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Analysis of temperature glide matching of heat pumps with zeotropic working fluid mixtures for different temperature glides

Benjamin Zühlendorf^{1a}, Jonas Kjær Jensen^b, Stefano Cignitti^c, Claus Madsen^d and Brian Elmegaard^e

^{a,b,e} Department of Mechanical Engineering, Technical University of Denmark, Nils Koppels Allé, Building 403, 2800 Kgs. Lyngby, Denmark, bezuhs@mek.dtu.dk, jkje@mek.dtu.dk, be@mek.dtu.dk

^c Process and Systems Engineering Center (PROSYS), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søtofts Plads, Building 229, 2800 Kgs. Lyngby, Denmark, steci@kt.dtu.dk

^d Danish Technological Institute, Gregersensvej, 2630 Taastrup, Denmark, clma@teknologisk.dk

Abstract:

The present study demonstrates the optimization of a heat pump for an application with a large temperature glide on the sink side and a smaller temperature glide on the source side. The study includes a numerical simulation of a heat pump cycle for binary mixtures based on a list of 14 natural refrigerants. This approach 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. The exergy destruction due to heat transfer, which is solely caused by the fluid having a non-ideal temperature profile was quantified and an indicator describing the glide match was defined to analyze its influence on the performance. The results indicated, that a good glide match can contribute to an increased performance. The increase in performance was dependent on the boundary conditions and reached up to 20 % for a simple cycle and up to 27 % if the 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, Glide matching, 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 flows and thus finite capacity flow reservoirs. When heat is removed or added from or to a fluid with a finite heat capacity, the temperature of the fluid changes. The temperature glides in heat sink and source pose additional challenges for 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

¹ Corresponding Author:

Email addresses: bezuhs@mek.dtu.dk (B. Zühlendorf); jkje@mek.dtu.dk (J. K. Jensen); steci@kt.dtu.dk (S. Cignitti); clma@teknologisk.dk (C. Madsen); be@mek.dtu.dk (B. Elmegaard)

compression heat pump, the Lorenz cycle can be approached by using a zeotropic mixture, experiencing 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, reducing exergy destruction due to heat transfer.

Besides the possible improvements resulting from beneficial exploitation of the 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 a single component are compensated by another component. Several studies, e.g. [7–9] have analyzed the combination of CO₂ with hydrocarbons (HC) in numerical and experimental studies, showing an increased coefficient of performance (COP) as well as secondary effects such as a reduced high pressure compared to pure CO₂ systems and a reduced flammability 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 numerical 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 [13] presented methods to compare the performance of pure and mixed refrigerants. Itard [14] studied wet compression-resorption heat pump cycles and analyzed the influence of the temperature glide match on the overall performance for 7 binary and 2 ternary mixtures. She concluded an optimal thermodynamic performance for a minimum sum of the mean temperature differences in the heat exchangers and derived recommendations to identify promising mixtures for the wet compression-resorption cycle. She highlighted a higher potential for using mixtures for applications with a high temperature increase in the sink combined with low absolute temperature lifts between source inlet and sink outlet temperature, without accounting for the temperature glide in the heat source.

Summarizing these studies, it can be summarized that there remains a lack of knowledge about the potential performance increase which could be obtained by using mixed working fluids dependent on the boundary conditions, including both sink and source, and furthermore, how this is related to the choice of the working fluid mixture.

Opposing the increase in efficiency, the use of zeotropic mixtures and a resulting match of the temperature glides require an increased heat transfer area, because the temperature difference is reduced and due to the diffusion resistances during phase change which decrease the convective heat transfer [1,15]. The tradeoff between additional investment in heat exchanger area and an increased performance is dependent on the physical and economic boundary conditions and needs to be analyzed for each application, regardless of whether pure or mixed refrigerants are considered. Others

[16–18] have shown that the increased performance can cover the additional investment and thus, result in an increased net present value using a mixture.

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 the temperature glides in source and sink as well as on the mean 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 present work consequently aims to analyze under which boundary conditions the use of zeotropic mixtures is reasonable. The study has furthermore analyzed to what extent the matching of the temperature profiles in the sink and source heat exchangers relate to the overall performance and derived recommendations to be used during cycle and working fluid design.

