INTEGRATED DESIGN OF WORKING FLUID MIXTURES AND ORGANIC RANKINE CYCLES (ORC) IN THE CONTINUOUS-MOLECULAR TARGETING (COMT) FRAMEWORK

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ABSTRACT

Organic Rankine Cycles (ORCs) provide power by exploiting low-temperature heat of renewable sources or waste heat. To enhance the efficiency of ORCs, binary mixtures have been proposed as working fluids. Using a working fluid mixture leads to a temperature glide during evaporation and condensation and thus to a better match between the temperature profile of the heat source and the working fluid. We present a method for the integrated optimization the working fluid mixture, i.e., its components and its composition, and the ORC process parameters. Mixture properties are calculated by the PC-SAFT equation of state. In our design framework, the so-called continuous-molecular targeting (CoMT), the pure component parameters are relaxed in the optimization to allow for a simultaneous optimization of the working fluid mixture and the process. However, the resulting optimal mixture components do in general not coincide with any real fluid. Real fluids are identified in the second step of the CoMT framework, the structure-mapping. In this paper, only the CoMT optimization is employed to quantify the potential benefit of working fluid mixtures. The results show that mixtures are not always thermodynamically beneficial and that their benefit depends on the conditions under which the ORC system is finally installed.

1. INTRODUCTION

Organic Rankine Cycles (ORCs) convert low-temperature heat to power. Typically, the exergy content of such sources is low. Thus, efficiency of the cycle is crucial. To enhance the power output, mixtures have been proposed as working fluids (Angelino and Colonna, 1998). Mixtures have a temperature glide, i.e., the temperature is not constant during the phase-change. Due to the temperature glide, a better match of the temperature profile of working fluid and (sensible) heat source is achieved (see figure 1). Better matching of heat source and working fluids is equivalent to less exergy destruction and thus thermodynamically favorable (Heberle et al., 2012). Therefore, zeotropic mixtures can enhance the efficiency of an ORC system (Angelino and Colonna, 1998; Wang and Zhao, 2009; Heberle et al., 2012). Also economically, mixtures were found to be outperforming pure components. Oyewunmi et al. (2014) state lower investment cost by 20 - 30 % when comparing a mixture to a pure component. However, the comparison of the performance of mixtures and pure working fluids might still be biased by the selection of reference pure working fluids and selection of mixtures for assessment. Only the comparison of optimal working fluid mixture to an optimal pure component enables an unbiased analysis.

The selection of an optimal pure component working fluid is already non-trivial (Quoilin et al., 2013; Bao and Zhao, 2013). The selection of an optimal working fluid *mixture* introduces further complexity. Approaches based on trial and error are prohibitive as the combinatorial nature of the problem cannot

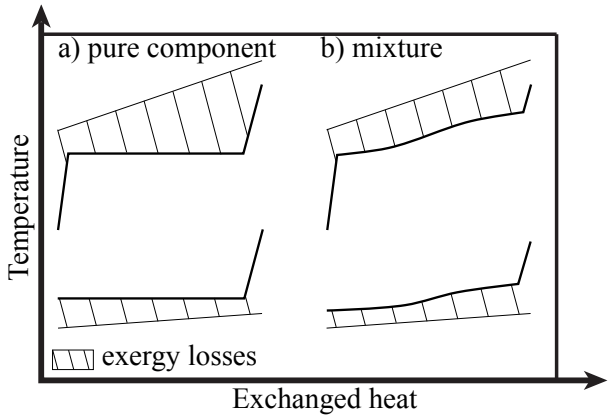

Figure 1: Comparison of the exergy loss during the heat exchange between heat source/sink (thin lines) and the working fluid (thick line), which is a) a pure fluid and b) a mixture. The inlet and outlet temperatures as well as the minimal approach temperature is kept constant. The hatched areas between heat source/sink and working fluid profile reflect the exergy loss due to heat transfer.

