Beyond Temperature Glide: The Compressor is Key to Realizing Benefits of Zeotropic Mixtures in Heat Pumps

Dennis Roskosch, Valerius Venzik, Johannes Schilling, André Bardow, and Burak Atakan*

Zeotropic mixtures are widely discussed as alternative refrigerants for vapor-compression cooling appliances and heat pumps. Mixtures can increase efficiency due to their nonisothermal phase change. In theoretical studies, zeotropic mixtures show significant benefits for efficiency if the temperature glide of the mixture matches the temperature change in the heat transfer fluids. Such large benefits have never been observed in experiments. First, this article clarifies the gap between simulations and experiments. Second, it is shown how zeotropic mixtures could increase efficiency in real plants. The analysis is based on experimental results from a heat pump with three zeotropic mixtures and on theoretical studies that also include a physical compressor model. The compressor performance is shown to depend strongly on composition. Therefore, the compressor efficiency is the key parameter for large benefits of zeotropic mixtures beyond well-matching temperature glides. Based on these findings, a fluid database is screened for fluids with well-matching temperature glides and high compressor efficiencies, utilizing a physical compressor model. As a result of the screening, the zeotropic mixture R152a/R32 is identified. The corresponding simulations show that zeotropic mixtures can achieve large benefits in heat pump efficiency if the pure components have similar and high compressor efficiencies.

1. Introduction

Cooling and heating processes are essential for humankind. While heating is usually still based on burning fossil fuels, cooling devices are mostly electricity-driven vapor-compression cycles. For 2018, the United Nations Environment Programme (UNEP)[1] estimated the worldwide number of cooling appliances at 3.6 billion. The electricity consumption of these appliances is estimated at around 3900 $\mathrm{TWh\,a^{-1}}$, corresponding to 17% of the world's total electricity demand. For the future, the UNEP forecasts a strong increase in cooling appliances up to 9.5 billion until 2050. The heating sector is also changing because the energy transition emphasizes electricity also for heating. Heat pumps play a crucial role in this context[2] as they convert electricity to heat with high efficiency. Today, the most common heat pump process is the electricity-driven vapor-compression heat pump, which also has the largest potential for the future. Consequently, the number of electricity-driven vapor-compression cycles will probably increase even more than already predicted for cooling appliances.

The growing electricity demand for cooling and heating should be satisfied with minimal environmental impact (mainly greenhouse gas [GHG] emissions). For vapor-compression cycles, the GHG emissions can be divided into direct emissions due to emissions of refrigerants with global warming potential (GWP) and indirect emissions due to the generation of electricity used to run the processes. According to the Technology and

Dr. D. Roskosch, Prof. A. Bardow
Energy and Process Systems Engineering Lab
ETH-Zürich
Tannenstrasse 3, Zürich 8092, Switzerland
E-mail: droskosch@ethz.ch

Dr. D. Roskosch, Dr. J. Schilling, Prof. A. Bardow
Institute of Technical Thermodynamics
RWTH Aachen University
Schinkelstraße 8, Aachen 52062, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/ente.202000955.

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Prof. A. Bardow
Institute of Energy and Climate Research – Energy Systems Engineering (IEK-10)
Forschungszentrum Jülich GmbH
Wilhelm-Johnen-Straße, 52425 Jülich, Germany

Dr. V. Venzik
Institute for Energy Efficient Buildings and Indoor Climate, E.ON Energy Research Center
RWTH Aachen University
Mathieustr. 10, Aachen 52074, Germany

Dr. V. Venzik, Prof. B. Atakan
Institute of Thermodynamics
University of Duisburg-Essen
Lotharstraße 1, Duisburg 47057, Germany

Economic Assessment Panel to the Montreal Protocol,[3] about 80% of the climate impact of cooling cycles is from indirect emissions and 20% from direct emissions.

Both direct and indirect emissions of cooling appliances and heat pumps can be reduced by zeotropic mixtures: on the one hand, the GWP and other essential criteria such as flammability can be adjusted by the targeted selection of fluid pairs.[4] On the other hand, zeotropic mixtures have a high potential for coefficient of performance (COP) increase due to their nonisothermal phase change.[5,6] This temperature change during isobaric evaporation and condensation is known as temperature glide. The extent of the temperature glide generally depends on the constituents of a mixture and its composition x.[5,6] The fundamental thermodynamic idea of using zeotropic mixtures is that the nonisothermal phase change better matches the temperature change in typical heat sources and sinks.[6] Matching of the temperature profiles minimizes exergy losses in the heat exchangers, and thus increases the COP.

Mixtures have already been proposed that achieve the desired thermodynamic properties such as low GWP (e.g., R404A, R452A),[4] but these mixtures mostly have a negligible temperature glide. In turn, the targeted use of a temperature glide is not yet industrial practice, even though it has been discussed in science for many decades.[7–9] In particular, the targeted selection of suitable fluid pairs for a specific application is still challenging.

The available publications on zeotropic mixtures are mostly theoretical studies and a few experimental studies. The theoretical studies aim either to show the general potential of zeotropic mixtures or to identify potentially suitable fluid pairs for a specific application. McLinden and Radermacher[10] compared pure and mixed refrigerants. Considering an ideal vapor-compression cycle by assuming isobaric heat exchangers and an isentropic compressor, the mixtures R22/R114 and R22/R11 were investigated over the whole composition range (from pure to pure fluid). For both mixtures, the authors found an increased COP for a specific composition compared with the respective pure components. The COP increase reached up to 18% for a large temperature difference of 25 K for the secondary heat transfer fluid. Based on their results, the authors concluded that the better the temperature glide of the mixture would match the temperature change in the secondary heat transfer fluids, the higher would be the COP increase in zeotropic mixtures. Similar results are also found by Yan et al.[11] for propane/isobutane mixtures in a vapor-compression refrigeration cycle with separation condensation, by Stoecker and Walukas[7] for R12/R114 mixtures in a domestic refrigerator, and by Zühlsdorf et al.[12] for different mixtures of hydrocarbons and hydrofluoroolefins in booster heat pumps. In another study, Zühlsdorf et al.[6] investigated the temperature glide matching in more detail. For 14 natural refrigerants, the authors conducted process simulations for several mixtures under various compositions. They found large COP increases up to 27% for zeotropic mixtures if the temperature change in the heat source is significant. All these theoretical studies show that a zeotropic mixture improves the COP significantly if only the temperature glide well matches the temperature change in the heat transfer fluids.

