

Propane-isobutane mixtures in heat pumps with higher temperature lift: an experimental investigation

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Abstract

The shift towards renewable energies leads to an increased interest in heat pumps, not only for floor heating at temperatures around 40 °C, but also for providing hot water at higher temperatures (> 60 °C). To reach the goal of a climate neutral process, it is important to use refrigerants with low global warming potentials. Zeotropic mixtures are discussed to potentially increase the coefficient of performance (*COP*) of a heat pump compared to pure fluids. The present work experimentally analyses a compression heat pump process of such fluids; five mixtures of propane and isobutane are investigated here. The influence of composition, compressor frequency, inlet temperature of the working fluid into the evaporator and the inlet temperature of the secondary fluid water into the condenser are researched. Besides the *COP*, the destroyed exergy of the components are evaluated, finding the most relevant losses. It is shown that the *COPs* for a temperature lift of 33 K are above 3 for the mixtures, while at a higher temperature lift of 53 K the *COP* is around 2. Furthermore, a strong impact of the compressor efficiency on the process was found, that changes with the composition, due to composition dependent pressure and density variations. The results show that the advantage of the zeotropic mixture within the heat exchangers is limited by their low contribution to the total specific exergy destruction compared to the compressor. The often-neglected changes in electro-mechanical losses get important, when the pressure ratios are changing with composition, as shown experimentally.

Keywords: thermal heat pump, hydrocarbon working fluids, working fluid mixtures, higher temperature lift.

1. Introduction

Heat pumps gain more and more in importance, due to their efficiency and possibility to be driven by work, because the world energy increasingly stems from renewable sources. At the same time, fluorocarbons have to be replaced as working fluids, due to their global warming potential (GWP) [1]. Natural refrigerants like hydrocarbons are an option to replace them and were investigated within several cycles [2-6], due to their low GWP and their good accessibility. Further, zeotropic refrigerant mixtures are a good way to achieve lower exergetic losses in heat exchangers when sensible heat sources and sinks are used, because the temperature difference between the working fluid and the secondary fluid throughout the heat exchange is reduced. While heat pumps are mainly used for low temperature lifts, the interest in higher temperature heat pumps (HTHP) rises [3, 5, 7-9], which provide secondary fluid exit temperatures of 50 °C to 100 °C using heat sources around 5 - 20 °C. Possible applications for HTHPs are the warm water distribution with a needed temperature of around 60 °C or conventional house heating systems with entering heat flows at 50 to 70 °C; they could replace natural gas heaters. High exergetic efficiencies and low CO₂ emissions can be reached, if the electrical energy is provided from renewables. In the field of water heating, Zhang et al [10] evaluated the *COP* of a process depending on the pipe length of the heat exchangers and the refrigerant amount. They used ambient air as the heat source and R22 as the refrigerant. The

temperature of the secondary fluid was increased to 55 °C and the *COP* strongly depended on the temperature of the ambient air and the charge of the system.

Chaichana et al [11] compared the hydrocarbons propane, propene, isobutane, and n-butane as refrigerants for a solar-powered heat pump for the provision of hot water, varying the temperatures of evaporation and condensation. The mass flow rates, operating pressures, compressor inlet temperatures and *COP* were compared. Propane and propene showed good performance in their study for condensing temperatures of up to 70 °C.

Chang et al [12] also compared the pure fluids isobutane, n-butane, propane and propene. They considered the zeotropic mixtures of isobutane/propane and n-butane/propane. The substances were compared in a test plant at low secondary fluid temperatures of 21.1 °C in the condenser and 8.3 °C in the evaporator. The mixture isobutane/propane (mass ratio 50/50) led to a 7 % higher coefficient of performance compared to the reference case with R22. The mixture of n-butane/propane (mass ratio 75/25) increased the *COP* by about 11 %.

Park et al [13] investigated propane and propene as pure refrigerants as well as the mixture of these two substances, also as an alternative to R22. In addition, a ternary mixture of propane/propene/DME was measured. They found an increase in the *COP* compared to R22 for all used refrigerant except for pure propene, with the ternary mixture showing the highest increase of 5.7 %.

Bamigbetan et al [14] investigated a cascade heat pump that can provide energy at 115 °C using residual heat. This cascade heat pump with a heating capacity of 20 kW was operated with propane and butane. They concluded that this system with an average *COP* of 3.1 in the temperature range of 58 to 72 °C is the better alternative to electrical heaters or gas boilers.

There are also several theoretical studies available, investigating zeotropic mixtures in heat pumps. For example, Guo et al [8] evaluated recuperative high-temperature heat pump cycles with subcritical zeotropic mixtures. The performance analysis for hot water supply from 15 °C to 99 °C with an air heat source was investigated for fluids like hexane, R431 0mee, propane, propene and R32 as refrigerant and studied the effect of pressures and mixture compositions on cycle *COP* and exergy utilisation. Higher *COP*s of 5.063 and 5.011 were reached for n-hexane/propene and R431 0mee/R32 with a reduction of exergy destruction due to a good temperature match between working fluid and heat sink. Also, the results were compared to CO₂ heat pump cycles and showed an increase in *COP* by up to 8.88 % with operation pressures below 2 MPa.

Mota-Babiloni et al [15] simulated and optimised high-temperature heat pump cascades with internal heat exchangers. They used low GWP working fluids like pentane, isobutane, propane, HCFO-1233zd(E), HCFO-1224yd(Z) and HFO-1336mzz(Z) as working fluids and optimised the *COP* of the cascade with an algorithm. They found the maximum *COP* of 3.15 for pentane/butane mixtures. An option with low flammability was a cascade with HFO-1366mzz(Z)/HFO-1234ze(E) which showed a good performance. In this study the low stage internal heat exchanger had a low impact on the high stage discharge temperature.

Zühlsdorf et al [16] investigated the increase of the performance of a booster heat pump that heats a district heating water stream from 40 °C to 60 °C. They screened 18 possible fluids like propane, pentane, propylene, isobutane or R1234yf and considered the pure fluids as well as the possible mixtures of them. The mixture with 50 % isobutane and 50 % pentane showed the best performance with an *COP* of 9.01. By analysing the complete system of low temperature district heating, they found the overall system *COP* increasing from 13 % to 22 % when using working fluid mixtures in the central and booster heat pump units.

In a further study, Zühlsdorf et al [17] demonstrated the optimization of a heat pump regarding the temperature glide. They investigated the temperature glide matching for 14 natural refrigerants and their mixtures. It was found that the *COP* increases by up to 27 %, when there is a large temperature change in the heat source along heat transfer. Furthermore, they

concluded that a good temperature match in the heat sink and source improve the *COP*, but an optimal match does not necessarily lead to an optimal *COP*.

