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Exergy-based analysis of irreversibilities for heat pump working fluids and cycle layouts

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Abstract:

The use of zeotropic mixtures in well-designed heat pump cycles enables considerable performance improvements. Temperature glide matching of the heat exchange processes and recovery of expansion losses by internal heat exchange decrease the exergy destruction and yield higher cycle performances. A case study for supply to district heating is presented, indicating increases in COP from 4.3 for a pure fluid in a standard cycle to 5.2 for a zeotropic mixture in a cycle with optimized internal heat exchange. As these improvement potentials are difficult to quantify by conventional and advanced exergy analysis, a new approach was suggested. For deriving a meaningful benchmark for cycle optimization, the exergy destruction was distinguished into a contribution describing the irreversibilities from the respective components operating with an ideal working fluid and cycle design and another contribution resulting from the cycle and working fluid being non-ideal. In addition, the exergy destruction was related to the COP, enabling an intuitive interpretation of the exergy-based analyses.

Keywords:

Cycle design; exergy; exergy destruction; heat pump; irreversibility; Lorenz cycle; refrigerant; temperature glide matching; working fluid; zeotropic mixtures.

Biographical notes:

B. Zühlsdorf is a consultant at the Danish Technological Institute in the division of Energy and Climate. His main research activities lie within the field of energy engineering and thermal systems and aim at the development of technical solutions for sustainable energy systems. In this context, he focusses on the electrification of heat supply with a special interest in heat pump systems for industry and district heating. His work focusses on the design and optimization of heat pump cycles by cycle layout optimization, working fluid selection and improved process integration. Furthermore, his work comprises the development of digital twins for large-scale heat pump and refrigeration systems, to better exploit the technical potentials of such systems. His studies are based on the application and development of various methods, including energy, exergy and economic analysis.

Jonas Kjær Jensen is a Research Scientist at the Department of Mechanical Engineering, Technical University of Denmark. His research is within the field of energy engineering and applied thermodynamic with a special interest in refrigeration and heat pump technology. His research focuses on improving the thermodynamic and economic performance of heat pumps and refrigeration systems through advanced cycle layouts, advanced refrigerant selection and advanced control strategies. He further has extensive experience on modelling zeotropic mixture cycles and absorption processes as well as advanced analysis and assessment methods such as exergy and exergoeconomic analysis. Jonas Kjær Jensen is the author of more than 30 peer-reviewed publications.

Brian Elmegaard is Professor and Head of section of Thermal Energy at the Department of Mechanical Engineering, DTU Technical University of Denmark. His research interest covers the advancement of thermal systems for assisting the green transition of modern society within the fields of industrial and domestic heating and cooling solutions. Present work covers optimization of heat pump systems with respect to cycles and working fluids as well as their integration in the energy systems. The work is based on application and studies of advanced methods like pinch analysis and exergy-based methods. The research is carried out in collaboration with industrial and academic partners in several national and international projects. Brian Elmegaard is the Danish delegate for the International Energy Agency's Technology Collaboration Program on Industrial Energy-related Technologies and Systems. He teaches applied thermal engineering at Bachelor, Master and PhD levels.

1. Introduction

Heat pumps enable sustainable and electricity-based heat supply in several applications, such as domestic heating or supply of heat to industrial process or district heating networks (Connolly and Vad Mathiesen, 2014; David *et al.*, 2017; Zühlsdorf *et al.*, 2019). The thermodynamic performance of heat pumps is strongly dependent on the working fluid and the cycle layout. The choice of the working fluid is furthermore subject to legislative restrictions ensuring a limited environmental impact of the working fluid, which facilitates the search for suitable alternatives.

The choice of the working fluid and the cycle layout accordingly became the focus of various recent studies. Domanski et al. (2014) studied the limitations for hypothetical pure fluids which were based on the corresponding states model while disregarding the limitation of being constrained by the actual availability of real molecules that could resemble such a fluid. Their study confirmed the fundamental trade-off among capacity and thermodynamic performance. McLinden et al. (2014) complemented this study by an analysis of potential real pure fluids. Recently, McLinden et al. (2017) concluded the range of promising replacement fluids to be rather limited. They furthermore outlined the dependency of the cycle layout and the working fluid with respect to an optimal thermodynamic performance.

Harby (2017) reviewed the possibilities for using mixtures of hydrocarbons as replacement fluids and indicated an increased flexibility considering a limited number of pure fluids, which are suitable as long-term replacements. The performance improvements obtainable by using zeotropic mixtures were found to be related to matching the temperature glides in the secondary cycles with the working fluid. The first methods for determining promising working fluids were developed by

(McLinden and Radermacher, 1987; Högberg, Vamling and Berntsson, 1993). Zühlsdorf, Jensen and Elmegaard (2019) analyzed different approaches for comparing working fluids and suggested a procedure for identifying high-performance working fluids. It was demonstrated that zeotropic working fluid mixtures could yield a considerable increase in thermodynamic performance in applications in which the heat source and heat sink are experiencing a reasonable temperature glide. The improvements could mainly be associated with an improved match of the temperature profiles of the heat source and sink with the working fluid. It was furthermore found that the potential performance increase was dominated by the glide match in the source (Zühlsdorf, Jensen, *et al.*, 2018) and that the optimal cycle design and the optimal working fluid were interdependent. The presented approaches did however require a sophisticated procedure for the selection of the working fluid.

Other studies focused on the development of a more advanced cycle layout, which enabled adjustment of the temperature glide of just one mixture and thereby obtaining a similar effect. Jensen et al. (2015) studied the performances of hybrid ammonia-water absorption-compression heat pumps and outlined different advantages, such as higher heat supply temperatures and improved thermodynamic performances. Van De Bor et al. (2014) studied the integration of a compression-resorption heat pump into various case studies and confirmed optimal thermodynamic performances for good temperature glide matches. Gudjonsdottir et al. (2017) studied the impact of adding carbon dioxide to a mixture of ammonia and water in a wet compression-resorption heat pump cycle and found different advantageous aspects, such as a decreased pressure ratio and increased overall performances. These studies document that the combined optimization of the cycle layout and the working fluid may lead to considerable performance increases. Exploiting these potentials does however require sophisticated methods for the evaluation of different alternatives.

Advanced exergy analysis (Bejan, Tsatsaronis and Moran, 1996; Tsatsaronis and Morosuk, 2012; Morosuk, Tsatsaronis and Schult, 2013) is a suitable tool for quantifying the interdependencies among the components, e.g., to describe the impact of the compressor efficiency on the condenser performance, by distinguishing endogenous and exogenous contributions. It is furthermore suitable for the quantification of the maximum performances for a given system using components of different efficiencies, e.g., to determine what efficiency could be reached with a very large, but technically feasible heat exchanger area, by distinguishing between an avoidable and unavoidable contribution (Tsatsaronis and Park, 2003). Kelly et al. (2009) compared different approaches for the calculation of the endogenous and exogenous contributions to the exergy destruction, enabling association of the exergy destruction with the component where it was caused rather than with the component in which it occurred.

