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Improving efficiency of heat pumps by use of zeotropic mixtures for different temperature glides

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Abstract:

The present study demonstrates the optimization of a heat pump for an application with a large temperature glide on the sink and a smaller temperature glide on the source side. The study includes a simulation of a heat pump cycle for all possible binary mixtures from a list of 14 natural refrigerants, which enables a match of the temperature glide of sink and source with the temperature of the working fluid during phase change and thus, a reduction of the exergy destruction due to heat transfer. The model was evaluated for four different boundary conditions. For a separated evaluation of the irreversibility solely caused by the fluid properties, the exergy destruction in the heat exchangers has been distinguished accordingly and an indicator quantifying the glide match has been defined to analyse the influence on the performance. It was observed that a good glide match can contribute to an increased performance. Dependent on the boundary conditions a performance increase of 20.0 % for a simple cycle was observed and 26.9 % increase if the required superheating can be avoided. The temperature glide match in the source was identified to have a higher influence on the performance than in the sink.

Keywords:

Heat pump, Zeotropic mixture, Temperature glide, Exergy efficiency.

1. Introduction

Heat pumps constitute an energy efficient and sustainable possibility for heat supply in domestic and industrial applications. Different approaches are followed to improve the performance and thus increase the competitiveness in a broad range of applications. Challenging conditions can result from the characteristics of heat sink and source, which are in many cases single phase. When heat is removed or added from or to a fluid with a finite heat capacity, the temperature of the fluid changes. The temperature glide in heat sink and source are additional challenges for an efficient heat pump integration.

Radermacher and Hwang [1] show, that a heat pump cycle with a pure fluid and thus, a constant temperature during phase change, conforms with the Carnot cycle which is beneficial for heat sources and sinks with minor or no temperature glide. For larger temperature glides in heat sink and source, the Lorenz cycle shows an enhanced performance. Retaining the layout of a conventional vapor compression heat pump, the Lorenz cycle can be approached by using a zeotropic mixture, which experiences a temperature glide during evaporation and condensation. A sophisticated choice of the refrigerant mixture can improve the heat pump performance by matching the temperature profiles during heat addition and removal to and from the cycle and thus, reduction of exergy destruction through heat transfer.

Besides the possible improvements resulting from beneficial exploitation of temperature glides, mixtures offer the possibility to obtain favorable thermodynamic and physical properties by combining a limited set of fluids. After the phase out of popular refrigerants with high global warming potentials (GWP) and ozone depletion potentials (ODP) by the Montreal protocol [2], the Kyoto protocol [3] and especially after extension to hydrofluorocarbons (HFC) by the amendment from Kigali [4,5], it is important to enlarge the range of potential applications for accepted alternatives. The mixing of natural refrigerants widens their range of applications and thus, their competitiveness [6].

It is additionally possible to design the mixtures in such a way, that unfavorable medium properties of the single components are compensated by the other components. Several studies, e.g. [7–9] have analyzed the combination of CO_2 with hydrocarbons (HC) in simulation and experimental studies, yielding an increased coefficient of performance (COP) and secondarily effects such as a reduced high pressure side when compared with pure CO_2 systems and a reduced flammability when compared to pure HC systems.

Nevertheless, the possible benefits resulting from zeotropic mixtures imply increased requirements during design and operation, to ensure that the mixture characteristics are used beneficially. Especially the temperature glide matching requires an increased knowledge and effort during cycle design in order to increase the cycle performance [10]. A mismatch of the temperature glide resulting from an insufficient design or from composition shift due to leakage during operation [11] can decrease the performance.

Many simulation-based and experimental studies were conducted in order to optimize the heat pump performance for a specific application by choosing from a limited set of mixtures and analyze operational issues in experimental setups, e.g. [12]. A comprehensive review about this topic was conducted by Mohanraj et al. in [6]. McLinden and Radermacher present methods to compare the performance of pure and mixed refrigerants [13] whereas there remains a lack of knowledge for the influence from temperature glide matching on the cycle performance for different boundary conditions and methods to choose the refrigerant accordingly.

Opposing the increase in efficiency, the use of zeotropic mixtures and a resulting match of the temperature glides require an increased heat transfer area, since the temperature difference is reduced and due to the diffusion resistances during phase change which decrease the convective heat transfer characteristics [1,14]. Nevertheless, the tradeoff between additional investment in heat exchanger area and an increased performance is very dependent on the physical and economic boundary conditions and need to be analyzed for each application, regardless if pure or mixed refrigerants are considered. That the increased performance can cover the additional investment and thus, result in an increased net present value for using a mixture has among others been shown by [15].

From the state of the art, it can be summarized that zeotropic mixtures can constitute a promising alternative to pure working fluids, as long as they are chosen according to the application. The possible performance increase of using mixtures depends on the boundary conditions, such as temperature glides in source and sink and temperature lift. The diversity of the different heat pump applications creates a demand for an analysis of the potential performance increase resulting from use of zeotropic mixtures dependent on different temperature profiles of heat source and sink.

The presented work has consequently aimed to analyze under which boundary conditions the use of zeotropic mixtures is reasonable. Furthermore, it has been investigated, how much the matching of the temperature profiles in each sink and source heat exchanger contributes to the overall performance increase in order to develop knowledge which can be used during cycle and working fluid design.

2. Methods

2.1. Simulation Procedure

In order to analyse for which applications the use of zeotropic mixtures is beneficial, a case with different boundary conditions was defined, representing a range of possible applications. In general, several combinations of temperature glides in heat source and sink are possible. The glide on both sides can be minor or zero, if the heat capacity rate is high, or large if the capacity rate is low. Also combinations of a high glide in the sink with a small glide in the source and vice versa are possible.

Nevertheless, typically the heat sink has a certain temperature glide, while different heat sources offer a range from small to large glides.

For this case, it is assumed, that the heat source consists of a stream with a temperature of 40 °C, which would represent a high share of industrial excess heat [16]. The source is used to heat another stream from 40 °C to 80 °C, which is within a common temperature range for low temperature processes [17]. The outlet temperature of the heat source is not fixed and will be varied from 35 °C (Case I), to 30 °C (Case II), 25 °C (Case III) and 20 °C (Case IV). This setup can represent a booster heat pump for a low temperature district heating network on the consumer side [18] for which the return temperature is not defined by other parameters or an industrial application in which a heat stream of a process can be exploited by cooling it down to any temperature, while heating another process stream to a useable temperature, e.g. for feeding it to a conventional district heating network or reusing it on site [19]. Especially when latent heat from condensation of moist air is recovered, the temperature glide on the source side is small.