The reviewed theoretical studies show that *COPs* can be increased significantly by using zeotropic mixtures when the temperature glides match the temperature change in the heat transfer fluids. Roskosch et al [18] investigated the reason, why theoretical studies often predicting a high increase in *COP* for zeotropic mixtures, while they were often not found in experiments. They found that the change in composition also changes the compressor efficiency, which in modelling studies most often is set constant, leading to the observed discrepancies. It was concluded that a zeotropic mixture is most beneficial for the performance when the compressor efficiency is nearly constant over the composition and when the temperature glide matches the temperature change in the heat transfer fluids. As mentioned in the reviews [2, 9], the experimental study of HTHP especially with hydrocarbons was not carried out often, but is promising as seen from the brief literature review. Thus, the present experimental investigation evaluates propane/isobutane mixtures as working fluids, using heat from water at environmental conditions and delivering secondary fluid enthalpy flows at 40 °C or 60 °C, aiming to determine *COPs* and the exergy destruction in the different components as a function of mixture composition.

2. Experimental

The used simple compression heat pump system consists of a compressor, an evaporator, a condenser, an expansion valve, and a working fluid reservoir. The simplified system is shown in Figure 1.

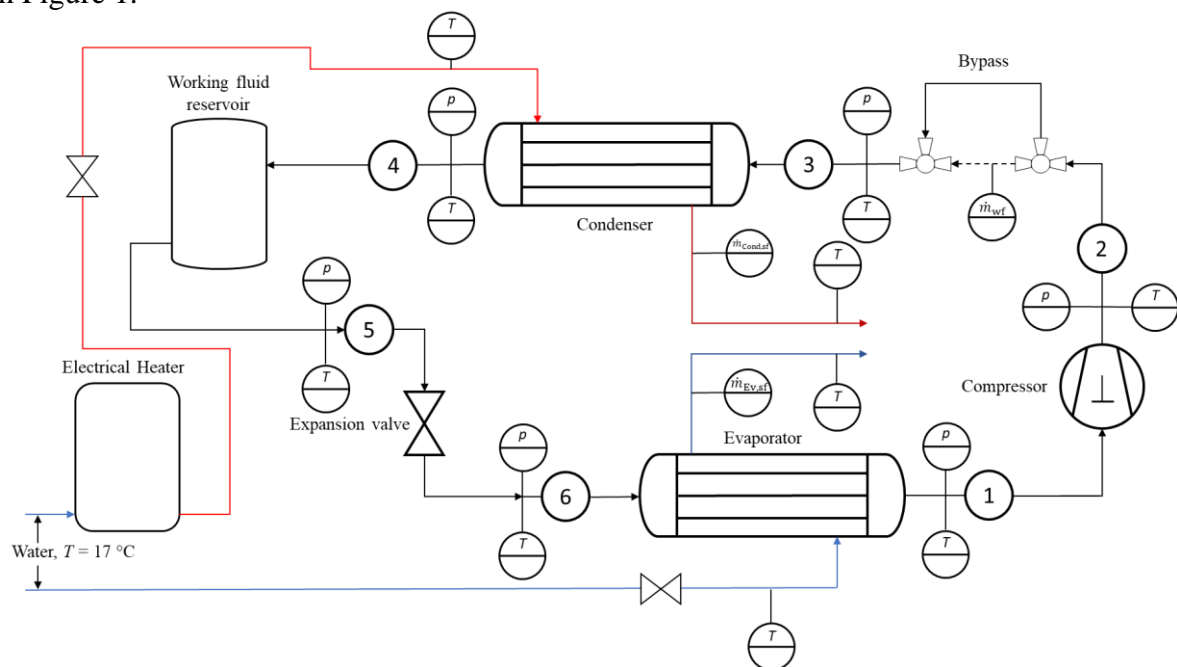


Fig 1: Schematic View of the used compression heat pump.

A semi-hermetic piston compressor (GEA Bock HGHC12P) increases the pressure between states 1 and 2. It has two cylinders, two pole pairs and a maximum power consumption of 2.2 kW. With a frequency inverter, the rotation speed can be varied continuously between 35 and 70 Hz. The actual frequency of the compressor is the AC frequency divided by the pole pair number of two. Thus, an AC frequency of 50 Hz leads to an RPM of 1500 min^{-1} . In the reference case, the frequency is 1500 min^{-1} and is varied down to 1050 min^{-1} . The stroke volume V_{stroke} of the compressor is 61.74 dm^3 , which is needed for the calculation of the theoretical volumetric flow rate. The electrical power consumption of the compressor is

measured at the outlet clamps of the inverter. A minimum superheating of the working fluid of 3 °C at the suction side is needed to protect the compressor. The maximum outlet temperature of the compressor is 120 °C due to the limit of the PTFE outlet seal. Reniso Synth 68 from Fuchs is used as machine oil with the thermophysical properties given in Table 1.

Table 1: Thermophysical properties of Synth 68.

Property	Value
Density at 15 °C	835 kg/m ³
Flash point (Cleveland)	260 °C
Kinematic viscosity at 40 °C	68 mm ² /s
Kinematic viscosity at 100 °C	10.5 mm ² /s
Pourpoint	-57 °C

Water was used as the secondary fluid in both counter-flow tube-in tube heat exchangers, its entrance temperature can be raised to 60 °C with an electric heater; this was varied in the experiments. In the evaporator, water with an inlet temperature of 17 °C and a mass flow rate of around 7 kg/min was used throughout. With this mass flow rate, an evaporator outlet temperature of the working fluid of nearly 17 °C is reached for all operation points. The throttling is realised with the help of a needle valve. The fine adjustment of the needle valve ensures the investigation of a wide range of operating points and allows to control the temperature at the evaporator inlet. The evaporator has an inner tube diameter of 10 mm (wall thickness: 1 mm) and an inner diameter of the outer tube of 16 mm. This results in an annular gap of 2 mm in which the water flows. The evaporator has a length of 14 m. The condenser has an annular gap of 2 mm and an inner tube diameter of the outer tube of 19 mm. The condenser has a total length of 22 m. To compensate the different needed working fluid mass loads at different operation points, a refrigerant reservoir is installed before the needle valve. In this way the system must not be refilled for operation point changes.

The water mass flow rates were measured with an Optiflux 4050 flow meter from KROHNE. Furthermore, the flow rate of the working fluid can be measured with a Coriolis flow meter MFS3081 K 1.5 E from KROHNE for calibration purposes. The use of the Coriolis flow meter causes heat losses and high pressure drops; thus, we followed the procedure from our previous work on the same system and determined the flow rates from the energy balance in the evaporator, the difference was determined there to be around 2 % [19]. Thus, the bypass shown in Fig. 1 was used for all the measurements presented here.

For monitoring and evaluating the processes, 6 pressure sensors and a total of 38 temperature sensors are installed in the system. The pressure sensors are located at the inlet and the outlet of the main components of the system (point 1 - 6 in Fig. 1). A temperature sensor is also installed at each of these points. The water temperatures at the inlets and outlets of the heat exchangers are also recorded. These pressure and temperature measurement points are shown in Fig. 1. The remaining temperature sensors are installed in the heat exchangers. Thus, the temperature profile inside the heat exchangers can be recorded and evaluated but are not discussed here. The information about the used pressure and temperature sensors within the system including their ranges and accuracies are summarized in Table 2.

