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Techno-economic optimization of high-temperature heat pumps using pure fluids and binary mixtures

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Abstract

Electrically driven high-temperature heat pumps (HTHPs) are becoming a promising and cost-effective technology to replace fossil-fuel driven boilers through residual heat recovery and revalorization. HTHPs are however often designed and optimized in terms of thermodynamic performance, neglecting financial aspects such as the levelized cost of heat (LCOH). In this study, the heat pump design and operating conditions are optimized by minimizing the LCOH. This is done for a wide set of working fluids and boundary conditions. Both subcritical, transcritical and supercritical cycles, as well as (zeotropic) binary mixtures, are considered. Depending on the boundary conditions, both pure fluids as well as (zeotropic) binary mixtures, mostly operating in the subcritical region, are financially attractive. The potential benefits of zeotropic mixtures are twofold: (1) more favorable operating conditions and (2) higher COPs. Transcritical cycles only showed to be attractive for large temperature glides at the heat sink side. The results also shows that the financial and thermodynamic optima differ in many cases. One reason for this is that working fluids with a high COP often induce high compressor inlet volume flow rates, resulting in high compressor costs.

Keywords: High-temperature heat pumps; binary mixtures; pure working fluids; techno-economic

1. Introduction

High-temperature heat pumps (HTHPs) are an emerging technology, allowing for efficient electrification in the industrial heating sector. It is expected that HTHPs will soon be able to supply process heat up to 200 °C [1]. By reaching supply temperatures of 200 °C heat pumps could deliver 37 % of the process heat demand in the European industry [2]. Consequently, there is an increasing amount of research on working fluids and cycle configurations for these HTHPs. This research mainly focusses on achieving a maximum COP and therefore minimal electricity use.

However, some working fluids with a high COP may require large compressors, or multiple compression stages, while configurations with a high COP may be more complex and therefore expensive. The discrepancy in thermodynamic and financial optima for some boundary conditions has been shown for organic Rankine cycles [3]. For HTHPs however, less research is performed on financially optimal heat pump cycles and working fluids. Moreover, if a financial analysis is performed it is typically done for just one application. In addition, the amount of working fluids screened and configurations considered is often not complete.

This research focusses on the selection of optimal working fluids for HTHPs, by optimizing and analyzing the levelized cost of heat (LCOH) for each working fluid. Both pure working fluids as well as binary (zeotropic) mixtures are considered as candidates. For this purpose, a financial framework is developed and applied to a large set of generic data, rather than to one, or a limited amount of, case studies(s).

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2. Methods

In this section, the financial framework is first explained. Afterwards, an overview of the refrigerant candidates is given. Subsequently, the large set of generic boundary conditions, to which the financial framework will be applied, is presented. Finally, the post-processing of the results is explained. In this procedure, working fluids may be eliminated because they violate technical constraints.

2.1. Financial framework

The financial framework is an extension of the thermodynamic simulation and optimization framework developed by Vieren et al. [4,5]. This framework allows for optimizing the COP for pure fluids and binary (zeotropic) mixtures, both in the subcritical, transcritical and supercritical regime. A single-stage heat pump cycle was chosen as reference cycle, with the option for an internal heat exchanger (IHX). Based on the obtained optimal, or sub-optimal working fluids, more advanced cycles can be modelled. The optimization framework maximizes the COP of the heat pump cycle by varying the superheat (ΔT_{sh}), subcooling (ΔT_{sc}), pressure during heat delivery (p_{high}) and pressure during heat extraction (p_{low}). For operation above the critical point, ΔT_{sh} and ΔT_{sc} are defined with respect to the critical point. For the binary mixtures, the molar fraction of the components is also optimized.