However, these theoretical studies mostly contradict the available experimental studies. Chang et al.[13] investigated propane/isobutane and propane/n-butane mixtures in a heat pump test rig that was operated in cooling and heating mode. Propane reached the highest COPs of all pure components. For the cooling mode, the COPs are increased for mixtures. The highest COPs are about 16% higher than those of the pure components isobutane or n-butane but only increased by 7% compared with propane. For the heating mode, no benefit of a mixture was obtained; here, propane had always the highest COP. Only small benefits of mixtures compared with the better pure component were also reported by Park et al.[14] for ethane/propane mixtures, and by Venzik et al. for isobutane/propene mixtures[5] and isobutane/propane mixtures.[15] The main results of these studies can be summarized as follows: the COPs of both pure components differ, and the maximum COP is often observed for a specific composition. However, the COP of the best mixture composition is just a few percentage points higher compared with the better performing pure fluid. In particular, the COP maximum is generally not located at the composition with the best matching temperature glide but is shifted to higher fractions of the better performing pure fluid.

The significant differences between simulations and experiments suggest that at least one crucial parameter has been lacking in the simulation models used. The resulting fundamental questions are: is it generally impossible to achieve the theoretically predicted COP benefits of mixtures in real plants? Or did we just considered the wrong mixture components so far? These questions lead to the following approach in this work.

We compare experimental results from a water/water heat pump test rig with simple simulations and explain the origin of the deviations between usual models and experiments. The experimental results of three zeotropic mixtures are then analyzed in more detail. We figure out why zeotropic mixtures do not achieve the expected COP benefits in experiments, even if the temperature glide matches the temperature changes in the heat transfer fluids. The fluid-dependent compressor efficiency, which is usually neglected in theoretical studies, is shown to be particularly important here (Section 3). Based on these findings, we propose a compressor-based criterion for the targeted selection of mixture components, in addition to the usual criterion to find mixtures with well-matching temperature glides. The compressor criterion is solely based on the compressor efficiencies of the pure components (Section 4), enabling a preselection without the knowledge of mixture properties. By utilizing a physical compressor model to calculate fluid-dependent compressor efficiencies,[16] the criterion is applied to fluid selection from a database. One mixture is selected that fulfills the criterion and has a well-matching temperature glide. The selected mixture is then tested in a process simulation over the whole composition range. The results show that zeotropic mixtures can achieve a large COP increase if the pure components fulfill our criterion of high and similar compressor efficiencies.

2. Experimental Section

The vapor-compression cycle considered in our study is a basic water/water heat pump (**Figure 1**). The schematic represents both the test rig in simplified form and the simulation model. Figure 1 also defines thermodynamic states. The evaporation temperature is defined as the temperature at the evaporator inlet $T_{ev} = T_4$; the condensation temperature refers to the dew point

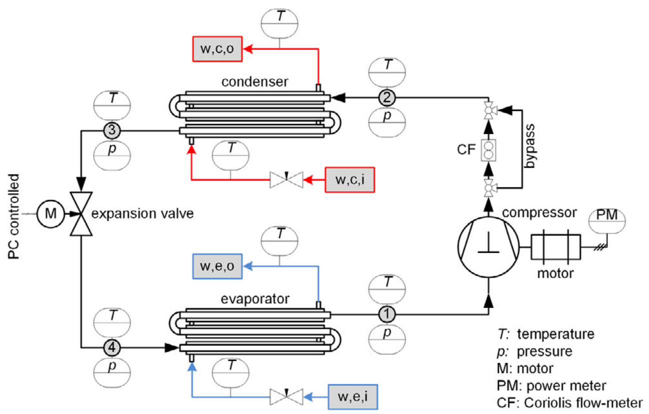

Figure 1. Schematic of the vapor-compression heat pump of experiment and simulation. Gray background fields define thermodynamic states.

temperature at the condenser inlet pressure $T_{con} = T_{sat}(p_2, q = 1, x)$. The subsequent sections give detailed information about the considered heat pump cycle (Section 2.1), the experimental setup (Section 2.2), and the simulations (Section 2.3). The definitions of the discussed parameters and variables are provided in Section SI1, Supporting Information.

2.1. Considered Heat Pump Cycle

As case study, a conventional water/water heat pump is considered, which feeds an underfloor heating system for central heating.[17] The underfloor heating system is represented by a fixed temperature change in the water flowing through the condenser. The water enters the condenser at $T_{w,c,i} = 25\,°C$ and is heated to $T_{w,c,o} = 35\,°C$. To achieve a temperature difference of 10 K, the water mass flow rate through the condenser is a function of the rejected heat flow rate, and thus depends on the mixture (components and composition x). The heat source of the heat pump is given by water entering the evaporator at $T_{w,e,i} = 17\,°C$ with a constant mass flow rate of 7.5 kg min^{-1}. The evaporation temperature is kept constant at $T_{ev} = 0\,°C$. The whole process operates in steady state.