2. Methods

2.1. Simulation Procedure

The benefits of using zeotropic mixtures as working fluid were analyzed by a number of cases with different boundary conditions, representing a range of possible applications. In general, several combinations of temperature glides in heat source and sink are possible, but typically the consumption glide on the sink side is given while the cooling of the heat sources may offer a potential range of glides.

For this study, it was 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 [19]. The source is used to heat another stream from 40 °C to 80 °C, which is within a common temperature range for industrial low temperature processes [20]. The outlet temperature of the heat source is not fixed and will be varied in the cases as shown in Table 1.

Table 1: Definition of boundary conditions for considered cases

Case Number	Heat Source $T_{\text{source,in}} \rightarrow T_{\text{source,out}}$	Heat Sink $T_{\text{sink,in}} \rightarrow T_{\text{sink,out}}$
I	40 °C $\rightarrow$ 35 °C	40 °C $\rightarrow$ 80 °C
II	40 °C $\rightarrow$ 30 °C	
III	40 °C $\rightarrow$ 25 °C	
IV	40 °C $\rightarrow$ 20 °C	

This setup can represent a booster heat pump for a low temperature district heating network on the consumer side [21] for which the return temperature is not defined by other parameters or an industrial application in which an excess 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 [22]. Especially when latent heat from condensation of moist air is recovered, the temperature glide on the source side can be small.

As a basis for the analysis a model for the heat pump 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 vapor compression cycle as shown in Figure 1. It consists of the minimum amount of required components and represents the simplest possible heat pump solution. Therefore, the analysis focused solely on the influence gained from using mixtures and included the possibility to derive recommendations for possible adjustments of the cycle layout.

Figure 1: Flow sheet of modelled heat pump (left) and diagram with temperature profiles over transferred heat for case II with 10 % CO₂ – 90 % DME as working fluid (right)

The heat pump process described 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 subcritically or supercritically, while the low pressure side is always below the critical point.

The model was based on the First and Second Law of Thermodynamics and includes energy and mass balances for all components. The heat exchangers were modelled as separate control volumes according to single-phase and two-phase flow, disregarding if they are manufactured as one component. This distinction diminishes for transcritical processes, which was for numerical reasons assumed at pressures 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 $\Delta T_{pinch,min} = 5 \text{ K}$ was 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 [23]. While fixing the condensation pressure by setting the minimum temperature difference to the minimum required pinch temperature difference yields the maximum COP for subcritical processes, this may not always be applicable for transcritical processes. The pressure has therefore been optimized for transcritical pressures with respect to COP considering a boundary on the minimum temperature difference, which corresponds to defining the pressure by the pinch point temperature difference as suggested by [23]. It may be noted, that the optimal gas cooler pressure resulted only in very exceptional cases in a minimum temperature difference larger than the minimum required pinch point temperature difference.

The compression process was modelled with an isentropic efficiency of $\eta_{\text{comp, is}} = 0.8$ while losses from the electrical motor to the environment were disregarded. The volumetric heating capacity VHC relates the supplied heat load to the volume flow rate at the inlet of the compressor and indicates the size of the component. In order to protect the compressor from wet compression a minimum superheating temperature difference of $\Delta T_{\text{SH}} = 5 \text{ K}$ is considered at both inlet and outlet of the compressor. For additional analyses of the influence of the superheating on the COP the simulations were repeated without superheating.

The throttling process was assumed to be isenthalpic.

The model was implemented in Matlab [24] and used medium properties from Refprop [25] with the recommended state of the art models for the 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 was conducted as described in [26]. The exergy flow rates $\dot{E}$ were calculated for the mass flows at each state point as well as for the consumed power. The dead state was defined as $T_0 = 25 \text{ °C}$ and $p_0 = 1 \text{ bar}$. The exergy destruction $\dot{E}_D$ was defined as the difference between all exergy flows entering and leaving a control volume, which is equivalent to the difference between the exergy fuel $\dot{E}_F$ and exergy product $\dot{E}_P$. The exergy fuel and product were defined as the desired and invested exergetic effect and therefore dependent on the function of the component. For dissipative components, such as the throttling valve, no meaningful definition of the product can be found according to [26].

$$\dot{E}_D = \dot{E}_F - \dot{E}_P = \sum_{i=1 \dots k} \dot{E}_i \quad (1)$$

The exergy destruction describes the irreversibilities within the components as an absolute value. Since the absolute energy flows in the different components can vary, the exergy destruction varies as well and is therefore not an optimal measure for comparisons of performance. A supplementing indicator is the exergy efficiency, defined as the ratio of the exergetic product over the exergetic fuel.