Table 2: Used sensors with manufacturer, type, measuring ranges and accuracies.

Sensor	Manufacturer	Type	Range	Accuracy
Temperature	Sensor Electric	PT-1000 type AA	-5 - 120 °C	$0.1 + 0.005 \cdot T$ [°C]
Pressure	ICS Schneider Messtechnik	IMP331	<u>Position 1 and 5:</u> 0 - 10 bar (absolute)	0.1 %
			<u>Others:</u> 0 - 25 bar (absolute)	

The influence of the mixture composition of propane and isobutane, the evaporator inlet temperature, the compressor frequency, and the condenser inlet temperature of water on the heat pump performance was investigated here and were varied. Since only some of the parameters can be selected independently, it was decided to control both temperatures at the evaporator inlet together with the mass flow rate of the secondary fluid, allowing a straightforward analysis of the exergy destruction in the evaporator. Also, the entrance temperature and the temperature difference of the water in the condenser were kept constant, because these are typical design variables of heat pumps. By keeping these values constant, the outlet temperature of the water in the evaporator, and the secondary fluid mass flow rate in the condenser differ for every operation point and are used for the evaluations. Furthermore, the minimum superheating was met for every data point, while the superheating value varied overall throughout the study since it was controlled for the actual evaporator inlet temperature. Also, the working fluid is subcooled at the outlet of the condenser for the presented work. The process values set in this way are shown in Table 3.

Table 3: Investigated process boundary conditions.

Parameter	Used values
Mole fraction isobutane, $x_{C_4H_{10}}$	0, 0.25, 0.5, 0.75, 1
Compressor frequency, n_{comp}	1500 min ⁻¹ , 1050 min ⁻¹
Working fluid inlet temperature evaporator, $T_{evap, in}$	0 °C, 4 °C, 8 °C
Secondary fluid inlet temperature evaporator, $T_{evap, sf, in}$	17 °C
Secondary fluid inlet temperature condenser, $T_{cond, sf, in}$	40 °C, 60 °C
Secondary fluid temperature difference condenser, $\Delta T_{cond, sf}$	10 °C
Temperature lift, T_{lift}	33 K, 53 K

The temperature lift is defined as the effective total temperature difference achieved between the evaporator inlet and the condenser outlet temperature of the secondary fluid. Thus, the temperature lifts are 33 K and 53 K.

The target mole fractions of 0.25, 0.5 and 0.75 that are filled into the system, did not correspond to the mixtures circulating during operation. These differed somewhat because the more volatile propane accumulated in the gas phase of some parts of the system, such as the refrigerant reservoir. So, the circulating mixture contains a slightly higher amount of isobutane. The composition of the circulating mixture was determined with the help of the assumption that the expansion valve is isenthalpic and thus the mole fractions could be calculated iteratively with the data from RefProp [20], until the enthalpy of a composition before and after the expansion valve were the same. This method was proposed and used by different authors

before [21, 22]. It was found that the range of the difference to the target mole fractions is from 0.011 to 0.045.

There are several potential sources of error in this experimental work. At first there are systematic errors. For example, oil from the compressor transported with the working fluid, fluctuations in the values while logging the data at an operation point or heat losses throughout the system. There were different approaches to prevent those errors and minimize the uncertainties. Before logging in the data, a steady operation point was reached for all values. To reduce the statistical error in the fluctuation of the values while operating the system, the data logging was carried out for 5 min (the values are captured every second) and afterwards the mean values were used for the calculations. Furthermore, the measurements were repeated two times. Heat losses are reduced by using polyurethane insulation (thickness: 20 mm) for the whole system, with an additional stone wool insulation (thickness: 30 mm) for the heat exchangers. Besides the approaches to reduce the systematic error, the statistical errors due to the uncertainties of the sensors (See Table 2) were analysed for this system in previous work [19]. From error propagation it was shown that the uncertainty is in a range between 0.18 and 3.51 % for the various derived values. For example, the calculated error of the compressor power consumption is 0.36 %, for the *COP* 2.22 % and for the specific exergy loss in the condenser 3.51 %. The error increases for the parameters with a higher contribution of the secondary fluid values to the calculation, due to the temperature sensitivity of the enthalpy and entropy of water. Overall, the repetition measurements showed the same range of error for the present work. Another mentionable source of error is the uncertainty of the equations of state that are used by RefProp [20] for calculating the mixture properties. The authors of the equations for isobutane and propane used within RefProp indicated their uncertainty to be within 1 - 3 % [23, p. 190]. Finally, the reproducibility of the measured data at different days was within 2.5 %.

3. Calculation

In the following, the most important equations necessary for the evaluation of the experimental data will be introduced and discussed. The *COP* is defined as the ratio of the determined net heat flow rate transferred to the secondary fluid (sf) in the condenser to the consumed compressor power:

$$COP = \frac{|\dot{Q}_{H,sf}|}{P_{comp,el}} \quad (\text{Eq. 1})$$

To analyse the process details, the exergy destruction in different parts are examined. These are generally determined by the difference between entering and exiting exergy flows \dot{E} . The exergies, when the contributions of kinetic and potential energy changes are neglected, are given by:

$$\dot{E}_i = \dot{m}_i \cdot ((h_i - h_u) - T_u \cdot (s_i - s_u)) \quad (\text{Eq. 2})$$

In this equation \dot{m}_i, T, h, s are mass flow rate, temperature, specific enthalpy, and specific entropy, respectively. An ambient (subscript: u) temperature of 25 °C and an ambient pressure of 1 bar were used in this work as dead state. Using Eq. 2, the incoming and outgoing exergy flows can be determined for each component and the difference can be calculated as exergy destruction.

Various efficiencies can be defined for the compressor to characterise it. In the present work, the electro-mechanical (subscript: em) compressor efficiency is used with:

$$\eta_{\text{comp,em}} = \frac{P_{\text{comp,wf}}}{P_{\text{comp,el}}} = \frac{\dot{m}_{\text{wf}} (h_{\text{comp,out}} - h_{\text{comp,in}})}{P_{\text{comp,el}}} \quad (\text{Eq. 3})$$

It represents the ratio of the power delivered to the working fluid (subscript: wf) $P_{\text{comp,wf}}$ and the electrical power consumed by the compressor $P_{\text{comp,el}}$ and takes the electro-mechanical losses in the compressor into account.