As a basis for the analysis a model for the heat pump model is implemented and simulated for each case and all possible refrigerants and binary refrigerant mixtures.

2.2. Heat Pump Model

2.2.1. Thermodynamic Model

The heat pump model was implemented for a simple vapour compression cycle as shown in Fig. 1. It consists of the minimum amount of required components and represents the simplest possible heat pump solution. Therefore, the analysis focuses solely on the influence gained from using mixtures and includes the possibility to derive recommendations for possible adjustments of the cycle layout.

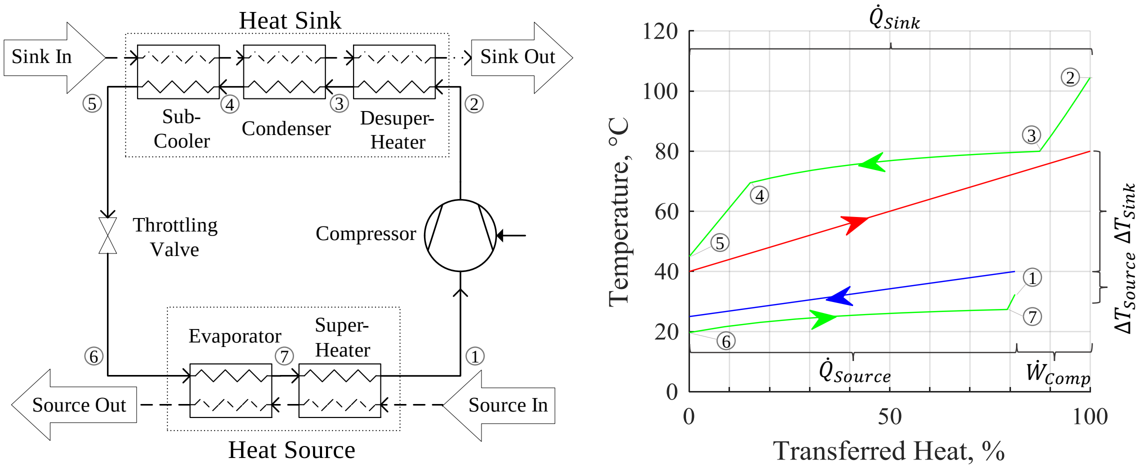

Fig. 1. Flow sheet of modelled heat pump (left) and diagram with temperature profiles over transferred heat for case II with 10 % CO_2 – 90 % DME as working fluid (right)

The heat pump process describes a working fluid which receives heat from the heat source at low pressure (6 → 1), before it is compressed to a higher pressure (1 → 2) in order to reject heat to the heat sink at high temperatures (2 → 5), before it is expanded to the low pressure again (5 → 6). The heat rejection can occur sub- or transcritically, while the low pressure side is always below the critical point.

The model is based on the first and second law of thermodynamics and includes energy and mass balances for all components. The heat exchangers are in the model divided into individual units according to single-phase and two-phase. Each of these is modelled as a separate heat exchanger, disregarding if they are manufactured as one component. This distinction diminishes for transcritical processes, which is for numerical reasons assumed above 95 % of the critical pressure. The heat exchangers implying phase change are discretized in steps of equal amounts of transferred heat along the flow direction to enable the calculation of temperature profiles during the phase change. A discretization in 15 state points for the condenser and 10 for the evaporator was found to provide sufficient accuracy with an acceptable tolerance.

In order to calculate condensation and evaporation pressure a minimum pinch point temperature difference of $\Delta T_{\text{pinch,min}} = 5$ K has been introduced. The possible performance gain from subcooling is always completely exploited by defining the temperature T_5 by the pinch point temperature difference above the sink inlet temperature. For the subcooled processes fixing the condensation pressure by setting the minimum temperature difference to the minimum required pinch temperature difference yields the maximum COP, while this is not always valid for transcritical processes. In the transcritical region the pressure is optimized with respect to COP considering a boundary on the minimum temperature difference.

The compression process is modelled with an isentropic efficiency of $\eta_{\text{comp,is}} = 0.8$ while losses from the electrical motor to the environment are disregarded. In order to protect the compressor from wet compression a minimum superheating temperature of $\Delta T_{\text{SH}} = 5$ K is considered. For additional analyses the simulations were repeated without superheating, see Appendix A.

The throttling process is assumed to be isenthalpic.

The model is implemented in Matlab [20] and uses medium properties from Refprop [21] with the recommended state of the art equations of state and mixing parameters for all modelled fluid mixtures.

2.2.2. Exergy Analysis

In order to identify the inefficiencies in the systems an exergy analysis is conducted as described in [22]. For the calculation of the exergetic fuel $\dot{E}_F$ and exergetic product $\dot{E}_P$ the exergy flow rate $\dot{E}$ is calculated for each state point, defining the dead state at $T_0 = 25$ °C and $p_0 = 1$ bar. The exergetic fuel and product are defined depending on the function of the component. For dissipative components, such as the throttling valve, fuel and product are defined by in and out flowing exergy streams. For all components and the system the exergy destruction can be determined by an exergy balance:

$$\dot{E}_D = \dot{E}_F - \dot{E}_P \tag{1}$$

The exergy destruction describes the irreversibilities within the components as an absolute value. Since the absolute heat transfer in the different components can vary, the exergy destruction varies as well and thus, is not an optimal measure for comparisons of performance. The more representative variable is the exergy efficiency as the ratio of the exergetic product over the exergetic fuel. Nevertheless, it can hardly be used to compare components of different types, since it accounts for all exergy destruction within the component, irrespective of the function and the sources of irreversibilities. Furthermore, it does not contain information if the exergy destruction could be avoided by e.g. an optimal mixture having a constant temperature difference along the transferred heat.

Therefore we suggest distinguishing between two contributions as shown in Fig. 2, i.e., exergy destruction $\dot{E}_{D,\text{pinch}}$ which is caused by the nature of the component or process and cannot be avoided even with an ideal fluid and an additional exergy destruction $\dot{E}_{D,\text{fluid}}$ which accounts for the difference between ideal and real working fluids. The sum of the exergy destruction from both contributions yield the total exergy destruction occurring within the component $\dot{E}_{D,\text{component}}$.

$$\dot{E}_{D,\text{component}} = \dot{E}_{D,\text{pinch}} + \dot{E}_{D,\text{fluid}} \tag{2}$$

If the heat exchanger is assumed to be an ideal component with an infinite heat exchanger area, the exergy destruction related to the pinch $\dot{E}_{D,\text{pinch}}$ would diminish, but still the exergy destruction accounting for the difference between a real and an ideal fluid $\dot{E}_{D,\text{fluid}}$ would contribute to the total components exergy destruction.

