approach leads to suboptimal solutions.

25 Thus, recent reviewers recommend to directly integrate the fluid selection
 into the process optimization to obtain overall optimal solutions [2, 11, 18, 19].
 An integrated design approach captures the interdependency of process and
 fluid, but leads to a large scale complex non-convex mixed integer nonlinear
 programming (MINLP) problem [20], since a discrete degree of freedom is added
 30 to the process optimization for each working fluid. Thus, systematic solution
 approaches for the integrated design of process and fluid have been proposed.
 Recently, Linke et al. [11] reviewed systematic approaches for the integrated
 design of ORCs: Papadopoulos et al. [21] show the merits of CAMD for ORC
 working fluids considering pure working fluids. In a first stage, a set of pure
 35 working fluid candidates is obtained using a CAMD formulation within a multi-
 objective optimization. The working fluid candidates are assessed in subsequent
 process optimizations. The optimization problem is solved by simulated anneal-
 ing. The approach is extended for identifying working fluid mixtures and also
 for allowing a process-level objective function [22]. The fluid properties are pre-
 40 dicted using a group contribution (GC) method and the cubic Peng-Robinson
 equation of state (EoS). Palma-Flores et al. [23] also present an optimization-
 based CAMD approach using a GC approach and a cubic EoS to predict the fluid
 properties. In a first stage, they perform a single-objective optimization to ob-
 tain a set of pure working fluid candidates. The optimization problem is solved
 45 by deterministic optimization. In a second stage, the working fluid candidates
 are assessed in a process simulation using 3 different process configurations.

CAMD approaches are commonly based on a set of target properties. If these
 target properties are defined a priori, the application of CAMD approaches has
 become relatively straight forward, e.g., for working fluid design for ORC appli-

50 cations [21, 23], solvent design [5, 24], polymer design [25, 26], and refrigerant
 design [9, 25, 27] as recently reviewed by Ng et al. [28]. However, a priori defi-
 nition of favorable target properties is challenging. Targeting approaches have
 been proposed, which aim at identifying favorable fluid properties, so called tar-
 gets. These targeting approaches allow solving the integrated design problem
 55 in two stages: In the first stage, targets are identified and fluids are designed
 in a second stage based on these targets. Eden et al. [29] present a targeting
 approach for process and product design based on property clustering tech-
 niques. Bardow et al. [3] integrate the design of process and solvent in the
 continuous-molecular targeting (CoMT) framework, which combines a model
 60 of the process and a thermodynamically consistent model of the working fluid,
 the perturbed-chain statistically associating fluid theory (PC-SAFT) equation
 of state [30]. The CoMT framework directly leads to molecular targets. CoMT
 has been applied to solvent design [3, 6] and ORCs [31] for integrated design of
 process and fluids. In a first stage of the CoMT framework, the pure component
 65 parameters representing the working fluid in PC-SAFT are relaxed leading to
 a nonlinear programming (NLP) problem. The NLP results in a hypothetical
 optimal working fluid, the target, along with the corresponding optimal pro-
 cess parameters. In a second stage, real working fluids, which show similar
 performance as the hypothetical optimal working fluid, are identified. Within
 70 this second stage, the so-called structure-mapping, a second degree Taylor ap-
 proximation of the objective function is used to estimate the objective function
 value of the real working fluids. The structure-mapping allows the selection of
 working fluids from a database [31]. Schilling et al. [32] proposed an adaptive
 refinement of the Taylor approximation for the database search. Lampe et al. [1]
 75 extend the structure-mapping by a CAMD formulation and a GC approach for
 PC-SAFT [33] to identify novel fluids during structure-mapping, in the so-called
 CoMT-CAMD approach. Thereby, the previous database search is transformed
 into a mixed-integer quadratic programming (MIQP) problem considering the
 Taylor approximation as objective function.

80 A targeting approach has also recently been proposed by Roskosch and Atakan for the integrated design of heat pumps using the cubic Peng-Robinson EoS [8]. In this approach, optimal thermo-physical properties (e.g., critical pressure, critical temperature) are identified in a first stage. In a second stage, working fluids with similar properties are identified from a database.

85 Progress in the numerical techniques and improved MINLP solvers enable the integrated design in one-stage using even modern thermodynamic models of the fluid. Pereira et al. [34] present an optimization-based one-stage approach for integrated solvent and process design using the statistical associating fluid theory for potentials of variable attractive range (SAFT-VR) to model the sol-
 90 vent. The search space of the considered fluids is still limited to linear alkanes, but the approach shows the merits and relevance of a physically-based solvent model for fluid design. Zhou et al. [35] present an approach for integrated solvent and process design combining a model for reaction kinetics and a GC method. Here, solvent descriptors determined from quantum chemical density
 95 functional theory calculations enable the simultaneous optimization of process operations and the molecular structure of the solvent. Recently, Burger et al. [4] proposed a hierarchical approach for integrated design of process and solvent using simplified short-cut models of the process and SAFT- γ Mie as solvent model.

100 In this work, we present a one-stage approach for the integrated design of ORC process and working fluid using a detailed process model and a modern model of the working fluid, the PC-SAFT EoS. This approach is based on the two-stage CoMT-CAMD approach presented by Lampe et al. [1]. However, the two-stage approach is conceptually avoided. Instead, the CAMD of novel fluids
 105 is directly combined with the process model and the fluid model. Thereby, the full process-level objective function and constraints are linked to the molecular design optimization. The adapted CoMT-CAMD approach is linked to an outer-approximation formulation to identify molecular structures in one stage. We therefore call the approach 1-stage CoMT-CAMD. The link is enabled by
 110 the deterministic MINLP solver DICOPT, which combines the CoMT problem

with outer-approximation. 1-stage CoMT-CAMD identifies the optimal working fluid and the corresponding process parameters in one single optimization of the MINLP problem. Due to the efficient solution procedure, multi-objective optimization can be employed to capture trade-offs within the fluid design. A preliminary version of this work has been presented in a conference paper [36]. The paper is structured as follows: In Section 2, the problem formulation of the MINLP as well as the CAMD-based fluid model is presented. In Section, 3, the one-stage approach is applied to a single and a multi-objective optimization of two ORC design case studies. In Section 4, advantages and disadvantages of the one-stage approach are discussed based on the case studies. In Section 5, conclusions are drawn.

2. Integrated one-stage design of process and working fluid

The presented 1-stage CoMT-CAMD approach for the integrated design of process and working fluid requires a model of the process and a model of the working fluid describing its properties at different states. Here, the fluid is modeled by the PC-SAFT equation of state. This fluid model is extended by a CAMD formulation and a GC approach based on PC-SAFT to integrate the fluid design as degree of freedom into the optimization. The extended fluid model is coupled with the process model to capture all process-related trade-offs. A detailed description of the MINLP problem formulation is given in Section 2.1. In Section 2.2, the extended working fluid model is described.

2.1. Problem formulation for integrated design of process and working fluid

A generic MINLP problem formulation for integrated design of process and working fluid is presented by Gani [20]. Originally, a single-objective optimiza-

tion is considered. Here, we also employ multi-objective optimization. The full problem can thus be formulated as:

$$\begin{aligned}
& \max_{x, y^S} (f_1(x, \theta), f_2(x, \theta), \dots, f_k(x, \theta))^T \\
& \text{s.t.} \quad \left. \begin{aligned} g_1(x, \theta) &\leq 0 \\ g_2(x, \theta) &= 0 \end{aligned} \right\} \text{ process model} \\
& \quad \quad \quad \left. \begin{aligned} \theta &= h(x, z) \end{aligned} \right\} \text{ PC - SAFT} \\
& \quad \quad \quad \left. \begin{aligned} z &= GC \cdot y^S \\ F_1 \cdot y^S &= 0 \\ F_2 \cdot y^S &\leq 0 \end{aligned} \right\} \text{ CAMD and GC approach} \\
& \quad \quad \quad x_{\text{lb}} \leq x \leq x_{\text{ub}} \in \mathbb{R}^n \\
& \quad \quad \quad y_{\text{lb}}^S \leq y^S \leq y_{\text{ub}}^S \in \mathbb{Z}^l
\end{aligned} \tag{1}$$