2.2. Experimental Setup

The test rig for the heat pump was presented in detail by Venzik et al.[5] and is summarized here. The test rig mainly consists of a reciprocating compressor, two heat exchangers, and an expansion valve. Other equipment, such as sight glasses or additional valves, are neglected in Figure 1, for clarity. A schematic that contains the whole equipment is given in Venzik et al.[5] Compared with the test rig setup shown in Venzik et al.,[5] additional tubes and valves are used in this study to bypass the Coriolis flowmeter (Figure 1). In this study, the Coriolis flowmeter was bypassed because it induces high pressure losses, which influence the compressor behavior. However, the Coriolis flowmeter was utilized for controlling the mixture composition.[5]

The semihermetic reciprocating compressor has two cylinders and maximal electrical power consumption of 2.2 kW. The compressor is operated at an electrical frequency of 50 Hz leading to a rotational speed of 1450 rpm; the displacement is 5.4 $m^3\,h^{-1}$.

Both heat exchangers are counter-flow double-pipe heat exchangers; the refrigerant is in the inner pipe and the water in the annulus. Adjustable valves control the water flows. The heat exchangers are long enough to ensure that they do not limit the heat transfer for any of the investigated mixtures.

A needle valve is installed as an expansion valve and is adjusted by the experimenter. A valve without control characteristic enables the experimenter to set the evaporation temperature independently. The water mass flow rate in the condenser is also a degree of freedom and adjusted to achieve the desired water temperature change of 10 K at any time. The condensation temperature is not directly controllable but results, in steady-state operation, from the equilibrium of the entire process. The resulting condensation temperatures depend on the vapor–liquid-equilibrium (VLE) behavior of the used refrigerant, and thus slightly change with the mixture and mixture composition.

To determine the thermodynamic states, digital temperature and pressure sensors are installed between all parts of the test rig (Figure 1). In addition, a power meter measures the electrical power consumption of the compressor. Exact specifications of the measurement equipment are given in the study by Venzik et al.[5] The measured data are recorded and processed using LabView;[18] further thermodynamic state variables such as enthalpy and entropy are calculated using Refprop Version 9.1.[19]

The measurement accuracy was already evaluated previously[20] using error propagation, according to guide to the expression of uncertainty in measurement (GUM). The calculations were based on given tolerances from the measurement equipment manufacturers and were conducted for a typical operation point, assuming a coverage factor of 1. For directly measured variables such as temperature and pressure, the statistical errors are below $\pm 0.1\%$. Statistical errors for derived variables, such as COP or compressor efficiency, are less than $\pm 2.2\%$. In addition to statistical errors, reproduction measurements showed errors below $\pm 2\%$ for all variables.

2.3. Modeling

The simulations are based on thermodynamic cycle calculations. Only the main parts of the heat pump cycle are considered: compressor, condenser, expansion valve, and evaporator. In contrast to the test rig, some assumptions are made for simplification: 1) Both heat exchangers are isobaric. 2) The whole test rig is adiabatic to the environment. 3) The state change in the compressor is described by an overall compressor efficiency, defined as the ratio of isentropic power P_{is} to consumed electrical power P_{elec}

$$\eta_{comp} = \frac{P_{is}}{P_{elec}} \tag{1}$$

4) The change in the thermodynamic state in the expansion valve is isenthalpic $h_3 = h_4$.

In addition, the evaporator outlet (state 1) is at the evaporation pressure $p_{sat}(T_{ev}, x)$ and a temperature of $T_1 = 17\,°C$; this temperature also always results in the experiment due to the water inlet temperature for the evaporator and the large heat transfer area of the evaporator. The condenser outlet (state 3) is assumed as saturated liquid at condensation pressure. Analogous to the experiments, the evaporation temperature is set to 0 °C.

The condensation temperature is the only remaining degree of freedom of the simulations. The standard approach in the literature for heat pump simulations calculates the condensation temperature by a minimum temperature approach. Usually, the minimum approach temperature is estimated. Here, we use the minimum approach temperature observed in our experiments. All experiments showed a similar minimum approach temperature of about $\Delta T_{\min} = 0.2$ K. By using the minimum approach temperature observed in the experiments, we aim to reproduce the behavior of the test rig in the simulations. Thus, the condensation temperature T_{con} is always calculated as the minimum value while fulfilling the minimum approach temperature $\Delta T_{\min}$. This calculation is numerically implemented by an optimization (cf. Section SI1, Supporting Information).

The overall compressor efficiency η_{comp} is either set to a fixed value or calculated by a compressor model, as indicated in the results section. As compressor model, we implemented a semi-physical compressor model taken from our earlier work.[16] This model for reciprocating compressors predicts overall and volumetric efficiencies depending on the inlet state, the outlet pressure, and the refrigerant. The model was specially developed for fluid extrapolation and can handle both pure fluids and mixtures. The fitting to a specific compressor is straightforward: just the geometric specifications (e.g., bore and stroke) of the compressor and one set of overall and volumetric efficiencies for one operation point with one refrigerant are needed. In previous work,[16] the compressor model was validated with numerous experimental results obtained for different pure fluids and mixtures at various operation points. Mean deviations of $\pm 3.0\%$ for the predicted overall compressor efficiencies were calculated. The model fit to the compressor installed in our test rig led to a relative clearance volume of $c_{\text{cl}} = 0.1$ and a friction pressure of $p_{\text{fr}} = 80.12$ kPa, which are the two fitting parameters of the compressor model. The compressor model only requires usual thermal and caloric state variables, which are either available from fluid databases or can be calculated by equations of state for numerous substances.