The isentropic efficiency is defined as the ratio of the isentropic compressor power and the power delivered to the fluid:

$$\eta_{\text{comp,is}} = \frac{P_{\text{comp,is}}}{P_{\text{comp,wf}}} = \frac{w_{\text{comp,is}}}{w_{\text{comp,wf}}} \quad (\text{Eq. 4})$$

With the inlet state of the working fluid and RefProp [20], the isentropic enthalpy (h) at the outlet of the compressor was calculated and used to determine the isentropic compressor work per mass flow of working fluid $w_{\text{comp,is}}$:

$$w_{\text{comp,is}} = h_{\text{comp,out,is}} - h_{\text{comp,in}} \quad (\text{Eq. 5})$$

The real outlet state of the compressor was used to calculate the specific work delivered to the fluid $w_{\text{comp,wf}}$ from the measured data, assuming an adiabatic compressor:

$$w_{\text{comp,wf}} = h_{\text{comp,out}} - h_{\text{comp,in}} \quad (\text{Eq. 6})$$

The volumetric efficiency is defined as the quotient of the effective volumetric flow rate (\dot{V}) into the compressor, as calculated from the density $\rho_{\text{comp,in}}$ and the mass flow rate \dot{m}_{wf} and the geometrically highest possible volumetric flow rate:

$$\lambda_{\text{comp}} = \frac{\dot{V}_{\text{comp,in}}}{\dot{V}_{\text{theoretical}}} = \frac{\dot{m}_{\text{wf}}}{\rho_{\text{comp,in}} \cdot n_{\text{comp}} \cdot V_{\text{stroke}}} \quad (\text{Eq. 7})$$

The latter is calculated from the compressor frequency n_{comp} and stroke volume V_{stroke} . The working fluid mass flow rate was determined from the energy balance across the evaporator, which was assumed to be adiabatic, because of the small temperature difference to the environment [19]. Thus, the mass flow rate can be calculated from:

$$\dot{m}_{\text{wf}} = \dot{m}_{\text{evap,sf}} \cdot \frac{(h_{\text{evap,sf,in}} - h_{\text{evap,sf,out}})}{(h_{\text{evap,wf,in}} - h_{\text{evap,wf,out}})} \quad (\text{Eq. 8})$$

By using the working fluid mass flow rate and the specific work delivered to the fluid (Eq. 6), $P_{\text{comp,wf}}$ is determined from the obtained data from the system.

4. Discussion and Results

In the following, first, the COP change with mixture composition and further parameters are presented, before going through the different devices aiming to get some insights into the reasons for the found dependencies. The influence of the mixture composition, the compressor frequency and the temperature lift on the COP is shown for different operating points in Fig. 2. The COP is plotted as a function of the isobutane mole fraction for all combinations of compressor frequency and temperature lift and the different evaporator inlet temperatures.

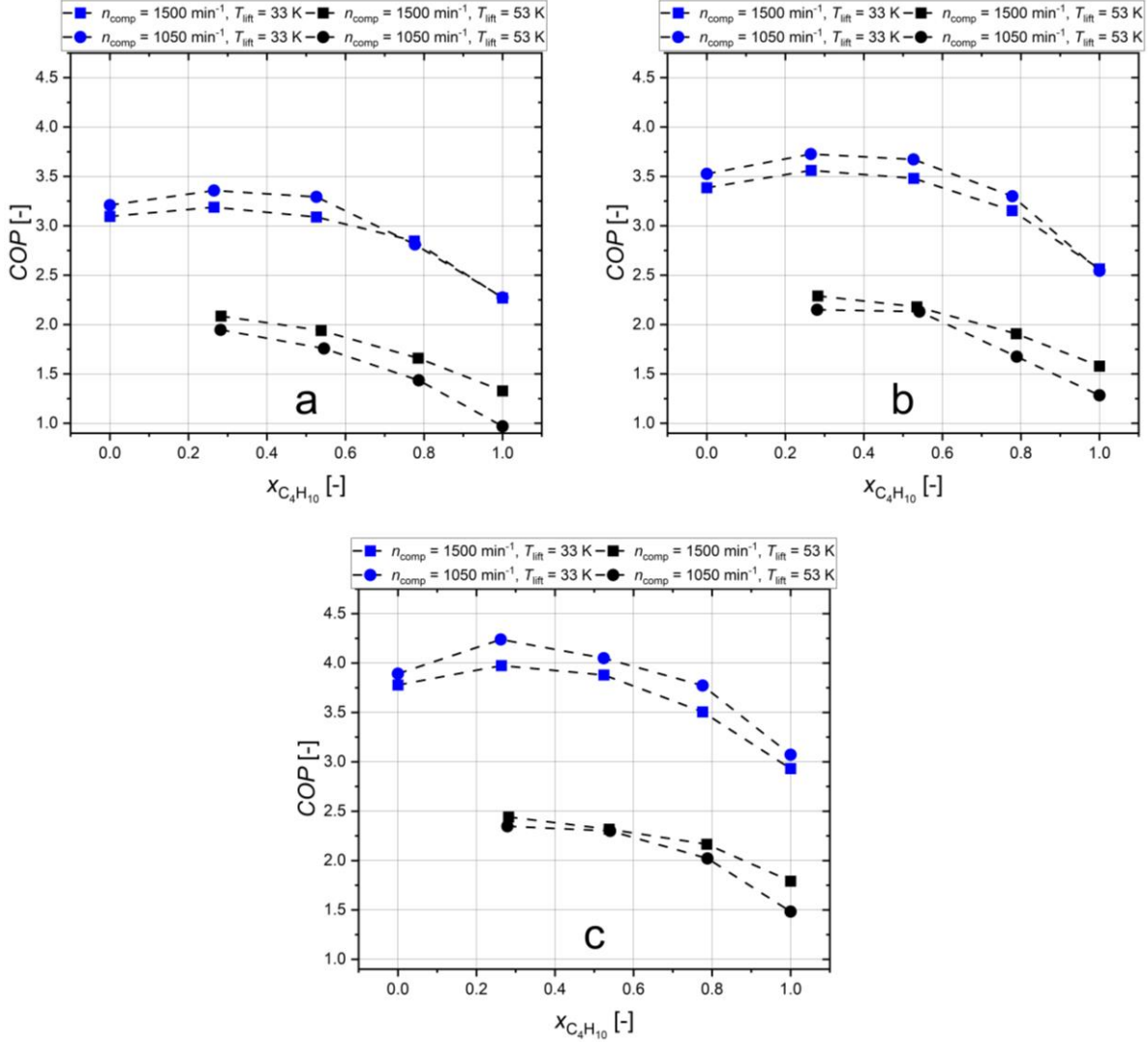


Fig 2: COP depending on the mole fraction of isobutane for a) $T_{evap, in} = 0 \text{ }^\circ\text{C}$, b) $T_{evap, in} = 4 \text{ }^\circ\text{C}$ and c) $T_{evap, in} = 8 \text{ }^\circ\text{C}$.