Because the LCOH is a function of the COP, the developed thermodynamic framework acts as a well-suited basis. Next to changing the objective function from COP to LCOH, the main adaptions to the existing model are:

- Removal of the constraints on the pinch point temperature difference (PPTD). From a thermodynamic point of view the COP would be maximal for a PPTD of 0 K. This would however require infinitely large heat exchangers. Therefore, a PPTD of 5 K in the heat exchangers was imposed in the thermodynamic model. In this financial analysis however, a low PPTD will be automatically penalized by a strong increase in heat exchanger costs, while the COP increases only marginally.
- Introduction of multiple compression stages. In the financial model, multiple compression stages will be considered if the compression ratio is high. This was not done in the thermodynamic model, because the use of multiple compression stages will not drastically influence the COP. For the financial model however the impact can be much higher. A maximum compression ratio per stage of 6 is selected.

2.1.1. Levelized cost of heat

The LCOH is the average net present cost of the heat production (€/kWh$_{th}$) over the lifetime of the heat generating system. The LCOH is calculated by use of Eq. 1.

$$LCOH = \frac{C_{CAPEX} + \sum_{t=1}^{n} \frac{C_{OPEX,t}}{(1+i)^t}}{\sum_{t=1}^{n} \frac{Q_t}{(1+i)^t}} \tag{1}$$

With C_{CAPEX} the capital expenditure (€), $C_{OPEX,t}$ the operational expenditure at year t (€/year), n the heat pump lifetime (year), i the interest rate (%) and Q_t the amount of heat produced at year t (kWh$_{th}$/year).

2.1.1.1. Capital expenditure

The capital investment cost of the heat pump (C_{CAPEX}) is determined according to the preliminary and study cost estimation method of Turton et al. [6], providing estimates in the accuracy range of -25 % to +40 %. In addition to the equipment purchase costs, the method also accounts direct and indirect project expenses, contingency and fees and auxiliary facilities.

First the purchasing cost of each component (C^0) was determined. An overview of each component cost function can be found in Table 1.

Table 1: Overview of the bare module cost (C^0) of each component.

Component	Cost equation	Variable	Reference
Plate heat exchanger	$C^0_{hex} = 0.88 \cdot (1600 + 210A^{0.95})$	A: Heat transfer surface (m²)	[7]
Reciprocating compressor	$C^0_{comp} = 19\,850 \cdot \left(\frac{\dot{v}_{comp,i}}{279.8}\right)^{0.73}$	$\dot{v}_{comp,i}$: Volume flow rate at the compressor inlet (m³/h)	[8]
Compressor drive	$C^0_{drive} = 10\,710 \cdot \left(\frac{\dot{W}_{drive}}{250\,000}\right)^{0.65}$	$\dot{W}_{drive}$: Power use of the electrical drive (W)	[8]
Expansion valve	$C^0_{valve} = 114.5 \cdot \dot{m}_{ref}$	$\dot{m}_{ref}$: Mass flow rate of the refrigerant (kg/s)	[9]

The heat exchanger cost is based on the heat transfer area, which is based on heat transfer coefficients (HTCs). These HTCs depend on the working fluid, Reynolds number and Prandtl number. Since a large set of pure working fluids and binary mixtures will be screened, it is not feasible to implement heat transfer correlations. Moreover, high uncertainties are expected for the binary mixtures. Therefore, fixed HTCs, depending on the phase of the working fluid or secondary medium, are chosen in this high-level analysis. An overview of the selected HTCs can be found in Table 2. The HTC for the liquid phase, two-phase and gas phase where determined based on extrapolation of overall HTCs reported in the VDI Heat Atlas [10]. For the supercritical phase the same HTC is chosen as for the liquid phase.

Table 2: Overview of the considered heat transfer coefficients for each phase.

Phase	Heat transfer coefficient α [W/(m²K)]
Liquid	2000
Two-phase	3000
Gas	100
Supercritical	2000

In order to account for inflation the cost functions reported in Table 1, which are derived in the past, are adjusted to the year 2021 by use of the chemical engineering plant cost index (CEPCI) [8]. The indexed purchased equipment cost is used to calculate the bare module cost (C_{BM}) of each component. This cost also accounts additional direct costs (e.g. labour) and indirect costs (e.g. engineering expenses) for each component. The bare module cost is found by multiplying the purchased equipment cost (C^0) with a bare module cost factor (F_{BM}):

$$C_{BM} = C^0 \cdot F_{BM} \tag{2}$$

An overview of the bare module cost factor of each component can be found in Table 3.