In this study, fluid properties are calculated either by using Refprop Version 10[21] or by applying the Peng-Robinson equation of state (EOS)[22] combined with a polynomial correlating the temperature dependence of the isobaric ideal gas heat capacity. The fluid database used for the Peng-Robinson EOS property model is composed of different sources[21,23,24] and is given in Section SI3, Supporting Information. The fluid property model used for calculation is indicated in the results section.

3. Zeotropic Mixtures: Theory and Real Life

3.1. Temperature Glide

In this work, we used three zeotropic mixtures of alkanes and alkenes: isobutane (R600a)/propane (R290), isobutane (R600a)/propene (R1270), and *n*-butane (R600)/propene (R1270). These pure fluids and their mixtures have frequently been discussed in the literature for heat pumps and chillers.[13,14,25,26] Mixtures of alkanes and alkenes usually form zeotropic mixtures, while their vapor pressures and temperature glides match well with the requirements of typical heat pump and chiller applications. C_3 and C_4 alkanes/alkenes are particularly suited for the temperature range of the considered case study on domestic heat pumps. With the chosen mixtures, our analysis thus covers a set of promising candidate mixtures for heat pumps. Several compositions in the entire range between the pure fluid states were investigated for the mixtures isobutane/propane and isobutane/propene. The mixture *n*-butane/propene could only be investigated up to an *n*-butane fraction of 80 mol% because higher fractions of *n*-butane lead to pressures below the ambient pressure. We avoided subatmospheric pressures in the test rig due to the risk of forming an ignitable mixture by the intake of ambient air.

Figure 2a shows the temperature glide for the considered mixtures as a function of mole fraction. The values refer to an isobaric state change from dew to bubble point at the respective condensation temperatures (defined at dew point). The selected mixtures cover a wide range of temperature glides, which are close to the temperature change in the condenser water flow (10 K). However, the mixtures differ in the composition dependence of the temperature glide. In particular, the

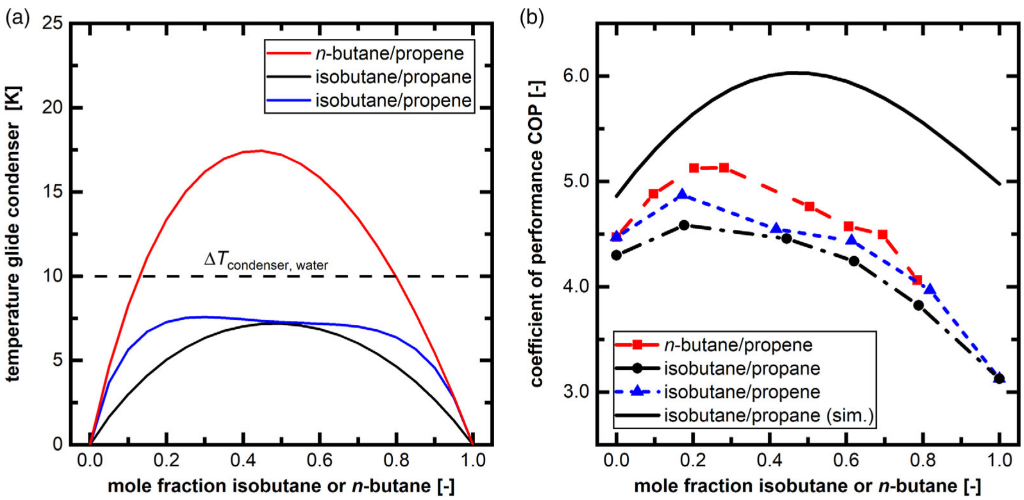

Figure 2. a) Theoretical temperature glide for the condenser and b) COP as function of mole fraction. Lines with symbols (b): measured results. Symbols refer to measured points; estimated errors are below the symbol size. Solid line (b): model results for isobutane/propane, $\eta_{\text{comp}} = \eta_{\text{comp,propane}}$, using Refprop.[21]

mixture isobutane/propane has a broad range with similar temperature glides.

Figure 2b shows COPs of the heat pump cycle as a function of the mole fraction of isobutane or *n*-butane. Both experimental results and simulations are shown. The simulation refers to the model given in Section 2.3 while assuming a constant overall compressor efficiency of $\eta_{comp} = 0.56$ for all compositions. This overall compressor efficiency corresponds to the measured compressor efficiency of pure propane.

The model results show the typical COP composition dependency for zeotropic mixtures of simple thermodynamic cycle calculations:[6,12] both pure fluids have similar COPs, while a specific composition shows a distinctive COP maximum. Such results are often shown in the literature and are the basis of the great expectations in using zeotropic mixtures. However, reality shows a different picture: the experimental results strongly differ from the simulation. All investigated mixtures show a similar behavior: the COPs of the respective pure components of the mixture differ, while the maximum COP is still achieved for a certain composition. This maximum is only significant compared with the pure component with the lower COP, here isobutane or *n*-butane. In comparison, the maximum COP is just slightly better than the other pure component. Other previous studies observed similar findings.[13,14] Still, the experimental results show that the COP increase due to the use of a zeotropic mixture can be improved if the temperature glide matches the temperature change in the heat transfer fluids. As shown in Figure 2a, the temperature glides of the mixtures isobutane/propane and isobutane/propene are smaller than the temperature change in the condenser water flow of 10 K for all compositions. The mixture *n*-butane/propene shows temperature glides between 0 and 17.5 K. Due to the higher and, thus, better fitting glide, *n*-butane/propene reaches the highest COP and shows the largest COP increase in the mixture compared with both pure fluids.

In summary, there is a great discrepancy between the expectations from theoretical studies and what is actually observed in experiments. The critical question is: how can we achieve the predicted large COP increase by zeotropic mixtures in practice?