Morosuk and Tsatsaronis (2008) conducted an advanced exergy analysis for an absorption refrigeration machine. Suggestions for the optimization of the system were derived from the results and found to be more comprehensive than comparable studies. Jensen et al. (2015) performed an exergoeconomic optimization of a hybrid ammonia-water absorption-compression heat pump for heat supply in a spray drying facility for finding the design with an optimal economic performance. Yan, Cui and Yu (2015) applied energy and exergy analysis to a condenser separation cycle using a mixture of R290 and R600a in domestic refrigerators. Promising configurations were identified in terms of energy efficiency and volumetric capacity, while construction and operability might imply challenges. Stegou-Sagia and Papadaki (2006) presented an exergy analysis for the analysis of two zeotropic mixtures as replacements for R22 in heat pumps, considering two different climatic conditions. Tyagi *et al.* (2010) analyzed a flexible cascade heat pump using seawater as heat source and sink for different operating conditions in which only heating, cooling or both services were used. Dincer and Naterer (2010) evaluated the exergy efficiency and sustainability indicator for a R134a heat pump system for various boundary conditions and controlling modes. Based on the exergy efficiency and the environmental impact, optimal operating points were derived. Ouadha, En-nacer and Imine (2008) performed a model-based analysis of a water-to-water heat pump using R290 as refrigerant. The study comprised energy and exergy analysis for evaluating the heat pump in heating and cooling mode and the heat exchange processes were found to have a dominating impact on the performance. Sarkar, Bhattacharyya and Gopal (2004) presented an optimization of a transcritical CO_2 heat pump cycle based on energy and exergy analyses before design guidelines were derived. Sarkar and Bhattacharyya (2009) presented an assessment of CO_2 blends with butane and isobutane in heat pump applications and identified high-performing mixture compositions.

Lecompte *et al.* (2014) presented an exergy analysis of zeotropic mixtures for Organic Rankine Cycles (ORC) in which it was found, that the exergy analysis implied considerable advantages compared to the First Law analysis, as it revealed the irreversibilities in the different components. Garg *et al.* (2013) studied the suitability of blends of CO_2 with isopentane and propane in ORC cycles. The study considered the variation of the irreversibilities in the different components, as well as relations of temperature glide matching.

From the review of the advanced exergy analysis in refrigeration and heat pump systems as well as Organic Rankine cycles, it may be concluded that advanced exergy analysis is generally a suitable method for evaluating the performance and the limitations of a given system i.e. for a given cycle layout and working fluid.

The advanced exergy analysis mainly seeks to determine the avoidable endogenous and avoidable exogenous exergy destruction rates as these are the irreversibilities that can be reduced by improving the design of the components that form the studied system. So far, the attempts of analyzing the unavoidable exergy destruction were limited to the analysis of efficiencies of the remaining components. Typically, the unavoidable exergy destruction rates are conceptually allocated to limitations of component performance such as maximum achievable isentropic efficiencies for compressors or turbines or minimum achievable pinch points in heat exchangers, of either endogenous or exogenous origin. However, it was shown by Zühlsdorf, Jensen, *et al.* (2018) and will be further elaborated in the present work, that the unavoidable exergy destruction is only partially caused by component ineffeciencies while also the choice of cycle layout and working fluid influences the amount of irreversibility. Gaining a deeper understanding of how the choice of cycle and working fluid affects the performance will thus give an indication as to which extent the system is best improved by improving the components or by improving the cycle layout or choice of working fluid.

Recently, Penkuhn and Tsatsaronis (2017) presented the so called decomposition method to peform the advanced exergy anaylsis. This methods imposes a superstructure for system to better identify the idealized process need to make the relevant distictions. Similar to this approach, it is suggested to idealize sub-systems and processes in order to determine the endogenous and exogenous exergy destruction. The work from Penkuhn and Tsatsaronis (2017) is formulated on a generic level and leaves various options for the application, while further studies are recommended as the basis for supplementing and consolidating the approach.

Morosuk and Tsatsaronis (2009) applied advanced exergy analysis for evaluating a set of working fluids for a refrigeration cycle. It was observed that the share of unavoidable exergy destruction in refrigeration machines depended on the working fluid. In the context of optimizing the cycle performance by the working fluid choice, these variations may be understood as the potential improvements obtainable by the choice of an optimal working fluid, thus highlighting the need to distinguish between components, cycle layout and working fluid-induced irreversibilities. Morosuk and Tsatsaronis (2009) indicated moderate improvement potentials for the analyzed case, while it was shown in e.g., (Zühlsdorf, Jensen, *et al.*, 2018; Zühlsdorf, Meesenburg, *et al.*, 2018; Zühlsdorf, Jensen and Elmegaard, 2019) that these improvement potentials may become considerable in applications with large temperature glides and for the utilization of zeotropic working fluid mixtures with a good temperature glide match. In order to exploit the potentials for minimizing the irreversibilities without the limitations of predefined cycles, it is important to develop a suitable method which is based on the optimal processes as a benchmark, rather than on the preselected system.

This paper therefore presents an approach for quantifying the maximum achievable performance for an optimal cycle layout and working fluid choice under consideration of realistic component efficiencies. (Zühlsdorf, Jensen, *et al.*, 2018) suggested distinguishing between a contribution that is associated with the heat exchanger and one contribution that is associated with the choice of the working fluid and the cycle layout. In this article, the method was extended to the entire cycle layout. Furthermore, a relation is derived to describe the dependency between the exergy destruction and the coefficient of performance COP, enabling an intuitive interpretation of the saving potentials and quantifying the deviations from an ideal theoretical cycle by different contributions of exergy destruction.

2. Methods

The presented analysis was based on numerical models and conducted for a heat pump system for which pure working fluids and zeotropic working fluid mixtures were evaluated for two different cycle layouts. In the following, the considered cycle layouts and the corresponding modelling assumptions are explained. Subsequently, the relation between the exergy destruction and the COP is derived, before an approach for splitting the exergy analysis into different contributions is presented for both the heat exchange processes and the temperature lifting process.

2.1. Heat pump cycles and working fluids

Two different cycle layouts are considered during the analysis. Figure 1 shows a standard (std) cycle in which the working fluid receives heat from the heat source at a low pressure, before it is compressed to reject heat to the heat sink. In the standard cycle, the working fluid is subsequently throttled to the low pressure. Figure 2 shows the layout of a cycle with an internal heat exchanger (IHX), in which the working fluid is further subcooled before the throttling valve, while preheating the suction line of the compressor. Thereby, part of the work which otherwise is dissipated in the throttling valve, is recovered and used for preheating the gas in the suction line of the compressor, which may yield reduced compression work. The internal heat exchanger allows furthermore reducing the superheating inside the evaporator and possibly shifting some of the evaporation process to the internal heat exchanger. This is expected to improve the temperature glide matching and allow for operation with higher evaporation pressures, which in turn yields a higher cycle efficiency. The optimal definition of the cycle depends on the case and the selected medium and will be analyzed for specific examples.

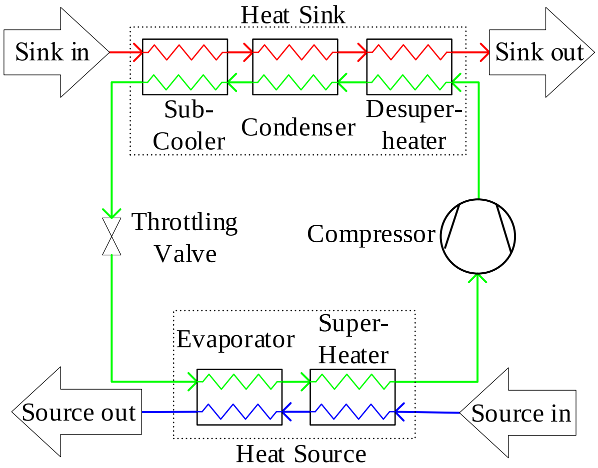

Figure 1. Standard heat pump cycle (std), (Zühlsdorf, 2019)

