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Integrated design of ORC process and working fluid using PC-SAFT and Modelica

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Abstract

Organic Rankine Cycles (ORC) use low-temperature heat to generate electrical power. To use the full potential of a heat source, the ORC has to be tailored to the specific application. Tailoring a cycle means an integrated design of both process and working fluid. This integrated design leads to complex mixed-integer nonlinear program (MINLP) optimization problems. To avoid this complexity, working fluid candidates are commonly preselected using heuristic guidelines; subsequently, the process is optimized for the set of preselected working fluids. However, the preselection can fail, leading to suboptimal solutions.

An approach for integrated design of ORC process and working fluid is the Continuous-Molecular Targeting–Computer-aided Molecular Design (CoMT-CAMD) approach. CoMT-CAMD employs the physically-based Perturbed-chain Statistical Associating Fluid Theory (PC-SAFT) equation of state as thermodynamic model of the working fluid. In PC-SAFT, each working fluid is described by a set of pure component parameters. In a first step, the so-called CoMT step, the discrete pure component parameters are relaxed resulting in a hypothetical optimal working fluid and the corresponding optimal process. In a second step, real working fluids with similar properties are identified using Computer-aided Molecular Design and a second-order Taylor approximation of the objective function around the hypothetical optimum. So far, the process models in CoMT-CAMD were implemented in a procedural programming language, which hinders the reusability, the use for more complex processes and dynamic simulations. In this work, we integrate CoMT-CAMD into the object-oriented modelling language Modelica. For this purpose, Modelica is directly linked to PC-SAFT. Thereby, already existing model libraries for Modelica can be used to model the ORC process. The resulting design approach is applied to the integrated design of an ORC process and working fluid for a geothermal power station.

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Keywords: Modelica; PC-SAFT; fluid design; Computer-aided Molecular Design; optimization

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1. Introduction

Organic Rankine Cycles (ORC) generate electrical power from low temperature heat [1]. Low temperature heat sources can be, e.g., waste heat, solar heat or geothermal heat. To use the full potential of a heat source, the ORC has to be tailored to the specific application. For tailoring a cycle, both process and working fluid have to be optimized simultaneously. Today, the fluid selection and process optimization are usually performed in 2 steps [2]: In a first step, a preselection of potential working fluids is carried out based on heuristic guidelines and experience. Subsequently, the preselected working fluids are assessed in individual process optimizations. However, the preselection relies on heuristic guidelines. If the heuristics fail, the 2-step approach leads to suboptimal solutions.

Therefore, the fluid selection has to be integrated into the process optimization to obtain overall optimal solutions [2]. However, such an integrated design leads to a challenging mixed-integer nonlinear programming (MINLP) optimization problem [3]. Thus, systematic solution approaches for the integrated design of ORC process and working fluid have been developed as recently reviewed by Linke et al. [2]: Papadopoulos et al. presented an approach for the integrated design of ORC process and working fluid mixtures based on a process-level objective function and Computer-aided Molecular Design (CAMD) [4]. A CAMD-based design approach for pure working fluids is proposed by Palma-Flores et al. [5]. Here, working fluid candidates are selected using multi-objective optimization and subsequently assessed in three ORC flowsheet configurations. Integrated design approaches for fluids and processes are also addressed for further engineering problems such as solvent design in chemical engineering. An approach for the integrated design of process and solvent has been presented by Pereira et al. for the absorption of CO₂ [6]. Herein, the search space is limited to linear alkanes, but this approach shows the advantages of an integrated design of processes and solvents. Recently, the same group extended their work by Burger et al. to a hierarchical approach for the integrated design of solvent and process using simplified shortcut models [7].