Nevertheless, it can hardly be used to analyze the improvement potentials, since it determines the overall exergy destruction by an outer balance equation, rather than locating the origin of the irreversibilities within the component. It does furthermore not contain information about whether or not the exergy destruction could be avoided by e.g. an optimal mixture having a constant temperature difference along the transferred heat.

Therefore, we suggested to distinguish between two contributions as shown in Figure 2, i.e., exergy destruction $\dot{E}_{D, \text{pinch}}$ which is caused by the nature of the component having a finite heat transfer area and cannot be avoided even with an ideal fluid and an additional exergy destruction $\dot{E}_{D, \text{fluid}}$ which accounts for real working fluid being non-ideal. The sum of the exergy destruction from both contributions yield the total exergy destruction occurring within the component $\dot{E}_{D, \text{component}}$.

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

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 the exergy destruction accounting for the difference between a real and an ideal fluid $\dot{E}_{D, \text{fluid}}$ would still contribute to the total components exergy destruction.

Figure 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 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 with a constant capacity rate between the temperatures T_1 and T_2 , the thermodynamic average temperature $\bar{T}_{1-2} = (T_1 - T_2)/\ln(T_1/T_2)$ is introduced, [26]. Using this relation, the exergy balance defines the exergy destruction as:

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

The indices “hot” and “cold” refer to the ideal fluid during condensation and the heat sink stream in the sink heat exchanger and in the heat source heat exchanger to the heat source stream and the ideal fluid during evaporation, respectively.

Using Equation 3 and the definition of the thermodynamic average temperature for streams with a constant heat capacity, the exergy destruction in sink and source due to the pinch point temperature difference ΔT_{pinch} can be directly expressed as a function of this temperature difference:

$$\dot{E}_{D,pinch,source} = T_0 \dot{Q}_{source} \frac{1}{T_{source,in} - T_{source,out}} \ln \left(\frac{T_{source,out}}{T_{source,in}} \left(\frac{T_{source,in} - \Delta T_{pinch}}{T_{source,out} - \Delta T_{pinch}} \right) \right) \quad (4)$$

$$\dot{E}_{D,pinch,sink} = T_0 \dot{Q}_{sink} \frac{1}{T_{sink,out} - T_{sink,in}} \ln \left(\frac{T_{sink,out}}{T_{sink,in}} \left(\frac{T_{sink,in} + \Delta T_{pinch}}{T_{sink,out} + \Delta T_{pinch}} \right) \right) \quad (5)$$

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 $\dot{E}_{D,component}$ over $\dot{E}_{D,pinch}$:

$$\pi_{glide} = \frac{\dot{E}_{D,component}}{\dot{E}_{D,pinch}} = \frac{\dot{E}_{D,fluid} + \dot{E}_{D,pinch}}{\dot{E}_{D,pinch}} \quad (6)$$

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

This definition enables additionally to determine the share of exergy destruction caused by the fluid being non-ideal on the entire exergy destruction of the system $y_{D,\text{fluid}}^*$ and thereby represents the potential decrease in exergy destruction by finding an optimal fluid:

$$y_{D,\text{fluid}}^* = \frac{\dot{E}_{D,\text{fluid}}}{\dot{E}_{D,\text{total}}} \quad (7)$$

The factor can be used to analyze the potential performance increase that can be obtained by better matching the temperature profiles in either sink or source, e.g. $y_{D,\text{fluid},\text{source}}^* = \dot{E}_{D,\text{fluid},\text{source}}/\dot{E}_{D,\text{total}}$, or to highlight the total potential reduction of exergy destruction $y_{D,\text{fluid},\text{total}}^* = (\dot{E}_{D,\text{fluid},\text{source}} + \dot{E}_{D,\text{fluid},\text{sink}})/\dot{E}_{D,\text{total}}$.

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 were considered in the design of the binary mixtures can be defined according to different aspects. No strong correlation could be observed in a previous study [16], which relates specific medium properties to the performance of a heat pump, when using the fluid as a component in a working fluid mixture. It therefore seemed 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 the possibility to use mixed working fluids enlarges variety of working fluids substantially compared to a limited set of pure fluids. This obviates the need to consider fluids with unfavorable characteristics such as high ODP or GWP.