be tackled efficiently. Thus, systematic methods for the design of working fluid mixtures are needed (Molina-Thierry and Flores-Tlacuahuac, 2015). Based on their pioneering work for pure fluids (Papadopoulos et al., 2010), Papadopoulos et al. (2013) identify high-performance working fluid mixtures by computer-aided molecular design (CAMD). In their approach, the constituting equations enforcing the feasibility of the component are skipped for one component and an optimal second component is identified. The result is used to limit the search space for the second component and the problem is solved to identify a mixture. Mavrou et al. (2015) compared the resulting mixtures to other proposed mixtures and confirm that the designed mixtures perform better. Furthermore, methods have been developed to select a mixture from a database of components by genetic algorithms (Andreasen et al., 2014).

The continuous-molecular targeting computer-aided molecular design (CoMT-CAMD) framework developed by the authors enables the selection of an optimal working fluid by simultaneously optimizing working fluid and process parameters (Lampe et al., 2014b). Due to the discrete nature of working fluid selection, the simultaneous optimization would lead to a mixed-integer nonlinear program (MINLP) of prohibitive size and complexity. In CoMT-CAMD, the simultaneous optimization is still achieved by exploiting the PC-SAFT equation of state (Gross and Sadowski, 2001, 2002). In PC-SAFT, each working fluid is represented by a set of pure component parameters. These pure component parameters are relaxed to continuous values during the optimization. The relaxation allows for optimization of working fluid and process in a single nonlinear program (NLP). The optimization in the relaxed search-space is the first step of CoMT-CAMD, the continuous-molecular targeting (CoMT). The resulting set of optimal pure component parameters does in general not coincide with the pure component parameters of any real working fluid. Real working fluids are identified in a second step, the so-called structure-mapping. The structure-mapping can be based on a database of existing fluids (Lampe et al., 2014b) or novel working fluids can be generated using CAMD (Lampe et al., 2014a). The CoMT-CAMD framework has also been applied successfully to solvent selection (Bardow et al., 2010; Stavrou et al., 2014).

In this paper, the CoMT-step of the framework is extended for the optimization of binary working fluid mixtures. The extension of the framework allows for the design of an optimal working fluid mixture simultaneously with the optimization of the process itself. The mixture components, the composition and the key process parameters are the degrees of freedom for the optimization. In section 2, the formulation of the integrated mixture and process design is introduced. The continuous-molecular targeting framework is used to identify the optimal working fluid mixture. The resulting optimal hypothetical mixture is compared to the result of the same optimization for a pure component in a case-study (sec. 3). The optimal hypothetical mixture and the hypothetical pure component fluid provide an upper bound on the possible performance for real fluids. Thus, the comparison of an optimal working fluid mixture

to an optimal pure working fluid allows to quantify the potential benefit of employing a working fluid mixture. The results show that mixtures are not always beneficial and that their benefit depends on the conditions under which the ORC system is finally installed.

2. GENERAL PROBLEM FOR WORKING FLUID MIXTURE OPTIMIZATION

In the continuous-molecular targeting, the working fluid mixture and the process are optimized simultaneously. For the formulation of the optimization problem, a generic model of the process is employed.

$$
\begin{aligned}
\min_{x,z_1,z_2,x_{\mathrm{wf}}} \quad & f(x,\theta) && \text{objective function} \\
\text{s.t.} \quad & g_1(x,\theta) \leq 0 && \text{process model inequalities} \\
& g_2(x,\theta) = 0 && \text{process model equalities} \\
& \theta = h(x,z_1,z_2,x_{\mathrm{wf}}) && \text{PC-SAFT} \\
& A\,z_1 \leq b && \text{convex hull (fluid 1)} \\
& A\,z_2 \leq b && \text{convex hull (fluid 2)} \\
& x_{\min} \leq x \leq x_{\max} \in \mathbb{R}^n && \text{process variables} \\
& 0 \leq x_{\mathrm{wf}} \leq 1 \in \mathbb{R} && \text{mixture composition} \\
& z_{\min} \leq z_1, z_2 \leq z_{\max} \in \mathbb{R}^m && \text{mixture components.}
\end{aligned}
\tag{1}
$$