Our group proposed the so-called Continuous-Molecular Targeting–Computer-aided Molecular Design (CoMT-CAMD) approach for the integrated design of process and solvents for CO₂ absorption [8]. This approach has also been successfully applied for the integrated design of ORC processes and working fluids [9]. In CoMT-CAMD, the physically-based Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [10] equation of state is used to model the working fluid. In PC-SAFT, a working fluid is represented by a set of pure component parameters. In a first step, the so-called CoMT step, the pure component parameters of PC-SAFT are relaxed during the integrated design of process and working fluid transforming the MINLP into a nonlinear program (NLP). The result of the CoMT step is a hypothetical optimal working fluid, the so-called target, and the corresponding optimal process conditions. In the second step, the so-called structure-mapping, real working fluids with similar properties as the target are identified. For this purpose, the objective function values of real working fluids are estimated using a second-order Taylor approximation of the objective function around the target. A CAMD formulation allows designing promising working fluids by solving the resulting mixed-integer quadratic program (MIQP) [11].

Previously, CoMT-CAMD was implemented in a procedural programming language which hinders the reusability of the equipment models, fast development and easy adaptation of processes, as well as the consideration for more complex systems and dynamic simulations. These shortcomings can be overcome by using a programming language suited for object-oriented and equation-based modeling like Modelica [12].

In this work, we present the CoMT-CAMD approach for the integrated design of ORC process and working fluid based on Modelica process models. The object-oriented and equation-based modeling with Modelica enables the reusability of models as well as using existing model libraries (see reference [13] for a dynamic ORC library from Casella et al.), easy drag-and-drop flowsheeting and modeling of complex processes within CoMT-CAMD.

In section 2, the general framework of CoMT-CAMD is presented. The integration of CoMT-CAMD in Modelica is shown in section 3. In section 4, the resulting design approach is applied for the design of a geothermal ORC application, while conclusions are drawn in section 5.

2. CoMT-CAMD approach for integrated design of ORC process and working fluid

The Continuous-Molecular Targeting–Computer-Aided Molecular Design (CoMT-CAMD) approach for integrated design of process and working fluid was originally proposed by Bardow et al. (2010). In CoMT-CAMD,

the thermodynamic properties of the working fluid are calculated using the PC-SAFT equation of state [10]. The CoMT-CAMD approach consists of two main steps, the CoMT step and the structure-mapping step (Figure 1).

In the CoMT step, the pure component parameters describing a working fluid in PC-SAFT are treated as continuous degrees of freedom transforming the MINLP into an NLP. In this way, the pure component parameters and the process conditions can be optimized simultaneously using standard NLP solvers. The result of the CoMT step is the so-called target, i.e., the set of PC-SAFT pure component parameters of a hypothetical optimal working fluid and the corresponding optimal process conditions.

In the structure-mapping step, real working fluids are identified which best match the performance of the target. In order to estimate the process performance of real fluids, a second-order Taylor approximation of the objective function around the hypothetical optimum is used as assessment criterion. The real working fluid with the best performance can either be identified from a database of known working fluids [9] or designed using Computer-Aided Molecular Design (CAMD) [11]. To design promising working fluids with CAMD, the molecular structure of the working fluids is linked to PC-SAFT using the homosegmented group contribution approach of PC-SAFT [14]. The molecular structure of the most promising working fluid is identified using the second-order Taylor approximation as objective function. This leads to an efficient mixed-integer quadratic programming (MIQP) optimization problem.

To overcome shortcomings of the Taylor approximation, it is advisable to not only design one single working fluid but to obtain a ranking of candidates. This can be accomplished by performing the MIQP repeatedly utilizing integer cuts [15] to exclude previous solutions from the design space. Finally, individual process optimizations are performed for the best working fluid candidates to obtain the real objective function values as well as the corresponding process conditions. The whole workflow of the integrated process and molecular design is shown in Figure 1.

Details on the CoMT step are described in section 2.1 before the PC-SAFT equation of state is discussed in section 2.2. The structure-mapping step with CAMD is explained in more detail in section 2.3 and the final process optimizations in section 2.4.