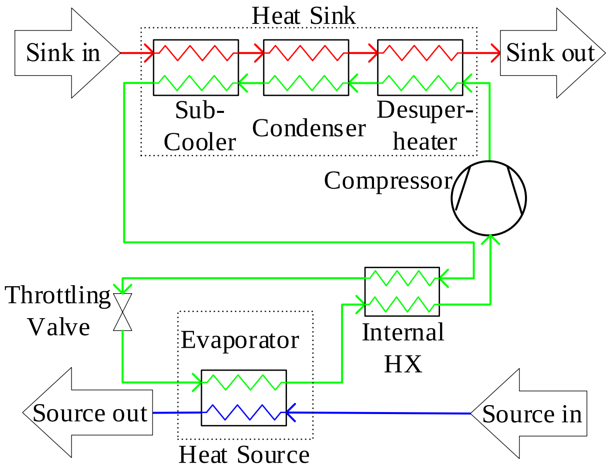

Figure 2. Heat pump cycle with internal heat exchanger (IHX), (Zühlsdorf, 2019)

The pressure levels were defined by minimum pinch point temperature differences in the heat exchangers of ΔT_{pinch} = 2.5 K. The outlet temperature of the subcooler was defined by the pinch point temperature difference to the sink inlet temperature, as this yielded a maximum subcooling and the highest thermodynamic performance. The compressor was modelled with an isentropic efficiency of 80 % and no heat losses to the environment were considered. No losses were considered for the motor.

As the main indicator of the thermodynamic performance, the coefficient of performance COP was introduced as the ratio of the supplied heat $\dot{Q}_{\mathrm{Sink}}$ and the power supplied to the compressor $\dot{W}_{\mathrm{Comp}}$.

$$\mathrm{COP} = \frac{\dot{Q}_{\mathrm{Sink}}}{\dot{W}_{\mathrm{Comp}}} \tag{1}$$

As an indicator of the size of the compression equipment and thereby of the investment cost, the volumetric heating capacity VHC was considered. It relates the supplied heat flow rate $\dot{Q}_{\mathrm{Sink}}$ to the volume flow rate at the suction line of the compressor $\dot{V}_1$.

$$\mathrm{VHC} = \frac{\dot{Q}_{\mathrm{Sink}}}{\dot{V}_1} \tag{2}$$

The cycles were evaluated by use of numerical models, which were based on mass and energy balances and accessed fluid properties from Refprop (Lemmon, Huber and McLinden, 2013). The numerical models are documented and accessible at (Zühlsdorf, Jensen and Elmegaard, 2018).

In this study, the analysis focused on the optimization of the working fluid choice in combination with the cycle layout. Therefore, propane (R290), butane (R600) and all possible binary mixtures of these were considered. Furthermore, the impact of the internal heat exchanger and the state of the working fluid at the outlet of the evaporator were analyzed.

The analysis is presented for a case study in which a heat sink of constant capacity was heated from 40 °C to 70 °C, while a heat source of constant capacity was cooled from 20 °C to 10 °C. The heat rate supplied to the heat sink was maintained constant throughout the analysis. The case corresponds to an application as it may be found in industrial applications, or for supply of district heating. The heat source is typical for the heat recovery from process cooling, while the heat sink corresponds to temperature profiles of heating applications. The case was however selected as an exemplary case without a specific application, since the main objective is presenting the developed approach.

2.2. Relating exergy destruction to deviations from ideal theoretical cycle in terms of COP

Exergy based methods were found to be a meaningful tool for allocating irreversibilities to different sources. The main criterion for the evaluation of the thermodynamic performance of heat pumps remains however to be the COP.

In order to enhance the understanding of the impact of the different rates of exergy destruction, it may be meaningful to relate these contributions to the COP. Accordingly, a relation was derived which describes the deviation of the real cycle with exergy destruction from the ideal Lorenz cycle without exergy destruction. This relation was presented in (Zühlsdorf, 2019) and is summarized in the following. It may be noted that the supplied heat and thereby the exergy product of the heat pump was kept constant throughout this analysis. The relations were derived for an application in which all temperatures were above the dead state.

The exergy balance of the ideal Lorenz cycle without exergy destruction was defined as shown in Eq. 3. For the Lorenz cycle, the exergy product $\dot{E}_{\mathrm{P}}$ and exergy fuel $\dot{E}_{\mathrm{F}}$ are equal and defined as the sum of the power of the compressor $\dot{W}_{\mathrm{Lor}}$ and the exergy rate supplied by the heat source $\dot{Q}_{\mathrm{source,Lor}}\left(1 - \frac{T_0}{\bar{T}_{\mathrm{source}}}\right)$.

$$\dot{E}_\mathrm{P} = \dot{E}_\mathrm{F} = \dot{E}_\mathrm{F,comp,Lor} + \dot{E}_\mathrm{F,source,Lor} = \dot{W}_\mathrm{Lor} + \dot{Q}_\mathrm{source,Lor}\left(1 - \frac{T_0}{\overline{T}_\mathrm{source}}\right) \tag{3}$$

For a real cycle, exergy destruction $\dot{E}_\mathrm{D}$ occurs, and the compressor power $\dot{W}_\mathrm{real}$ and the exergy rate supplied by the source are adjusted by $\dot{Q}_\mathrm{source,real}\left(1 - \frac{T_0}{\overline{T}_\mathrm{source}}\right)$.

$$\dot{E}_\mathrm{P} + \dot{E}_\mathrm{D} = \dot{E}_\mathrm{F} = \dot{E}_\mathrm{F,comp,real} + \dot{E}_\mathrm{F,source,real} = \dot{W}_\mathrm{real} + \dot{Q}_\mathrm{source,real}\left(1 - \frac{T_0}{\overline{T}_\mathrm{source}}\right) \tag{4}$$

As the product was maintained to be constant throughout the analysis, Eq. 6 could be derived by combining Eq. 3 and 4.

$$\dot{W}_\mathrm{real} - \dot{W}_\mathrm{Lor} = \left(\dot{Q}_\mathrm{source,Lor} - \dot{Q}_\mathrm{source,real}\right)\left(1 - \frac{T_0}{\overline{T}_\mathrm{source}}\right) + \dot{E}_\mathrm{D} \tag{5}$$

In addition, Eq. 6 can be derived by combining the energy balances for an ideal ($\dot{Q}_\mathrm{source,Lor} + \dot{W}_\mathrm{Lor} = \dot{Q}_\mathrm{Sink}$) and a real system ($\dot{Q}_\mathrm{source,real} + \dot{W}_\mathrm{real} = \dot{Q}_\mathrm{Sink}$). For the definition of the energy balances, no heat losses to the environment were considered.

$$\dot{Q}_\mathrm{source,Lor} - \dot{Q}_\mathrm{source,real} = \dot{W}_\mathrm{real} - \dot{W}_\mathrm{Lor} \tag{6}$$

Using this relation in combination with Eq. 4 allows the definition of a relation between the additional power spent in the compressor in the real case ($\dot{W}_\mathrm{real}$ - $\dot{W}_\mathrm{Lor}$) and the exergy destruction $\dot{E}_\mathrm{D}$.

$$\dot{W}_\mathrm{real} - \dot{W}_\mathrm{Lor} = \frac{\overline{T}_\mathrm{source}}{T_0}\dot{E}_\mathrm{D} \tag{7}$$