The first step is to go back to the reason for using the temperature glide of zeotropic mixtures in heat pumps: the temperature glide can reduce the exergy losses in the heat exchangers and the gap between the thermodynamic mean temperatures of evaporation T_L and condensation T_H. Both effects increase COP, in particular, if the temperature glide of the mixture matches the temperature change in the heat transfer fluids. **Figure 3** shows the specific exergy losses in the evaporator (Figure 3a) and the ratio of both thermodynamic mean temperatures T_H/T_L (Figure 3b) derived from the experiments. The trends for the condenser are similar to those of the evaporator. The experimental results show that zeotropic mixtures actually reduce exergy losses. As predicted by theory, the minima of the exergy losses as well as of the temperature ratios are located at compositions with temperature glides that well match the heat source and sink temperature regimes (Figure 2a). Thus, zeotropic mixtures indeed reduce exergy losses and the gap between the thermodynamic mean temperatures. Still, the COP maxima are found for higher mole fractions of propane or propene (Figure 2b). Thus, the COP composition dependency cannot solely depend on the match of the temperature glide and the thermodynamic mean temperature ratios: there has to be another crucial physical effect.

3.2. The Compressor is the Heart of the Matter

The compressor is the central part of a vapor-compression heat pump from an exergetic point of view. Although the compressor efficiency is known to strongly depend on fluid properties and on the operation point,[5,16] theoretical studies usually use constant efficiencies for all mixtures and operation points. Thus, the fluid dependence of the compressor efficiencies is a promising candidate to explain the large deviations between simulations and experiments, as investigated later.

Figure 4 shows the experimental results of the overall compressor efficiencies (Figure 4a) and the specific exergy losses in the compressor and the evaporator (Figure 4b) for the three

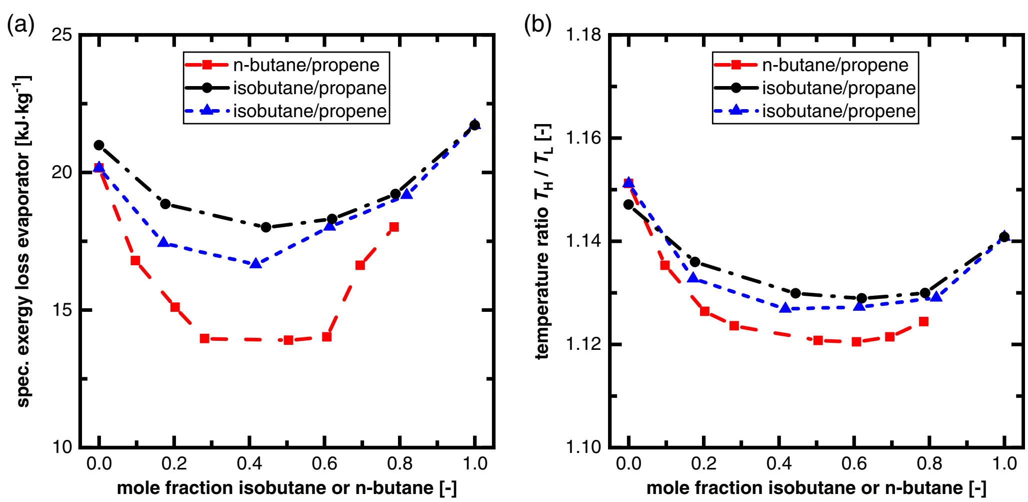

Figure 3. a) Measured specific exergy loss in the evaporator and b) ratio of thermodynamic mean temperatures as function of mole fraction. Symbols refer to measured points; estimated errors are below the symbol size.

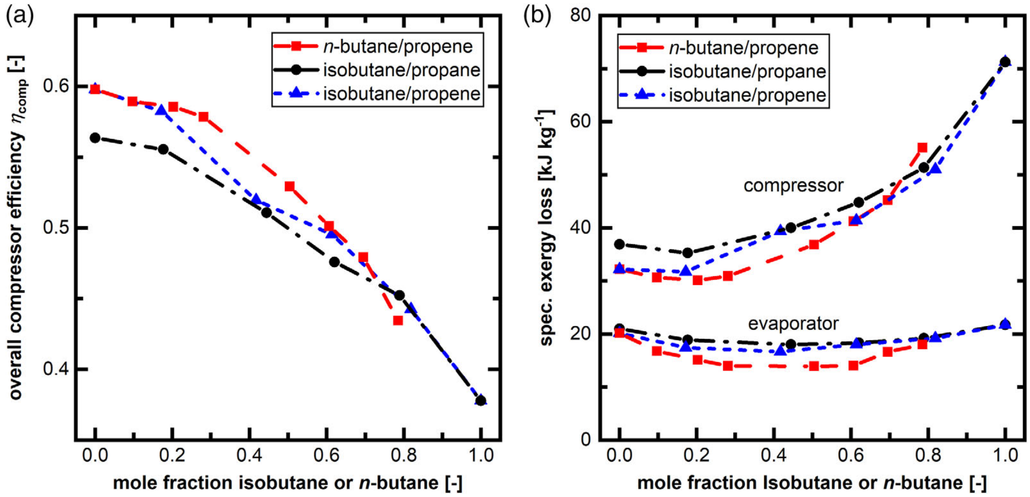

Figure 4. a) Overall compressor efficiency η_{comp} and b) specific exergy loss in the compressor and the evaporator as function of mole fraction. Symbols refer to measured points; estimated errors are below the symbol size.

investigated mixtures. The overall compressor efficiency is quite similar for all mixtures but strongly depends on the composition. The efficiencies of isobutane and *n*-butane are significantly smaller than for propane and propene. The exergy losses in the compressor show a reversed trend: compositions with small compressor efficiencies have high exergy losses and vice versa. The compressor exergy losses are significantly larger than the exergy losses from evaporation and depend more strongly on composition (Figure 4b). Thus, the compressor efficiency dominates the efficiency of the whole heat pump cycle.