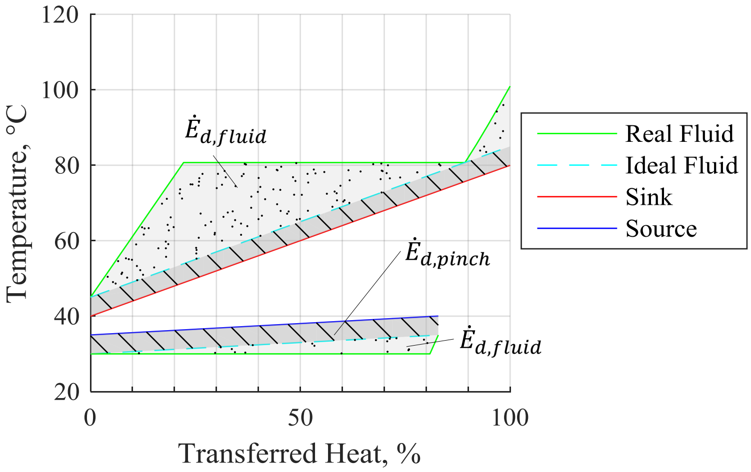

Fig. 2. Diagram with temperature profiles over transferred heat with exergy destruction highlighted

The exergy destruction accounting for the minimum temperature difference can be determined by an exergy balance in between the ideal fluid and the sink or source stream accordingly. In order to calculate the exergy flow $\dot{E}_Q$ of a heat flow rate $\dot{Q}$ which is rejected or received linearly between the temperatures T_1 and T_2, the thermodynamic average temperature $\overline{T}_{1-2} = (T_1 - T_2)/\ln(T_1/T_2)$ is introduced, [22]. Using this relation, the exergy balance defines the exergy destruction as:

$$\dot{E}_{D,\text{pinch}} = \left(1 - \frac{T_0}{\overline{T}_{\text{hot}}}\right)\dot{Q} - \left(1 - \frac{T_0}{\overline{T}_{\text{cold}}}\right)\dot{Q} = T_0\,\dot{Q}\,\frac{\overline{T}_{\text{hot}} - \overline{T}_{\text{cold}}}{\overline{T}_{\text{hot}}\,\overline{T}_{\text{cold}}} \tag{3}$$

As an indicator to describe the match of the temperature profiles we introduce the temperature matching indicator π_{glide} as the ratio of the total exergy destruction $\dot{E}_{D,\text{component}}$ over $\dot{E}_{D,\text{pinch}}$:

$$\pi_{\text{glide}} = \frac{\dot{E}_{D,\text{component}}}{\dot{E}_{D,\text{pinch}}} = \frac{\dot{E}_{D,\text{fluid}} + \dot{E}_{D,\text{pinch}}}{\dot{E}_{D,\text{pinch}}} \tag{4}$$

For an optimal match of the temperature profiles the matching efficiency will approach $\pi_{\text{glide}} = 1$ whereas it increases with an increasing mismatch.

This definition enables additionally to determine the share of exergy destruction caused by the fluid enthalpy-temperature profile on the entire exergy destruction of the system $y_{D,\text{fluid}}$ and thereby represents the possible decrease of inefficiencies in the system by fluid optimization:

$$y_{D,\text{fluid}} = \frac{\dot{E}_{D,\text{fluid}}}{\dot{E}_{D,\text{total}}} \tag{5}$$

The introduced distinction between exergy destruction which could potentially be avoided by finding an optimal fluid and exergy destruction resulting from component inefficiencies cannot be applied to the compression and expansion process, since these processes convert mechanical work into internal energy, which can theoretically be reversible for any fluid. In these cases properties of the real fluids do not cause any additional exergy destruction.

2.3. Refrigerant Screening

The list of fluids which are considered in the design of the binary mixtures can be defined according to different aspects. Since no straight relation between medium properties of the pure components and the cycle performance of the mixture could be observed, it seems promising to assemble the group of pure fluids for designing the mixtures with fluids covering a broad range of typically relevant medium characteristics, such as the normal boiling point and the critical point. Considering that already a small number of pure fluids results in a high number of possible mixed working fluids obviates the need to consider fluids with unfavorable characteristics, that remain unfavorable also in a mixture, such as ozone depletion potential (ODP) or global warming potential (GWP).

Considering these aspects, the group of commonly used natural refrigerants and the two higher boiling hydrocarbons (HC) n-Hexane and Heptane are chosen for this study as shown in Table 1. The natural refrigerants entail a good and low-cost availability, experiences from being proven working fluids, limited toxicity, low environmental impact and good miscibility among each other.

The miscibility has been analyzed using a group contribution method as proposed in [23]. Immiscibility of the fluids would result in two liquid phases with different compositions, so called miscibility gaps, which could have unfavorable influences on the operation. The fluids above the dashed line in Table 1 are widely miscible with each other with minor miscibility gaps in the mixtures including ethers. Especially mixtures with DME have miscibility gaps, whereas DEE shows good miscibility with the other fluids. The ethers are fully miscible. The miscibility of the fluids above the dashed line with water and ammonia is limited over the complete required range of pressure and temperature. Based on this, all possible binary mixtures among the fluids 1 to 14 and among water and ammonia are considered in the study, while it needs to be analyzed when a mixture including the ethers shows promising results, if the specific composition lies in the region of limited miscibility.

The increased flammability of the natural refrigerants is accepted, since it is assumed that technically and economically feasible solutions exist [24]. Furthermore, R290 and R601 are commonly used in commercial products [25] and considered as suitable for industrial applications [26].

Table 1. List of fluids considered in the design of binary mixtures above dashed line and additionally considered fluids below dashed line, [27,28]

No.	Name of Fluid	Ref. No.:	Type	ODP -	GWP -	Normal Boiling Point, °C	Crit. Temp. °C	Crit. Pressure bar	Safety Class
1	Methane	R-50	HC	0	25	-161.5	-82.6	46.0	A3
2	Ethylene	R-1250	HO	0	6.8	-103.8	9.2	50.4	A3
3	Ethane	R-170	HC	0	2.9	-88.6	32.2	48.7	A3
4	CO_2	R-744		0	1.0	-	31.0	73.8	A1
5	Propylene	R-1270	HO	0	3.1	-47.6	91.1	46.7	A3
6	Propane	R-290	HC	0	3.0	-42.0	96.7	42.5	A3
7	Dimethyl ether (DME)	R-E170	HC	0	1.0	-24.0	127.3	53.4	A3
8	Iso-Butane	R-600a	HC	0	3.0	-11.7	134.7	36.3	A3
9	n-Butane	R-600	HC	0	3.0	-0.5	152.0	38.0	A3
10	Iso-Pentane	R-601a	HC	0	4.0	27.8	187.3	33.8	A3
11	Ethyl ether (DEE)	R-610	HC	0	4.0	34.6	193.7	36.4	A3
12	Pentane	R-601	HC	0	4.0	36.1	196.6	33.7	A3
13	n-Hexane		HC			68.7	234.5	30.3	
14	Heptane		HC			98.4	267.0	27.4	
15	Ammonia	R-717		0	0.0	-33.3	132.4	112.8	B2
16	Water	R-718		0	0.2	100.0	373.9	220.6	A1

The model will be evaluated for all pure components and all possible binary mixtures at 9 compositions resulting from the fluids in Table 1. This procedure produces a comprehensive set of 833 thermodynamic cycle simulations per case which is used as a basis for analyses of the relation between the temperature glide matches and the performance.