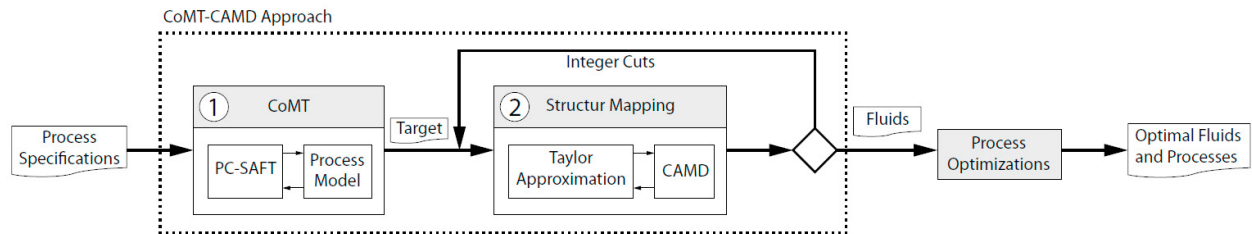


Figure 1: Workflow of the CoMT-CAMD approach

2.1. Continuous-Molecular Targeting (CoMT)

The Continuous-Molecular Targeting (CoMT) is the first step of the integrated process and working fluid design with CoMT-CAMD. The thermodynamic behavior of the working fluids is described with the PC-SAFT equation of state based on pure component parameters. The PC-SAFT pure component parameters are relaxed in the CoMT step and optimized simultaneously with the process conditions. By treating the discrete PC-SAFT pure component parameters as continuous variables, the optimization problem is transformed from a mixed-integer nonlinear programming (MINLP) into a nonlinear program (NLP) problem [11]:

$$\begin{aligned}
 & \max_{x,y} f(x,y) \\
 & s. t. \left. \begin{aligned} g_1(x,y) &\leq 0 \\ g_2(x,y) &= 0 \end{aligned} \right\} \text{"process model"} \\
 & h(x,y) = 0 \quad \text{"PC-SAFT"} \\
 & Ay \leq b \quad \text{"convex hull"} \\
 & x_{min} \leq x \leq x_{max} \in \mathbb{R}^m \\
 & y_{min} \leq y \leq y_{max} \in \mathbb{R}^l.
 \end{aligned} \tag{1}$$

Here, x and y denote the vectors containing the process degrees of freedom (e.g., pressure levels) and the PC-SAFT pure component parameters, respectively. The objective function $f(x, y)$ is a process-based performance measure such as the net power output or efficiency. The process model is formulated in terms of inequality constraints $g_1(x, y)$ and equality constraints $g_2(x, y)$. The PC-SAFT equation of state $h(x, y)$ is used to compute the thermodynamic properties (e.g., enthalpies) of the working fluids. Bounds are set both on the process degrees of freedom x and the PC-SAFT pure component parameters y . Additionally, linear inequality constraints $Ay \leq b$ are used to set up a convex hull around the region in the design space of the PC-SAFT pure component parameters where real molecules can be found (see references [9,11] for details). This ensures that the optimization in the CoMT step results in a hypothetical optimal working fluid with properties similar to those of real fluids.

The results of the optimization in the CoMT step are the PC-SAFT pure component parameters y^* for the hypothetical optimal working fluid, the so-called target, and the corresponding optimal process conditions x^* . As the parameters y^* do generally not correspond to the pure component parameters of a real working fluid, the result of the CoMT step is used for the identification of the most suitable real working fluids in the structure-mapping step.

2.2. PC-SAFT Equation of State

The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) [10] is a physically-based equation of state model for the residual Helmholtz energy. In PC-SAFT, molecules are considered as chains of hard spheres (segments) which may interact with each other. Pure components are described based on typically 3 to 7 pure component parameters. As only non-polar and non-associating working fluids are considered in this work, 3 pure component parameters are sufficient: the segment number m , the segment diameter σ and the segment dispersion energy ε/k .