Table 3: Bare module factor (F_{BM}) for each component, according to Turton et al. [6].

Component	F_{BM}
Plate heat exchanger	1.16
Positive displacement compressor	2.4
Compressor drive	1.5
Expansion valve	2

The total module cost (C_{TM}), which equals the capital expenditure, is the summation of each bare module costs with an additional 15 % and 3 % added for contingency costs and fees respectively:

$$C_{TM} = 1.18 \cdot \sum_{i=1}^{n} C_{BM,i} = C_{CAPEX} \tag{3}$$

2.1.1.2. Operational expenditure

The yearly operational expenditure is determined by the total yearly electricity use and the yearly maintenance cost:

$$C_{OPEX} = c_{el} \cdot \left(\frac{\dot{Q}_{process}}{COP}\right) \cdot h_a + f_{maint} \cdot C_{CAPEX} \tag{4}$$

The total yearly electricity use is determined by the specific electricity costs c_{el} (€/kWh$_{el}$), the electricity use rate (kW$_{el}$) and the annual operation hours h_a (h). The electricity use rate is determined by dividing the heat demand rate of the industrial process ($\dot{Q}_{process}$) by the COP. The yearly maintenance cost is calculated as a fraction (f_{maint}) of the capital expenditure.

2.1.2. Financial boundary conditions

For the computation of the LCOH, several external parameters are required that depend, amongst others, on the type of industry and country where the HTHP is to be integrated. In this work financial boundary conditions are chosen that represent a typical energy-intensive industry in Belgium, as shown in Table 4.

Table 4: Overview of the considered financial boundary conditions.

Parameter	Value	Reference
Heat pump lifetime (n)	15 year	[8,11,12]
Interest rate (i)	5 %	-
Maintenance cost fraction (f_{maint})	0.06	[12]
Annual operating hours (h_a)	7000 h	[12,13]
Specific electricity cost (c_{el})	0.0806 €/kWh$_{el}$	[14]

For the specific electricity cost, the bi-annual electricity costs reported by Eurostat for Belgium between 2016-2020 [14] is averaged. This was done for the prices reported in the yearly electricity consumption range of 500 MWh$_e$ to 2000 MWh$_e$. According to Eurostat, most of the EU non-household consumers fall in this use range.

2.2. Refrigerant selection

Regarding the pure working fluids, a selection is made based on the REFPROP10.0 database [15]. The following selection criteria are applied:

- Ozone depletion potential (ODP) of approximately zero.
- Global warming potential (GWP) below 150.
- National Fire Protection Association (NFPA) 704 instability grade of 0.
- Thermally stable up to 200 °C or higher.

Based on the selection of the pure working fluids a pool of binary mixtures is made. From this pool, mixtures where both components have a critical temperature below 160 °C are eliminated, because the goal is to study these mixtures in the subcritical region. All these working fluids are examined for the configuration with and without IHX.

2.3. Operational boundary conditions

First the financial model is applied to two boundary conditions reported in earlier work of Vieren et al. [4], where the COP was optimized by this simulation framework. The temperature levels of the two selected boundary conditions can be found in Table 5.

Table 5: Temperature data of the two selected case studies.

Case study (source-sink)	Heat source inlet temperature	Heat source outlet temperature	Heat sink inlet temperature	Heat sink outlet temperature
Sensible-sensible	120 °C	100 °C	160 °C	180 °C
Latent-sensible	100 °C	100 °C	120 °C	180 °C

After these cases are discussed, an estimate of the financial performance for the selected refrigerants is formulated for a wide range of generic boundary conditions. The generic data is classified in four groups depending on the nature of the heat source or sink. An overview of the classifications, and the amount of datapoints (i.e. boundary conditions) selected, can be found in Table 6.

Table 6: Overview of the four classifications depending on the nature of the heat source or sink.