The process model comprises an objective $f(x,\theta)$ (e.g. net power output, efficiency, or second law efficiency) as well as inequality and equality constraints $g_1(x,\theta)$ and $g_2(x,\theta)$, respectively. The process model depends on two vectors of variables: the optimized process parameters x (e.g., mass flow rate, or pressure level) and thermo-physical properties of the working fluid θ (e.g., enthalpies, or entropies of each state point). The thermo-physical properties θ are calculated by PC-SAFT ($\theta = h(x,z_1,z_2,x_{\mathrm{wf}})$). In PC-SAFT, binary mixtures are defined by their composition x_{wf} and two sets of pure component parameters z_1 and z_2. For the optimized process parameters, bounds can be derived based on the application of the ORC system (e.g., upper and lower pressure level). To limit the search space of the pure component parameters z_i, we construct a convex hull around a database of known pure components. The convex hull yields a set of linear constraints $A\,z_i \leq b$ for both of the mixture components. Thus, the complete search space of working fluids is feasible for each component.

The simultaneous optimization of mixture and process in eq. (1) identifies the optimal process parameters x^* as well as an optimal working fluid mixture represented by the components z_i^* and the composition x_{wf}^*. The optimization is performed as one single nonlinear program and no discrete degrees of freedom are introduced. However, the resulting optimal mixture components z_i^* do in general not coincide with any real fluid. Real fluids are identified in the second step of the CoMT-CAMD framework, the structure-mapping. In this paper, only the first step of the method is employed. This CoMT step does not identify real components, but yields an upper bound for the performance of any working fluid mixture, as the relaxed problem contains all discrete solutions.

Optimization problem (1) is a nonconvex NLP. In nonconvex problems, multiple local minima can occur. In fact, the search space is symmetric in the compounds of the mixture and thus there at least are two globally optimal solutions, which both represent the same mixture: For any combination of two components z_1 and z_2, and their composition x_{wf}, an identical symmetric solution can be obtained by exchanging the fluids (i.e., $\bar{z}_1 = z_2$ and $\bar{z}_2 = z_1$) and adapting the composition (i.e., $\bar{x}_{\mathrm{wf}} = 1 - x_{\mathrm{wf}}$). The symmetry of the search space can be prevented by a symmetry breaking constraint, e.g., bounding the mixture composition to $x_{\mathrm{wf}} \leq 0.5$. Symmetry breaking constraints should be employed when global optimization is used to speed up the optimization (Liberti and Ostrowski, 2014). For local search algorithms, symmetry breaking constraints are not always beneficial (Prestwich and Roli, 2005), as additional local minima can be introduced to the problem. In this work, optimization is performed using sequential quadratic programming (SQP) implemented in Matlab (2012) based on (Han, 1977; Powell, 1978, 1979)

Table 1: Specification of the heat source for the generic example.

Parameter	Symbol	Value
heat source mass flow rate	$\dot{m}_{\mathrm{HS}}$	$50\ \frac{\mathrm{kg}}{\mathrm{s}}$
heat source specific heat capacity	$c_{p,\mathrm{HS}}$	$4.185\ \frac{\mathrm{kJ}}{\mathrm{kg\ K}}$
heat source inlet temperature	$T_{\mathrm{in,HS}}$	$270\ ^{\circ}\mathrm{C}$

on a standard desktop PC (Core i5 CPU, 1.7 GHz with 4 GB RAM) using the default settings. To prevent the solver from converging to a local optimum, different starting values have been used.