Since residual properties are calculated with PC-SAFT, an additional caloric property is needed as reference to enable the calculation of absolute caloric properties. In this work, we consider the heat capacity of the ideal gas as reference. As all thermodynamic properties have to be described solely based on PC-SAFT pure component parameters in the CoMT step, the ideal gas heat capacity is calculated using a Quantitative Structure-Property Relationship (QSPR) with PC-SAFT pure component parameters as inputs [11]. Additionally, another QSPR model is used to obtain molar masses [11]. Thus, all relevant thermodynamic properties are calculated consistently and solely based on PC-SAFT pure component parameters.

2.3. Structure-Mapping using Computer-Aided Molecular Design (CAMD)

In this work, Computer-Aided Molecular Design (CAMD) is used in the structure-mapping to design real working fluids with an objective function value close to the target from the CoMT step. In contrast to searching for candidates in a databank of known working fluids, both known and new fluids can be considered with CAMD. To facilitate the molecular design, a measure is needed to predict the expected performance of designed fluids in the considered process. The performance should be predicted solely based on the PC-SAFT pure component parameters y to avoid time-consuming process optimizations during the structure-mapping. Thus, a second-order Taylor approximation $\hat{f}(y)$ around the hypothetical optimum y^* from the CoMT step is used as performance measure calculated as:

$$\hat{f}(y) = f^{opt}(y^*) + \left. \frac{df^{opt}}{dy} \right|_{y=y^*} \cdot (y - y^*) + \frac{1}{2} \cdot (y - y^*)^T \cdot \left. \frac{d^2f^{opt}}{dy^2} \right|_{y=y^*} \cdot (y - y^*). \quad (2)$$

where f^{opt} is the maximal objective function value achievable in a process optimization for a fixed set of PC-SAFT pure component parameters y .

The CAMD formulation optimizes the molecular structure with respect to the Taylor approximation $\hat{f}(y)$ as performance measure. For the evaluation of $\hat{f}(y)$, the PC-SAFT pure component parameters y are calculated from the molecular structure of the working fluids. For this purpose, Lampe et al. [11] use the homosegmented group contribution (GC) approach of PC-SAFT from Sauer et al. [14], which we also use in this work. The set of functional groups includes all non-polar groups used by Lampe et al. [11] so that alkanes, alkenes, 1-alkynes, benzenes, cyclohexanes and cyclopentanes are considered in this work. The set of functional groups can be easily extended in further studies. The CAMD problem is formulated as an MIQP [11]:

$$\begin{aligned}
 & \max_n \hat{f}(y) \\
 & \text{s. t.} \quad GC(n) = y \\
 & \quad \quad FEAS(n) \leq 0 \\
 & \quad \quad Ay \leq b \\
 & \quad \quad n \in \mathbb{Z}^0
 \end{aligned} \tag{3}$$

Here, a molecule is described based on the functional groups constituting its molecular structure represented by the vector n . The pure component parameters y are calculated from the molecular structure ($GC(n) = y$). A feasible connectivity of the functional groups constituting a molecule is ensured by additional constraints ($FEAS(n) \leq 0$) [16]. Moreover, a convex hull ($Ay \leq b$) as described in section 2.1 is also used in the structure-mapping.

The result of the MIQP is the optimal molecular structure, which optimizes the second-order Taylor approximation. As there are inaccuracies in the models and methods, it is desired to obtain not only one working fluid, but a ranking of candidates from the structure-mapping step. Consequently, the MIQP is solved repeatedly using integer cuts [15] to exclude previous solutions from the design space and get a ranking of promising fluids.

2.4. Final process optimizations

In the structure mapping, a second-order Taylor approximation of the objective function is used as performance measure. However, this Taylor approximation does not exactly match the real process performance achievable with a given working fluid. Thus, the candidate ranking from the structure-mapping step may differ from the real ranking. Therefore, individual process optimizations are performed for the identified working fluids from the structure-mapping to refine the ranking.