The values for pure propane (mole fraction of 0) could not be recorded for a temperature lift of 53 K, because the maximum pressure in the system would exceed the limit of 20 bar. The lowest measured COP here is 0.97 (below 1, due to experimental uncertainties) for $0 \text{ }^\circ\text{C}$, 1050 min^{-1} and a temperature lift of 53 K at an isobutane mole fraction of 1. The highest measured COP is 4.24 for $8 \text{ }^\circ\text{C}$, 1050 min^{-1} and a temperature lift of 33 K at an isobutane mole fraction of 0.262. Overall, it can be seen that the COP increases, as expected from the reversible (Carnot) limit, with increasing evaporator inlet temperature. The trends of the COP dependencies are similar for the different temperatures, therefore, the results for the evaporator inlet temperature of $4 \text{ }^\circ\text{C}$ are discussed in more detail.

COPs between 2.54 and 3.73 are found for the lower temperature lift of 33 K, as seen in Fig. 2 (b), which are higher than those for the higher temperature lift, where values between 1.28 and 2.29 are observed. Within a composition-variation series, pure isobutane leads throughout to the lowest *COPs*; the highest *COPs* are found for isobutane mole fraction of 0.25, but the increase of the *COP* from pure propane to the maximum is only around 5 %. As mentioned before, the circulating mole fraction differed from 0.25 and was determined to be 0.267. The *COP* for pure propane as refrigerant is higher than for pure isobutane, the latter *COPs* always being the lowest of each series.

The optimal zeotropic mixture increases the *COP* compared to the pure refrigerants. This can be attributed to the temperature glide that occurs for mixtures, leading to a better matching between working fluid temperatures and secondary fluid temperatures and reduces the exergy losses in the heat exchangers, as will be discussed later. With the rising temperature glide, the temperature difference between working fluid and secondary fluid is lower and, in addition, the pressure ratio in the compressor decreases. As an example, the measured temperature glides in the condenser are plotted in Fig. 3 as a function of the isobutane mole fraction for a compressor frequency of 1500 min^{-1} and an evaporator inlet temperature of $4 \text{ }^\circ\text{C}$.

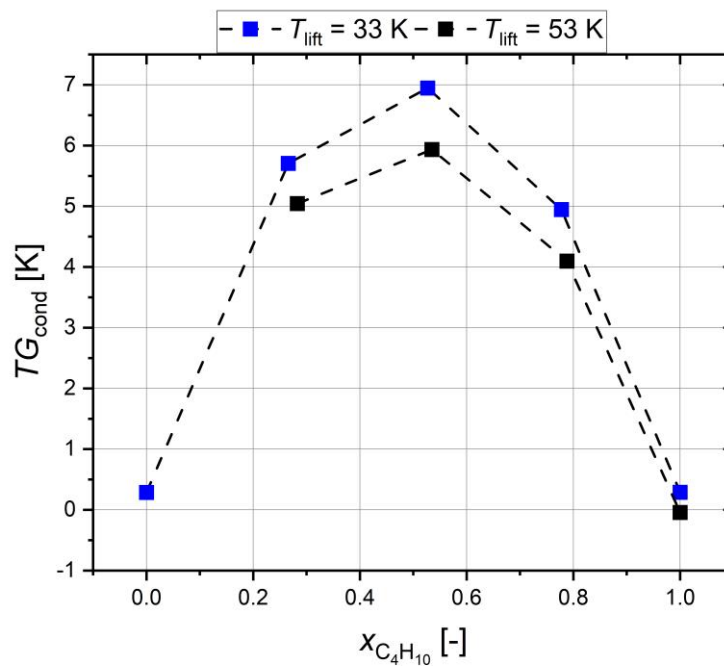


Fig 3: Temperature glide in condenser depending on isobutane mole fraction at $T_{\text{evap, in}} = 4 \text{ }^\circ\text{C}$ and $n_{\text{comp}} = 1500 \text{ min}^{-1}$ for both temperature lifts.

For ideal mixtures, the largest temperature glide is expected at a mole fraction of 0.5, here the highest temperature glide is found at a fraction of 0.527 and is 5.94 K for a temperature lift of 53 K and 6.95 K for 33 K. The small, but not vanishing temperature glide for the pure fluids is caused by the pressure drop in the condenser. In general, the temperature glide is larger at lower temperature lifts of the heat pump (33 K here), because the condensation pressure is lower, and thus, the difference between boiling point and dew point is increased. The larger temperature glide approaches the temperature change of 10 K of the secondary fluid, and this better temperature matching in the heat exchanger leads to a lower exergy destruction. By comparing Figs. 3 and 2, it is noticed that the operating point with the highest *COP* is not found for the mixture with the highest temperature glide, but at a mole fraction of 0.267. Thus, the positive effect of the temperature glide must be superimposed by another dependency. From previous

work, the variation in compressor efficiency with composition was suspected, which may be a direct or an indirect effect, as discussed next.

To examine the influence of the compressor, the change of the COP with the compressor frequency can be considered first by regarding Fig. 2 once more. It is seen that the influence of the compressor frequency is changing between the low and the high temperature lift. For a high temperature lift the COP is lower for the lower frequency, while for the 33 K lift, the opposite behaviour is observed, and the COP is higher at 1050 min^{-1} . The increase of the COP for the lower temperature lift can be explained by a reduction of the compressor losses, due to lower friction losses as also discussed in previous work [24]. The inverse finding is astonishing and justifies a closer look at this opposing behaviour. For the nominal isobutane mole fraction of 0.25, Table 4 compares the three compressor efficiencies, the isentropic, the electro-mechanical, and the volumetric efficiency, as a function of frequency and temperature lift, all for an evaporator inlet temperature of 4 °C.

Table 4: COP , isentropic and electro-mechanical efficiency and volumetric efficiency for $T_{\text{evap, in}} = 4$ °C and a target mole fraction of 0.25 depending on the compressor frequency and temperature lift.

	1500 min^{-1}	1050 min^{-1}	1500 min^{-1}	1050 min^{-1}
	33 K	33 K	53 K	53 K
COP (-)	3.56	3.73	2.29	2.15
$\eta_{\text{comp, is}}$ (-)	0.619	0.631	0.637	0.642
$\eta_{\text{comp, em}}$ (-)	0.951	0.975	0.920	0.890
λ_{comp} (-)	0.731	0.725	0.640	0.608

The COP increases for the lower temperature lift from 3.56 to 3.73 with decreasing compressor frequency, while the COP increases from 2.15 to 2.29 with frequency for the higher temperature lift. The isentropic efficiency is increasing with frequency reduction for both, but for the lower temperature lift, the increase is higher with 1.94 % compared to 0.78 % for the higher lift. Only for the electro-mechanical efficiency, an opposing behaviour as for the COP is noticed, it increases by 2.52 % for the 33 K lift and decreases 3.26 % for the 53 K lift. The volumetric efficiency is increasing with frequency for both temperature lifts but for the lower lift the decrease is only 0.82 %, while for the higher lift 5 %.