Herein, the process model encompasses one or more objective functions ($f_1(x, \theta)$, $f_2(x, \theta), \dots, f_k(x, \theta)$), equality constraints $g_2(x, \theta)$ as well as inequality constraints $g_1(x, \theta)$. Since an equilibrium fluid model is currently employed, any objective function based on equilibrium properties can be considered (e.g., net power output, thermal or exergy efficiency). Recently, PC-SAFT has been extended to calculate transport properties [37, 38]. The knowledge of transport properties would also allow equipment sizing and thus the use of economic objectives. The process model depends on two kinds of variables: process variables x (e.g., mass flow rate or pressure levels) and fluid properties θ (e.g., enthalpies or entropies) at different states. Non-thermodynamic properties (e.g., global warming potential (GWP) or flammability) could be added to the model as demonstrated in earlier CAMD approaches [21]. In general, structural degrees of freedom can also be considered on the process level to represent different flowsheets. Here, we consider only continuous variables. The fluid properties θ are calculated by the fluid model $\theta = h(x, z)$. Here, the working fluid is modeled by the PC-SAFT EoS. The fluid properties depend on both the process variables x and a set of pure component parameters z representing the fluid. To integrate the

fluid design as degree of freedom in the process optimization, a CAMD formulation is employed allowing the design of novel promising working fluids. In this CAMD formulation, each working fluid is characterized by its molecular structure y^S . The vector y^S represents the number of functional groups constituting the molecular structure of the fluid (see Section 2.2). To link the pure component parameters z of PC-SAFT to the vector y^S representing the molecular structure, a GC approach is added to connect PC-SAFT and the CAMD formulation. With this GC approach, the pure component parameters z of PC-SAFT are calculated from the molecular structure $z = GC \cdot y^S$. To ensure structural feasibility of the molecular structure, additional linear constraints $F_1 \cdot y^S = 0$ and $F_2 \cdot y^S \leq 0$ are added to the problem formulation [39, 40].

The full MINLP problem from Problem (1) for the integrated design of process and working fluid depends on continuous process variables x and integer variables y^S representing the molecular structure of the working fluid. The MINLP is solved by outer-approximation [41], which is extended by an equality relaxation problem. Series of nonlinear program (NLP) subproblems and mixed-integer program (MIP) master problems are solved: Initially, all integer variables are relaxed to calculate a hypothetical optimum by solving the resulting NLP. The hypothetical optimum represents an upper bound on the objective function. This relaxed NLP corresponds exactly to the CoMT problem in the CoMT-CAMD approach [3]. Based on outer-approximation, an MIP master problem is then solved to identify an integer point with similar properties as the hypothetical optimum. The MIP master problem defines a tighter upper bound on the objective function. Afterwards, the integer variables are fixed and the resulting NLP is solved. The solution represents a lower bound on the objective function. The last two steps are repeated until the objective function value of the NLP solution is lower than the lower bound (for details on outer approximation see Floudas [42]). We use the software GAMS (version 24.6.1) [43] and the deterministic MINLP solver DICOPT [44] with the subsolvers SNOPT [45] and BARON [46] to solve the NLPs and MIPs, respectively.

180 1-stage CoMT-CAMD is based on the two-stage CoMT-CAMD approach presented by Lampe et al. [1]. Both approaches use the same CAMD formulation, GC approach and fluid model (Figure 1). Also, 1-stage CoMT-CAMD initially solves the CoMT problem to identify a hypothetical optimal working fluid by relaxation of the pure component parameters, the so-called target. However in the two-stage CoMT-CAMD approach, a decomposition is employed and CAMD is not directly integrated into the fluid and process design. Thus, a second stage, the structure-mapping, is needed to identify real working fluids based on an approximation of the objective and constraints. Additionally, a predefined convex hull is required in the CoMT problem for the two-stage approach.

185 Schilling et al. [32] propose an adaptive strategy refining the approximation in the structure-mapping iteratively for database search. 1-stage CoMT-CAMD systematically refines approximations of the objective and constrains based on the outer-approximation formulation. This strategy enables the identification of real working fluids in a single stage. The integration of CAMD into the one-stage design procedure for fluid and process also removes the need to estimate the convex hull around the structurally feasible working fluids, which is otherwise needed in the first stage of the two-stage approach.

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The resulting MINLP problem can be solved as a single-objective or a multi-objective optimization. The solution of a single-objective optimization is one single optimal working fluid and the corresponding optimal process parameters. CAMD should usually provide a list of candidates to allow considering aspects not covered by the model or model inaccuracies. We therefore use integer cuts [42] to obtain a ranked list of optimal working fluids (Figure 1). Here, the MINLP is solved repeatedly, wherein the previous solutions are excluded from the feasible design space. To reduce computation effort, the CoMT solution of the first MINLP is saved and set as initial value for the subsequent MINLPs.

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The identified ranking can be assessed for further criteria. The solution of a multi-objective optimization is a Pareto front of potential working fluids. The Pareto front can be generated using multi-objective optimization methods (e.g.,

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Figure 1: Comparison of the frameworks of a) the two-stage CoMT-CAMD approach [1] and b) 1-stage CoMT-CAMD. Integer Cuts can be used to obtain a ranked list of optimal working fluids. The accuracy of the ranking can be increased by a final process optimization considering pure component parameters fitted to measurement data if available.

210 normalized normal constraint method [47], epsilon-constraint method [48] or
more advanced methods [49]).

Finally, it is also important to take into account that the GC approach intro-
duces uncertainties in the result [33], which can have significant impact on the
performance [22]. To increase accuracy of the result, a final process optimiza-
215 tion can be performed for each identified working fluid using pure component
parameters fitted to measurement data for vapor-liquid equilibrium (VLE) and
liquid densities if available (Figure 1). The impact of the uncertainties of the
GC approach is discussed in Section 4.2.

2.2. CAMD based on group-contribution PC-SAFT

220 To enable the integrated design of process and working fluid, the working
fluid is modeled by the perturbed-chain statistical associating fluid theory (PC-
SAFT) equation of state [30] including contributions for polar components [50,
51]. In this fluid model, working fluids are represented by a set of 3 to 7
pure component parameters. In the presented work, non-associative and non-
225 quadrupolar working fluids are regarded within the fluid design. Thus, 4 pure
component parameters are sufficient to describe each working fluid: the segment
number m , the segment diameter σ , the segment dispersion energy ϵ/k , and the
dipole moment μ . The vector z is defined by a combination of these pure
component parameters $z = (m, m\sigma^3, m\epsilon/k, \mu)^T$. These parameter combinations
230 are a convenient choice since they are the basic variables in the employed GC
approach [33].

The PC-SAFT EoS is based on the residual Helmholtz energy. Using a
Helmholtz energy model ensures a consistent picture of all equilibrium properties
of the fluid. Absolute caloric properties can be calculated if a reference property
is known. For this purpose, we use the heat capacity of the ideal gas c_p^{ig} .
The two-stage CoMT-CAMD approach needs quantitative structure-property
relationships (QSPR) to calculate the ideal gas heat capacity c_p^{ig} and the molar
mass since only the pure component parameters z were known. In the presented
1-stage CoMT-CAMD approach, the molecular groups y^S are available during

design. Thus, the heat capacity of the ideal gas c_p^{ig} can be calculated from the molecular structure of the working fluid y^{S} by Joback’s first-order group-contribution method [52] (see Appendix A.1 for details). Caloric properties such as the absolute enthalpy h can thus be calculated for a given pressure p and temperature T based on an arbitrary reference temperature T_0 by:

$$h = h^{\text{res}}(p, T, z) + h^{\text{id}}(y^{\text{S}}, T) = \underbrace{h^{\text{res}}(p, T, z)}_{\text{PC-SAFT}} + \int_{T_0}^T \underbrace{c_p^{\text{ig}}(y^{\text{S}}, \tilde{T})}_{\text{Joback}} d\tilde{T}, \quad (2)$$

where h^{res} denotes the residual contribution calculated with PC-SAFT and h^{id} denotes the ideal contribution calculated from the heat capacity of the ideal gas c_p^{ig} . The molar mass is also calculated exactly from the molecular structure of the working fluid avoiding the QSPR model used in the two-stage design.