Heat source	Heat sink	Datapoints
Latent	Latent	4
Latent	Sensible	12
Sensible	Latent	12
Sensible	Sensible	36

Each datapoint has a heat sink outlet temperature between 160-200 °C, whereas the heat source inlet temperature varies between 80-120 °C. Because the degrees of freedom increase when the secondary stream is of sensible nature (addition of a temperature glide next to the absolute temperature level), more datapoints are selected in these scenarios. However, less datapoints are selected compared to the COP optimization [4] due to the increased complexity and therefore computational power.

Important to note is that whilst the COP computation of the developed framework is independent of the capacity of the heat pump system, the LCOH is not because non-linear cost functions are used. In this work a heat pump with a heating capacity of 500 kW_{th} is considered.

2.4. Post-processing

After the pool of refrigerants is simulated, the results are post-processed. During post-processing working fluids which require a compressor discharge pressure above 60 bar are discarded. The reason is that few compressors exist for pressures above 60 bar, except for CO2. Moreover, for the binary mixtures a minimum deviation in molar fraction and LCOH from the respective pure fluids is imposed. A minimum deviation of respectively 2 mol % and 2 % is selected so that there is a clear distinction between pure working fluid and binary mixture.

3. Results

3.1. Sensible-sensible boundary condition

An overview of the financially best performing working fluids for the 'sensible-sensible boundary condition' can be found in Table 7. This table reports the working fluid, molar fraction of the first component, number of stages, use of an IHX, COP, LCOH and the specific investment cost (c_{inv}) of the 5 best performing fluids. The specific investment cost is obtained by dividing the capital expenditure (Eq. 3) by the heating capacity (500 kW_{th}).

Table 7: Overview of the financially best performing refrigerants for the 'sensible-sensible boundary condition'.

Working fluid	Molar fraction first component	Stages	IHX	COP	LCOH [€/kWh_{th}]	$c_{,inv}$ [€/kW_{th}]
Methanol/ammonia	0.685	1	No	3.84	0.0290	372
Cis-2-Butene/methanol	0.585	1	Yes	3.56	0.0305	363
Benzene/methanol	0.648	1	Yes	4.10	0.0307	512
Cyclobutene/toluene	0.955	1	Yes	3.45	0.0309	351
Cyclobutene/heptane	0.963	1	Yes	3.46	0.0310	357

Based on the reported results it can be observed that the financially most attractive refrigerants are (zeotropic) binary mixtures. These binary refrigerants are made up entirely of natural refrigerants, or more specifically, of hydrocarbons and ammonia. To reveal the potential of these mixtures, the results of the respective pure working fluids with the largest molar fraction are reported in Table 8.

Table 8: Overview of the financially best performing pure refrigerants for the ‘sensible-sensible boundary condition’.

Working fluid	Stages	IHX	COP	LCOH [€/kWh$_{th}$]	c_{inv} [€/kW$_{th}$]
Cyclobutene	1	Yes	3.37	0.0317	357
Methanol	2	No	3.71	0.0331	528
Cis-2-Butene	1	Yes	3.18	0.0339	396
Benzene	2	Yes	3.82	0.0400	871

Comparing these tables shows that mixtures are able to increase the COP and decrease the specific investment costs compared to the pure fluids. One of the reasons for the increase in COP can be explained by the non-isothermal phase change of these mixtures. This may result in a better temperature match between refrigerant and secondary medium, decreasing the exergy destruction. As an example, the T,Q-diagram of both methanol/ammonia and pure methanol is given in Figure 1, where it can be observed that methanol/ammonia results in a better temperature match. Moreover, the pressure levels shown in the figure indicate that the addition of ammonia to methanol increases the pressure levels. As the increase in evaporator pressure is relatively more outspoken compared to the condenser pressure, the compression ratio decreases from about 8 to 5.7, resulting in the possibility of using one compression stage. Moreover, mixing the pure fluids may result in a lower volume flow rate at the compressor inlet compared to one of the pure constituents and therefore a lower compressor cost. For the methanol/ammonia mixture for example the volume flow rate at the compressor inlet is 0.083 m³/s whereas for pure methanol a flow rate of 0.130 m³/s at the inlet of the compressor is needed.