3. Results

Fig. 3 gives an overview of the calculated COP of the heat pump for all possible mixture combinations for the introduced four cases. Each line represents the COP of one binary mixture with a composition varying from zero to one for the less volatile component x_2. For some cases technically feasible results were not obtained, e.g. because the evaporation process is transcritical due to a too low critical temperature. These points are not included and cause discontinuities in some curves.

The maximum achievable COP decreases from case I to IV with an increasing temperature glide and thereby lower absolute temperatures in the heat source. The obtained COPs decrease accordingly, whereas additional analysis has shown that the best exergetic efficiencies are for all four cases in a range between 50 % and 52 %.

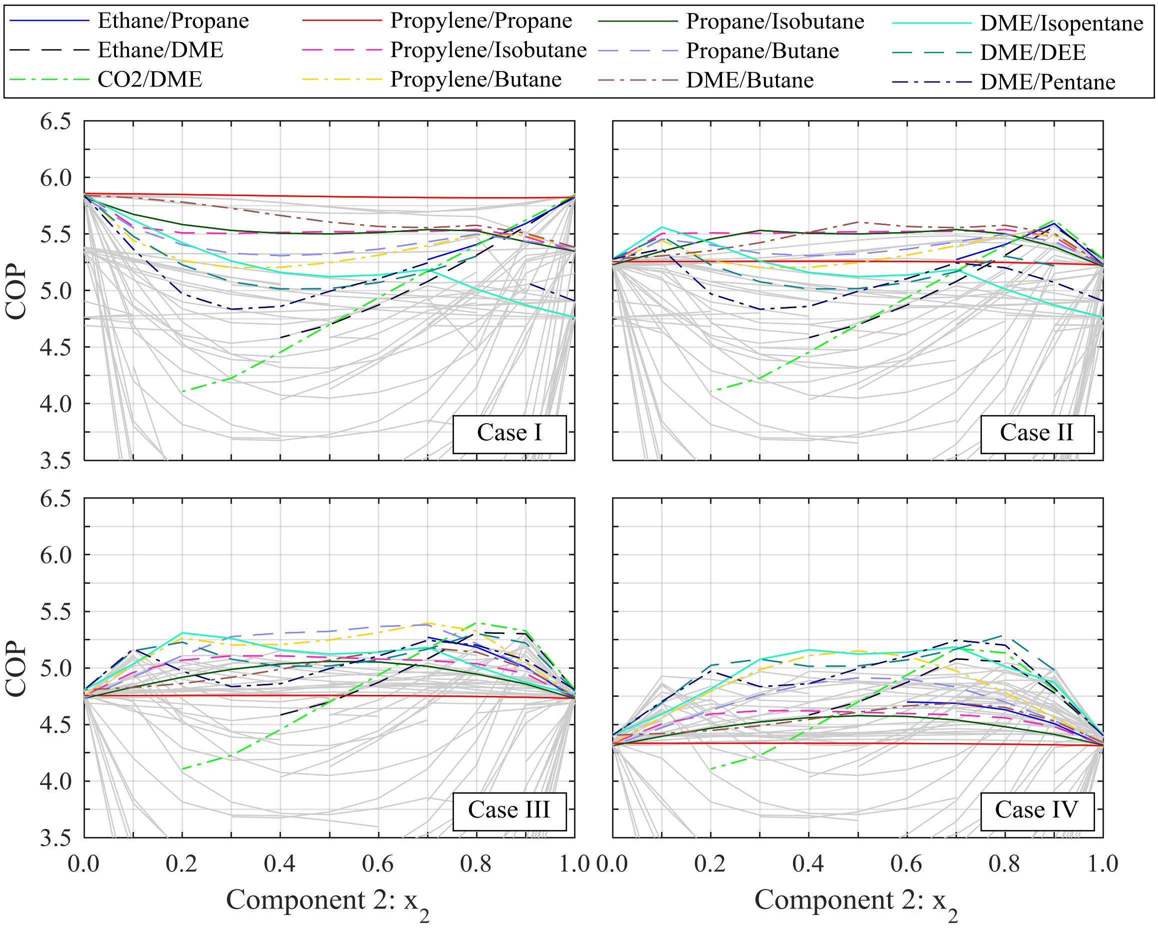

Fig. 3. COP for all cases with 5 K superheating for all mixtures over the composition of the less volatile component 2. Selected mixtures are labelled while other mixtures are included as grey shaded, representing the general solution space.

It can be seen in Fig. 3 and Table 2 that the performance increase from utilizing mixtures improves with a larger temperature glide in the heat source. For case I, the best performance is obtained by pure working fluids while case IV shows a significant increase in COP between the best pure and mixed working fluid.

The best performance in case I is represented by propylene, DME and Propane with a COP between 5.85 and 5.82. The glide matching indicator for the source π_{so} is between 1.53 and 1.54 whereas the sink shows a higher mismatch. The good temperature glide in the evaporator for the pure fluids stems from a temperature glide of 5 K in the heat source and a minimum required superheating of 5 K, which causes the pinch point temperature difference at the inlet and outlet of the heat sink and thus, already a good temperature match. In some cases the superheating by the heat source can be avoided by using e.g. an internal heat exchanger. Therefore the same set of simulations was repeated for zero superheating as shown in Fig. 4. It can be noticed that the results for the cases without superheating of 5 K correspond well to the cases with 5 K higher temperature glide in the source.