This finally enables the definition of a relation for the COP, which is solely dependent on temperatures of the heat source $\overline{T}_\mathrm{source}$ and the heat sink $\overline{T}_\mathrm{sink}$, the dead state temperature T_0, and the ratio of the exergy destruction and the exergy product $\frac{\dot{E}_\mathrm{D}}{\dot{E}_\mathrm{P}}$. Therefore, the relation from equation 7 is inserted into the definition of the COP, before both the nominator and the denominator are divided by $\dot{Q}_\mathrm{sink}$. Finally, the definition for the exergy product ($\dot{E}_\mathrm{P} = \dot{Q}_\mathrm{sink}\left(1 - \frac{T_0}{\overline{T}_\mathrm{Sink}}\right)$) was used to eliminate $\dot{Q}_\mathrm{sink}$ from the equation.

$$\begin{aligned}\mathrm{COP} = \frac{\dot{Q}_\mathrm{sink}}{\dot{W}_\mathrm{real}} = \frac{\dot{Q}_\mathrm{sink}}{\dot{W}_\mathrm{Lor} + \frac{\overline{T}_\mathrm{source}}{T_0}\dot{E}_\mathrm{D}} = \frac{1}{\frac{1}{\mathrm{COP}_\mathrm{Lor}} + \frac{\overline{T}_\mathrm{source}}{T_0}\frac{\dot{E}_\mathrm{D}}{\dot{Q}_\mathrm{sink}}} \\ = \frac{1}{\frac{1}{\mathrm{COP}_\mathrm{Lor}} + \frac{\overline{T}_\mathrm{source}}{T_0}\left(1 - \frac{T_0}{\overline{T}_\mathrm{sink}}\right)\frac{\dot{E}_\mathrm{D}}{\dot{E}_\mathrm{P}}}\end{aligned} \tag{8}$$

For zero exergy destruction, the COP corresponds to the $\mathrm{COP}_{\mathrm{Lor},}$ while the COP decreases for an increasing exergy destruction. It may however be noted that the relation between the COP and the exergy destruction $\dot{E}_\mathrm{D}$ is nonlinear.

In the presented analysis, this relation was used to visualize the dependencies of the potential improvements in COP that could be obtained by reductions in exergy destruction. The dead state was assumed to be at 1 bar and 1 °C. This may be considered as the conditions of the ambient, while the heat source might be a stream originating from cooling an industrial process. The impact of the dead state temperature was analyzed in a parameter study and no impact on the general applicability of the method was observed.

2.3. Associating exergy destruction with the actual process or the cycle layout and the working fluid

Recent studies on the optimization of heat pump systems by selecting the working fluid and the cycle layout have demonstrated a considerable potential for improvements in thermodynamic performance (Zühlsdorf, Jensen, *et al.*, 2018; Zühlsdorf, Meesenburg, *et al.*, 2018; Zühlsdorf, Jensen and Elmegaard, 2019). This optimization approach focused to some extent on the reduction of what was considered as unavoidable exergy destruction by advanced exergy analysis (Morosuk and Tsatsaronis, 2009). While advanced exergy analysis was found to be suitable for identifying the amount of unavoidable exergy destruction for a pre-defined system, it did not include further conclusions about what amount of exergy destruction could be omitted by optimizing the cycle layout and the working fluid.

As a method that is addressing this aspect sufficiently, we suggest deriving the scenario for the optimal performance with realistic component efficiencies from an idealized cycle, rather than from a predefined cycle as it is suggested in conventional exergy analysis (Morosuk and Tsatsaronis, 2009).

The suggested concept is derived and demonstrated by the example of vapor compression heat pumps using pure and mixed refrigerants. The ideal cycle for vapor compression heat pumps and refrigeration systems is the Lorenz cycle (Lorenz, 1894), consisting of heat rejection at the thermodynamic average temperature of heat source and sink and an isentropic compression and expansion. Heat pump and refrigeration cycles comprise accordingly a heat exchange process in which heat is obtained at a low temperature from the heat source, and one in which heat is rejected at higher temperature to the heat sink. Additionally, there are various approaches used to realize the temperature lift between the heat source and the heat sink. In a conventional one-stage vapor compression cycle, the temperature lift is realized by a compression and an expansion process. There are however various approaches that are combining compression and expansion process to obtain higher system performances. The compression and expansion process are therefore summarized in a lumped *temperature lift process* within the further analysis.

The optimal performance that may be obtained in each process, is determined by the *optimal feasible scenario,* which is described by an optimal cycle layout and working fluid under consideration of realistic component efficiencies. This enables quantifying the amount of exergy destruction that solely results from the actual process, and accordingly distinguishing it from the exergy destruction that is induced by the real cycle layout and working fluid. This exergy destruction constitutes accordingly the potential to improve the thermodynamic cycle performance.

The exergy destruction is accordingly separated into two contributions. The part of the exergy destruction that occurs during the process *i* when operating with an optimal fluid and cycle layout (index: “opt. C&F”) is described by $\dot{E}_{\mathrm{D,process,i-opt.C\&F}}$ and associated with the process itself. The the remaining part stems from deviations of the real fluid and cycle layouts from the ideal process (index: “real C&F) and is denoted as $\dot{E}_{\mathrm{D,process\ i-real\ C\&F}}$. The sum of both contributions yields the total exergy destruction occurring during process i $\dot{E}_{\mathrm{D,process\ i}}$.

$$\dot{E}_{\mathrm{D,process\ i}} = \dot{E}_{\mathrm{D,process\ i-opt\ C\&F}} + \dot{E}_{\mathrm{D,process\ i-real\ C\&F}} \tag{9}$$

In the following, this concept is adopted to the heat transfer processes with heat source and sink and the lumped temperature lift process.

2.3.1. Heat transfer process with heat source and sink

The optimal feasible scenario for the heat transfer processes is defined by a balanced heat exchange process. It was demonstrated in (Zühlsdorf, 2019) and (Zühlsdorf, Jensen, *et al.*, 2018) that a sophisticated working fluid choice among zeotropic mixtures may allow to approach the balanced heat transfer processes closely. Figure 3 introduces a respective example. It shows the temperature-heat-diagram of the standard cycle using butane for an exemplifying application. The temperature profiles of the working fluid during evaporation and condensation do not match with the temperature profiles of source and sink. The diagram includes furthermore the areas highlighting the temperature mismatches, which are causing the exergy destruction due to heat transfer. Aiming to reduce the temperature differences within the heat exchanger, and thereby the exergy destruction, while respecting a minimum pinch point temperature difference yields a balanced heat exchanger as the optimal process and is depicted by the *ideal fluid* in the temperature-heat-diagram. The balanced heat exchanger defines the amount of exergy destruction $\dot{E}_{\mathrm{D,HX-opt.C\&F}}$, which is associated with the heat exchanger equipment and considered to be inevitable even with an ideal fluid. The temperature profile of butane is deviating from the ideal process, which yields an increased mismatch and accordingly the exergy destruction that can be associated with the fluid being non-ideal $\dot{E}_{\mathrm{D,fluid}}$.