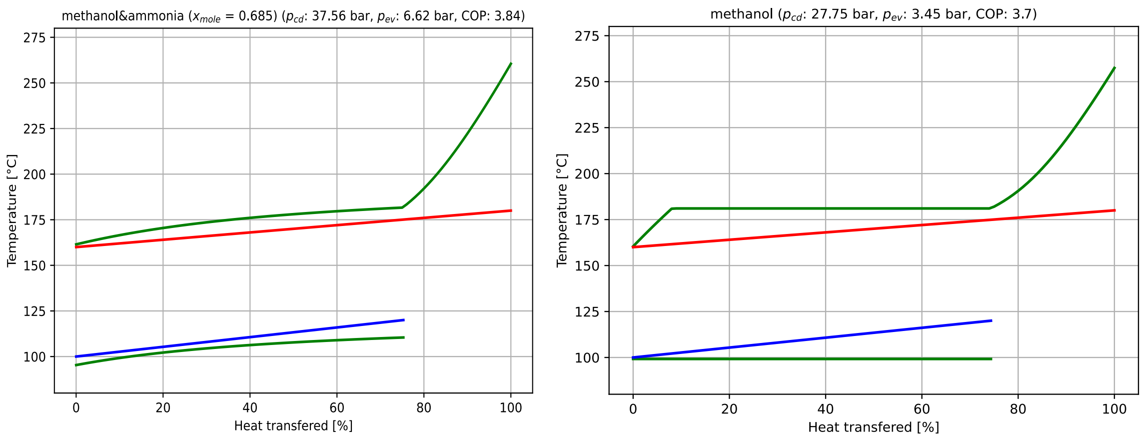

Figure 1: T,Q-diagram of methanol/ammonia and methanol for the ‘sensible-sensible boundary condition’.

Table 7 and Table 8 also demonstrates that the financially most attractive heat pump does not necessarily have the highest COP. Benzene for example has a COP of 3.82 which is about 13 % higher than for cyclobutene (3.37). However, the LCOH of a heat pump with benzene is 26 % higher compared to a heat pump with cyclobutene. This is because a heat pump with benzene would have a specific investment cost of 871 €/kW$_{th}$, compared to 357 €/kW$_{th}$ for cyclobutene. The investment cost of the benzene heat pump is high because of the high pressure ratio resulting in the need for two compression stages, and the high volume flow rate resulting in large compressors. Both the high-pressure ratio and high volume flow rate are caused by the low evaporation pressure, associated to the high normal boiling point (NBP) of benzene (80.1 °C).

3.2. Latent-sensible boundary condition

An overview of the financially best performing working fluids for the ‘latent-sensible boundary condition’ can be found in Table 9, which has the same structure as Table 7.

Table 9: Overview of the financially best performing refrigerants for the 'latent-sensible boundary condition'.

Working fluid	Stages	IHX	COP	LCOH [€/kWh$_{th}$]	c_{inv} [€/kW$_{th}$]
Cyclobutene	1	No	4.16	0.0249	278
Cis-2-Butene	1	No	4.27	0.0255	306
R1233zd(E)	1	No	4.33	0.0258	332
R1234ze(Z)	1	No	4.27	0.0259	325
R1224yd(Z)	1	No	4.24	0.0265	345

Table 9 shows that all best performing working fluids are pure fluids. These fluids operate as transcritical cycles. For applications with a large temperature glide at the heat sink side and a small or zero temperature glide at the heat source side, these cycles are able to provide a good temperature match. In fact binary mixtures were able to increase the COP and LCOH, but only in such a minor degree that they were eliminated by the post-processing. Both natural refrigerants (i.e. hydrocarbons) and synthetic refrigerants hydrofuoloro-olefins (HFOs) and hydrochlorofluro-olefins (HCFOs) are found to be well performing. Again, the working fluid with the highest COP is not necessarily the working fluid showing the best financial aspects. This is shown in Figure 2, where the LCOH of the 100 best performing refrigerants is plotted as a function of the COP, showing no correlation between the two parameters. This is an important result: even though a higher COP inherently lowers the LCOH by reducing electricity consumption, other factors determine the financial optimum. The figure also shows that for the best performing fluids, the optimized LCOH does not show large variations. This is partly due to the large number of working fluids simulated. It should also be noted that due to the uncertainty in LOCH, the working fluid with the lowest simulated LCOH may not have the lowest LCOH in practice. Therefore, the generalized selection matrix will show the best performing refrigerant types (e.g. hydrocarbons or mixtures of HFOs) rather than a single working fluid.