3. ILLUSTRATIVE EXAMPLE

The comparison of mixtures of existing working fluids to existing pure components in the literature shows advantages for the mixtures compared to pure components. However, this comparison can be misleading when a good mixture is compared to a bad pure component. Eq. (1) yields an optimal hypothetical mixture and the corresponding process parameters. The same optimization can be performed for a pure working fluid by enforcing a composition of $x_{\mathrm{wf}} = 0$. This allows for the identification of an optimal hypothetical pure working fluid. The results of both optimizations can be used for a unbiased assessment of the potential benefit of mixtures.

To assess the potential of mixtures, a generic example of an ORC system is used. Changing the model for the cooling of the cycle allows to identify how the cold side effects the optimal mixture. A recuperated ORC is considered. The minimal temperature difference to heat source and heat sink are $\Delta T_{\mathrm{min}} = 0\ \mathrm{K}$. The heat source is defined by a mass flow rate of hot water (see table 1). The degrees of freedom x for the process are the pressure levels for evaporization p_{evap} and condensation p_{cond} as well as the mass flow rate of working fluid $\dot{m}_{\mathrm{wf}}$. The system is optimized for an optimal net power output

$$P_{\mathrm{net}} = \dot{m}\ \left[(h_4 - h_5) - (h_2 - h_4)\right]\ ,$$

where the enthalpies are calculated assuming boiling liquid after the condenser (state 1) and saturated steam after the evaporator (state 4). To calculate the enthalpy after the turbine (state 5) and after the pump (state 2), constant isentropic efficiencies of turbine and condenser are assumed ($\eta_{\mathrm{T}} = \eta_{\mathrm{P}} = 0.85$). For the recuperator, a minimal approach temperature of $\Delta T_{\mathrm{min}}^{\mathrm{regen}} = 30\,^{\circ}\mathrm{C}$ is assumed.

For the cooling of the system, different options and model formulations are employed in the following to demonstrate their effect on the optimal working fluid mixture.

3.1 Constant Cooling Temperature

The most simple model of a cooling system assumes a constant lower temperature limit. The lower limit is selected according to a considered cooling system. For this example, a lower temperature limit of $70\ ^{\circ}\mathrm{C}$ is considered. Eq. (1) is used to optimize two sets of pure component parameters z_1 and z_2 as well as the optimal mixture composition x_{wf}.

For a constant cooling temperature, the resulting optimal mixture is basically a pure component ($x_{\mathrm{wf}}^{*} = 0.005$). The illustration of the cycle in a T,h-diagram in figure 2 allows to identify the properties of the working fluid leading to optimality: The working fluid is fitted optimally between the temperature profiles of the heat source and heat sink. As the lower temperature level is constrained by a constant temperature, the temperature glide of a mixture cannot be exploited for the condensation (states 5'-1). For the heating of the system, working fluid and mass flow rate are selected to allow for a minimal temperature difference in the preheating (states 2'-3). This combination of the practically pure working fluid and process is not the most efficient cycle, regarding thermal efficiency. The deficit in efficiency is overcome by matching preheating and heat source such that the heat source is cooled down as far as possible. Thus, the cycle is optimal with respect to the net power output.

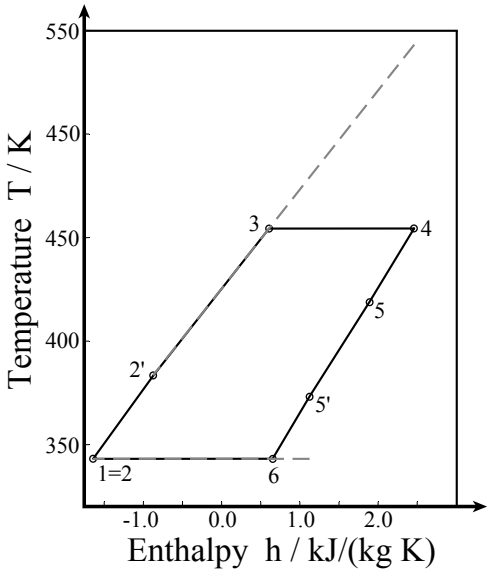

Figure 2: Resulting ORC from the CoMT-optimization for a constant lower temperature limit.