Based on this, the group of commonly used natural refrigerants and the two higher boiling HCs, n-Hexane and Heptane, are chosen for this study as shown in Table 2. The natural refrigerants entail a good and low-cost availability, limited toxicity, low environmental impact and good miscibility among each other, while being established working fluids.

The miscibility has been analyzed using a group contribution method as proposed in [27]. 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 2 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. In case a mixture including the ethers appears to be a promising solution, further analysis with respect to the miscibility is required.

Table 2: List of fluids considered in the design of binary mixtures above dashed line and additionally considered fluids below dashed line, [28–30]

No.	Name of Fluid	Ref. No.:	Type	ODP	GWP _{100yr.}	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 increased flammability of the natural refrigerants is accepted, since it is assumed that technically and economically feasible solutions exist [31]. Furthermore, R290 and R600a are commonly used in commercial products [32] and considered suitable for industrial applications [33].

The model was evaluated for all pure components and all possible binary mixtures at 9 compositions resulting from the fluids in Table 2. This procedure produced a comprehensive set of 833 thermodynamic cycle simulations per case which is used as a basis for analyzing the relation between the temperature glide matches and the performance.

3. Results

Figure 3 gives an overview of the calculated COP of the heat pump for all possible mixture combinations for cases I to IV and Table 3 presents an overview of the best performing pure and mixed working fluids for each case. All four cases assumed the same supply temperature by heating water from 40 °C to 80 °C and the same heat source inlet temperature of 40 °C, while case I was defined by cooling down the heat source by a temperature difference of 5 K, which increased stepwise to 20 K for case IV. 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, no technically feasible results were 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 decreased from case I to IV with an increasing source temperature glide and thereby a lower mean temperature in the heat source. The obtained COPs decreased accordingly, whereas additional analysis showed that the best exergetic efficiencies for all four cases were in the range of 50 % to 52 %.

It can be seen in Figure 3 and Figure 4 that the performance increased from utilizing mixtures is improved with a larger temperature glide in the heat source. For case I, the best performance was obtained by pure working fluids while case IV showed a significant increase in COP between the best pure and mixed working fluid.

Figure 3: COP for all cases with minimum 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.

Propylene, DME and Propane showed the best performance in case I with a COP between 5.85 and 5.82. The glide matching indicator for the source π_{so} was between 1.53 and 1.54 whereas the sink shows a higher mismatch.

Case II assumes a temperature glide of 10 K in the source stream, which caused an increased mismatch in the source for the pure fluids. DME and Propylene have values of $\pi_{so} = 2.05$, while the temperature glide can be approached better by mixtures. The two best mixtures 10 % CO₂ – 90 % DME and 50 % DME – 50 % Butane have a source temperature glide match of 1.56 and 1.59, respectively. The maximum 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.

Table 3: Simulation results for best performing mixtures and pure fluids for each case and a minimum of 5 K superheating

Medium	COP	π_{so} -	π_{si} -	p_{ev} bar	p_{co} bar	VHC kJ/m ³
Case I						
Propylene	5.85	1.53	2.80	13.1	35.7	9,508
DME	5.84	1.54	3.43	6.8	22.6	6,106
Propane	5.82	1.53	2.92	10.8	31.1	8,093
Butane	5.38	2.24	3.61	2.5	11.0	2,512
Isobutane	5.34	2.28	3.48	3.6	14.4	3,308
Pentane	4.91	3.34	3.74	0.6	4.1	721
Case II						
10 % CO ₂ – 90 % DME	5.62	1.56	2.96	7.5	25.1	6,564
50 % DME – 50 % Butane	5.61	1.59	3.14	4.8	17.3	4,329
10 % Ethane – 90 % Propane	5.60	1.42	2.58	12.3	35.9	8,761
10 % Ethane – 90 % Propylene	5.57	1.48	2.50	14.5	39.5	10,060
DME	5.28	2.05	3.42	5.9	22.5	5,368
Propylene	5.26	2.05	2.80	11.5	35.5	8,467
Case III						
30 % Propylene – 70 % Butane	5.40	1.47	2.84	4.0	15.0	3,573
30 % Propane – 70 % Butane	5.38	1.42	2.98	3.9	14.8	3,475
10 % CO ₂ – 90 % DME	5.32	1.56	2.97	7.0	25.0	6,138
80 % DME – 20 % Isopentane	5.31	1.89	2.87	4.5	17.2	4,112
Pentane	4.81	2.48	3.74	0.6	4.1	693
DME	4.80	2.58	3.42	5.1	22.3	4,701
Case IV						
20 % DME – 80 % DEE	5.29	1.33	2.47	1.2	6.1	1,312
30 % DME – 70 % Pentane	5.24	1.62	2.00	1.2	6.1	1,330
30 % DME – 70 % Isopentane	5.19	1.74	2.20	1.7	8.0	1,757
50 % Propylene – 50 % Butane	5.15	1.52	2.56	5.0	18.6	4,270
Isopentane	4.41	2.98	3.69	0.6	5.0	747
DME	4.41	3.10	3.42	4.4	22.2	4,101