The finding that a higher compressor frequency is beneficial for a high temperature lift but disadvantageous for a low frequency regarding the COP can be rationalized from these numbers: if $P_{\text{comp, el}}$ from Eq. 1 is expressed with the electro-mechanical and the isentropic compressor efficiency, the influence of the latter gets obvious:

$$COP = \eta_{\text{comp, is}} \cdot \eta_{\text{comp, em}} \cdot \frac{\dot{Q}_{\text{H, sf}}}{\dot{m}_{\text{wf}} \cdot (h_{\text{comp, out}} - h_{\text{comp, in}})} \quad (\text{Eq. 9})$$

But also, the composition influences further operating conditions. To examine this, the mass flow rate, the density at the inlet of the compressor, the volumetric efficiency and the pressure

ratio of the compressor (outlet pressure divided by the inlet pressure) for a temperature lift of 33 K are given in Table 5.

Table 5: Isobutane mole fraction dependence of the density at the compressor inlet, working fluid mass flow rate, the volumetric efficiency and the pressure ratio; all for $n_{\text{comp}} = 1500 \text{ min}^{-1}$ and $T_{\text{lift}} = 33 \text{ K}$

$x_{\text{C}_4\text{H}_{10}}$ (-)	$\rho_{\text{comp, in}}$ (kg/m ³)	\dot{m}_{wf} (kg/s)	λ_{comp} (-)	π_{comp} (-)
0	9.75	0.0110	0.7299	3.457
0.267	8.09	0.0092	0.7312	3.417
0.527	6.59	0.0074	0.7225	3.509
0.778	5.26	0.0057	0.6979	3.695
1	4.15	0.0044	0.6763	4.078

With increasing isobutane mole fraction, the density of the mixture entering the compressor, as well as the working fluid mass flow rate, decrease almost linearly. The volumetric efficiency dependence of the compressor is non-linear; a maximum of 0.7312 for an isobutane fraction of 0.267 is observed and it decreases slightly towards pure propane and stronger towards pure isobutane. A high volumetric efficiency means a better utilisation of the compressor (see Eq. 7). Also, the pressure ratio is lowest for the isobutane mole fraction of 0.267 and the highest for pure isobutane, the trend resembles the one of the volumetric efficiency. The combination of the highest volumetric efficiency, the lowest pressure ratio, and the high working fluid mass flow rate, at a mole fraction of 0.267, leads to a high total compressor efficiency and a high *COP*.

Furthermore, the mixture composition influences the heat transfer to the secondary fluid and thus the *COP*. To underline this, the composition-dependence of the heat transferred per mass-unit of fluid (q) in the condenser is shown in Fig. 4.

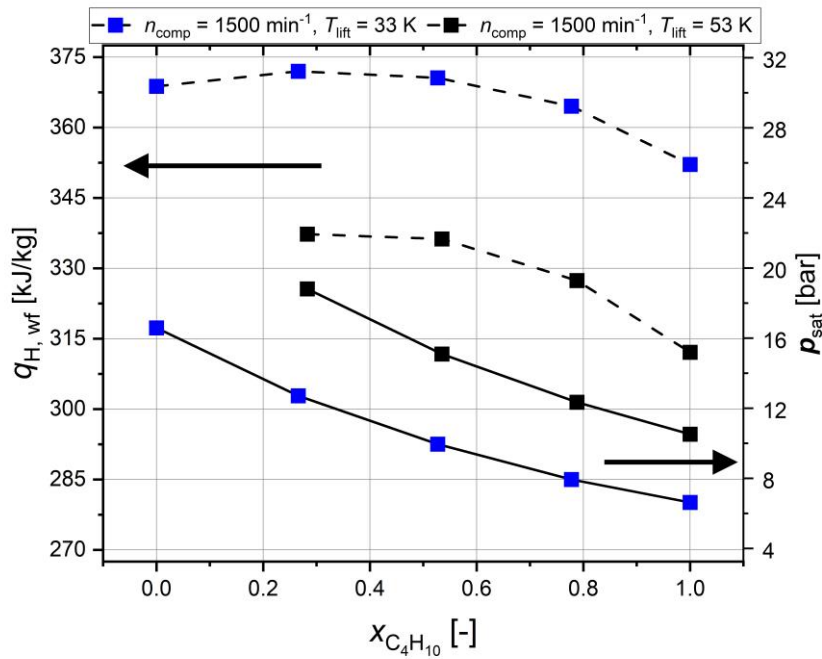


Fig 4: Heat transferred per mass-unit (dashed line) and saturation pressure in the condenser depending on the isobutane mole fraction at $n_{\text{comp}} = 1500 \text{ min}^{-1}$ and $T_{\text{evap, in}} = 4 \text{ }^{\circ}\text{C}$ for both temperature lifts.

The composition dependence of the heat transferred per mass-unit in the condenser is similar to the course at the same conditions in Fig. 2 for both temperature lifts with a maximum at an isobutane mole fraction of 0.267. This behaviour is mainly due to the composition dependence of the condensation enthalpy, which makes up the largest part of the heat transferred to the secondary fluid in the condenser. The condensation enthalpies associated with the temperature glides (shown in Fig. 3), and the heat transfer rates in the condenser (related to the working fluid) are listed in Table 6. The boundary conditions are the same as in Fig. 4.

Table 6: Specific condensation enthalpies, condenser heat flow rates, and temperature glide in the condenser for isobutane mole fractions at $n_{\text{comp}} = 1500 \text{ min}^{-1}$, $T_{\text{lift}} = 33 \text{ K}$ and $T_{\text{evap, in}} = 4 \text{ }^{\circ}\text{C}$.

$x_{\text{C4H10}} (-)$	$\Delta h_{\text{cond}} (\text{kJ/kg})$	$\dot{Q}_{\text{H, wf}} (\text{kW})$	$TG (\text{K})$
0	288.55	4.06	0.286
0.267	310.15	3.41	5.706
0.527	315.92	2.73	6.947
0.778	312.29	2.07	4.946
1	300.94	1.53	0.290

From Table 6 it is seen that the condensation enthalpy increases with rising temperature glide up to the maximum of 315.92 kJ/kg at an isobutane mole fraction of 0.527, while the enthalpy of 310.15 kJ/kg for a mole fraction of 0.267, however, is not far below and much higher than the propane enthalpy of evaporation of 288.55 kJ/kg. The heat flow rate in the condenser decreases with increasing isobutane mole fraction due to the decreasing mass flow rate (see

table 5), with the maximum heat flow rate for pure propane. Thus, for pure propane, the heat flow rate does not rise sufficiently to compensate for the larger mass flow rate obtained, resulting in a small decrease of the heat flow rate compared to the one determined with a mole fraction of 0.267. For a mole fraction of 0.527, the condensation enthalpy and the temperature glide are both maximal, but the mass flow rate is low, due to the lower density of the mixture. The result is that for the mixture with an isobutane fraction of 0.267 the condenser heat flow rate is the highest and the ratio of $\dot{Q}_{H,sf}$ and \dot{m}_{wf} is maximal.

Finally, the fluid dependent specific exergy destruction of all components are shown to analyse their influence on the system performance and the *COP*. The specific exergy destruction depending on the isobutane mole fraction for a compressor frequency of 1500 min^{-1} , a temperature lift of 33 K (a) and 53 K (b) with an evaporator inlet temperature of $4 \text{ }^\circ\text{C}$ are shown in Fig. 5.