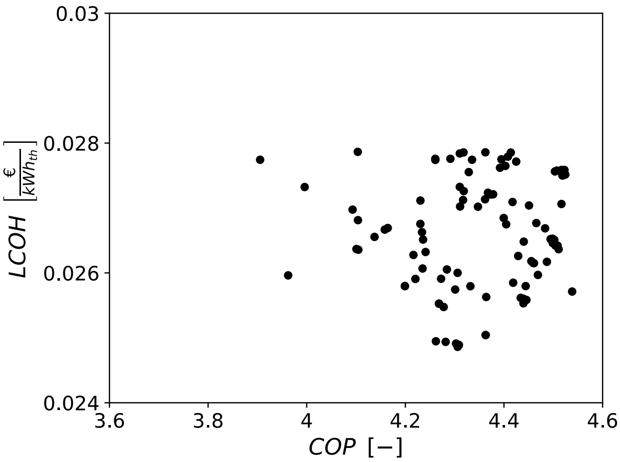

Figure 2: LCOH as a function of the COP for the 100 best performing working fluids of the 'latent-sensible boundary condition'.

3.3. Selection matrix

Based on a large amount of simulated boundary conditions, explained in Table 6, the results are generalized in the form of a 'selection matrix', as shown in Table 10. This selection matrix reports the best performing working fluid(s) for each type of heat source and sink. Since flammability concerns may prevent the installation of the heat pump, and the cost of ATEX related regulations is not considered, a distinction is made between flammable refrigerants and non/mildly-flammable refrigerants. As the feasibility also depends on the absolute temperature levels, it is also indicated for which temperature level (low, medium and high, within the studied temperature ranges) of heat source and/or heat sink the working fluid is recommended. Water for example is only recommended for high source temperatures, because for low source temperatures the evaporation pressure is low, resulting in high suction volume flow rates. Cyclobutene, cis-2-butene or HFOs and HCFOs on the other hand are only recommended for lower heat sink temperatures, as for high heat sink temperatures the compressor discharge pressure becomes too high (> 60 bar), resulting in elimination by the post-processing.

Table 10: Generalization of the financially best performing refrigerant for the different classifications of heat sources and heat sinks.

		Heat source	
		Latent	*Sensible*
Heat sink	*Latent*	**Near-azeotropic mixtures** **Flammable:** ➢ Mixtures of hydrocarbons (always) ➢ Mixtures of water and hydrocarbons (medium T_{source}) **Non/mildly flammable:** ➢ None **Pure fluids** **Flammable:** ➢ Acetone, methanol, ethanol (always) ➢ Cyclobutene (low T_{source} and T_{sink}) **Non-flammable:** ➢ Water (high T_{source}) ➢ HFOs and HCFOs (low T_{source} and T_{sink})	**Zeotropic mixtures** **Flammable**: ➢ Mixtures of hydrocarbons and mixtures of hydrocarbons and ammonia (always) ➢ Mixtures of water and hydrocarbons (medium T_{source}) **Non/mildly-flammable**: ➢ Water/ammonia (high T_{source}) **Pure fluids** **Flammable**: ➢ Cyclobutene, Cyclopentane, Cis-2-Butene (low T_{sink}) ➢ Acetone, Methanol, Ethanol (high T_{sink}) **Non/mildly-flammable**: ➢ Water (high T_{sink} and T_{source}) ➢ HFOs and HCFOs (low T_{sink} and T_{source})
	Sensible	**Zeotropic mixtures** **Flammable:** ➢ Mixtures of hydrocarbons (high T_{sink}) ➢ Mixtures of hydrocarbons and water or ammonia (high T_{source} and high T_{sink}) **Non/mildly-flammable:** ➢ None **Pure fluids** **Flammable:** ➢ Cyclobutene and Cis-2-Butene (low T_{sink}) **Non/mildly-flammable**: ➢ HFOs and HCFOs (low T_{sink}) ➢ Water (high T_{source} and T_{sink})	**Zeotropic mixtures** **Flammable:** ➢ Mixtures of hydrocarbons and mixtures of hydrocarbons and ammonia (always) ➢ Mixtures of water and hydrocarbons (medium T_{source}) **Non/mildly-flammable:** ➢ Water/ammonia (medium T_{source})