The performance gain from using mixtures reached 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 corresponds 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 while 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 were 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 was in both cases larger than 3.5.

The pressure ratios of the presented best cases were mostly below 4 for moderate absolute pressures which can be assumed as technologically feasible. The volumetric heating capacities VHC vary between 700 kJ/m³ for fluids with low evaporation pressures and reaches up to more than 10,000 kJ/m³ for higher evaporation pressures, indicating a relatively high heat supply rate with compact compression equipment.

The good temperature glide in the evaporator for the pure fluids stemmed from the source temperature glide of 5 K and the minimum required superheating of 5 K. This caused the pinch point temperature difference to be located at both the inlet and outlet of the heat source and thus, a good temperature match. In some cases the superheating by the heat source can be avoided by using e.g. an internal heat exchanger. The same set of simulations was therefore repeated for zero superheating as shown in Figure 4. It may be noted 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.

Figure 4: COP for all cases with minimum 0 K superheating for all simulations 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.

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 showed unfavorable 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.

Figure 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 COP the exergetic efficiency was chosen to indicate the performance.

Figure 5 indicates a similar trend of fluids with a good performance for all four cases. The solutions with a good performance accumulated for low glide match indicators in the source and a moderate mismatch in the sink between 3 (case I) and 2 (case IV). There were 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, only few solutions could be found 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. Especially for the cases with low source glides, these solutions were mostly transcritical solutions with a good match on the sink side and a moderate glide match on the source side.

Figure 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 color, transcritical cycles are marked with a black +

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

The diagrams in Figure 5 show that a large range of possible temperature profiles is covered, 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 Figure 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.

Figure 7: Temperature-Heat-Diagram for subcritical cycle with a good glide match on the source side, a moderate glide match on the sink side and a good COP

Figure 8: Temperature-Heat-Diagram for a transcritical cycle with a good glide match on both the source and sink side and a moderate COP

Figure 9: Temperature-Heat-Diagram for a subcritical cycle with a good glide match on the source side, a moderate glide match on the sink side and a good COP

Figure 10: Temperature-Heat-Diagram for a subcritical cycle with a poor glide match on the source side, good glide match on the sink side and a moderate COP

The diagram on the right hand side of Figure 6 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 color. 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 Figure 7 to Figure 10 show temperature – heat load diagrams for relevant and characteristic cases. Figure 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.

Figure 9 and Figure 10 show cases in which either the source or sink had a good glide match while the other glide match was moderate without significantly reducing the COP. The exergy destruction caused by the mismatch of the fluid in source and sink for the case shown Figure 9 are $y_{D,fluid,source}^* = 5.5 \%$ and $y_{D,fluid,sink}^* = 25 \%$, whereas for the case of Figure 10 they contribute with $y_{D,fluid,source}^* = 26 \%$ and $y_{D,fluid,sink}^* = 2.5 \%$.

4. Discussion

The presented work has analyzed 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 improvement 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 feasibility of reducing the required minimum superheating depends on the equipment and can be enabled by different approaches. Comprehensive studies of compression equipment, which is capable of handling liquid during compression, was conducted by Ferreira [34]. Another measure to enable operation without superheating within the evaporator is the utilization of an internal heat exchanger.

The miscibility of the considered mixtures was analyzed and binary mixtures with DME were identified to be potentially immiscible, which would result in a system with two liquid phases of 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 analyzed. 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 analyzed 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 non-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. The tendency of an increased COP for an improved glide match corresponds to the findings of Itard [14], who reported an optimal COP for a minimum sum of mean temperature differences in the heat exchangers. Nevertheless, Figure 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 Figure 9 and Figure 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 unfavorable 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 [35]. The theoretical potential of decrease in exergy destruction is around 25 % for the presented cases.