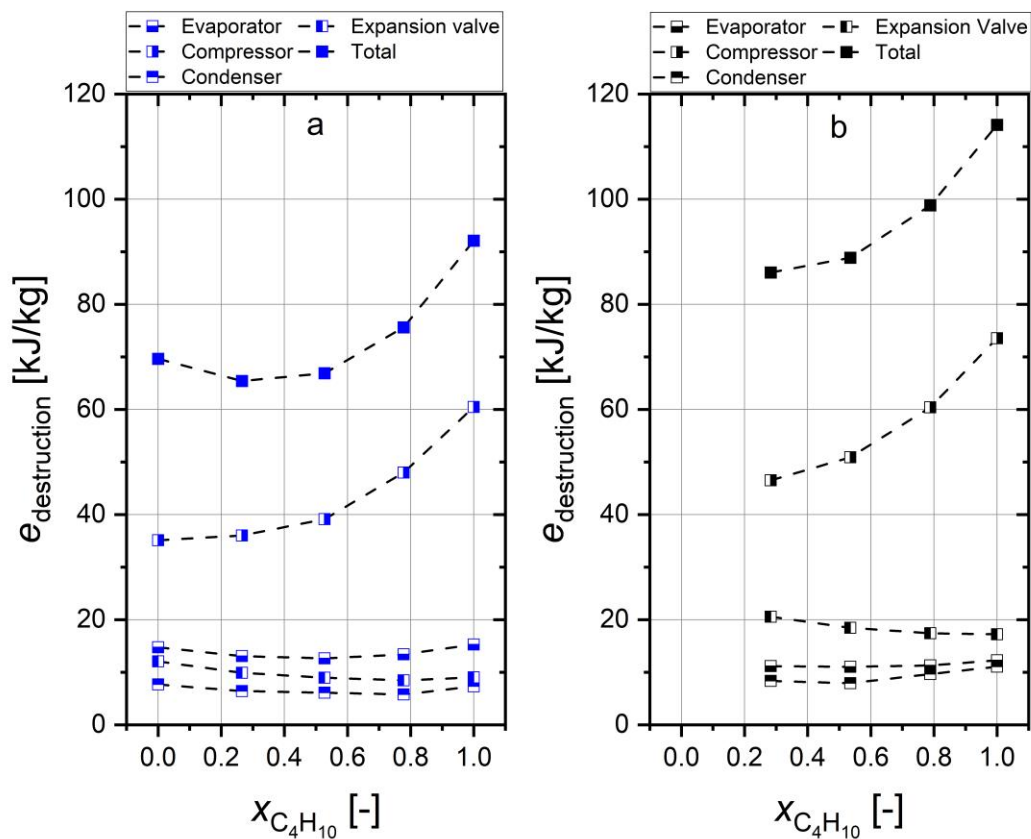


Fig 5: Specific exergy destruction depending on the isobutane mole fraction at $n_{\text{comp}} = 1500 \text{ min}^{-1}$ for $T_{\text{evap, in}} = 4 \text{ }^\circ\text{C}$ and (a) $T_{\text{lift}} = 33 \text{ K}$ (b) $T_{\text{lift}} = 53 \text{ K}$.

For T_{lift} of 33 K it is seen that the total specific exergy losses are in the range between 65 kJ/kg and 92 kJ/kg. The lowest exergy destruction is found for a mole fraction of 0.267 and the highest for pure isobutane. The losses with pure propane and with a mole fraction of 0.5 are only slightly above the minimum. The exergy destruction in the condenser is lowest, with values between 5.8 kJ/kg and 7.7 kJ/kg. The component with the next highest irreversibilities is the expansion valve (8.5 kJ/kg - 12.1 kJ/kg). The evaporator leads to slightly higher destruction of 12.6 kJ/kg to 15.3 kJ/kg, while the compressor shows the largest irreversibilities between 35 kJ/kg and 60 kJ/kg. As expected for a temperature glide, the specific exergy destruction in the condenser is highest for the pure refrigerants. The observed low increase of around 5 % of the maximum *COP* for mixtures compared to pure propane can be explained here too. The contribution of both heat exchangers to the total exergy loss is only around 25 % for 33 K.

Thus, the possibility to reduce the exergy destruction with increasing the temperature glide is limited by the low share of the heat exchangers on the losses. With increasing temperature lift (53 K in b) the contribution of the heat exchangers to the total exergy destruction decreases to around 21 %, so that the reduction potential gets even lower with higher temperature lifts. Because of this, the *COP* range from minimum to maximum for different mixture compositions decreases from 1.19 for 33 K to 1.01 for 53 K (see Fig. 2).

In comparison to the heat exchangers, the compressor has a very high share of the total exergy destruction. It contributes between 50.4 % and 65.67 % and the courses of the total exergy destruction follows the one of the compressor so that it can be concluded that the compressor is the most important component for the total exergy destruction of the process and has a main influence on the *COP* too. To address this further, a closer look shall be taken at the electrical and isentropic specific work of the compressor for a temperature lift of 53 K in Fig. 6.

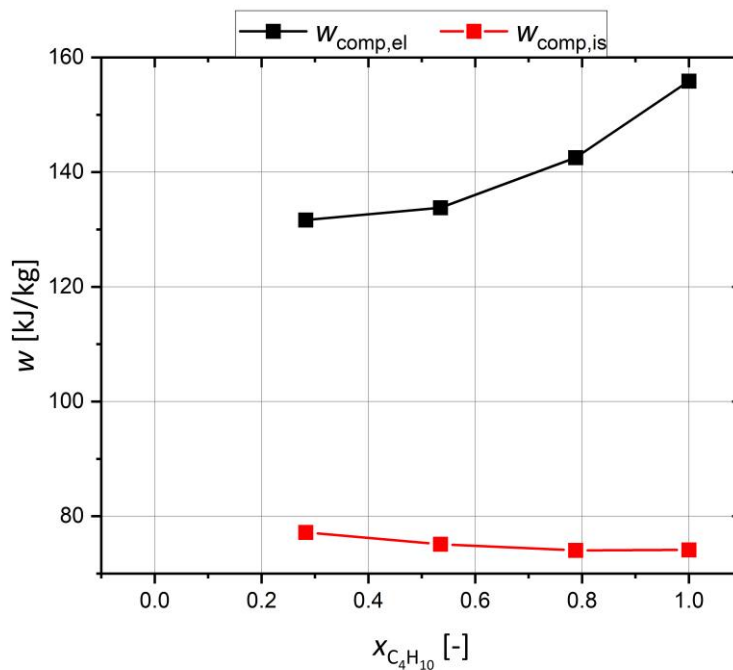


Fig 6: Specific electrical and isentropic compressor work depending on the isobutane mole fraction at $n_{comp} = 1500 \text{ min}^{-1}$, $T_{lift} = 53 \text{ K}$ and $T_{evap, in} = 4 \text{ }^\circ\text{C}$.