To connect the PC-SAFT EoS to a CAMD formulation, the homosegmented GC approach from Sauer et al. [33] is employed. This so-called GPC-SAFT approach relates the pure component parameters of PC-SAFT to the molecular structure of the fluid. The group contributions are fitted to VLE data and liquid densities from a database for a range of pure fluids. Here, we limit the molecular design space of the CAMD formulation to prevent extrapolation from this database. Thereby, we use the highest accuracy of the CAMD formulation (see Section 4.2 for details). The limit is considered in the inequality constraints $F_2 \cdot y^{\text{S}} \leq 0$ in Problem (1). In GPC-SAFT, the pure component parameters are calculated by the mixing rules of Vijande et al. [53]:

$$\begin{aligned} p_1 &:= m = \sum_{i \in I} n_i \cdot m_i, \\ p_2 &:= m \cdot \sigma^3 = \sum_{i \in I} n_i \cdot m_i \cdot \sigma_i^3, \\ p_3 &:= m \cdot \epsilon/k = \sum_{i \in I} n_i \cdot m_i \cdot (\epsilon/k)_i, \\ p_4 &:= \mu = \sum_{i \in I} n_i \cdot \mu_i, \end{aligned} \quad (3)$$

where n_i is the number of groups of type i in the molecular structure represented by the vector $y^{\text{S}} = (n_1, n_2, \dots, n_m)^{\text{T}}$. The vector $\tilde{z}_i = (m_i, \sigma_i, (\epsilon/k)_i, \mu_i)^{\text{T}}$ contains

the group contributions to the pure component parameters (see Appendix A.2 for details). In this work, 20 functional groups are employed: $-\text{CH}_3$, $-\text{CH}_2-$, >CH- and >C< for alkanes, $=\text{CH}_2$, $=\text{CH-}$ and >C= for alkenes, $-\text{C}\equiv\text{CH}$ for 1-alkynes, $\text{>C}^{\text{Arom}}=$, $\text{<CH}^{\text{Arom}}=$, $\text{>CH}^{\text{Pent}}-$, $\text{<CH}_2^{\text{Pent}}-$, $\text{>CH}^{\text{Hex}}-$ and $\text{<CH}_2^{\text{Hex}}-$ for cyclic components with alkyl side groups, $-\text{CH}=\text{O}$ for aldehydes, $\text{>C}=\text{O}$ for ketones, $-\text{O}-\text{CH}_3$ and $-\text{O}-\text{CH}_2-$ for ethers, $-\text{O}-\text{CH}=\text{O}$ for formates and $-\text{O}-(\text{C}=\text{O})-$ for esters.

SAFT approaches were shown to provide accurate predictions of fluid behavior [54]. However, calculations are more demanding than for classical EoS, e.g., cubic EoS. Therefore, we perform all process calculations and all thermodynamic calculations of PC-SAFT in external equations basically providing a black-box model to GAMS. GAMS forwards the working fluid parameters calculated from the molecular structure y^{S} as well as the process variables x to the external equations. The working fluid parameters are the pure component parameters of PC-SAFT z , the parameters needed for Joback’s GC method and the molar mass. The external equations return the objective function value f , the process constraints g and h and first-order derivatives of these values to the optimization problem in GAMS (for details on external equations in GAMS see chapter 28 in [43]). Hereby, stable computations are enabled. However, the external calculations prevent the use of global MINLP solvers, which still rely on models given in explicit form [55]. To also capture possible local maxima, we employ integer cuts [42] to generate a ranking of candidates.

3. Case studies and results

The presented 1-stage CoMT-CAMD approach is demonstrated in two case studies for integrated design of ORC process and working fluid. In case study 1, a geothermal ORC at 120 °C based on Heberle and Brüggemann [14] is tailored using a single-objective optimization to demonstrate the general applicability of the approach (Section 3.1). Additionally, multi-objective optimization for the generation of combined heat and power is presented. In case study 2 (Sec-

tion 3.2), the process model is extended by a detailed model for preliminary turbine design [56]. The integrated design of the extended process and working fluid is performed for a solarthermal ORC with regenerator at 380 °C based on
 270 Casati et al. [57].

3.1. Case study 1: Geothermal ORC

In case study 1, the 1-stage CoMT-CAMD approach is applied to the integrated design of process and working fluid of a subcritical, non-regenerated ORC based on Heberle and Brüggemann [14] (Figure 2). Water from a geothermal
 275 well is considered as a heat source with an inlet temperature of $T_{\text{HC,in}} = 120^\circ\text{C}$ and a constant mass flow rate of $\dot{m}_{\text{HC}} = 66 \text{ kg s}^{-1}$ (Table 1).

Figure 2: ORC process of case study 1 in (a) flowsheet and (b) temperature-entropy diagram.

The integrated design of process and working fluid is first performed based on a single-objective optimization. Here, the net power output P_{net} is considered as objective function, since for geothermal applications the heat source is given and we want to get the most power out of it. Thus, the net power output is more appropriate as the performance index than the thermal efficiency of the process [18]. The net power output P_{net} is calculated as:

$$f_1 = P_{\text{net}} = |P_T| - |P_P| = \dot{m}_{\text{wf}} \cdot (\eta_{\text{s,T}} \cdot |h_{4,\text{s}} - h_3| - \eta_{\text{s,P}}^{-1} \cdot |h_{2,\text{s}} - h_1|), \quad (4)$$

where $\dot{m}_{\text{wf}}$ denotes the mass flow rate of the working fluid. The power output of the turbine P_T is calculated from an isentropic expansion in the turbine

considering the constant isentropic turbine efficiency $\eta_{s,T}$ and the isentropic
 280 enthalpy drop $h_{4,s} - h_3$ between the states 4s and 3, where the state 4s denotes
 the state at $p_{4,s} = p_{\text{cond}}$ and $s_{4,s} = s_3$ (Figure 2 b). In a similar way, the
 power input of the pump P_P is calculated from an isentropic compression in the
 pump considering the constant isentropic pump efficiency $\eta_{s,P}$ and the isentropic
 enthalpy drop $h_{2,s} - h_1$ between the states 1 and 2s, where the state 2s denotes
 285 the state at $p_{2,s} = p_{\text{evap}}$ and $s_{2,s} = s_1$. For the sake of clarity, the state 2s is
 not illustrated in Figure 2 b, since it is almost identical to state 2.

The process variables $x = (\dot{m}_{\text{wf}}, p_{\text{cond}}^{\text{red}}, p_{\text{evap}}^{\text{red}}, \Delta T_{\text{sh}})^T$ are: the mass flow rate
 of the working fluid $\dot{m}_{\text{wf}}$, the reduced operating pressures of the condenser $p_{\text{cond}}^{\text{red}}$
 and the evaporator $p_{\text{evap}}^{\text{red}}$ and the degree of superheating at turbine inlet ΔT_{sh} .
 Reduced pressures p^{red} are calculated by:

$$p^{\text{red}} = \frac{p}{p^{\text{crit}}}, \quad (5)$$

where p denotes the absolute pressure and p^{crit} denotes the critical pressure
 of the working fluid. We prefer reduced pressures as process variables instead
 of absolute pressures as reduced pressures allow easy bound constraints to en-
 290 sure only subcritical processes (here: $p^{\text{red}} < 0.8$). This leads to more stable
 computations. Pressure drops in evaporator and condenser are neglected in
 this case study ($p_2 = p_3 = p_{\text{evap}}$ and $p_1 = p_4 = p_{\text{cond}}$). Feasible heat trans-
 fer is ensured by constraining the minimum approach temperature ΔT_{min} in
 the heat exchangers. Additionally, the absolute pressure levels of the cycle are
 295 constrained to minimal and maximal absolute pressures p_{min} and p_{max} . Fur-
 thermore, the minimal and maximal reduced pressures $p_{\text{min}}^{\text{red}}$ and $p_{\text{max}}^{\text{red}}$ are also
 determined to constrain the reduced pressures. Feasible cooling in the condenser
 is ensured by a minimal allowed temperature $T_{\text{cond}}^{\text{min}}$. The size of the designed
 molecular structures is limited by a maximal number of functional groups (i.e.,
 300 $\sum_i n_i \leq n_{\text{max}} = 25$). This corresponds to 9,411 structurally feasible molecular
 structures fulfilling the constituting equations. The number of feasible molecu-
 lar structures is obtained by solving repeatedly a feasibility problem using the
 CAMD constraints only and integer cuts to exclude previous solutions.