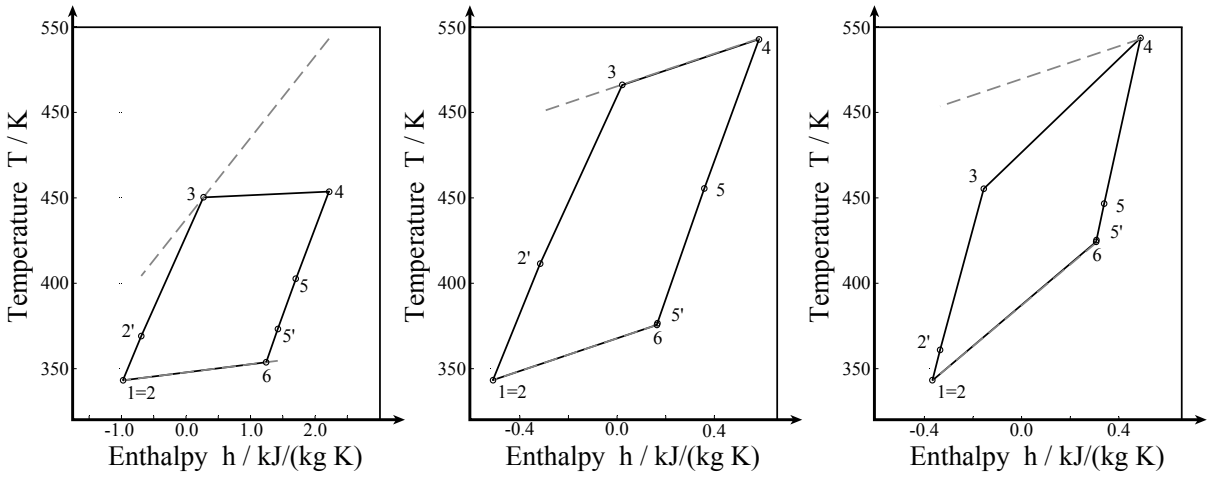

Figure 3: Resulting ORC from the CoMT-optimization for a cooling source with constant mass flow rate of a) $500\ \frac{\mathrm{kg}}{\mathrm{s}}$**, b)** $50\ \frac{\mathrm{kg}}{\mathrm{s}}$ **and c)** $20\ \frac{\mathrm{kg}}{\mathrm{s}}$**.**

The assumption of a constant lower temperature limit leads to the identification of a pure working fluid: due to the constant lower temperature of the cooling system, a pure working fluid already enables an optimal match for a constant lower temperature limit. The effect of a sensible heat carrier in the cooling system is considered in the following.

3.2 Fixed Mass Flow Rate of Cooling Agent

In this section, the cooling system is modeled in the same way as the heat source; i.e., a mass flow rate of cooling agent is supplied with a specified temperature. Three different mass flow rates are assessed to show the effect of a variation of the value of this parameter ($500\ \frac{\mathrm{kg}}{\mathrm{s}}$, $50\ \frac{\mathrm{kg}}{\mathrm{s}}$, and $20\ \frac{\mathrm{kg}}{\mathrm{s}}$). The value of $50\ \frac{\mathrm{kg}}{\mathrm{s}}$ corresponds to the same heat capacity flow rate $(\dot{m}\, c_p)_{\mathrm{HS}}$ as for the heat source.

In figure 3a, the result of the optimization is shown for a flow rate of $\dot{m}_{\mathrm{CS}} = 500\ \frac{\mathrm{kg}}{\mathrm{s}}$. The result is a mixture with a composition of $x_{\mathrm{wf}} = 0.29$ (see table 2). The temperature glide follows the cooling agent exactly. To enable the perfect match of cooling agent and working fluid the condensation pressure p_{cond} and the mass flow rate $\dot{m}_{\mathrm{wf}}$ are selected to the according values. The evaporization pressure p_{evap} is chosen to exploit the minimal allowed temperature difference to the heat source.