Interestingly, binary mixtures almost always show to be (near-) optimal, also for boundary conditions where the temperature glide of the heat source and sink differ, or there are no temperature glides at all. As an example, the T,Q-diagram of acetone/water is shown for a sensible (120-90 °C) latent (160 °C) boundary condition (Figure 3.a) and a latent (120 °C) latent (200 °C) boundary condition (Figure 3.b). From Figure 3.a it can be observed that for the optimized pressures and molar fraction the temperature glide of the acetone/water mixture during condensation is rather small (~10 °C) compared to the temperature glide during vaporization (~20 °C), resulting in a decent temperature match. For other molar fractions and pressures, the temperature glide of the mixture during evaporation and condensation may approach zero (i.e. near-azeotropic mixture) as shown in Figure 3.b. In these scenarios binary mixtures do not necessarily increase the COP (although in this case they did), but they may result in better operational parameters and therefore financial aspects. The only scenario where the potential of zeotropic mixtures is limited, is for boundary conditions with large temperature glides as the heat sink ($\geq$ 60 °C) and small to zero temperature glide at the heat source, as has been shown in section 3.2.

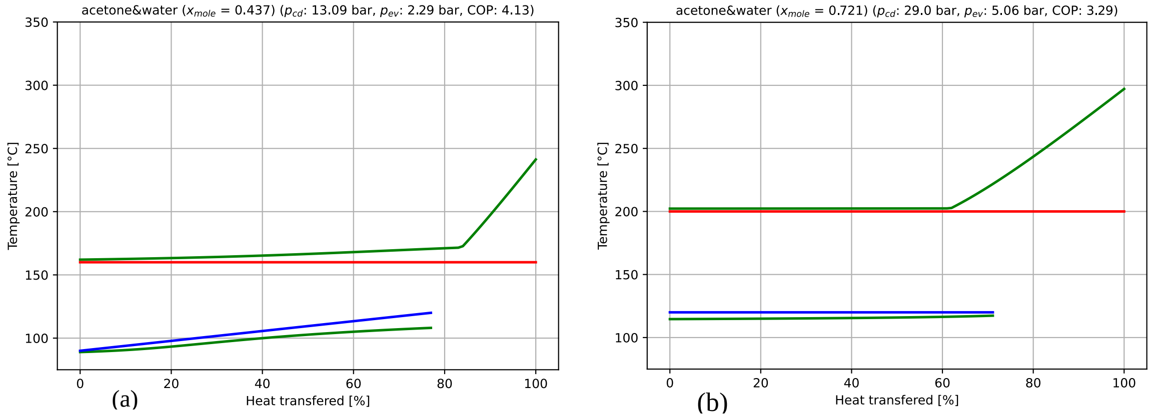

Figure 3: Optimized T,Q-diagram for acetone/water for a sensible (120-90 °C) latent (160 °C) boundary condition and latent (120 °C) latent (200 °C) boundary condition.

The reported (near-) optimal working fluids are, or consist of at least one, highly flammable hydrocarbon. If these highly flammable working fluids are not taken into consideration the options are limited. Generally, HFOs and HCFOs show the best feasibility if the source and sink temperature are low. For higher temperatures (where the pressure of the HFOs and HCFOs becomes too high) water is recommended. In some scenarios, addition of ammonia to the water can have beneficial effects in financial performance.