Table 1: Specifications of the ORC based on Heberle and Brüggemann [14].

Parameter	Symbol	Value
Flow rate (heat carrier)	$\dot{m}_{\text{HC}}$	66 kg s^{-1}
Temperature (heat carrier)	$T_{\text{HC}}^{\text{in}}$	$120 \text{ }^{\circ}\text{C}$
Heat capacity (heat carrier)	$c_{\text{p,HC}}$	$4.2 \text{ kJ kg}^{-1} \text{ K}^{-1}$
Isentropic turbine efficiency	$\eta_{\text{s,T}}$	0.8
Isentropic pump efficiency	$\eta_{\text{s,P}}$	0.9
Min. approach temperature	ΔT_{min}	10 K
Min. abs. pressure	p_{min}	1 bar
Min. red. pressure	$p_{\text{min}}^{\text{red}}$	10^{-5}
Max. abs. pressure	p_{max}	50 bar
Max. red. pressure	$p_{\text{max}}^{\text{red}}$	0.8
Min. cooling temperature	$T_{\text{cond}}^{\text{min}}$	$20 \text{ }^{\circ}\text{C}$
Max. number of groups	n_{max}	25

The optimal net power output of the target calculated in the CoMT problem
 305 is $P_{\text{net}} = 1.84 \text{ MW}$. This target would apply for a hypothetical fluid and gives an
 upper bound on the performance possible for all fluids which can be described
 by GPC-SAFT. A ranking of the 10 best real working fluids is identified by
 the 1-stage CoMT-CAMD approach using integer cuts (Table 2). The approach
 identifies mainly alkanes and alkenes demonstrating the good performance of
 310 these families of working fluids. Propane proves to be the best working fluid
 for this ORC application with $P_{\text{net}} = 1.59 \text{ MW}$, which is 13.7% lower than
 the hypothetical target. Notably, two non-conventional polar working fluids,
 dimethyl ether and ethyl methyl ether, are identified showing the potential to
 generate new and promising working fluids. For the sake of completeness, the
 315 optimal process parameters of the identified working fluids are given in Appendix
 B.

To validate the resulting ranking, a subset of the molecular structures consid-
 ered in CAMD is generated and a brute-force process optimization is performed.

Table 2: Top 10 molecular structures identified by the 1-stage CoMT-CAMD approach with integer cuts for case study 1, the net power output and the rank (real) from an individual process optimization of 458 validation structures (=composed of less or equal than 10 functional groups).

Rank	Name	P_{net} / MW	Rank (real)
-	Target	1.84	-
1	Propane	1.59	1
2	Propene	1.57	2
3	Dimethyl ether	1.53	8
4	Isobutane	1.56	3
5	Isobutene	1.55	5
6	n-Butane	1.55	4
7	Neopentane	1.55	6
8	1-Butene	1.54	7
9	2-Butene	1.53	10
10	Ethyl methyl ether	1.53	9

The ranking contains only small molecular structure with $\sum_i n_i \leq n_{\text{max}} = 10$.
 320 Thus, all molecular structures are generated, which are composed of less or equal
 than 10 functional groups. This subset of molecular structures, the validation
 set, contains 458 working fluids. This subset is comparatively small. How-
 ever, the computational effort to confirm global optimality of the solution using
 enumerative search is already enormous. Furthermore, we suppose that larger
 325 molecular structures show unfavorable properties for power generation at the
 temperature level of this case study as no large molecules were identified in the
 1-stage CoMT-CAMD optimization. Each molecular structure of the validation
 set is tested by performing an individual process optimization. The resulting
real ranking serves as a measure for the quality of the ranking calculated by
 330 the 1-stage CoMT-CAMD approach. The approach identifies the top 10 of the
 global optimal working fluids of the limited search space nearly in the correct
 order. Thus, the local solver seems to perform well but integer cuts are required

to find all good solutions. To evaluate the computation effort, the numbers of function evaluations of the process model are compared: The individual process optimization of the 458 working fluids requires 75,523 function evaluations. Whereas, the 1-stage CoMT-CAMD approach needs 3,188 function evaluations to calculate a ranking of 10 working fluids despite the limited search space for individual process optimization considering only 5 % of the possible fluids. This computation effort corresponds to a saving of 95.8 %. The saving increases if all molecular structures would be considered for validation without limiting of the search space. The result shows that the 1-stage CoMT-CAMD approach is accurate and efficient for integrated design of process and working fluid.

The efficient computations allow the extension to multi-objective optimization. For this purpose, a combined heat and power application is considered. For all identified working fluids, the outlet temperature of the heat carrier $T_{\text{HC,out}}$ is higher than 50 °C. Due to the constraint of the minimal approach temperature in the evaporator, further cooling of the heat carrier reduces the evaporator temperature and, thus, the evaporator pressure. This reduction in turn decreases the thermal efficiency and net power output. Therefore, further cooling of the heat carrier temperature is prevented in the optimization. To further exploit the heat source, the remaining thermal energy of the heat carrier can be used to cover a heat demand.

Generation of combined heat and power (CHP) is favorable for geothermal applications of ORCs [14]. Heberle and Brüggemann [14] show that a connection in series of ORC and heat generation is an efficient CHP concept. For serially-connected heat generation, the heat is supplied by the heat carrier after leaving the evaporator of the ORC. The maximal heat supply temperature is thus limited by the ORC outlet temperature of the heat carrier $T_{\text{HC,out}}$. A rise of the outlet temperature of the heat carrier enhances heat generation, but reduces the ORC heat input and, thus, the net power output of the ORC. To capture the trade-off between heat and power generation, we employ multi-objective optimization within the integrated design of process and working fluid.

In addition to the net power output P_{net} (Equation (4)), the ORC outlet temperature of the heat carrier $T_{\text{HC,out}}$ is considered as second objective function calculated by:

$$f_2 = T_{\text{HC,out}} = T_{\text{HC,in}} - \frac{\dot{Q}_{\text{ORC,in}}}{\dot{m}_{\text{HC}} \cdot c_{\text{p,HC}}} = T_{\text{HC,in}} - \frac{\dot{m}_{\text{wf}} \cdot (h_3 - h_2)}{\dot{m}_{\text{HC}} \cdot c_{\text{p,HC}}}, \quad (6)$$

where $\dot{Q}_{\text{ORC,in}}$ denotes the ORC inlet heat flow calculated from the mass flow rate of the working fluid $\dot{m}_{\text{wf}}$ and the enthalpies h_i at the states 2 and 3.

365 The Pareto front is calculated using the normal constraint method [47]. Since we use a local MINLP solver, non-Pareto optimal solutions could be identified. Therefore, the normal constraint method is repeated, where the direction of movement of the normal constraint is changed. Both resulting Pareto fronts are superimposed and filtered according Pareto dominance to increase the accuracy
370 of the solution.

As seen for the single-objective optimization, propane maximizes the net power output (Figure 3). Here, the outlet temperature of the heat carrier is comparatively low ($T_{\text{HC,out}} = 58^\circ\text{C}$). The polar working fluid acetaldehyde is optimal for low net power output and high outlet temperatures. Depending on
375 the required heating temperature, the working fluid can be selected to maximize the net power output. Overall, 4 working fluids are identified along the Pareto front. Ethylacetylene shows the highest heat carrier outlet temperatures for a wide range of the net power output. Thus, ethylacetylene shows interesting thermodynamic fluid properties for CHP applications as it can cover a wide
380 range of operation conditions. In summer for example, the heat demand is low and the ORC can be operated in a range of high net power output. While during winter time, the heat demand is high and the ORC can be operated in a range of high outlet temperatures of the heat carrier using the same working fluid. The suppliers of ethylacetylene report that it is chemically stable at the thermal
385 conditions of the considered ORC cycle and that isomerization has only to be expected above 200°C [58]. However, ethylacetylene is highly reactive and its applicability as ORC working fluid has to be proved. A closer study reveals that ethyl methyl ether shows a similar performance as ethylacetylene and thus also

Figure 3: Pareto front for generation of combined heat and power in case study 1, which results from a multi-objective optimization of the net power output P_{net} versus the ORC outlet temperature of the heat carrier $T_{\text{HC,out}}$.

interesting thermodynamic fluid properties for CHP applications. The average
 390 deviation between the net power output of ethyl methyl ether and ethylacetylene
 is 0.65 % indicating practically equal performance of the working fluids.