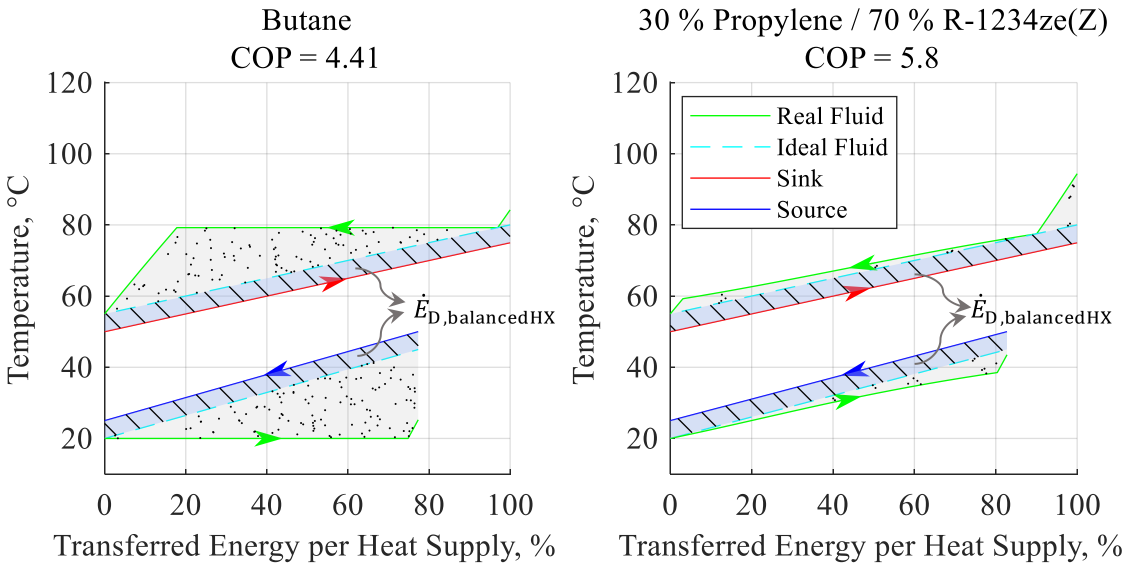

Figure 3. Temperature-heat-diagram of the pure fluid butane (left) and a mixture of 30 % propylene / 70 % R-1234ze(Z) (right), including a balanced heat exchange process and the respective exergy destruction $\dot{E}_{D,balancedHX}$ as well as the temperature mismatch for the real fluid, (Zühlsdorf, 2019)*. The cycles were calculated using the numerical models as described in section 2.1.*

The exergy destruction $\dot{E}_{\mathrm{D,HX-opt.C\&F}}$ associated with the minimum pinch point temperature difference, which results from the heat transfer of $\dot{Q}$ from a stream with a thermodynamic average temperature $\bar{T}_{\mathrm{hot}}$ to a stream with a thermodynamic average temperature $\bar{T}_{\mathrm{cold}}$, can be obtained from an exergy balance and is defined as shown in Eq. 9.

$$\dot{E}_{\mathrm{D,HX-opt.C\&F}} = \left(1 - \frac{T_0}{\bar{T}_{\mathrm{hot}}}\right)\dot{Q} - \left(1 - \frac{T_0}{\bar{T}_{\mathrm{cold}}}\right)\dot{Q} = T_0\,\dot{Q}\,\frac{\bar{T}_{\mathrm{hot}} - \bar{T}_{\mathrm{cold}}}{\bar{T}_{\mathrm{hot}}\,\bar{T}_{\mathrm{cold}}} \tag{10}$$

The exergy destruction in the heat exchanger i associated with the fluid being non-ideal $\dot{E}_{\mathrm{D,HX}\,i\mathrm{-real\ C\&F}}$ is determined by the difference of the total exergy destruction in the heat exchanger i $\dot{E}_{\mathrm{D,HX}\,i}$ and the contribution associated with the pinch point $\dot{E}_{\mathrm{D,HX}\,i\mathrm{-opt.C\&F}}$.

$$\dot{E}_{\mathrm{D,HX}\,i} = \dot{E}_{\mathrm{D,HX}\,i-\mathrm{opt.C\&F}} + \dot{E}_{\mathrm{D,HX}\,i-\mathrm{real\ C\&F}} \tag{11}$$

The thermodynamic average temperature of a stream between temperature T_A and T_B with constant heat capacity can be calculated as $\bar{T}_{\mathrm{A-B}} = (T_\mathrm{A} - T_\mathrm{B})/\ln{(T_\mathrm{A}/T_\mathrm{B})}$ (Bejan, Tsatsaronis and Moran, 1996).

The heat flow for the heat exchange to the heat sink was defined by the application and maintained throughout the analysis. The heat flow rate for the heat source is dependent on the COP and may be obtained from an energy balance for the system under consideration of minimum pinch point temperature differences and a lumped efficiency for the temperature lift process as introduced in the subsequent chapter.

2.3.2. Temperature lift process

In a conventional one-stage vapor compression cycle, the temperature lift between the heat transfer processes is realized by a compression and an expansion process. The expansion process is often realized by throttling within the two-phase region and is hence causing irreversibilities, especially due to the formation of gas. In order to reduce these losses and recover some of the lost work, several approaches are used in practice. Such approaches include expansion devices, such as ejectors or expanders, or more complex cycle layouts, such as internal heat exchangers or multi-stage compression with open intercoolers and recovery of flash gas.

Considering the various possibilities for close integration of expansion and compression process it may be concluded that it is a meaningful approach to summarize these processes in one lumped process. We therefore suggest considering the compression and expansion process, including all associated processes such as internal heat exchange, as one *temperature lift process* with respect to the definition of an ideal reference process.

This reference process constitutes a process, which is the combination of both an ideal fluid and realistic component efficiencies that yield minimum irreversibilities. For the temperature lift process, we suggest assuming a lumped exergetic efficiency with respect to the minimum work that has to be invested to lift the temperature from the lower to the higher thermodynamic average temperature under consideration of the minimum pinch point temperature differences ΔT_pinch.

The maximum obtainable COP and thereby the minimum required work $\dot{W}_\mathrm{min}$ for lifting heat from one temperature to a higher temperature is defined by the Lorenz $\mathrm{COP}_\mathrm{Lor}$, which is obtained by the Lorenz cycle (Lorenz, 1894). The Lorenz cycle consists of isentropic expansion and compression processes and transfers the heat at the thermodynamic average temperatures of the source and sink. The $\mathrm{COP}_\mathrm{Lor}$ is accordingly solely dependent on the temperatures of the heat source and sink. The Lorenz cycle may be seen as a generalization of the Carnot cycle. For cases with no temperature glide of the sink and source the Lorenz cycle is identical to the Carnot cycle.

For a fixed heat supply rate $\dot{Q}_\mathrm{sink}$, and the assumption of feasible minimum pinch point temperature differences ΔT_pinch for the heat transfer processes, the minimum required work $\dot{W}_\mathrm{min}$ may be derived based on the thermodynamic average temperatures of the working fluid during heat exchange with the source $\bar{T}_\mathrm{wf,source}$ and the sink $\bar{T}_\mathrm{wf,sink}$.

$$\dot{W}_\mathrm{min} = \dot{Q}_\mathrm{sink}\left(\frac{\bar{T}_\mathrm{wf,sink} - \bar{T}_\mathrm{wf,source}}{\bar{T}_\mathrm{wf,sink}}\right) \tag{12}$$

Irrespective of the exact layout of the temperature lift process, it may be expected that it is associated with irreversibilities and that an amount of these irreversibilities cannot be avoided even when considering an optimal cycle layout and working fluid. The additional work to be invested for compensating the irreversibilities while maintaining the same heat supply may be estimated with a lumped efficiency $\eta_\mathrm{TL} = \frac{\dot{W}_\mathrm{min}}{\dot{W}_\mathrm{opt.C\&F}}$. This efficiency describes the ratio of the work in an ideal cycle and the work in a cycle with an optimal cycle layout and working fluid, while considering both the expansion process and the compression process as a lumped process. This approach was chosen, as the expansion and compression processes are closely linked and may generally be integrated with each other by a variety of approaches, which prohibits an independent consideration.

$$\dot{W}_{\mathrm{opt.C\&F}} - \dot{W}_{\mathrm{min}} = \dot{W}_{\mathrm{min}} \left(\frac{1}{\eta_{\mathrm{TL}}} - 1 \right) \tag{13}$$