Table 2: Resulting mixtures from the CoMT-optimization for different mass flow rates of cooling agent

Parameter	Unit	Values		
$\dot{m}_{\mathrm{CS}}$	$\frac{\mathrm{kg}}{\mathrm{s}}$	500	50	20
x_{wf}	–	0.29	0.1	0.16
m_1	–	1.84	1.91	1.85
σ_1	Å	3.41	4.32	4.15
$\left(\frac{\epsilon}{k}\right)_1$	K	503	489	543
m_2	–	2.04	1.84	1.84
σ_2	Å	4.36	3.91	3.32
$\left(\frac{\epsilon}{k}\right)_2$	K	392	400	392
p_{evap}	bar	1.26	8.68	5.13
p_{cond}	bar	0.05	0.13	0.25
$\dot{m}_{\mathrm{wf}}$	$\frac{\mathrm{kg}}{\mathrm{s}}$	57.0	15.2	12.5

The results for the varied mass flow of cooling source are similar to this result (figures 3b and 3c). The cooling agent is dominating the value for the temperature glide, regardless of the heat source properties. The optimal match of cooling agent and working fluid leads to a thermodynamically optimal cycle. However, only a comparison based on an economic objective function would give a final answer to the question, if mixtures can outperform pure components: the optimal cycles in this and the previous section exploit a perfect match of working fluid and cooling agent in the condenser. This leads to low temperature differences for the heat transfer and accordingly to large required heat exchange area. The larger heat exchange area might lead to prohibitive investment cost to employ the cycle in a ORC system.

3.3 Modeling of an Air-Cooled System

The comparison based on a constant mass flow rate of cooling agent in section 3.2 might lead to the conclusion that mixtures are performing better for real ORC systems. However, the assumption of a constant mass flow rate of the cooling agent might still be misleading. Besides the negative effect on the heat exchange area, the assumption of a constant mass flow rate of cooling agent is not valid for many applications: When an air-cooled system is employed, the amount of air for cooling the system is not limited by any constraint, in general. The amount of air that is fed to the system results from a tradeoff between cost for the compression of the air and the effectiveness of the cooling-system.

To reflect this tradeoff, a model for the compressor of an air-cooled system is employed. The model is based on a constant isentropic efficiency of the compressor $\eta_{\mathrm{comp}} = 0.75$. The mass flow rate of cooling agent is assumed to be the minimal mass flow rate allowing for the cooling of the cycle. Thus, effort for cooling at lower temperatures is considered in the optimization. The air is entering the compressor at $T_{\mathrm{air,in}} = 15\ ^{\circ}\mathrm{C}$ and fed to an heat exchanger. The pressure drop to be overcome by the compressor is $\Delta p = 0.01\ \mathrm{bar}$.

Under these conditions, the CoMT optimization results in a mixture (figure 4a and table 3). The optimal process has a lower temperature than the previous cases. The lower temperature is feasible, as the constraint on the lower temperature is less restrictive. A moderate temperature glide is employed (see figure 4a). The net power output optimal mixture with the optimal process is $P_{\mathrm{net}} = 2.76\ \mathrm{MW}$.

For an assessment of the effect of mixtures on the performance of the cycle, the optimization is performed for pure component working fluids. The optimal mixture and an optimal pure component are compared. Thus, the comparison is unbiased by the selection of a specific mixture and a set of pure components.