The presented example demonstrates the possibilities and merits of multi-objective optimization within 1-stage CoMT-CAMD.

3.2. Case study 2: Solarthermal ORC

395 The second case study discusses the integrated design of process and working
 fluid of a subcritical, solarthermal ORC application with regenerator based on
 Casati et al. [57] (Figure 4). The working fluid is directly heated and evaporated

Figure 4: ORC process of case study 2 in (a) flowsheet and (b) temperature-entropy diagram.

in the solar field composed of parabolic troughs. The fixed solarthermal heat input $\dot{Q}_{solar,in}$ can heat the working fluid up to a temperature limit of $T^{out,max}_{evap} =$
 400 380 °C (Table 3). Most commonly, constant isentropic turbine efficiencies are assumed during working fluid design, i.e., all working fluids achieve the same performance in the turbine. To capture the impact of the working fluid, we include a detailed model of a one-stage radial inflow turbine in the process model recently developed by Lampe et al. [56] for the two-stage CoMT-CAMD
 405 approach. The turbine model enables the preliminary design of the turbine. The isentropic efficiency of the turbine $\eta_{s,T}$ is calculated within the model depending on both the process parameters and working fluid properties. Additionally, the detailed turbine model constrains crucial turbine design parameters to ensure that the turbine can actually be built for the considered working fluid and
 410 process parameters. A detailed description of the equations of the model is given in Appendix C. More details on the combined design of working fluids, process and turbine will be presented elsewhere [59] (in preparation).

For solarthermal ORC systems, thermal efficiency is an appropriate performance index [18] and is considered as objective function here. Since condensation is enabled by an air-cooling system, the effort of the blower P_B is regarded in the thermal efficiency η_{th} calculated by:

$$f_1 = \eta_{th} = \frac{P_{net}}{\dot{Q}_{solar,in}} = \frac{|\eta_G \cdot P_T| - |P_P| - |P_B|}{\dot{Q}_{solar,in}}, \quad (7)$$

where η_G denotes the efficiency of the generator.

Table 3: Specifications of the ORC based on Casati et al. [57] and Lampe et al. [56].

Parameter	Symbol	Value
Transferred heat	$\dot{Q}_{\text{solar,in}}$	463 kW
Max. temperature at outlet	$T_{\text{evap}}^{\text{out,max}}$	380 °C
Generator efficiency	η_{G}	0.95
Mechanical pump efficiency	$\eta_{\text{mech,P}}$	0.9
Isentropic pump efficiency	$\eta_{\text{s,P}}$	0.7
Min. approach temperature	ΔT_{min}	10 K
Min. abs. pressure	p_{min}	0.05 bar
Min. red. pressure	$p_{\text{min}}^{\text{red}}$	10^{-5}
Max. abs. pressure	p_{max}	30 bar
Max. red. pressure	$p_{\text{max}}^{\text{red}}$	0.8
Min. temperature	$T_{\text{cond}}^{\text{min}}$	80 °C
Max. number of groups	n_{max}	25
Max. Mach number	$Mach_{\text{max}}$	0.9
Min. blade height	$b_{2,\text{min}}$	0.1 mm
Max revolutions per minute	RPM_{max}	70,000
Max. expansion ratio	SVR_{max}	150

The process variables $x = (\dot{m}_{\text{wf}}, p_{\text{cond}}^{\text{red}}, p_{\text{evap}}^{\text{red}}, \Delta T_{\text{sh}})^{\text{T}}$ are: the mass flow rate
of the working fluid $\dot{m}_{\text{wf}}$, the reduced operating pressures at condenser outlet
 $p_{\text{cond}}^{\text{red}}$ and evaporator outlet $p_{\text{evap}}^{\text{red}}$, and the degree of superheating at turbine inlet
 ΔT_{sh} . Here, fixed pressure drops are considered in the solar field, the regenerator
and the air-side of the condenser based on Casati et al. [57]. Again, the minimum
approach temperature, the absolute and reduced, minimal and maximal pressure
levels, the minimal cooling temperature and the maximal segment number are
specified. The detailed model of the turbine constrains the following design and
operating parameters of the turbine: the Mach number $Mach$, the revolutions
per minute RPM , the blade height b_2 and the expansion ratio SVR .

The working fluids identified by 1-stage CoMT-CAMD are given in Table 4. The optimal thermal efficiency of the hypothetical target calculated in the CoMT problem is 26.0%. Ethyl cyclohexane shows the best thermal efficiency with 25.6%, which is 1.7% lower than the hypothetical target. The ranking of 10 working fluids identified by the 1-stage CoMT-CAMD approach with integer cuts exhibits mainly cyclic components, e.g., substituted cyclohexanes, benzenes and cyclopentanes. Also identified are the non-conventional branched alkene 3,3,4,4-tetramethyl pent-1-ene and alkyne 3,3,4,4-tetramethyl pent-1-yne. No polar working fluid appears in the ranking. Again, the optimal process parameters of the identified working fluids are given in Appendix B.

As in case study 1, an individual process optimization of the 458 validation structures is performed serving as a measure for the quality of the ranking. Here, 9 of the top 10 working fluids of the limited design space are identified by the 1-stage CoMT-CAMD approach with integer cuts. The 5th best molecular structure is missed due to the local nature of the solver. The individual process optimization of the 458 molecular structures requires 54,181 function evaluations. Whereas, the one-stage approach needs only 3,039 function evaluations to calculate 10 working fluids considering a 20 times larger design space. This corresponds to savings of 94.4%.

The case studies show the power of the integrated design using 1-stage CoMT-CAMD: the efficient optimization allows for fluid design in multi-objective optimization and allows using detailed process models.

4. Discussion

The 1-stage CoMT-CAMD approach enables us to identify the optimal working fluid and the corresponding optimal process parameters in one single optimization problem. Additional integer cuts can be used to generate a ranked list of working fluid candidates. The 1-stage CoMT-CAMD approach can efficiently identify the most promising working fluids from existing databases but goes beyond by also generating new and promising molecular structures. The process

Table 4: Top 10 molecular structures identified by the 1-stage CoMT-CAMD approach with integer cuts for case study 2, the net power output and the rank (real) from an individual process optimization of 458 validation structures (=composed of less or equal than 10 functional groups).

Rank	Name	η_{th} / %	Rank (real)
-	Target	26.02	-
1	Ethyl cyclohexane	25.57	1
2	Dimethyl cyclohexane	25.44	2
3	1,2,3,4-tetramethyl cyclopentane	25.29	3
4	Ethyl benzene	25.18	7
5	Xylene	25.15	10
6	3,3,4,4-Tetramethyl pent-1-ene	25.14	11
7	Isopropyl cyclopentane	25.23	4
8	Ethyl methyl cyclopentane	25.18	6
9	3,3,4,4-tetramethyl pent-1-yne	25.16	8
10	Trimethyl cyclohexane	25.16	9

model enables capturing all process-related trade-offs in a multi-objective optimization. It is shown that an extension of the process model by a detailed
455 model of the process components, e.g., the turbine, is possible. Thereby, additional constraints on crucial design parameters can be used to increase practical relevance of the solution.

4.1. Non-thermodynamic fluid properties

In the presented work, we consider only thermodynamic equilibrium prop-
460 erties of the working fluid. Additional crucial working fluid properties are neglected, e.g., GWP, flammability, toxicity or thermal stability. Also, the ozone depletion potential (ODP) of the working fluids has to be considered for halogenated working fluids. If GC approaches are available, the non-thermodynamic fluid properties can be directly integrated into the CAMD formulation as, e.g.,
465 by Papadopoulos et al. [21]. If no predictive methods based on GC approaches

exist, the resulting ranking has to be assessed a posteriori. A posteriori assessment of the ranking allows capturing trade-offs. In this work, highly flammable working fluids are identified in both case studies. Thus, flammable working fluids show high performance. However, the investment costs of flammable
 470 working fluids are higher to ensure safety. This trade-off can be captured in an a posteriori assessment.