The typical experimental COP composition curves (Figure 2b) can be explained by combining the results: if we start in the plots at pure isobutane or *n*-butane and go to the COP maxima, the exergy losses decrease both in the evaporator and in the compressor (Figure 4b), and thus the COP increases strongly (Figure 2b). Now, we start at pure propane or propene, with increasing isobutane or *n*-butane fraction; the exergy loss in the evaporator decreases again. However, the compressor exergy loss decreases very slightly or remains nearly constant (Figure 4b). Thus, the COP increases just slightly, leading to a flat maximum (Figure 2b). Therefore, the behavior of the compressor is responsible for the merely flat maxima and the shifts of the maxima away from compositions with well-matching temperature glide, as observed in experiments. To be more precise, compressor behavior means the very different overall compressor efficiencies for the pure components and the trends for mixtures.

This finding is also confirmed by simulations if the simple process model of Figure 2b is enhanced by a compressor model accounting for fluid-dependent overall compressor efficiencies[16] (**Figure 5**). With the compressor model, the calculated COPs are all too large because further losses, such as pressure losses, are neglected by the model. However, these losses only lead to a constant offset, and thus the mixture behavior is fully captured by the model.

As a result of the analysis, zeotropic mixtures should not only show a temperature glide that matches the temperature change in the heat transfer fluids. The compressor efficiency should also remain nearly constant over the composition range or should even increase for the mixtures. We expect that the exergy losses in the heat exchangers then have a higher impact on the exergy loss of the whole cycle leading to a stronger exergy loss minimum and COP maximum.

4. Selection of Zeotropic Mixtures

The previous analysis showed that fluid pairs are beneficial with high compressor efficiencies over the whole composition range and a well-matching temperature glide. However, these characteristics are not helpful as criteria for mixture selection because

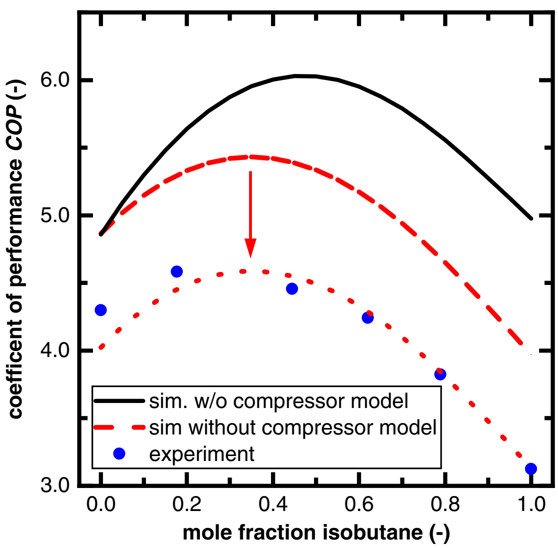

Figure 5. Coefficient of performance (COP) as function of isobutane mole fraction. Blue circles: experimental results; solid black line: model results without compressor model; dashed red line: model results with compressor model; and dotted red line: model results with compressor model shifted to the COP of pure isobutane. Mixture: isobutane/propane.

the decisive mixture properties are mostly unknown. However, the behavior of zeotropic mixtures is usually close to ideal mixtures facilitating the selection of promising fluid pairs.

For ideal mixtures, composition-dependent temperature glides can be calculated by Raoult's law just depending on the pure component vapor pressures. Calculations with Raoult's law show that the maximum temperature glide mainly depends on the ratio of vapor pressures of the pure components (cf. Section SI2, Supporting Information). The temperature glide is 0 K for a ratio of 1 (equal vapor pressures) but increases with an increasing ratio of vapor pressures. The desired temperature glide in this case study of about 8–10 K, e.g., requires a vapor pressure ratio from 3.0 to 3.5. As another characteristic of ideal mixtures, most state variables are linear functions of the composition. Accordingly, linear composition dependency of compressor efficiency promises to be a reasonable assumption for a first fluid screening. Figure 4a supports this assumption for the mixtures studied experimentally. Consequently, we expect that the compressor efficiencies are nearly constant with composition if the compressor efficiencies of the pure fluids are similar. Therefore, the screening for promising fluid pairs just requires the calculation of compressor efficiencies of pure fluids. In this work, we use the physical compressor model, as introduced in Section 2.3.

To test the findings, vapor pressures were calculated for 336 fluids from different substance groups (cf. Section SI3, Supporting Information). For all fluids with vapor pressures between 0.01 and 1 MPa at 0 °C, the overall compressor efficiency was calculated by the physical compressor model (cf. Section 2.3). The selected pressure range refers to the pressure limits of the test rig. Following the case study, the overall compressor efficiencies are calculated for an evaporation temperature of 0 °C, a compressor inlet temperature of 17 °C, and a condensation temperature of 33 °C. The condensation temperature is estimated to an average value because the condensation temperatures are, in reality, fluid dependent. Fluid properties are modeled by the Peng-Robinson EOS property model (cf. Section 2.3). Cubic equations of state have disadvantages regarding the accuracy, in particular, for polar molecules. However, the availability of fluid data for numerous substances is a great advantage for screening. **Figure 6** shows the calculated overall compressor efficiency as a function of vapor pressures at 0 °C for the 95 remaining fluids fulfilling the pressure limits.