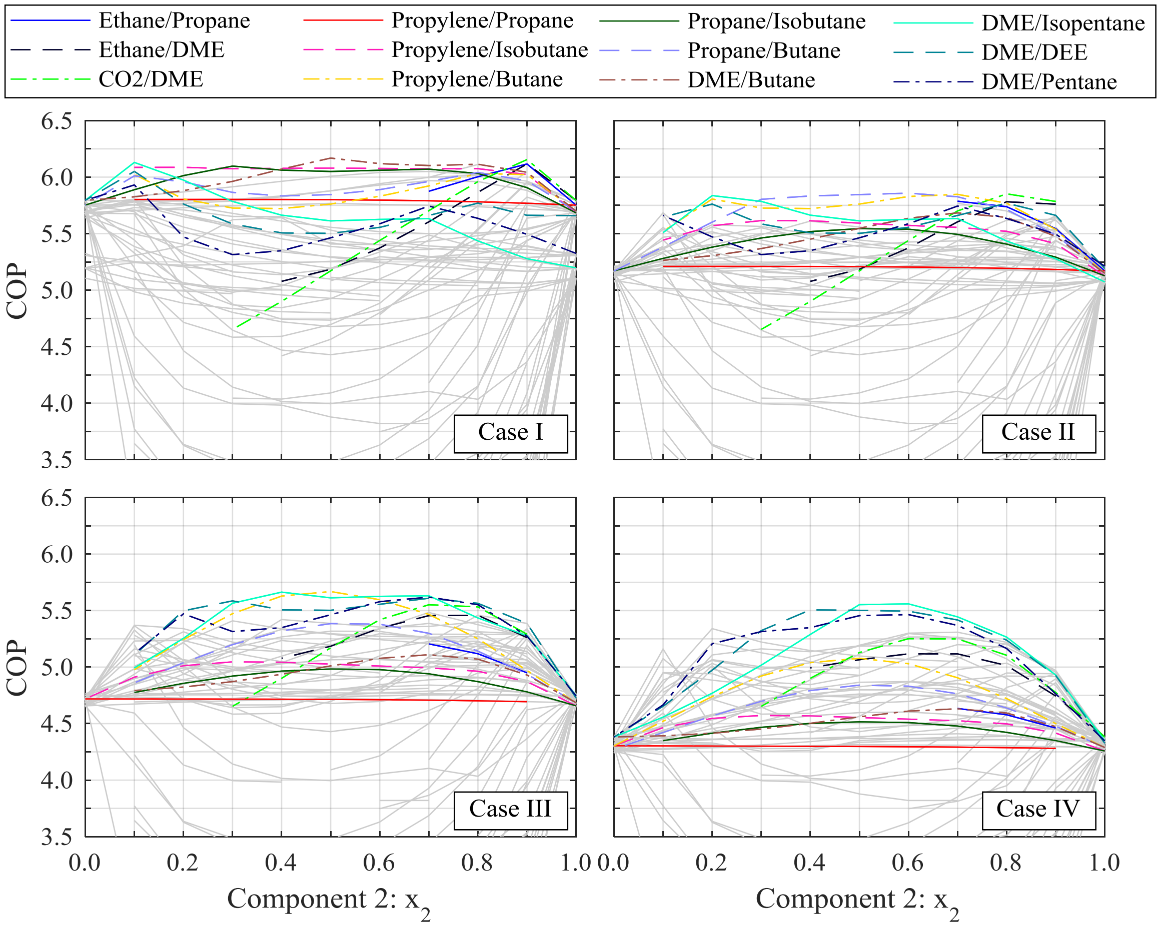

Fig. 4. COP for all cases without superheating for all simulations over comp. of component 2. Selected mixtures are labelled while other mixtures are included as grey shaded, representing the general solution space.

Case II assumes a temperature glide of 10 K in the source stream, which causes an increased mismatch in the source for the pure fluids. DME and Propylene have values for $\pi_{so} = 2.05$, whereas the temperature glide can be better approached by mixtures. The two best mixtures 10 % CO_2 – 90 % DME and 50 % DME – 50 % Butane have a source temperature glide match of 1.56 and 1.59, respectively. The COP obtained from the mixtures is 5.62, which is equal to an increase of 6.4 % when compared to the COP of the best pure fluid of 5.28.

The performance gain from using mixtures reaches 12 % for case III and 20 % for case IV. The simulations without superheating have shown an increase in COP from 4.38 to 5.56 which is equal to 27 % for Case IV. The values for the temperature glide match indicator in the source are around 1.5 for the best mixtures in Case III and IV whereas for the pure fluid they are approximately 2.5 for case III and 3.0 for case IV. The temperature glide match indicators in the sink are for the best solutions in case III below 3.0 and in case IV below 2.5, whereas the mismatch for the best pure fluids is in both cases larger than 3.5.

The pressure ratios of the presented best cases are mostly below 4 for moderate absolute pressures which can be assumed as technologically feasible.

The water ammonia mixtures did not show competitive COPs. The mixtures have a high and nonlinear temperature glide which resulted in a high mismatch on at least one side. All solutions have shown unfavourable operation conditions such as very high compressor discharge temperatures for a high share of water and high compressor discharge temperatures and high pressures for an increasing share of ammonia.

Table 2. Simulation results for mixtures and pure components with best performance for each case

Medium	COP	π_{so}	π_{si}	p_{ev}	p_{co}	Medium	COP	π_{so}	π_{si}	p_{ev}	p_{co}
		-	-	bar	bar			-	-	bar	bar
Case I						**Case II**					
Propylene	5.85	1.53	2.80	13.1	35.7	10 % CO_2 – 90 % DME	5.62	1.56	2.96	7.5	25.1
Dimethyl ether	5.84	1.54	3.43	6.8	22.6	50 % DME – 50 % Butane	5.61	1.59	3.14	4.8	17.3
Propane	5.82	1.53	2.92	10.8	31.1	10 % Ethane– 90 % Propane	5.60	1.42	2.58	12.3	35.9
Butane	5.38	2.24	3.61	2.5	11.0	10 % Ethane – 90 % Propyl.	5.57	1.48	2.50	14.5	39.5
Isobutane	5.34	2.28	3.48	3.6	14.4	DME	5.28	2.05	3.42	5.9	22.5
Pentane	4.91	3.34	3.74	0.6	4.1	Propylene	5.26	2.05	2.80	11.5	35.5
Case III						**Case IV**					
30 % Propyle. – 70 % Butane	5.40	1.47	2.84	4.0	15.0	20 % DME – 80 % DEE	5.29	1.33	2.47	1.2	6.1
30 % Propane – 70 % Butane	5.38	1.42	2.98	3.9	14.8	30 % DME – 70 % Pent.	5.24	1.62	2.00	1.2	6.1
10 % CO_2 – 90 % DME	5.32	1.56	2.97	7.0	25.0	30 % DME – 70 % Isopent.	5.19	1.74	2.20	1.7	8.0
80 % DME – 20 % Isopent.	5.31	1.89	2.87	4.5	17.2	50 % Propy. – 50 % Butane	5.15	1.52	2.56	5.0	18.6
Pentane	4.81	2.48	3.74	0.6	4.1	Isopentane	4.41	2.98	3.69	0.6	5.0
DME	4.80	2.58	3.42	5.1	22.3	DME	4.41	3.10	3.42	4.4	22.2

Fig. 5 shows the performance of all solutions for case I to IV over the glide matching indicators for sink and source. In order to allow comparisons between the cases with a different maximum achievable efficiency the exergetic efficiency is used to indicate the performance.