4.2. Uncertainties of the GC approach

GC approaches introduce uncertainties in the result, since the GC-calculated pure component parameters differ from pure component parameters individually
 475 adjusted to measurement data, in the following referred to as 'fitted pure component parameters'. These uncertainties can have a large impact on the performance [22]. Lampe et al. [31] show that small deviations in the pure component parameters of PC-SAFT can have a significant impact, as the slope and curvature of the objective function vary strongly. To evaluate the uncertainties
 480 due to the GC approach, an individual process optimization is performed for the identified working fluids of both case studies considering the fitted pure component parameters of the working fluids if available. Thereby, isomers of the identified molecular structure are individually regarded if fitted pure component parameters are available. Isomers cannot be resolved by the employed
 485 first-order GC approach. The result is compared to the objective function value with GC-calculated parameters (Figure 5). Isomers are shown by more than one dot for one rank.

The average error in the objective is 0.8%. The GC-calculated pure component parameters underestimate the performance for most of the identified
 490 working fluids in both case studies. The identified working fluids are composed of similar groups, so that the uncertainties of the GC approach results in a systematic deviation of the objective function. Overall, the GC approach is suitable to estimate the pure component parameters of PC-SAFT within the integrated design of process and working fluid using the 1-stage CoMT-CAMD
 495 approach. Since a list of candidates should be the output, the 1-stage CoMT-

Figure 5: Net power output of the Top 10 identified working fluids of case study 1 (top) and thermal efficiency of the Top 10 identified working fluids of case study 2 (bottom) computed with GC-calculated and fitted pure component parameters. Note that the y-axis is zoomed into the range containing the top candidates for better visualization of the differences.

CAMD approach allows for efficient and accurate generation of this list. As improved versions of the GC approach become available, they can be readily integrated.

Isomers could be captured within the optimization using a GC approach of higher order. Such an approach increases the number of integer variables and, thus, the computation effort. In both case studies, all isomeric members show small differences in the objective, with average differences of less than 0.4%. Thus, the efficient first-order GC approach based on PC-SAFT is sufficient to predict isomers by the same molecular structure. The isomers can still be distinguished in the a posteriori assessment of the ranking.

4.3. Comparison to the two-stage CoMT-CAMD approach

The presented 1-stage CoMT-CAMD approach builds upon the two-stage CoMT-CAMD approach presented by Lampe et al. [1]. In order to compare both approaches, the two-stage CoMT-CAMD approach is applied to case study 1. In the two-stage CoMT-CAMD approach, a second degree Taylor approximation function $P_{\text{net,ap}}$ of the objective function and a first degree Taylor approximation of the inactive set of constraints are used in the MIQP problem of the structure-mapping (see Section 1). The results of both approaches are compared in Table 5. In addition, the value of the approximation function $P_{\text{net,ap}}$ of the two-stage CoMT-CAMD is also shown for the working fluids identified by 1-stage CoMT-CAMD and the value of a process optimization P_{net} is shown for the working fluids identified by the two-stage CoMT-CAMD approach. The values of P_{net} and $P_{\text{net,ap}}$ are calculated using GC-predicted pure component parameters. As in Section 3, the results are compared to an individual process optimization of the 458 generated validation structures consisting of compounds of less or equal than 10 functional groups. The rank of the resulting real ranking is shown in column Rank (real).

The two-stage CoMT-CAMD approach identifies 7 working fluids of the Top 10. The identified working fluids are mostly overestimated by the approximation function. Especially, acetaldehyde and ethane are heavily overestimated and

Table 5: Comparison of the Top 10 working fluids of case study 1 identified by the 1-stage CoMT-CAMD approach and the two-stage CoMT-CAMD approach: Objective function value of a process optimization P_{net} , the value of the approximation function $P_{\text{net,ap}}$ and the real rank resulting from an individual process optimization considering a reduces parameter space.

1-stage CoMT-CAMD					two-stage CoMT-CAMD				
Rank	Name	P_{net}	$P_{\text{net,ap}}$	Rank	Rank	Name	$P_{\text{net,ap}}$	P_{net}	Rank
		MW	MW	(real)			MW	MW	(real)
1	Propane	1.59	1.58	1	1	Acetaldehyde	2.33	1.24	15
2	Propene	1.57	1.57	2	2	2-Butene	2.22	1.53	10
3	Dimethyl ether	1.53	1.72	7	3	Isobutene	2.19	1.55	5
4	Isobutane	1.56	1.83	3	4	Ethane	2.17	0.97	24
5	Isobutene	1.55	2.19	5	5	n-Butane	2.01	1.55	4
6	n-Butane	1.55	2.01	4	6	1-Butene	1.88	1.54	7
7	Neopentane	1.55	2.38	6	7	Isobutane	1.83	1.56	3
8	1-Butene	1.54	1.88	7	8	Dimethyl ether	1.72	1.53	8
9	2-Butene	1.53	2.22	10	9	Propyne	1.59	1.52	12
10	Ethyl methyl ether	1.53	2.89	9	10	Propane	1.59	1.58	1

thus mis-classified. Neopentane and ethyl methyl ester, which are identified by 1-stage CoMT-CAMD, show a high approximation function value, but they are excluded by the linear approximation of the constraints and thus not identified by the two-stage CoMT-CAMD approach. The presented 1-stage CoMT-CAMD approach thus improves the already good result of the two-stage CoMT-CAMD approach. The working fluids are classified more accurately and no working fluid is excluded by a coarse approximation of the constraints. The adaptive strategy for refinement of the approximation pursued by the outer-approximation strategy proves useful to improve the classification of the identified working fluids.

5. Conclusions

In this work, we present a one-stage approach for the integrated design of ORC process and working fluid, so-called 1-stage CoMT-CAMD. The approach identifies the optimal working fluid and the corresponding optimal process parameters in one single MINLP optimization problem using the modern PC-SAFT EoS to model the working fluid. Computational efficiency allows for a single-objective optimization and even allows for a multi-objective optimization.

1-stage CoMT-CAMD builds upon the two-stage CoMT-CAMD approach presented by Lampe et al. [1]. A detailed process model and a detailed fluid model are combined to capture all thermodynamic trade-offs. The process model is based on equilibrium thermodynamics depending on both process variables and thermodynamic properties of the working fluid. The fluid properties are calculated in a thermodynamically consistent way using the PC-SAFT equation of state. A CAMD formulation in combination with a GC approach for PC-SAFT is used to integrate the fluid design as degree of freedom within the optimization. The considered molecular families of the GC approach are: alkanes, alkenes, 1-alkynes, cyclic components with alkyl side groups, aldehydes, ketones, ethers, formats and esters. The resulting MINLP problem can be solved considering one or multiple process-related objective functions to capture all process-based

trade-offs. Here, we use the deterministic local MINLP solver DICOPT, which
 555 is based on outer approximation extended by a relaxation strategy.

The presented 1-stage CoMT-CAMD approach is successfully applied to the
 integrated design of process and working fluid of two ORC applications. In both
 case studies, over 9,000 structurally feasible molecular structures are covered in
 the optimization. In case study 1, a geothermal, non-regenerated ORC applica-
 560 tion is tailored by a single-objective optimization. Mainly alkanes and alkenes,
 but also non-conventional ethers are identified. To demonstrate multi-objective
 optimization, the case study is adapted for generation of combined heat and
 power. The resulting Pareto front identifies various working fluids and corre-
 sponding process conditions, which maximize the net power output, depending
 565 on the needed heating temperature. In case study 2, a solarthermal ORC ap-
 plication with regenerator is considered. The process model is extended by a
 detailed model for turbine design to demonstrate the possibility of modelling
 the components of the process in a more detailed manner. Crucial turbine de-
 sign parameters can be constrained within the optimization to ensure that the
 570 turbine can actually be built for the designed working fluid.