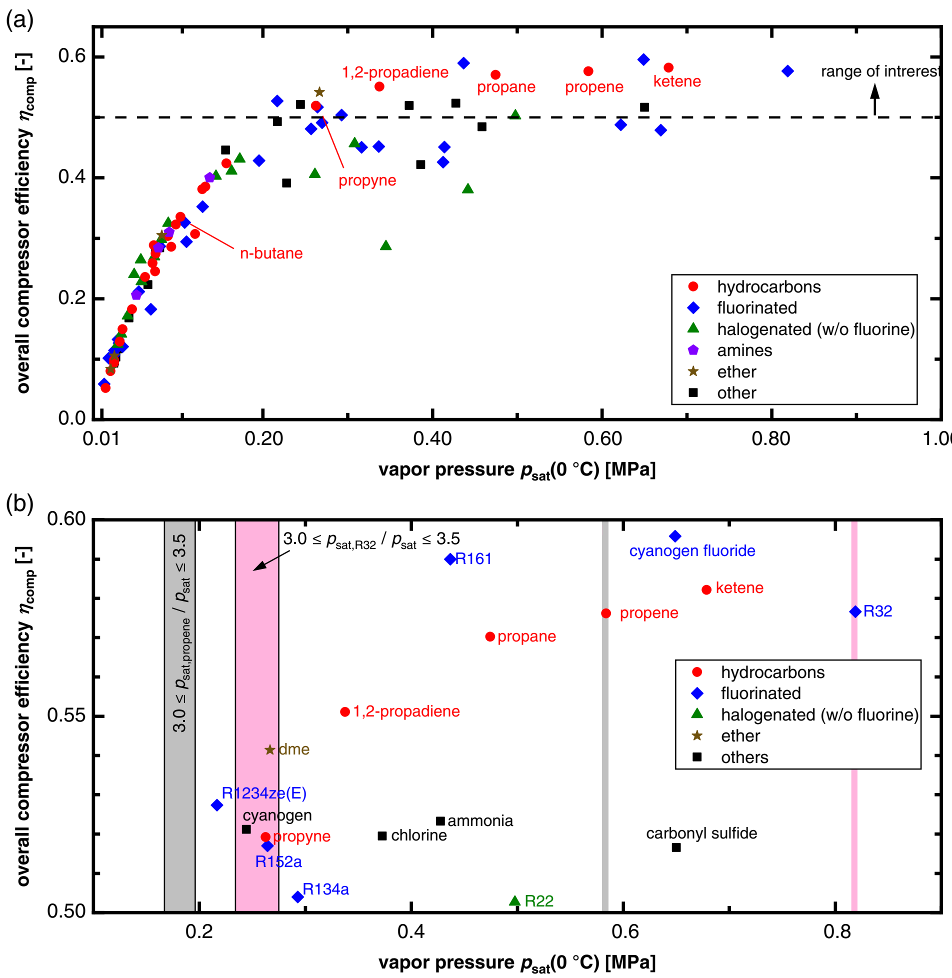

Figure 6. a) Calculated overall compressor efficiency η_{comp} as function of vapor pressure at 0 °C. Symbols refer to different substance groups. b) Zoom of (a) of the interesting range $\eta_{comp} \geq 0.50$.

Figure 6a shows the general trend of higher overall compressor efficiencies for larger vapor pressures. The relation between vapor pressure and overall compressor efficiency limits the opportunities of finding fluid pairs with different vapor pressures but similar overall compressor efficiencies. This trend applies, in particular, to the group of hydrocarbons (red circles). As mostly mixtures of alkanes or alkenes were investigated in the literature, hydrocarbons are of particular interest. If unstable substances, such as ketene, 1,2-propadiene, and propyne, are excluded from the analysis, there is no fluid pair of hydrocarbons with both similar compressor efficiencies and sufficient difference in vapor pressures. The screening results suggest that, at least within the normal operating conditions of heat pumps and refrigeration cycles, mixtures of hydrocarbons are not expected to improve the COP significantly. Thus, the analysis suggests that mixtures with at least one component from another molecular family than hydrocarbons have to be investigated.

Figure 6b shows the range of interest with higher compressor efficiencies ($\eta_{comp} \geq 0.5$), as shown in Figure 6, in more detail. Mixtures of fluid pairs with overall compressor efficiencies below this limit can achieve a significant COP increase compared with the pure components. However, the COP increase in these mixtures resulting from the temperature glide is expected to be too small to beat the pure fluid with the best overall compressor efficiency. Thus, only mixtures of pure fluids with high overall compressor efficiencies are reasonable to achieve a benefit against pure fluids. However, the search for appropriate fluid pairs remains challenging, even if other substance groups are included in the analysis (Figure 6b). In particular, the small number of fluids with high vapor pressures limits the possibilities. Here, just propene and R32 are suitable candidates. Ketene and cyanogen fluoride are chemically unstable, carbonyl sulfide is toxic, the use of R22 is prohibited, and propane already has a too-small vapor pressure to find a partner leading to a zeotropic mixture with the desired temperature glide between 8 and 10 K ($p_{sat} \leq 0.14$ MPa). For propene, no fluid lies precisely in the range of corresponding vapor pressures to achieve a temperature glide of 8–10 K (gray background).

Apart from hydrocarbons, mixtures of propene with the fluorinated substances within the range of 0.2 MPa $\leq p_{sat} \leq$ 0.3 MPa may be attractive (Figure 6b). Usually, alkanes and alkenes form azeotropic mixtures with fluorinated hydrocarbons (e.g., propane/R32[27] or propane/R1243zf[28]), which can have higher temperature glides as expected for zeotropic mixtures with similar vapor pressure ratios. Even though azeotropic mixtures might be promising, we follow previous studies and focus on zeotropic mixtures.