The diagrams show a similar trend of fluids with a good performance for all four cases. The solutions with a good performance accumulate for low glide match indicators in the source and a moderate mismatch in the sink between 3 (case I) and 2 (case IV). There are also solutions with an almost optimal glide match in the sink and an increased mismatch in the source between 4 (case I) and 3 (case IV) which have a moderate performance. Nevertheless, in the range of an optimal glide match with indicators for both sink and source of less than 2.2 for case I to 1.5 for case IV only few solutions could be found. Especially for the cases with low source glides, these solutions are mostly transcritical solutions with a good match on the sink side and a moderate glide match on the source side.

The diagrams show that the entire range of possible temperature profiles are available, while the dependency between the source glide match and exergetic efficiency shows a clearer pattern than for the sink. This dependency can be seen more clearly in Fig. 6, in which the glide match indicator of the source (left) and of the sink (right) are plotted over the exergetic efficiency for all cases superimposed on each other. The source glide match indicator varies between 1 and 15, while the exergetic efficiency can be low irrespective of a good glide match. Nevertheless, an increasing exergetic efficiency requires an enhanced temperature glide match. Thus, to obtain a good performance a good glide match in the source can be seen as a requirement.

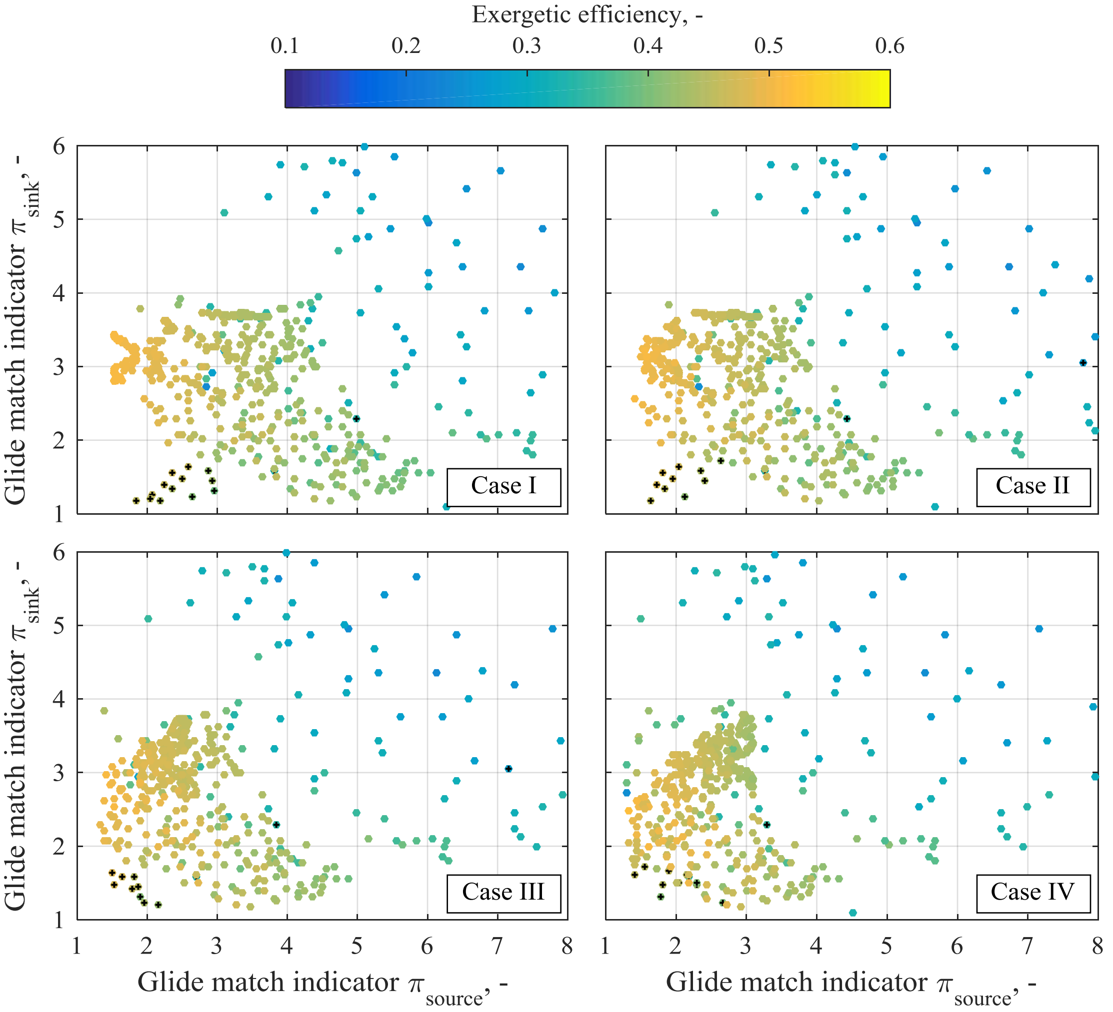

Fig. 5. Combinations of glide match indicators π of sink and source for all simulations for case I-IV with 5 K superheat with exergetic efficiency indicated by colour, transcritical cycles are marked with a black +