The variety of the results demonstrated the various possibilities, in which the medium properties influence the performance of the different components and accordingly the overall performance of the system. These manifold interdependencies imply the difficulty to define recommendations for selecting mixture components dependent on the boundary conditions. The presented results do furthermore include cases, which demonstrate that such recommendations as presented by Itard [14] are not generally applicable.

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 increase 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 analyzed 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	VHC	Volumetric heating capacity, kJ/kg
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	hot	Hot stream
1-7	State point numbers	in	Inlet
co	Condensation	is	Isentropic
cold	Cold stream	min	Minimum
comp	Compressor	out	Outlet
component	Related to component	P	Product
D	Destruction	pinch	Temperature difference
ev	Evaopration	si	Sink
F	Fuel	so	Source
fluid	Related to fluid	SH	Super heating
glide	Temperature glide	total	Related to complete system

References

- [1] Radermacher R, Hwang Y. Vapor Compression Heat Pumps with Refrigerant Mixtures. CRC Press; 2005.
- [2] UNEP - Ozone Secretariat, Programme UNE. Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer - 10th Edition. 2016.
- [3] United Nations. Kyoto Protocol To the United Nations Framework Convention on Climate Change. Kyoto: 1998.
- [4] Environmental Investigation Agency 2016. Kigali amendment to the montreal Protocol: A Crucial Step in the Fight Against Catastrophic Climate Change. 2016.
- [5] United Nations Environmental Programme. Report of the Twenty-Eighth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer. Kigali, Rwanda: 2016. doi:10.1002/9780470670590.wbeog931.
- [6] Mohanraj M, Muraleedharan C, Jayaraj S. A review on recent developments in new refrigerant mixtures for vapour compression-based refrigeration, air-conditioning and heat pump units. *Int J Energy Res* 2011;35:647–69. doi:10.1002/er.
- [7] Sarkar J, Bhattacharyya S. Assessment of blends of CO₂ with butane and isobutane as working fluids for heat pump applications. *Int J Therm Sci* 2009;48:1460–5. doi:10.1016/j.ijthermalsci.2008.12.002.
- [8] Kim JH, Cho JM, Kim MS. Cooling performance of several CO₂/propane mixtures and glide matching with secondary heat transfer fluid. *Int J Refrig* 2008;31:800–6. doi:10.1016/j.ijrefrig.2007.11.009.
- [9] Dai B, Li M, Ma Y, Dang C, Li M, Tian H, et al. Thermodynamic performance assessment of carbon dioxide blends with low-global warming potential (GWP) working fluids for a heat pump water heater. *Int J Refrig* 2014;64:942–52. doi:10.1016/j.ijrefrig.2014.11.009.
- [10] Rajapaksha L. Influence of special attributes of zeotropic refrigerant mixtures on design and operation of vapour compression refrigeration and heat pump systems. *Energy Convers Manag* 2007;48:539–45. doi:10.1016/j.enconman.2006.06.001.
- [11] Kruse H, Wiescholke F. Concentration Shift When Using Refrigerant Mixtures. *Ashrae Trans* 1997;103:747–55.
- [12] Venzik V, Roskosch D, Atakan B. Propene / isobutane mixtures in heat pumps: an experimental investigation. *Proc. ECOS 2016 - 29TH Int. Conf. Effic. COST, Optim. Simul. Environ. IMPACT ENERGY Syst.*, Portoroz, Slovenia: 2016, p. P552.
- [13] McLinden MO, Radermacher R. Methods for comparing the performance of pure and mixed refrigerants in the vapour compression cycle. *Int J Refrig* 1987;10:318–25. doi:10.1016/0140-7007(87)90117-4.
- [14] Itard L. Wet Compression-Resorption Heat Pump Cycles: Thermodynamic Analysis and Design. Delft University of Technology, 1998.
- [15] Kærn MR, Modi A, Jensen JK, Andreasen JG, Haglind F. An assessment of in-tube flow boiling correlations for ammonia-water mixtures and their influence on heat exchanger size. *Appl Therm Eng* 2016;93:623–38. doi:10.1016/j.applthermaleng.2015.09.106.
- [16] Zühlsdorf B, Bühler F, Mancini R, Cignitti S, Elmegaard B. High Temperature Heat Pump Integration using Zeotropic Working Fluids for Spray Drying Facilities. 12th IEA Heat Pump Conf. 2017, Rotterdam: 2017.
- [17] Ommen T, Jensen JK, Markussen WB, Reinholdt L, Elmegaard B. Technical and economic working domains of industrial heat pumps: Part 1 - single stage vapour compression heat pumps. *Int J Refrig* 2015;55:168–182. doi:10.1016/j.ijrefrig.2015.02.012.
- [18] Jensen JK, Ommen T, Markussen WB, Reinholdt L, Elmegaard B. Technical and economic working domains of industrial heat pumps: Part 2 - Ammonia-water hybrid absorption-compression heat pumps. *Int J Refrig* 2015;55:183–200. doi:10.1016/j.ijrefrig.2015.02.011.