3. CoMT-CAMD with Modelica

Previously, integrated design with CoMT-CAMD was based on process models implemented in a procedural programming language. The procedural programming language hinders the reusability of models as well as the investigation of process variants. To overcome these limitations, we present the integrated process and molecular design with CoMT-CAMD based on process modeling with Modelica [17]. Modelica is an object-oriented language for physical modeling which enables convenient model reuse and drag-and-drop flowsheeting [12,17].

As CoMT-CAMD is based on property predictions with PC-SAFT, functions for all relevant property calculations with PC-SAFT have to be available for process modeling with Modelica. For this purpose, a PC-SAFT implementation in FORTRAN 90 is coupled to Modelica models using the Modelica external function interface (see reference [17] for details). All Modelica functions required for the interface itself and for convenient use of PC-SAFT property calculations during process modeling are included in a Modelica package [18].

The whole workflow of the Modelica-based CoMT-CAMD approach is shown schematically in figure 2.

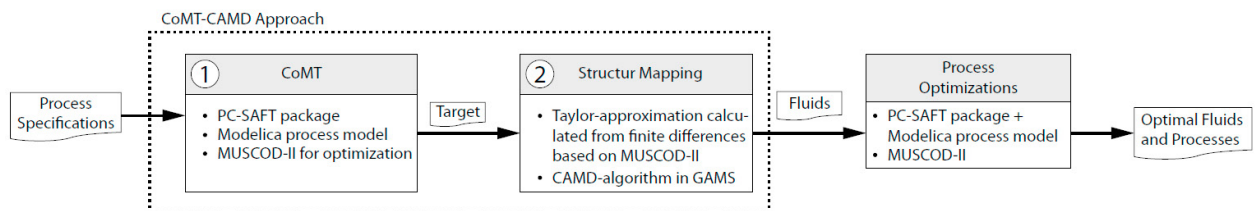


Figure 2: Workflow of the integrated molecular and process design with CoMT-CAMD including the tools used in the individual steps

For the CoMT step, the dynamic optimization package MUSCOD-II [19] is used to solve the NLP given in Problem (1). Even though the integrated design of process and working fluid is performed for steady state processes in this work, MUSCOD-II is used for optimization to demonstrate its potential for CoMT-CAMD and to open up possibilities for future extension of the approach to dynamic systems. The derivatives of the second-order Taylor approximation

required in the structure-mapping step (c.f. Section 2.2) are approximated with finite differences computed with MATLAB. The required objective function values are calculated using MUSCOD-II and the Modelica process models. The CAMD algorithm is implemented in the high-level modeling system GAMS (General Algebraic Modeling System) [20]. The solver CPLEX [21] is used to solve the MIQP problem given in Problem (3). The final process optimizations (c.f. Section 2.4) are performed with MUSCOD-II and the Modelica process models.

4. Case study: Design of a subcritical geothermal ORC power plant

The CoMT-CAMD approach based on process modelling with Modelica is applied for the integrated design of process and working fluid of a subcritical geothermal ORC power plant. The process is modeled by drag-and-drop flowsheeting using model libraries in Modelica. The specifications of the case study are presented in section 4.1. In section 4.2, the results of the integrated design of ORC process and working fluid are shown.

4.1. Specifications of the case study

In this case study, we consider a medium-scaled subcritical ORC without regenerator operating in steady-state based on Heberle and Brüggemann [22] (see Table 1). The working fluid is evaporated using geothermal water as heat source with an inlet temperature of $T_{HS}^{in} = 120\text{ °C}$. In the condenser, cooling water with an inlet temperature of $T_{CW}^{in} = 15\text{ °C}$ is used to enable condensation. The ORC flowsheet in Modelica and a qualitative temperature-entropy diagram of the considered ORC are shown in figure 3.