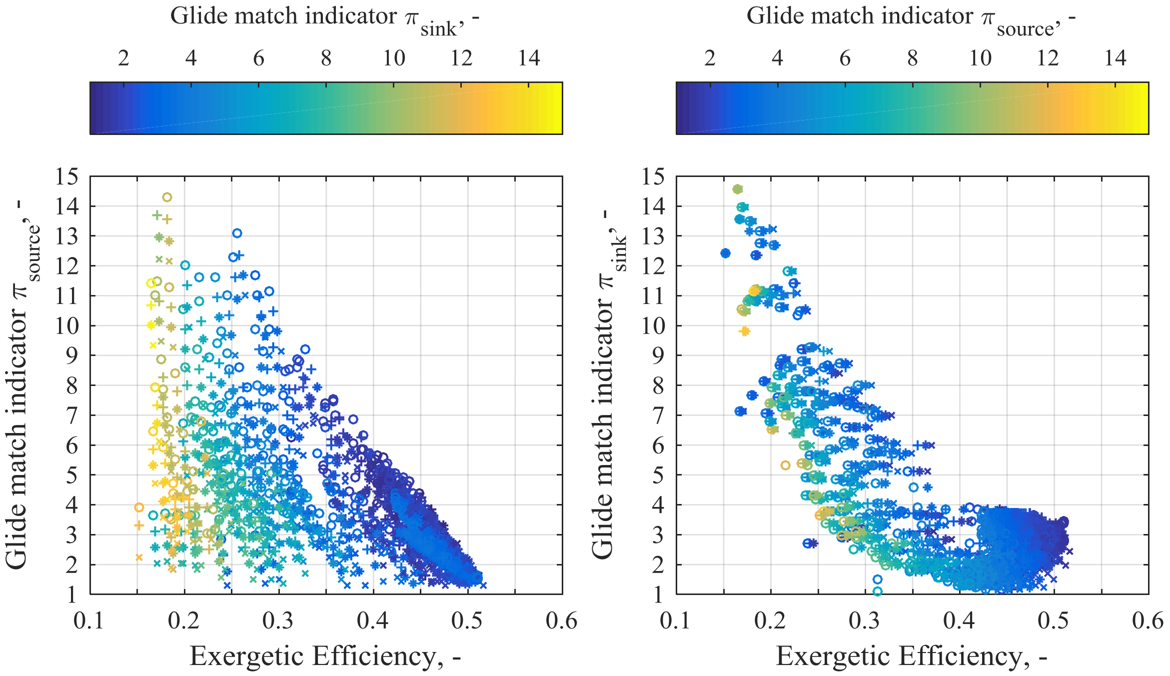

*Fig. 6. Glide match indicators for source (left) and sink (right) over exergetic efficiency with indication of respective other heat transfer process by colour for all cases indicated by marker (Case I: o, Case II: +, Case III: *, Case IV: x)*

The diagram on the right hand side shows a different pattern for temperature glide match in the sink over the exergetic efficiency. An increasing mismatch results in a decreased performance as well, whereas here a matching indicator below 4 enables exergetic efficiencies from 0.25 to 0.55. In this region the efficiency is dominated by the source side, which is indicated by the colour. While optimal glide matches in the sink result in an exergetic efficiency between 0.4 and 0.5, the highest exergetic efficiencies are obtained with a glide match indicator of approximately 3.

The diagrams in Fig. 7 to Fig. 10 show temperature – heat load diagrams for relevant and characteristic cases. Fig. 7 shows the mixture 10 % Ethane – 90 % Propane for case II which represents one of the best solutions in terms of COP and represents a good compromise between glide matches on both sides. The 80 % Ethane – 20 % Propylene mixture shows an almost perfect glide match in sink and source but a decreased COP compared to the best pure fluids for case II.

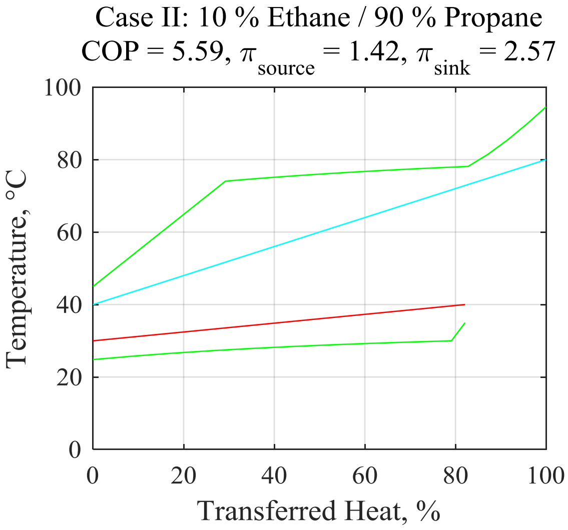
Case II: 10 % Ethane / 90 % Propane
COP = 5.59, π_{source} = 1.42, π_{sink} = 2.57

Fig. 7. Temperature-Heat-Diagram for a case with good COP and good glide match

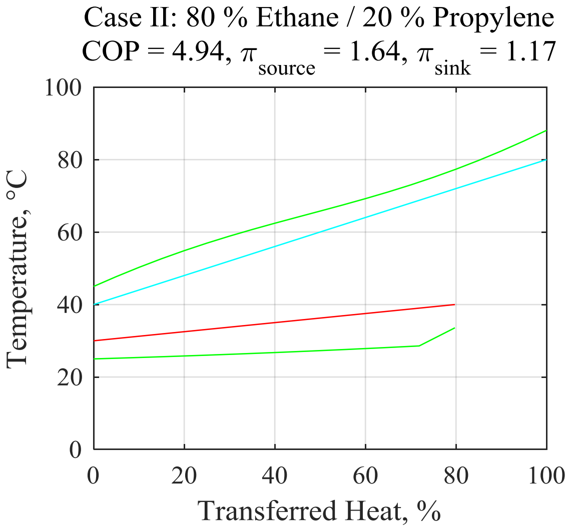
Case II: 80 % Ethane / 20 % Propylene
COP = 4.94, π_{source} = 1.64, π_{sink} = 1.17

Fig. 8. Temperature-Heat-Diagram for a case with a good glide match on the source side

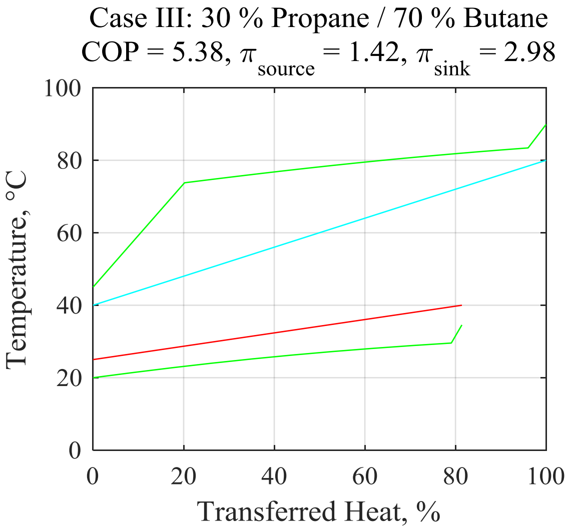
Case III: 30 % Propane / 70 % Butane
COP = 5.38, π_{source} = 1.42, π_{sink} = 2.98

Fig. 9. Temperature-Heat-Diagram for a case with a good glide match on the source side