The exergy destruction that is associated with the temperature lift and remains even for an optimal cycle and fluid $\dot{E}_{\mathrm{D,TL-opt.C\&F}}$ is derived analogously as Equation 7 dependent on the average temperature of the working fluid during heat transfer with the heat source $\overline{T}_{\mathrm{source,wf}}$ and the dead state temperature T_0.

$$\dot{E}_{\mathrm{D,TL-opt.C\&F}} = \dot{W}_{\mathrm{min}} \left(\frac{1}{\eta_{\mathrm{TL}}} - 1 \right) \frac{T_0}{\overline{T}_{\mathrm{source,wf}}} = \dot{Q}_{\mathrm{sink}} \left(\frac{1}{\eta_{\mathrm{TL}}} - 1 \right) T_0 \left(\frac{\overline{T}_{\mathrm{wf,sink}} - \overline{T}_{\mathrm{wf,source}}}{\overline{T}_{\mathrm{source,wf}} \cdot \overline{T}_{\mathrm{wf,sink}}} \right) \tag{14}$$

The lumped maximum efficiency depends on the technological advancements and requires a qualified assumption. For the current study, a lumped maximum efficiency of $\eta_{\mathrm{TL}} = 80\ \%$ was assumed, based on studies of different cycle layouts and under consideration of technically feasible components. In future studies, the definition of a reasonable efficiency might as well require analyzing different layouts

The total exergy destruction related to the temperature lift is the sum of the exergy destruction occurring in all components related to the temperature lift $\dot{E}_{\mathrm{D,TL}}$, such as compressor, expansion valve, internal heat exchanger and open intercooler. Analogously to the distinction in the heat exchanger, the exergy destruction is composed on a contribution that cannot be avoided even with an ideal fluid $\dot{E}_{\mathrm{D,TL\,-\,opt.C\&F}}$ and a contribution accounting for the cycle and fluid being nonideal $\dot{E}_{\mathrm{D,TL\,-\,real\ C\&F}}$.

$$\dot{E}_{\mathrm{D,TL}} = \sum_i \dot{E}_{\mathrm{D,TL,i}} = \dot{E}_{\mathrm{D,TL\,-\,opt.C\&F}} + \dot{E}_{\mathrm{D,TL\,-\,real\ C\&F}} \tag{15}$$

3. Results

3.1. Thermodynamic analysis

This section presents a basic thermodynamic analysis of the results to outline the potentials obtainable by different mixtures of the chosen combination of propane and butane and for different cycle layouts.

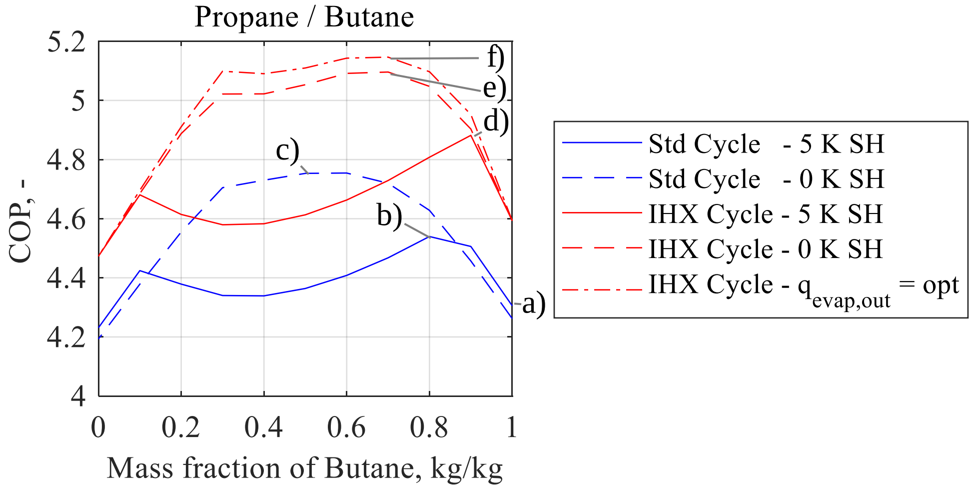

Figure 4. COP for the standard (Std) cycle and the internal heat exchanger (IHX) cycle with different fluid conditions at the outlet of the evaporator for mixtures of propane and butane, (Zühlsdorf, 2019)

Figure 4 shows the COP for all mixtures of propane and butane depending on the mass fraction of butane for different cycle layouts. The standard cycle with a minimum required superheating of 5 K inside the evaporator was included as a baseline. It was furthermore assumed, that the required superheating inside the evaporator could be reduced by e.g., an advanced control of the evaporator outlet enabled by the temperature glide of the mixtures, without adding a component. In addition to the standard cycle, the IHX-cycle was presented for three different assumptions. It was assumed that the outlet of the evaporator is i) superheated by 5 K, ii) in saturated conditions and iii) at an optimized outlet quality. All five scenarios were evaluated by use of the numerical models as described in section 2.1. for binary mixture compositions distributed equidistantly in with an interval of 10 % steps. Based on these results, six representative cases were selected for further evaluation and summarized in Table 1 and visualized by means of temperature heat diagrams in Figure 5.