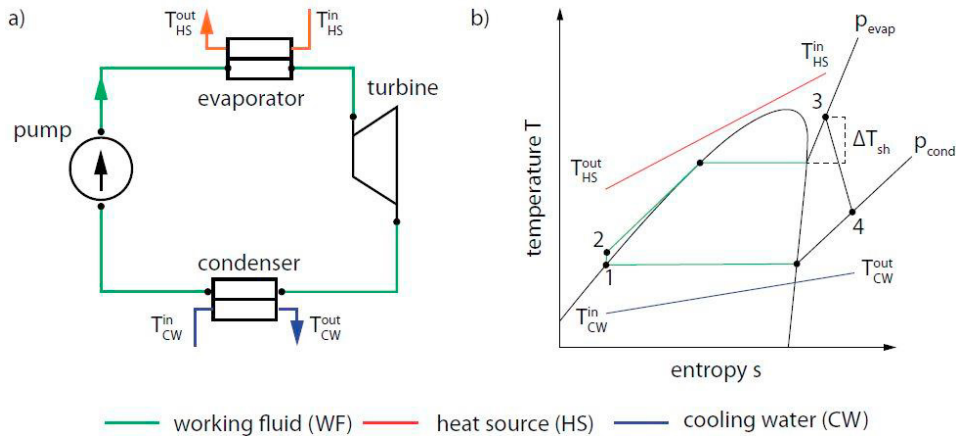


Figure 3: Flowsheet and qualitative temperature-entropy diagram of the ORC process

The net power output of the ORC power plant P_{net} is used as objective function for the integrated design of ORC process and working fluid and calculated as:

$$f = P_{net} = \eta_G \cdot (|P_T| - |P_P|) = \eta_G \cdot \dot{m}_{WF} \cdot (|h_4 - h_3| - |h_2 - h_1|), \quad (4)$$

where η_G denotes the generator efficiency, P_T the power output of the turbine, P_P the power input of the pump and h_i the specific enthalpy of state i . The rotating equipment is modelled by constant isentropic efficiencies $\eta_{is,P}$ for the pump and $\eta_{is,T}$ for the turbine. Pressure drops in the heat exchangers are neglected. The process degrees of freedom $x = (\dot{m}_{WF}, p_{cond}^{red}, p_{evap}^{red}, \Delta T_{sh})^T$ are the mass flow rate of the working fluid \dot{m}_{WF} , the reduced pressure levels ($p_i^{red} = p_i/p_{critical}$) of the condenser p_{cond}^{red} as well as the evaporator p_{evap}^{red} and the degree of superheating ΔT_{sh} . The inequality constraints of the process g_2 are the limitation on the absolute pressure levels (p_{min}, p_{max}) as well as the reduced pressure levels ($p_{min}^{red}, p_{max}^{red}$) and the steam quality at turbine outlet β_{min}^{turb} (see Table 1). The minimal approach temperature in the heat exchangers ΔT_{min}^{pinch} is additionally constrained to ensure feasible heat transfer.

Table 1: Specifications of the case study based on Heberle and Brüggemann [22].

Parameter	Symbol	Value	Parameter	Symbol	Value
heat source mass flow rate	\dot{m}_{HS}	66 kg/s	min./max. reduced pressure	$p_{min}^{red}/p_{max}^{red}$	0.01 / 0.8
heat source inlet temperature	T_{HS}^{in}	120 °C	cooling water inlet/ outlet temperature	T_{CW}^{in}/T_{CW}^{out}	15 °C / 20 °C
heat source/cooling water specific heat capacity	c_{HS}/c_{CW}	4200 J/ (kg K)	min. approach temperature	ΔT_{min}^{pinch}	5 K
min./max. absolute pressure	$p_{min}/$ p_{max}	1 bar / 50 bar	min. vapor fraction at turbine outlet	β_{min}^{turb}	0.95

4.2. Results

The CoMT-CAMD approach is applied for the integrated design of the presented ORC process and the working fluid using Modelica to model the process. Within CoMT-CAMD, a relaxation problem is initially solved in the CoMT step to identify a hypothetical optimal working fluid, the target, jointly with the corresponding optimal process conditions. For the considered case study, the target achieves an objective function value of $P_{net} = 1.95 MW$ (Table 2). The objective function value of the target is an upper bound of the objective function for real working fluids.