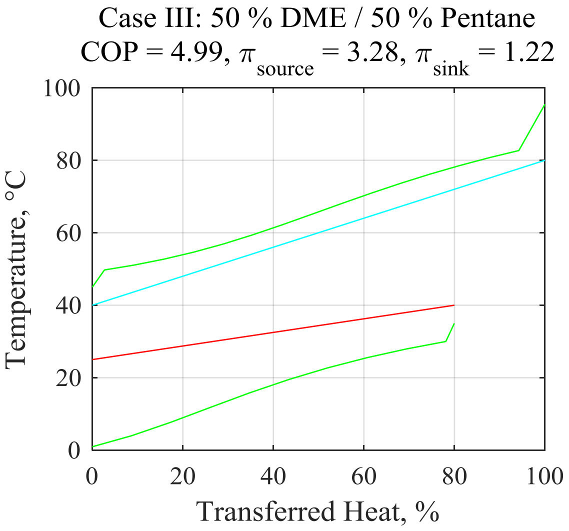
Case III: 50 % DME / 50 % Pentane
COP = 4.99, π_{source} = 3.28, π_{sink} = 1.22

Fig. 10. Temperature-Heat-Diagram for a case with a good match on the sink side

Figure Fig. 9 and Fig. 10 show cases in which either the source or sink match is good while the respectively other glide match is moderate but not so bad, that it would decrease the COP significantly. The exergy destruction caused by the mismatch of the fluid in source and sink for the case shown Fig. 9 are $y_{D,\text{fluid,source}}$ = 5.5 % and $y_{D,\text{fluid,sink}}$ = 25 %, whereas for the case of Fig. 10 they contribute with $y_{D,\text{fluid,source}}$ = 26 % and $y_{D,\text{fluid,sink}}$ = 2.5 %.

4. Discussion

The presented work has analysed the potential performance increase which can be achieved from a sufficient choice of a working fluid mixture. The choice of the working fluid and thus, also the possible performance increase is strongly dependent on the cycle layout. The shown case assumed a required minimum superheating of 5 K, which required a smaller temperature glide in the evaporator and thereby decreased the potential of zeotropic mixtures. The simulations of the cases without superheating showed an increased potential for zeotropic mixtures, whereas case I without the minimum 5 K superheating and 5 K temperature glide shows similar results as case II with no superheating and 10 K temperature glide.

The miscibility of the considered mixtures was analysed and binary mixtures with DME were identified to be potentially immiscible, which would result in a system with two liquid phases or different compositions. Since the results have shown that DME performs well in many mixtures, the miscibility of the specific composition at the required pressures and temperatures was analysed. The miscibility gaps occurred in all cases below operation temperatures, which yields a full miscibility of the components in the required range of pressure and temperature.

Different variables were analysed with respect to their usability and meaningfulness for evaluations of different working fluid mixtures and comparisons with other solutions. The introduced temperature glide matching indicator accounts for the exergy destruction due to the fluid being not ideal as a dimensionless, linear indicator. The exergy destruction of the fluid is put into relation to the heat transfer process and therefore can be used to compare processes with different loads in heat sink and source and among different simulations with varying overall efficiencies. If the exergy destruction is e.g. put into relation to a value which depends on the cycle performance, such as the exergetic fuel or overall exergy destruction, the results from different simulations cannot be compared to each other. The temperature glide match indicator represents a quantitative measure of the glide match and has proven to give meaningful results.

The results suggest a stronger dependency of the cycle performance on the glide match in the source than in the sink. This dependency is supported by the structure of equation 3 in which the absolute temperatures of the heat transfer process contribute squared in the denominator to the exergy destruction from heat transfer over a certain temperature difference. Assuming the heat to be transferred at the thermodynamic average temperature of sink stream (332.7 K) and source stream (310.6 K) the exergy destruction per unit transferred heat in the source is approximately 15 % higher than in the sink. An increasing mismatch will furthermore intensify this effect, since the temperature differences and thus the absolute temperatures diverge. Nevertheless, the higher heat load in the sink compensates this effect to some extent.

Different cases have been shown representing the different available combinations of temperature glides and accordingly different qualities in glide matching. Often a good compromise between both has shown to give good COPs. Nevertheless, Fig. 8 has shown a case with an optimal glide match and a COP which is not as optimal as the glide match suggests. Since the compressor and the throttling valve were modelled with the same efficiency it can be concluded that there are fluid properties influencing the exergy destruction in the remaining components to a relevant extent.

The cases presented in Fig. 9 and Fig. 10 show some inefficiencies due to heat transfer but based on the high COPs it can be assumed that the working fluids do not have an unfavourable effect on compressor and throttling valve. If in these cases the temperature glide match could be improved by any cycle adjustment while retaining the fluid and the remaining components constant, the exergy destruction in the component and thus, in the entire system would decrease and improve the performance. Possible cycle adjustments are extensively discussed for water ammonia systems [29]. The theoretical potential of decrease in exergy destruction is around 25 % for the presented cases.

5. Conclusion

The analyses have demonstrated a performance increase which can potentially be exploited by using zeotropic working fluid mixtures. The possible improvement in performance is dependent on the boundary conditions of sink and source and can be increased by cycle adjustments, such as no superheating. Whereas for case I with 5 K superheating and 5 K temperature glide in the source the best working fluid were pure fluids, a performance crease of 20 % in case IV with 5 K superheating and 27 % without superheating could be observed.

It has been shown that a good temperature match in sink and source can improve the performance significantly, while an optimal match does not necessarily result in an optimal COP. Furthermore there are other influences stemming from the fluid on the cycle which have not been further quantified and need to be analysed in further studies. The lack of relations between medium properties of the pure components or of the mixture creates a demand for a screening as demonstrated here in order to determine an optimal working fluid.

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Nomenclature

Latin symbols:

$\dot{E}$	Exergy flow rate, W	$\bar{T}$	Thermodynamic average temperature, K
$\dot{Q}$	Heat flow rate, W		
T	Temperature, °C or K	y	Exergy destruction ratio, -

Greek symbols

ΔT	Temperature Difference, K	π	Temperature glide matching efficiency
η	Efficiency, -		

Subscripts and superscripts

0	Dead state for exergy analysis	glide	Temperature glide
1-7	State point numbers	hot	Hot stream
co	Condensation	is	Isentropic
cold	Cold stream	min	Minimum
comp	Compressor	P	Product
component	Related to component	pinch	Temperature difference
D	Destruction	si	Sink
ev	Evaopration	so	Source
F	Fuel	SH	Super heating
fluid	Related to fluid	total	Related to complete system

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