- [19] Bühler F, Fridolin M, Huang B, Andreassen JG, Elmegaard B. Mapping of low temperature heat sources in Denmark. ECOS 2015 28th Int Conf Effic Cost, Optim Simul Environ Impact Energy Syst 2015.
- [20] Brückner S, Liu S, Miro L, Radspieler M, Cabeza LF, Lävemann E. Industrial waste heat recovery technologies: An economic analysis of heat transformation technologies. Appl Energy 2015;151:157–67. doi:10.1016/j.apenergy.2015.01.147.
- [21] Elmegaard B, Ommen TS, Markussen M, Iversen J. Integration of space heating and hot water supply in low temperature district heating. Energy Build 2016;124:255–64. doi:10.1016/j.enbuild.2015.09.003.
- [22] Bühler F, Nguyen T-V, Elmegaard B. Energy and exergy analyses of the Danish industry sector. Appl Energy 2016. doi:10.1016/j.apenergy.2016.02.072.
- [23] Besbes K, Zoughaib A, Carlan F De, Peureux J-L. Exergy Based Methodology for Optimized Integration of Heat Pumps in Industrial Processes. Int Refrig Air Cond Conf 2014.
- [24] The MathWorks Inc. MATLAB R2015b 2015.
- [25] Lemmon EW, Huber ML, McLinden MO. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1 2013.
- [26] Bejan A, Tsatsaronis G, Moran M. Thermal Design and Optimization. 1996. doi:10.1016/S0140-7007(97)87632-3.
- [27] Fredenslund A, Jones RL, Prausnitz JM. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. AIChE J 1975;21:1086–99. doi:10.1002/aic.690210607.
- [28] Bell IH, Wronski J, Quoilin S, Lemort V. Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp. Ind Eng Chem Res 2014;53:2498–508. doi:dx.doi.org/10.1021/ie4033999.
- [29] Wilson DP, Kujak S, Leary JMO, Kennoy DH, Kusmierz A, Patnaik V, et al. ASHRAE Standard 34-2007 - Designation and Safety Classification of Refrigerants. vol. 4723. Tullie Circle: 2008.
- [30] DS/EN 378-1:2016 - Danish Standard Refrigerating systems and heat pumps – Safety and environmental requirements - Part 1: Basic requirements, definitions, classification and selection criteria. vol. 8. Copenhagen: 2016.
- [31] Corberán JM, Segurado J, Colbourne D, González J. Review of standards for the use of hydrocarbon refrigerants in A/C, heat pump and refrigeration equipment. Int J Refrig 2007;31:748–56. doi:10.1016/j.ijrefrig.2007.12.007.
- [32] Danfoss. Danfoss - Refrigerants and Energy Efficiency. Hydrocarbons n.d. <http://refrigerants.danfoss.com/hydrocarbons/#/> (accessed January 31, 2017).
- [33] IEA Heat Pump Centre - Annex 35. Application of Industrial Heat Pumps - Final Report. Borås, Sweden: 2014.
- [34] Ferreira CAI, Zamfirescu C, Zaytsev D. Twin screw oil-free wet compressor for compression-absorption cycle. Int J Refrig 2006;29:556–65. doi:10.1016/j.ijrefrig.2005.10.006.
- [35] Jensen JK, Markussen WB, Reinholdt L, Elmegaard B. On the development of high temperature ammonia-water hybrid absorption-compression heat pumps. Int J Refrig 2015;58:79–89. doi:10.1016/j.ijrefrig.2015.06.006.