The 1-stage CoMT-CAMD approach identifies the most promising fluids
 from existing databases but furthermore also generates new and promising
 molecular structures. The case studies show that the first order GC-approach
 for PC-SAFT is a suitable method to estimate the pure component parameters
 575 of PC-SAFT within the integrated design of process and working fluid. The
 1-stage CoMT-CAMD approach improves the already good results of the two-
 stage CoMT-CAMD approach. Thus, the 1-stage CoMT-CAMD approach is an
 accurate and efficient method to tailor an ORC to a specific application.

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Appendix A. Group contribution values

785 Appendix A.1. Group contribution values for heat capacity of the ideal gas

The heat capacity of the ideal gas c_p^{ig} is calculated by Joback's first-order group-contribution method [52]:

$$c_p^{\text{ig}} = A + B \cdot T + C \cdot T^2 + D \cdot T^3, \quad (\text{A.1})$$

where T denotes the temperature. The parameters A , B , C and D are calculated from the molecular structure of the working fluid $y^S = (n_1, n_2, \dots, n_m)^T$ by:

$$\begin{aligned} A &= \sum_{i \in I} n_i \cdot A_i - 37.93 \frac{\text{J}}{\text{mol K}}, \\ B &= \sum_{i \in I} n_i \cdot B_i + 0.210 \frac{\text{J}}{\text{mol K}^2}, \\ C &= \sum_{i \in I} n_i \cdot C_i - 3.91 \cdot 10^{-4} \frac{\text{J}}{\text{mol K}^3}, \\ D &= \sum_{i \in I} n_i \cdot D_i + 2.06 \cdot 10^{-7} \frac{\text{J}}{\text{mol K}^4}. \end{aligned} \quad (\text{A.2})$$

The group contribution values A_i , B_i , C_i and D_i of groups of type i are given in Table A.6.

Appendix A.2. Group contribution values for GPC-SAFT

The group contribution values for GPC-SAFT used in equation (3) are given
790 in Table A.7.

Table A.6: Group contribution values for the calculation of heat capacity of the ideal gas by Joback's first-order group-contribution method [52].

Group	A_i $\frac{\text{J}}{\text{mol K}}$	B_i $10^{-2} \frac{\text{J}}{\text{mol K}^2}$	C_i $10^{-5} \frac{\text{J}}{\text{mol K}^3}$	D_i $10^{-8} \frac{\text{J}}{\text{mol K}^4}$
$-\text{CH}_3$	19.5	-0.808	15.3	-9.67
$-\text{CH}_2-$	-0.909	9.50	-5.44	1.19
$\rangle\text{CH}-$	-23.0	20.4	-26.5	12.0
$\rangle\text{C}\langle$	-66.2	42.7	-64.1	30.1
$=\text{CH}_2$	23.6	-3.81	17.2	-10.3
$=\text{CH}-$	-8.0	10.5	-9.63	3.56
$\rangle\text{C}=\text{O}$	-28.1	20.8	-30.6	14.6
$-\text{C}\equiv\text{CH}$	32.37	-0.70	10.267	-6.641
$\rangle\text{C}^{\text{Arom}}=$	-8.25	10.1	-14.2	6.78
$\nearrow\text{CH}^{\text{Arom}}=$	-2.14	5.74	-0.164	-1.59
$\rangle\text{CH}^{\text{Pent}}-$	-20.5	16.2	-16.0	6.24
$\nearrow\text{CH}_2^{\text{Pent}}-$	-6.03	8.54	-0.8	-1.80
$\rangle\text{CH}^{\text{Hex}}-$	-20.5	16.2	-16.0	6.24
$\nearrow\text{CH}_2^{\text{Hex}}-$	-6.03	8.54	-0.8	-1.80
$-\text{CH}=\text{O}$	30.9	-3.36	16.0	-9.88
$\rangle\text{C}=\text{O}$	6.45	6.70	-3.57	0.286
$-\text{O}-\text{CH}_3$	45.0	-7.13	26.4	-15.15
$-\text{O}-\text{CH}_2-$	24.591	3.18	5.66	-4.29
$-\text{O}-\text{CH}=\text{O}$	24.1	4.27	8.04	-6.87
$-\text{O}-(\text{C}=\text{O})-$	24.5	4.02	4.02	-4.52

Table A.7: Group contribution values for GPC-SAFT [33].

Group	m_i / -	σ_i / Å	$(\epsilon/k)_i$ / K	μ_i / D
—CH ₃	0.611,98	3.720,2	229.9	0.0
—CH ₂ —	0.456,06	3.89	239.01	0.0
>CH—	0.143,04	4.859,7	349.64	0.0
>C<	−0.669,7	−1.787,8	107.68	0.0
=CH ₂	0.369,39	4.026,4	289.49	0.0
=CH—	0.563,61	3.551,9	216.69	0.0
>C=	0.863,67	3.181,5	156.31	0.0
—C≡CH	1.327,9	2.942,1	223.05	0.0
>C ^{Arom} =	0.153,71	3.962,2	527.2	0.0
∕CH ^{Arom} =	0.423,35	3.727	274.41	0.0
>CH ^{Pent} —	0.033,14	7.719,0	1,297.7	0.0
∕CH ₂ ^{Pent} —	0.467,42	3.727,2	267.16	0.0
>CH ^{Hex} —	0.028,80	8.977,9	1,306.7	0.0
∕CH ₂ ^{Hex} —	0.394,96	3.912,6	289.03	0.0
—CH=O	1.577,4	2.803,5	242.99	2.455,6
>C=O	1.223	2.812,4	249.04	3.243,2
—O—CH ₃	1.653,9	3.069,7	196.05	1.386,6
—O—CH ₂ —	1.134,9	3.203,7	187.13	2.744
—O—CH=O	1.752,5	2.904,3	229.63	2.791,6
—O—(C=O)—	1.506,3	2.816,6	222.52	3.165,2

Appendix B. Optimal process parameters of the identified working fluids

Table B.8: Optimal process parameters of the top 10 molecular structures identified by the 1-stage CoMT-CAMD approach with integer cuts for case study 1.

Rank	Name	$\dot{m}_{\text{wf}}$ kg s ⁻¹	p_{cond} bar	p_{evap} bar	ΔT_{sh} K
-	Target	78.9	15.36	43.26	0
1	Propane	43.8	8.14	24.63	0
2	Propene	45.0	10.16	30.16	0
3	Dimethyl ether	37.4	5.92	19.26	0
4	Isobutane	40.9	2.78	9.30	0
5	Isobutene	40.0	2.47	8.75	0
6	n-Butane	38.6	2.17	7.59	0
7	Neopentane	43.5	1.18	4.34	0
8	1-Butene	38.8	2.66	8.95	0
9	2-Butene	36.3	2.05	7.34	0
10	Ethyl methyl ether	35.7	1.62	6.39	0

Table B.9: Optimal process parameters of the top 10 molecular structures identified by the 1-stage CoMT-CAMD approach with integer cuts for case study 2.

Rank	Name	$\dot{m}_{\text{wf}}$ kg s ⁻¹	p_{cond} bar	p_{evap} bar	ΔT_{sh} K
-	Target	0.92	0.21	29.99	41.8
1	Ethyl cyclohexane	0.86	0.21	28.42	58.0
2	Dimethyl cyclohexane	0.89	0.27	27.92	66.4
3	1,2,3,4-tetramethyl cyclopentane	0.94	0.18	25.75	57.8
4	Ethyl benzene	0.80	0.17	22.63	76.6
5	Xylene	0.79	0.15	20.74	79.7
6	3,3,4,4-Tetramethyl pent-1-ene	0.98	0.25	26.33	60.6
7	Isopropyl cyclopentane	0.86	0.24	28.63	68.2
8	Ethyl methyl cyclopentane	0.87	0.26	28.38	71.1
9	3,3,4,4-tetramethyl pent-1-yne	0.93	0.20	28.25	57.3
10	Trimethyl cyclohexane	0.93	0.14	20.92	62.7

Appendix C. Equations for the Turbine Model

In this work, we consider a one-stage radial inflow turbine developed by
795 Lampe et al. [56]. In the following, we use the notation of the states and
velocities as defined in Figure C.6. The working fluid enters the nozzle of the
turbine in state 1, the rotor in state 2 and leaves the turbine in state 3, as the
diffuser is neglected. Stagnation states of the working fluid are denoted by 0X,
when the working fluid recovers the kinetic energy from state X. The state 3ss
800 corresponds to an isentropic turbine, the state 3s to an isentropic rotor and a
real nozzle.