Table 2: Top 5 working fluids with the corresponding PC-SAFT pure component parameters as well as the net power output P_{net} , the pressure levels in the evaporator p_{evap} and in the condenser p_{cond} , the mass flow rate of the working fluid \dot{m}_{WF} and the degree of superheating ΔT_{sh} determined in individual process optimizations. The order is according to the ranking of the CAMD step. The sorted rank according to the results of the individual process optimizations is shown in parentheses.

Rank	Fluid	P_{net}	m	$\sigma/\text{\AA}$	$(\epsilon/k)/K$	$\dot{m}_{WF}/(kg/s)$	p_{cond}/bar	p_{evap}/bar	$\Delta T_{sh}/K$
-	target	1.95 MW	3.14	3.46	164.1	71.5	7.0	25.5	0
1 (2)	Propene	1.48 MW	1.52	3.76	243.5	47.1	11.0	32.0	0
2 (1)	Propane	1.50 MW	1.68	3.77	232.6	47.8	9.2	27.4	0
3 (3)	Isobutane	1.44 MW	1.91	3.88	247.6	41.4	2.8	9.3	0
4 (4)	1-Butene	1.43 MW	1.97	3.79	242.4	40.0	2.9	9.6	0
5 (5)	Propyne	1.41 MW	1.93	3.23	226.4	30.4	8.9	24.1	48.2

Real working fluids are identified in the structure-mapping using the Computer-aided Molecular Design formulation given in Problem (3). Integer-cuts are used to identify a ranking of 5 working fluids (Table 2). A final process optimization is performed for the identified working fluids to overcome shortcomings in the Taylor approximation (see section 2.4). For this case study, the Top 5 working fluids contain mainly short-chained alkanes and alkenes highlighting the good performance of these working fluid families for heat sources in a similar temperature range as in this case study. The best identified working fluid is propane with a net power output of $P_{net} = 1.50 MW$, which is 23.2 % lower than the target value. However, propane is identified as second working fluid. The second-order Taylor approximation in the CAMD step does not match the objective function perfectly resulting in a small deviation from the ranking calculated by final process optimizations. Thus, integer-cuts and a final process optimization are necessary to obtain an overall optimal solution.

On the process side, the mass flow rate \dot{m}_{WF} of the Top 5 working fluids is significantly lower than the mass flow rate of the target. The differences in pressure levels result from the different boiling temperatures of the working fluids, which are adapted to the temperatures of the heat source and the cooling water. In this case study, Propyne is the only working fluid in the Top 5 which is superheated in the evaporator.

5. Conclusion

In this work, we enable the integrated design of ORC process and working fluid with CoMT-CAMD based on object-oriented and equation-based modeling with Modelica. So far, CoMT-CAMD was implemented in a procedural programming language, which hinders the reusability, fast and easy development and adaptation of processes and application for more complex systems. These limitations are overcome by the presented CoMT-CAMD approach

based on object-oriented process modelling using the programming language Modelica. Here, the process model is written in Modelica, which enables easy drag-and-drop flowsheeting and the usage of existing model libraries to reduce programming effort for the development of new processes. The property calculations based on PC-SAFT are performed in Modelica external functions. A powerful optimization tool for optimal control problems, MUSCOD-II, is used in the CoMT step to identify a hypothetical optimal working fluid. Subsequently, a CAMD algorithm is used to identify real working fluids with similar properties as the hypothetical optimum.

We successfully apply the presented CoMT-CAMD approach based on object-oriented process modeling with Modelica to the integrated design of a geothermal ORC power plant. A ranking of the optimal working fluids and the corresponding optimal processes are efficiently identified with CoMT-CAMD. Thus, the integrated design of ORC process and working fluid can be applied based on fast and easy drag-and-drop process flowsheeting with Modelica.

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