For R32 (difluoromethane), a few fluids are identified within the desired range of vapor pressure (magenta background in Figure 6b), which are mainly also fluorinated hydrocarbons. The most promising fluid pair is R32 and R152a (1,1-difluoroethane) because both fluids are already established refrigerants which form zeotropic mixtures.[29] Due to their high GWPs ($GWP_{R152a} = 677$; $GWP_{R32} = 138$)[30], R32, as well as mixtures of R32 and R152a, is not expected having a great future as refrigerants. However, they are still approved, e.g., on the European continent, for heat pumps and chillers with a refrigerant charge smaller than 3 kg.[31] Mixtures of R32 and R152a were already tested and shown to be feasible in a vapor-compression cycle.[32]

To validate our criterion, we assessed various compositions of R152a/R32 with the simulation model, as given in Section 2.3. The overall compressor efficiency η_{comp} is calculated with the compressor model as a function of inlet state, outlet pressure, and mixture composition[16] (cf. Section 2.3). Fluid properties are calculated using Refprop Version 10,[21] showing good agreement with experimental data.[33] The process model has also been shown to reproduce the composition dependence of the COP well (Figure 5).

For the considered mixture R152a/R32, the overall compressor efficiency changes only slightly with mole fraction of R152a (**Figure 7**a). The temperature glide in the condenser, calculated for the composition-dependent condensation pressure, shows a

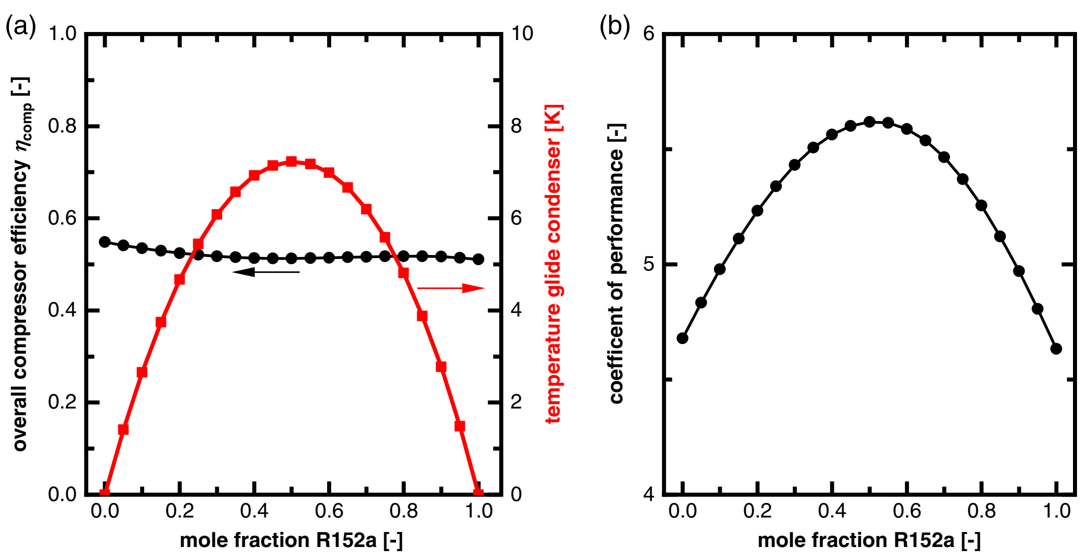

Figure 7. a) Overall compressor efficiency and condenser temperature glide, b) COP, all as function of mole fraction R152a. Mixture: R152a/R32.

symmetric dependence on mole fraction with a maximum value of 7.2 K at equimolar composition (Figure 7a).

We now observe the COP dependency that is expected from basic thermodynamic theory for zeotropic mixtures (Figure 7b): the composition with the highest COP is now at the composition with the best matching temperature glide (here the largest, equimolar composition). Even more interesting, the mixture shows now a significant COP increase at optimal composition compared with both pure components. Our simulation study thus confirms that zeotropic mixtures can be highly beneficial compared with pure fluids if the pure components of the mixture have similar compressor efficiencies and lead to a well-matching temperature glide. We believe that our criterion is useful for all vapor-compression cooling cycles and heat pumps where the exergy losses of the compressor dominate the overall exergy losses of the process, regardless of the specific temperature levels.

5. Conclusion

Starting point of our article was the promise of zeotropic mixtures to increase heat pump efficiency coming from basic theory, which is in conflict with experimental findings of small COP increase in zeotropic mixtures. Theoretical studies mostly show a strong COP increase at the composition with best-matching temperature glide. Experimental studies typically show that a specific composition indeed has a high COP increase compared with one pure component, but the COP is just slightly increased compared with the better pure component. Our experimental analysis shows that this gap between simulation and experiment is due to the composition-dependent compressor efficiency. We found that zeotropic mixtures can achieve large benefits in efficiency if: first, the compressor efficiency remains nearly constant over composition, and second, the temperature glide well matches the temperature change in the heat transfer fluids. For zeotropic mixtures, it was shown that the knowledge of vapor pressures and compressor efficiencies of the pure fluids is sufficient to select mixtures.

Based on the finding, we screened a fluid database for fluid pairs meeting the criterion and all other requirements. The overall compressor efficiencies were calculated by a compressor model which can easily be fitted to a specific piston compressor. One fluid pair was selected to test our criterion: R152a/R32. We tested this identified mixture by a cycle simulation that also includes the compressor model, which accounts for the mixture-dependent efficiency. The results show a strong COP increase compared with both pure components as desired from the thermodynamic theory. We are optimistic that a screening of a larger fluid database or a computer-aided molecular design would certainly identify even more sufficient fluid pairs. We are looking forward to future experiments to validate the usefulness of our criterion to select zeotropic mixtures in practice.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

compressor efficiency, heat pumps, refrigerants, temperature glide, zeotropic mixtures

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