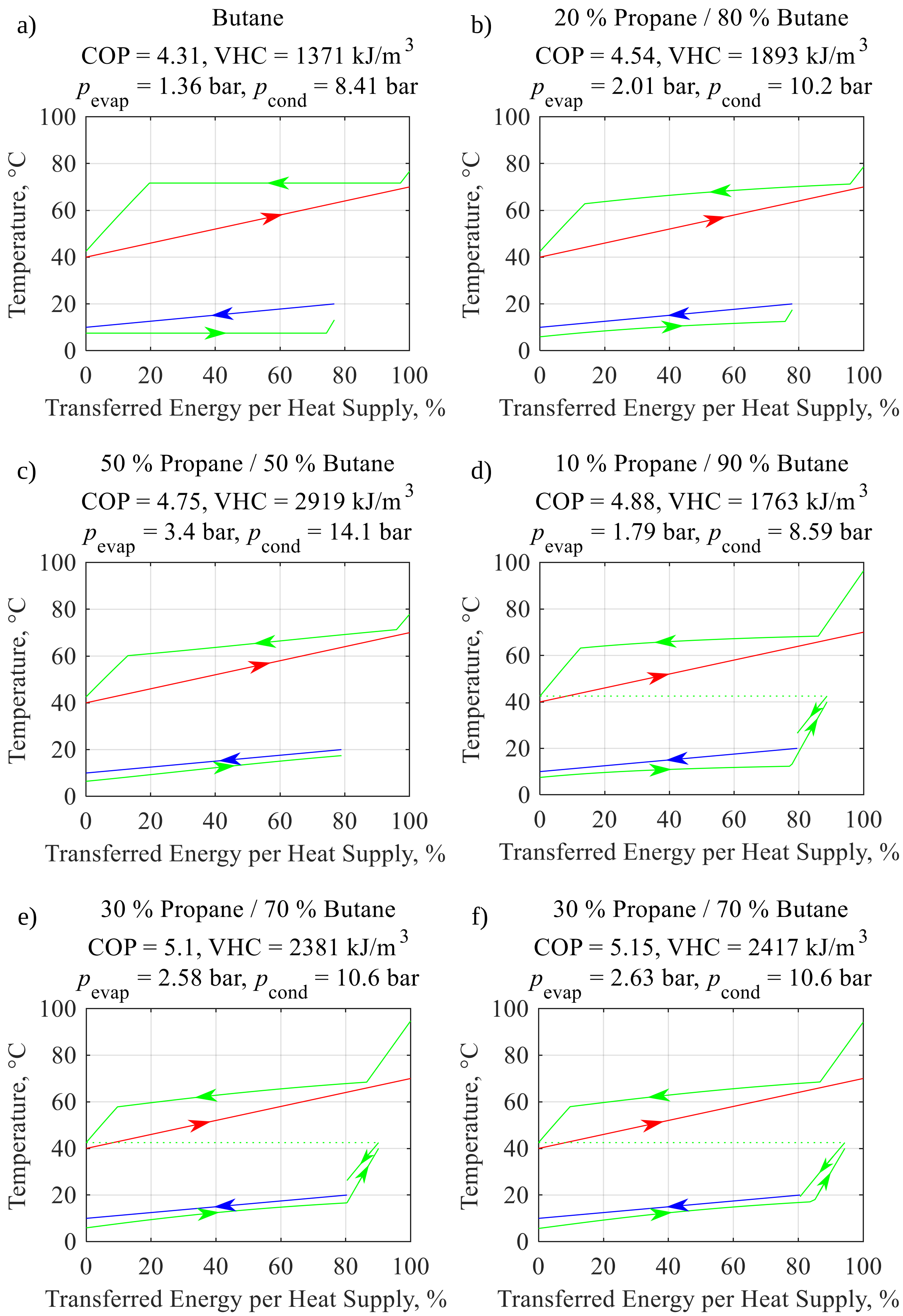

Figure 5. Temperature-heat-diagrams for cases a) to f) from Table 1, (Zühlsdorf, 2019)

Table 1. Summary of COP, volumetric heating capacity VHC and pressure levels for selected cases

Case	Cycle	Condition at evaporator outlet	Medium (Example)	COP, -	VHC, kJ/m^3	p_{evap}, bar	p_{cond}, bar
a)	Std-cycle	Superheated by 5 K	Butane	4.31	1371	1.4	8.4
b)			20 % Propane / 80 % Butane	4.54	1893	2.0	10.2
c)	Std-cycle	Superheated by 0 K	50 % Propane / 50 % Butane	4.75	2919	3.4	14.1
d)	IHX-cycle	Superheated by 5 K	10 % Propane / 90 % Butane	4.88	1763	1.8	8.6
e)	IHX-cycle	Superheated by 0 K	30 % Propane / 70 % Butane	5.10	2381	2.6	10.6
f)	IHX-cycle	Optimized quality	30 % Propane / 70 % Butane	5.15	2417	2.6	10.6

The diagram shows a COP of 4.3 for butane at (a), which is slightly higher than for propane for the standard cycle with 5 K superheating inside the evaporator. For the same cycle configuration, the COP could be increased to 4.5 for 20 % propane / 80 % butane (b). Assuming that the superheating inside the evaporator could be reduced benefitted mainly the mixtures with a good glide match on the source side and yielded a COP of 4.8 for 50 % propane / 50 % butane.

The results for the configuration in which an internal heat exchanger was considered and a minimum required superheating of 5 K inside the evaporator was assumed were similar to the standard cycle with minimum 5 K superheating inside the evaporator with a relatively constant offset of 0.25 in COP. This enabled a COP of 4.9 for 10 % propane / 90 % butane.

The reduction of the required superheating inside the evaporator showed a similar increase in COP for the IHX-cycle as it did for the standard cycle. The mixture 30 % propane / 70 % butane reached a COP of 5.1 with saturated conditions at the outlet of the evaporator, while it reached 5.15 for an optimized outlet quality. It may furthermore be noted that a higher concentration of propane yielded higher pressure levels and higher volumetric heating capacities.

Figure 5 shows the temperature-heat-diagrams for the cases described in Table 1. In case a), butane showed a mismatch of the temperature profiles on both the heat source and sink side. The temperature match on the source side was improved for all other cases, while an optimal match is obtained for the cases in which the superheating inside the evaporator was omitted. On the sink side, the temperature match was improved compared to butane, while a certain mismatch remained.

3.2. Exergy Analysis

The thermodynamic analysis documented considerable performance improvement potentials associated with the use of zeotropic working fluid mixtures for the selected case. This section presents the results of an exergy analysis and relates the contributions of exergy destruction to potential increases in COP. The exergy destruction in the heat exchangers was furthermore distinguished into a contribution associated with the pinch point temperature difference that could not be avoided with an ideal fluid and another contribution accounting for the fluid being non-ideal.

Figure 6 shows the different sources of exergy destruction $\dot{E}_D$ in relation to the exergy product $\dot{E}_P$ and relates these to the COP for the selected six cases. The COP approaches the Lorenz COP_{Lor} for zero exergy destruction and decreases non-linearly for an increasing exergy destruction. The potential increase in COP associated with the reduction of a unit of exergy destruction is accordingly higher for lower values of absolute total exergy destruction.

The exergy destruction associated with the pinch point temperature differences remains constant for the condenser and increases slightly for the evaporator. The slight increase results from the increasing heat flow rate in the evaporator at higher COPs. The exergy destruction in relation to the exergy product occurring in the compressor decreases from 22 % in a) to 18 % in e), which might result from decreasing temperature differences between compressor inlet and outlet. The irreversibilities associated with the throttling valve decrease considerably due to the introduction of the internal heat exchanger, which compensates the additional exergy destruction resulting from the heat transfer.