4. Discussion

A framework is developed that is capable of simulating single- and double-stage heat pump cycles, with and without internal heat exchanger. It is also able to simulate all the refrigerants in REFPROP 10.0 and the binary mixtures of these refrigerants. By assigning costs to the components of the heat pump, the financial performance over the lifetime of each heat pump cycle was estimated and ranked.

A preliminary financial screening is carried out for a wide range of generalized boundary conditions, rather than for a limited number of specific case studies. Generally, there is a common misconception in the literature that the payback period is used instead of LCOH. In such cases, the configurations with the optimum payback tend to be those with the lower investment costs, while they may not have the lowest LCOH, as has been shown in the work of Zühlsdorf et al. [19]. The LCOH is used in this work because it takes into account the period after the investment has been paid back. Moreover, the LCOH is independent of external boundary conditions such as gas prices. It is expected in this work that the calculated LCOH provides a good first estimate of the financial appraisal. The results showed that binary mixtures often have beneficial effects compared to their pure components, either by increasing the COP through improved temperature matching in the heat exchangers, or by improving the operating conditions due to the flexibility in thermophysical properties. Moreover, due to the presence of azeotropic behavior in the vapor-liquid equilibrium, these binary mixtures are also interesting for applications with no temperature glides. For applications where the temperature glides of the binary mixture cannot be matched with the secondary fluids, some authors even propose heat pump cycles with a variable mixture composition regulation, so that a satisfactory temperature match can be achieved in both condenser as evaporator [16], [17]. Nevertheless, the increase in COP for such cycles may not outweigh the additional cost. The only region where binary mixtures operating in the subcritical region are less interesting, is for applications with large temperature glides at the heat sink side. In such scenarios, pure fluids operating in the transcritical regime are the most favorable. In addition, in event of large temperature glides, zeotropic mixtures may experience fractionation and composition shift [18]. Furthermore, the results shows that there is a mismatch between thermodynamic and financial optima. The financially optimal working fluids do not have the highest COP. Furthermore, the best performing working fluid does also not have the lowest investment cost.

For the best performing working fluids reported in this work, the financial performance could be analyzed in more depth by (re)considering the following aspects:

1. The assumption of a fixed heat transfer coefficient. This assumption is particularly favorable for zeotropic mixtures, as these may experience a degradation of heat transfer [18]. Nevertheless, the breakdown of the LCOH showed that the contribution of the heat exchangers with respect to the total LCOH is often small.
2. The cost of the refrigerant, especially synthetic refrigerants shows to be more expensive [20].
3. The influence of material compatibility or pressure on the equipment costs.

4. The off-design behaviour.
5. An isentropic compression efficiency, which depends on the properties of the working fluid [21].
6. Influence of costs related to ATEX compliance.

In addition, there is a clear dependency of the results towards the considered financial boundary conditions reported in Table 4. Arpagaus et al. [22] showed that the electricity costs and operating hours in particular have a large impact on the LCOH, and thus could influence the most optimal heat pump cycle from a financial point of view. A sensitivity of the selection matrix towards these parameters could be included in future work.

5. Conclusion

A financial framework, able to optimize the LCOH of a heat pump is developed. This framework is used to give a preliminary indication of the financial appraisal for a broad range of pure fluids and binary mixtures. The model is applied to a large set of generic data.

The results show that there is a discrepancy between optimum COP and optimum LCOH. Consequently, selection of a refrigerant just based on maximal COP, may lead to a sub-optimal financial solution. Moreover, the selection matrix shows the optimal working fluid strongly depends on the boundary conditions. However, binary mixtures of natural refrigerants (hydrocarbons, ammonia and water) showed to be (near) optimal for a large range of boundary conditions. The potential of these mixtures is twofold: the COP can be improved by temperature matching in event of zeotropic mixtures and mixing working fluids allows for more advantageous operating conditions (e.g., lower compression ratio or lower volume flow rate).

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