In Fig. 6 it is seen that the specific electrical work ($w_{el} = P_{comp,el}/\dot{m}_{wf}$) of the compressor (black line) increases with the amount of isobutane in the mixture, similar to the behaviour of the exergy destruction in the compressor, while the needed isentropic work is slightly falling with isobutane content. Eq. 10 combines Eq. 3 and Eq. 4, and the electrical specific work can be divided into three parts: the specific isentropic work and the electro-mechanical and isentropic compressor efficiencies:

$$w_{comp,el} = w_{comp,is} \cdot \frac{1}{\eta_{comp,em} \cdot \eta_{comp,is}} \quad (\text{Eq. 10})$$

As the isentropic compressor work only decreases slightly with the isobutane mole fraction, as seen in Fig. 6 (red line), the change in the electro-mechanical and isentropic compressor efficiency is the reason for the increase of the electrical compressor work. To show this, the compressor efficiencies, the pressure ratio and the volumetric efficiency are shown in Fig. 7 as a function of the isobutane mole fraction.

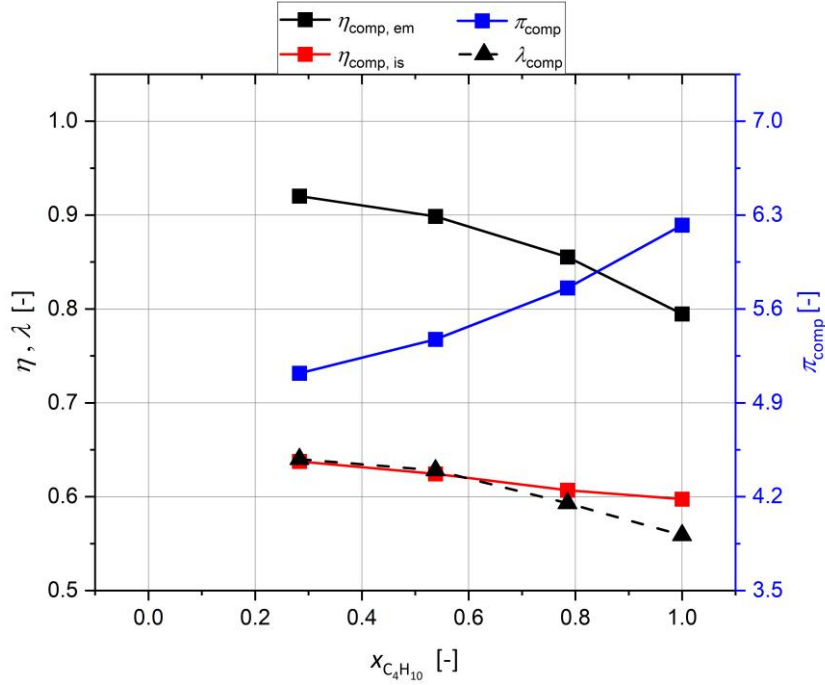


Fig 7: Internal compressor efficiency $\eta_{comp, em}$, isentropic efficiency $\eta_{comp, is}$, volumetric efficiency λ_{comp} and the pressure ratio π as a function of the isobutane mole fraction at $n_{comp} = 1500 \text{ min}^{-1}$, $T_{lift} = 53 \text{ K}$ and $T_{evap, in} = 4 \text{ }^\circ\text{C}$.

Interestingly, the electro-mechanical efficiency drops with the isobutane mole fraction. Because the electro-mechanics has not any direct relation to the working fluid, this must be due to the change in the mechanical variables, the pressure levels along the volume change. Therefore, the pressure ratio of the compressor is shown in blue in Fig. 7, which increases from 5.12 at $x_{C_4H_{10}} = 0.267$ to 6.22 for pure isobutane. This increase of the pressure ratio also leads to the decrease of the volumetric efficiency (dashed line) with the isobutane mole fractions. As a result of this, it is seen that both compressor efficiencies decrease with the isobutane mole fractions, but for $\eta_{comp, em}$ (black line) the reduction by 13.65 % is higher than for $\eta_{comp, is}$ (red line) which falls by 6.3 %. The courses of λ_{comp} and $\eta_{comp, em}$ are similar, λ_{comp} falls by 12.65 %. Thus, the utilisation of the compressor drops with isobutane mole fractions due to the pressure ratio and the volumetric efficiency, resulting in lower compressor efficiencies, causing the increase in the needed specific electrical work (Eq. 10 and Fig. 6). This altogether leads to the highest *COP* at a mole fraction of 0.267 within the investigated operation points.

5. Conclusions

Experimental results for the fluid dependence of the performance of a water-water compression heat pump system with higher temperature levels are presented. The temperature level for the secondary fluid water, which acts as heat source, was $17 \text{ }^\circ\text{C}$. The rejected heat was used to heat water to $50 \text{ }^\circ\text{C}$ and $70 \text{ }^\circ\text{C}$, respectively, both with a $10 \text{ }^\circ\text{C}$ temperature increase within the condenser. These temperature lifts of 33 K and 53 K are typical for a sustainable system providing hot water. The performance was investigated as a function of the evaporator inlet temperature, compressor frequency and isobutane mole fraction in a propane/isobutane working fluid mixture. Although, the use of this zeotropic mixture has a positive effect on the process due to the temperature glide and the associated higher condensation enthalpy, both effects on the *COP* are limited, because the mixture density varies monotonically and leads to lower working fluid mass flow rates with increasing isobutane mole fraction. The temperature glide reduces the heat-transfer

exergy destruction and therefore tends to increase the *COP*, but due to the low contribution of both heat exchangers to the total irreversibility of 21 – 25 %, this effect is limited and gets even smaller with higher temperature lifts. Compared to this, the compressor accounts for a high share of the total exergy destruction between 50 % and 66.67 %. It has a large influence on the process and especially the *COP*. The largest temperature glide is observed at an isobutane mole fraction of 0.527, but the highest *COP* is at 0.267. At this composition, the lowest specific compressor work is found, and it was shown that the higher compressor efficiencies are the reason for this. The efficiencies decrease with higher amounts of isobutane mainly through the reduction of the internal compressor efficiency that is caused by the decreasing volumetric efficiency and increasing pressure ratio of the compressor. Therefore, it can be concluded that the heat exchangers and with them the moderate temperature glide has a smaller influence than expected, while the change in working conditions lead to indirect effects, which influence the important compressor efficiency, leading to the found shift in the highest *COP* to a mole fraction of 0.267. From this it gets clear that using constant compressor efficiencies in cycle calculations for different fluid mixtures will not lead to reliable results. In this context, the often-neglected electro-mechanical efficiency-changes have to be characterized carefully. Finally, the advantage of zeotropic mixtures should gain in importance for mixtures with larger temperature glides used to heat secondary fluids with adapted temperature changes. This may be worth future investigations.

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