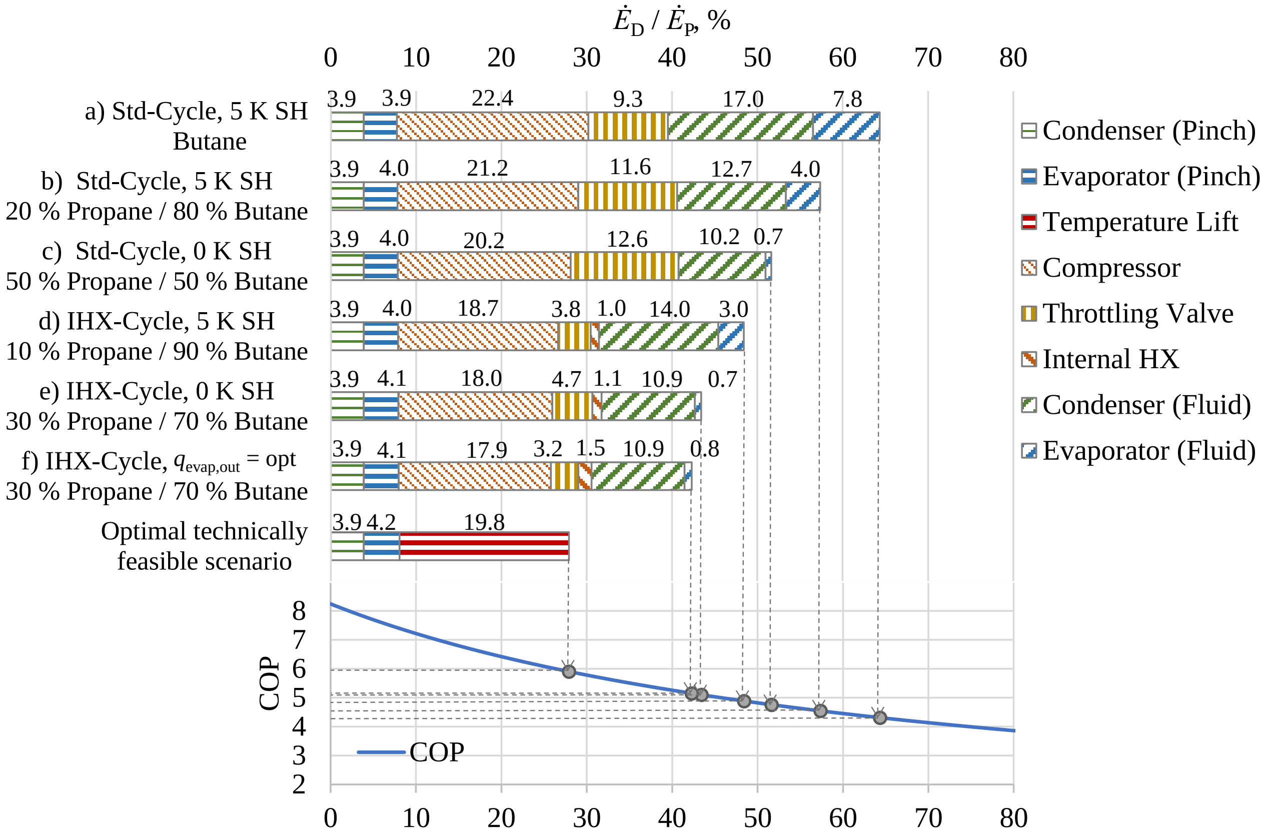

Figure 6. Overview of the exergy destruction per exergy product in relation to the COP for all considered cases, extended based on (Zühlsdorf, 2019)

The exergy destruction associated with the temperature profile of a real fluid deviating from an ideally matched working fluid decreases from 17 % for a) to 11 % for e), in the condenser, while it could be reduced to below 1 % for the evaporator. These findings are furthermore consistent with the observations from the temperature-heat-diagrams.

The optimal technically feasible scenario describes a case in which the heat transfer processes occur most optimally with matched temperature profiles and a lumped exergetic efficiency for the temperature lift process of 80 %. This scenario does thereby constitute a benchmark for the optimization of the remaining cycles. In this case, the exergy destruction from the condenser and the evaporator accumulate to 3.9 % and 4.2 % in relation to the exergy product, respectively. The best temperature lift process in case e) comprises the compressor with 17.9 %, the throttling valve with 3.2 % and the internal HX with 1.5 %, which accumulates to 22.6 %. The optimal technically feasible scenario suggests a minimum exergy destruction of 19.8 % of the exergy product, based on a lumped exergetic efficiency for the temperature lift process of 80 %, which was assumed to be a technically feasible benchmark for the given case.. Assuming this assumption to be a reasonable benchmark indicates that the irreversibilities associated with the temperature lift process in case e) are at a satisfying level.

4. Discussion

The study presented an exergy-based analysis of different working fluids and different cycle layouts. It highlighted the different contributions of irreversibilities in terms of exergy destruction and related these contributions to the deviations in COP from the theoretically ideal Lorenz COP_{Lor}.

The study was based on a specific example, and it was limited to the analysis of binary mixtures of propane and butane. It may be noted that the mixture of propane/butane was chosen as an example for the demonstration of the method. The temperature glides of these mixtures are relatively similar in both evaporation and condensation. This yields a moderate mismatch in the sink side, which cannot be avoided for the described case study considering propane/butane. Zühlsdorf et al. (Zühlsdorf, Jensen, *et al.*, 2018) outlined that the improved temperature glide matches might be obtained by other fluids, which are e.g., operating with a condenser pressure close to or above the critical pressure.

The exergy destruction in the heat source and heat sink heat exchangers was distinguished into two contributions. One contribution was associated with the heat exchanger equipment and the other with the fluid being nonideal. The exergy destruction associated to the heat exchanger equipment was considered to be unavoidable by optimizing the working fluid and the cycle layout. The results indicated that these contributions remained constant and were only impacted by the different heat flow rates in the evaporator resulting from the variations in COP and the constant heat sink capacity during the study. This distinction was found to be a meaningful quantification of the exergy destruction, which could be reduced by temperature glide matching with a sophisticated working fluid choice.

The ideal fluid with respect to the heat transfer process was identified as a fluid with an optimally matched temperature profile. This enabled determining the exergy destruction associated with the component when operating with an ideal fluid, without requiring specific medium properties. For the temperature lift process, we considered a similar approach as applied for the heat exchange process by dividing the irreversibilities into a contribution from the fluid and from the component. The definition of this is, however, less intuitive than the definition for the heat exchange processes, especially when considering the various possibilities for optimizing the performance. In order to substantiate this approach, it is illustrated by the example of a single-stage vapor compression cycle in the following. For the single-stage vapor compression cycle with a high isentropic compression efficiency and an isenthalpic expansion, the optimal fluid would have the following properties:

For compression it should be a gas which would require the lowest possible work for a given increase in pressure and temperature, respectively. Apart from the component requirement of a high isentropic efficiency, this would entail that the ideal fluid should be a gas with a low isentropic exponent and a high molecular mass. For more easily matching the heat exchange characteristics, the profile of dewpoint curve should preferably match the isentrope of the compression. For the expansion, the fluid should have a low change in density and an accordingly low amount of throttling losses.

However, a real fluid deviates from these ideal characteristics and causes accordingly irreversibilities in the described cycle layout. These irreversibilities may however be compensated by an adjusted cycle layout, considering measures such as an expansion device with work recovery, internal heat exchangers and/or open intercoolers with multi-stage compression and expansion. The optimal choice of the cycle layout and the respective measures for compensating the fluid non-idealities depends obviously on the fluid characteristics. It may therefore be concluded that a general benchmark for the temperature lift process is only meaningful when being defined as a lumped efficiency. Any attempt of defining it based on a more specific cycle layout might benefit specific working fluid characteristics.

5. Conclusions

The article presented an exergy-based analysis of different working fluids and cycle layouts and related the exergy destruction to deviations from a theoretically ideal Lorenz cycle in terms of COP. The study was based on a case study with fixed inlet and outlet conditions considering different mixtures of propane/butane.

The exergy destruction in the components were, in addition to a conventional exergy analysis, distinguished into a contribution solely resulting from the component efficiencies which remain for an ideal working fluid and a contribution accounting for the fluid being non-ideal. This distinction was found suitable for quantifying the optimization potential associated with temperature glide matching using zeotropic working fluids.

Furthermore, the exergy destruction was related to deviations from the Lorenz cycle in terms of COP. This enabled a more intuitive interpretation of the exergy destruction and the corresponding impact on the thermodynamic performance.

Both concepts may highlight the optimization potential in heat pump in refrigeration cycles and may thereby contribute to the development of high-performance heat pump cycles. The developed methodology appears promising to be applied for evaluating working fluids and cycle layouts for heat pump and refrigeration applications. The suggested concept of relating the exergy destruction to COP may be considered as a visual approach that is associating the irreversibilities with the main performance parameter, COP, in order to explain the impact of irreversibilities more intuitively.

Acknowledgments

Nomenclature

Latin symbols:

COP	Coefficient of performance, -
$\dot{E}$	Exergy flow rate, kW
p	Pressure, bar
$\dot{Q}$	Heat flow rate, kW
T	Temperature, °C
$\bar{T}$	Thermodynamic average temperature, °C
$\dot{V}$	Volume flow rate, m^3/s
VHC	Volumetric heating capacity, kJ/m^3
$\dot{W}$	Power, kW

Subscripts and superscripts:

Comp	Compressor
cold	Cold side
cond	Condensation
D	Destruction
evap	Evaporation
F	Fuel
fluid	Fluid
hot	Hot side
Lor	Lorenz cycle
P	Product
pinch	Pinch
real	Real cycle
Sink	Sink
Source	Source
0	Dead state

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