The isentropic efficiency of the turbine $\eta_{s,T}$ is calculated from loss coefficients
for the rotor ζ_R and nozzle ζ_N as well as fluid velocities as [60]:

$$\eta_{s,T} = \frac{h_{01} - h_{03}}{h_{01} - h_{3ss}} = \frac{\Delta w}{\Delta w + \frac{1}{2} \left(c_3^2 + w_3^2 \zeta_R + c_2^2 \zeta_N \left(\frac{T_3}{T_2} \right) \right)}, \quad (\text{C.1})$$

Figure C.6: a) Schematic of the radial turbine as well as the corresponding velocity triangles and b) Enthalpy-entropy diagram of the expansion process in the turbine

where $\Delta w = h_{01} - h_{03}$ denotes the specific work of the turbine. The loss coefficients for the rotor ζ_R and nozzle ζ_N are calculated by:

$$h_3 - h_{3s} = \frac{1}{2} w_3^2 \zeta_R \quad (C.2)$$

$$h_{3s} - h_{3ss} = \frac{1}{2} c_2^2 \zeta_N \frac{T_3}{T_2}. \quad (C.3)$$

We rewrite the isentropic efficiency as an implicit function for turbine efficiency $\eta_{s,T} = f(p_{01}, T_1, p_3, y)$. Using assumptions for the degree of reaction R [60, 61, 62]:

$$R = \frac{h_2 - h_3}{h_1 - h_3} = 0.15, \quad (C.4)$$

the exit velocity ratio Φ [63]:

$$\Phi = \frac{c_3}{U_2} = 0.25, \quad (C.5)$$

and the blade loading coefficient Ψ :

$$\Psi = \frac{U_2}{C_0} = 0.7, \quad (C.6)$$

we can express the velocities in Equation (C.1) in terms of these variables. c_2 can be expressed as

$$c_2 = \sqrt{2 (h_{02} - h_2)}. \quad (C.7)$$

An energy balance around the nozzle yields $h_{01} = h_{02}$. Using Equation (C.4) and neglecting the diffuser (state 3 = state 4) yields

$$c_2 = \sqrt{2 (h_{01} - h_3 - R (h_1 - h_3))} , \quad (C.8)$$

where $h_{01} = h_1 + \frac{1}{2}c_1^2 \overset{0}{=} h(p_1, T_1, y)$. The enthalpy $h(p, T, y)$ defined by pressure p , temperature T and the pure component parameters y can be calculated using PC-SAFT.

The next velocity in Equation (C.1), c_3 , can be expressed from the definition of Φ , Ψ (in Equation (C.5) and Equation (C.6), respectively) and the sprouting velocity $C_0 = \sqrt{2(h_{01} - h_{3ss})}$, which is the artificial velocity corresponding to a kinetic energy equal to the total enthalpy drop of an isentropic turbine

$$c_3 = \Phi \Psi C_0 = \Phi \Psi \sqrt{2(h_{01} - h_{3ss})} . \quad (C.9)$$

The relative velocity at the rotor outlet w_3 can be expressed using the velocity triangle in Figure C.6 as

$$w_3 = \sqrt{U_3^2 + c_3^2} = \sqrt{\left(U_2 \frac{D_3}{D_2}\right)^2 + c_3^2} \quad (C.10)$$

$$= \sqrt{\left(\Psi C_0 \frac{D_3}{D_2}\right)^2 + c_3^2} \quad (C.11)$$

and c_3 can be expressed as shown above. Inserting in Equation (C.1), using $h_{01} - h_{03} = \eta_{s,T} (h_{01} - h_{3ss})$ and canceling $h_{01} - h_{3ss}$ yields

$$\eta_{s,T} = \frac{\eta_{s,T}}{\eta_{s,T} + \Phi^2 \Psi^2 + \zeta_R \Psi^2 \left(\Phi^2 + \left(\frac{D_2}{D_3} \right)^2 \right) + \zeta_N (1-R) \left(\eta_{s,T} + \Phi^2 \Psi^2 \right) \frac{T_3}{T_2}} \quad (C.12)$$

ignoring the trivial solution of no power output $\eta_{s,T} = 0$ we obtain

$$\eta_{s,T} = \frac{1 - \Phi^2 \Psi^2 - \zeta_R \Psi^2 \left(\Phi^2 + \left(\frac{D_2}{D_3} \right)^2 \right) - \zeta_N (1-R) \Phi^2 \Psi^2 \frac{T_3}{T_2}}{1 + \zeta_N (1-R) \frac{T_3}{T_2}} \quad (C.13)$$

805 where the temperature ratio across the rotor $\frac{T_3}{T_2}$ is still depending on the efficiency of the turbine, but it has limited influence on the numerical value of the efficiency [60]. However, Equation (C.13) can be used to determine $\eta_{s,T}$ iteratively.

Using $p_3 = p_4$, T_3 can be expressed as $T(p_4, h_3)$. The enthalpy in state 3 can be expressed as

$$h_3 = h_{03} - \frac{1}{2}c_3^2 = h_{01} - (\eta_{s,T} + \Phi^2\Psi^2)(h_{01} - h_{3ss}) \quad (C.14)$$

where $h_{3ss} = h(p_4, s(p_1, T_1), y)$ and $h_{01} = h_1 = h(p_1, T_1, y)$ are known. Additional to the calculation of the isentropic efficiency of the turbine, the model allows for a preliminary design of the turbine. The blade height can be calculated from the mass flow at the rotor inlet.

$$b_2 = \frac{\dot{m}_{wf}}{\rho_2 c_{m2} \pi D_2} \quad (C.15)$$

The diameter of the inlet, in turn, can be calculated from conservation of mass flow rate through the rotor

$$\dot{m}_{wf} = \dot{m}_{wf,3} = \dot{m}_{wf,2} \quad (C.16)$$

$$\Leftrightarrow D_2 = \sqrt{\frac{4 \dot{m}_{wf}}{\rho_3 \Phi U_2 \pi \left(\frac{D_{3s}}{D_2}\right)^2 \left(1 - \left(\frac{D_{3h}}{D_{3s}}\right)^2\right)}} \quad (C.17)$$

where $\frac{D_{3s}}{D_2}$ and $\frac{D_{3h}}{D_{3s}}$ are fixed. The unknown meridonal velocity c_{m2} can be calculated from the velocity triangle, as

$$c_{m2}^2 = c_2^2 - c_{t2}^2 \quad (C.18)$$

and velocity c_2 is known from Equation (C.8). The tangential velocity c_{t2}^2 can be calculated from

$$c_{t2} = \frac{h_{01} - h_{03}}{\Psi \sqrt{2(h_{01} - h_{3s})}} \quad (C.19)$$

Finally, Equations (C.8), (C.15), (C.17), (C.19) yield

$$b_2^2 = \frac{\dot{m} \rho_3 \Phi \Psi \sqrt{h_{01} - h_{3s}} \left(\frac{D_{3s}}{D_2}\right)^2 \left(1 - \left(\frac{D_{3h}}{D_{3s}}\right)^2\right)}{4\rho_2^2 (2(h_{01} - h_3) - R(h_1 - h_3)) - \frac{(h_{01} - h_{03})^2}{2\Psi^2(h_{01} - h_{3s})}}, \quad (C.20)$$

where $\rho_2 = \rho(p_2, T_2, y)$ and $\rho_3 = \rho(p_3, T_3, y)$.

The speed of rotation can easily be calculated as

$$RPM = \frac{U_2}{D_2} \quad (C.21)$$

with Equation (C.17) and $U_2 = \Psi \sqrt{2(h_{01} - h_{3ss})}$. Finally, as all velocities are known, the Mach numbers in stage x can be calculated as

$$M_x = \frac{v_x}{w_x}, \quad (C.22)$$

810 where the speed of sound w_x is a function of PC-SAFT.