The result of the CoMT-optimization for the pure component is similar to the result of the mixture optimization (see figure 4b). The optimal pure component has pure component parameters close to com-

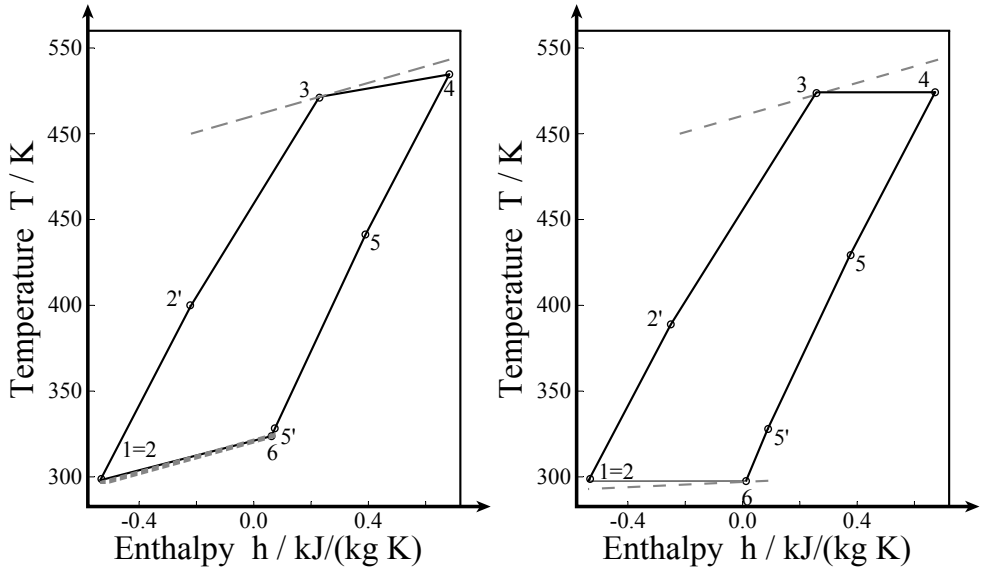

Figure 4: a) Result of the CoMT-optimization employing a model of and air-cooling system. b) Result of the CoMT-optimization for a pure component employing a model of and air-cooling system.

ponent 1 from the optimal mixture (table 3). The net power output of the pure component cycle is $P_{\mathrm{net}} = 2.69$ MW. Thus, the net power output is only 3 % lower than the value for the optimal mixture.

4. SUMMARY

The CoMT method for the integrated optimization of working fluid and process is extended to the design of working fluid mixtures. The optimization was applied successfully to the identification of optimal mixtures under different specifications for the application.

The hypothetical optimal mixture results in a optimal match of the heat transfer profile of the working fluid and the cooling agent in all examples. For a constant temperature of the cooling agent, the optimal working fluid is a pure component. When the mass flow rate of the cooling agent is constant, mixtures are preferable due to their ability to adapt to the temperature profile of the cooling agents.

Overall, the results show that pure component working fluids are competitive with mixtures and indeed optimal in some cases. By employing a model of the cooling system, the trade-off between the efficiency of the cycle and power consumption of the cooling system is reflected. For this case, a mixture is the

Table 3: Results of the CoMT-optimization using an air-cooled system.

Parameter	Unit	Pure component	mixture
x_{wf}	–	-	0.1
m_1	–	1.84	1.84
σ_1	Å	5.21	5.18
$\left(\frac{\epsilon}{k}\right)_1$	K	519	543
m_2	–	–	1.89
σ_2	Å	–	4.35
$\left(\frac{\epsilon}{k}\right)_2$	K	–	400
p_{evap}	bar	6.79	6.43
p_{cond}	bar	0.01	0.01
$\dot{m}_{\mathrm{wf}}$	$\frac{\mathrm{kg}}{\mathrm{s}}$	14.5	14.6

optimal solution. However, the difference to the optimal pure component working fluid is below 3 %. For the construction of a real ORC system, the small difference might favor the selection of a pure component for simplicity of the system design.

The comparison of mixtures to pure working fluids indicates that there are pure components that can compete with mixtures in terms of thermodynamical performance. Still, economic criteria will decide in practice about the use of working fluid mixtures. Thus, economic criteria should be included in the analysis in future work.

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