Optimal temperature matching in high-temperature heat pumps

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Extended Abstract

1. Introduction

Heat transfer within heat exchangers is the main source of exergy destruction in high-temperature heat pumps [Hu et al., 2017]. Matching the temperature profile of refrigerant and secondary medium is an effective approach to reduce exergy destruction. One way to achieve temperature matching in the heat exchangers is selecting refrigerants with an appropriate critical temperature. Depending on the refrigerant's critical temperature and the boundary conditions applied, three operational modes exist, namely: subcritical, transcritical and supercritical. Above the critical pressure, the refrigerant transfers heat associated to a temperature change. Whereas below the critical pressure, the temperature is constant during condensation or evaporation. A second approach is to make use of zeotropic mixtures that achieve non-isothermal phase change. In this paper, both transcritical and supercritical operation as zeotropic mixtures will be studied to achieve optimal temperature matching for heat sink outlet temperatures in the range of 160-200°C.

2. Methodology

In this work a selection of pure fluids and binary mixtures are simulated for a large set of boundary conditions by use of a thermodynamic framework. The thermodynamic framework, refrigerant selection and boundary conditions are briefly described in the upcoming sections.

2.1. Simulation framework.

The thermodynamic model allows for simulation of heat pump cycles, using pure refrigerants and binary mixtures, based on defined pressure levels, amount of superheat and subcooling[1] and a molar fraction for the mixtures. A single-stage heat pump cycle, optionally with the use of an internal heat exchanger (IHX), is used as reference cycle. More complex cycles (e.g. cycle with two compression stages and intercooling) can be derived based on the operating conditions of the single-stage heat pump cycle. The single-stage heat pump cycle is modelled by assuming compression with a fixed isentropic efficiency (75%) and isenthalpic expansion. No pressure drops and heat losses were considered in the heat exchangers and piping. Furthermore, an effectivity of 0.75 was used for the IHX.

A optimizer on top of the thermodynamic model allows for maximizing the COP by varying the pressure levels, superheat and subcooling and molar fractions for mixtures. A state-of-the-art global optimizer within SciPy was selected. The optimization algorithm includes several techniques to reduce the simulation time, such as multiprocessing or a design space dependent

[1] For operation above the critical point the superheat and subcooling are defined with respect to the critical point.

on the refrigerant. In addition, soft constraints are applied as such the pinch point temperature difference is kept at 5K and wet compression is avoided.

2.2. Refrigerant selection

All pure refrigerants within REFPROP10.0 with favorable environmental properties (ODP ≈ 0, GWP<150) are simulated. For zeotropic mixtures, all possible binary mixtures from the selected pool of pure refrigerants are considered. However, as the focus is on zeotropic mixtures operating in the subcritical region, mixtures where both components have a critical temperature below 160°C are not considered.

After simulation of the selected refrigerants, several technical constraints (see Table 1) are applied.

Table 1: Considered technical constraints in the post-processing of the fluid selection.

Parameter	Constraint
Pressure ratio (PR)	PR < 20
Evaporator[2] pressure (p_{ev})	p_{ev} > 0.5 bar
Condenser pressure (p_{cd})	p_{cd} < 45 bar

Furthermore, in case of mixtures, the miscibility is assessed in the postprocessing. No constraint is applied on the compressor outlet temperature since multiple techniques exists to reduce it, such as: intercooling, vapor- or liquid-injection, etc [Redón et al., 2014 and Shen et al., 2014]. With an analogous reasoning [Harby, 2017], no constraint is applied on the refrigerant flammability. However, scenarios where flammable fluids are not allowed will be considered.

2.3. Boundary conditions

Several relevant case studies and a set of 140 generic boundary conditions, covering a large range of heat sink and source temperature glides, are studied. For both, the heat sink outlet temperatures varies between 160-200°C. Two boundary conditions are further discussed in this study, namely a case with sensible heat source and sink and a case with latent heat source and sensible heat sink. The selected temperature levels of these generic boundary conditions can be found in Table 2.

Table 2: Temperature levels of the selected boundary conditions.

	Sensible-Sensible	Latent-Sensible
T_{source} (°C)	100 - 120	100
T_{sink} (°C)	160 - 180	120 - 180

3. Results and discussion

3.1. Sensible-Sensible boundary condition

The acquired results for the selected sensible-sensible boundary condition are given in Table 3. In this table, the five best performing fluids are shown. For these refrigerants the COP, p_{ev}, p_{cd}, PR, volumetric heating capacity (VHC) and Lorentz efficiency (η_{lor}) are given. Moreover, it is indicated whether or not the most optimal cycle makes use of IHX. For mixtures, the molar fraction of the first constituent is given within brackets.

Table 3: Properties of the five best performing fluids for the sensible-sensible boundary condition.

Refrigerant	COP [-]	p_{ev} [bar]	p_{cd} [bar]	PR [-]	VHC [kJ/m³]	η_{lor} (%)	IHX
acetone/toluene (0.48)	4.30	1.83	9.50	5.2	1754	58.2	✓

[2] For operation above the critical point the term evaporator/condenser are in fact not correct. Instead, one should use gas heater or cooler, but for the sake of simplicity evaporator and condenser will be used.

acetone/water (0.43)	4.22	2.69	16.19	6.0	3023	57.2	X
benzene/methanol (0.75)	4.16	2.97	15.24	5.1	2764	56.3	✓
ethanol/toluene (0.37)	4.15	1.65	10.74	6.5	1756	56.2	✓
ethanol/water (0.21)	4.10	1.50	12.81	8.5	2141	55.5	X

From Table 3 it can be concluded that the five best performing refrigerants are zeotropic mixtures. Acetone/Toluene has, with a COP of 4.30 (η_{lor}= 58.2%), the best performance. The other mixtures have similar performances. However, all five mixtures consists of at least one highly flammable fluid. When non-flammable or mildly flammable refrigerants would be targeted, water-ammonia allows for the best performance (COP = 3.87). The best performing pure fluid is toluene (COP = 3.85), whereas the best performing non-flammable or mildly flammable pure fluid is water (COP = 3.61).

Use of zeotropic mixtures allows for a COP increase of 12% compared to pure fluids when flammability is not an issue, and 7% when flammability is an issue. In addition, more advantageous operating conditions can be achieved by mixing working fluids. In Table 4, a comparison between water/ammonia and water is made. Next to the increase in COP (+7%), the evaporator pressure becomes above atmospheric level (+32%), pressure ratio decreases (-24%), the VHC increases (+25%) and the compressor outlet temperature ($T_{comp,out}$) decreases (-34.4°C). A minor disadvantage is a small increase in pressure level at the condenser (+7.6%).

Table 4: Technical comparison of water/ammonia mixture with pure water.

Refrigerant	COP [-]	p_{ev} [bar]	p_{cd} [bar]	RR [-]	VHC [kJ/m^3]	$T_{comp,out}$ [°C]
water/ammonia (0.94)	3.87	1.12	10.77	9.6	1725	438.9
water	3.61	0.85	10.01	11.9	1375	473.3

Pure working fluids operating in the transcritical or supercritical region all had lower COPs.

3.2. Latent-Sensible boundary condition

The acquired results for the selected latent-sensible boundary condition are given in Table 5. The table has the same layout as Table 3, used for the sensible-sensible boundary condition.

Table 5: Properties of the five best performing fluids for the latent-sensible boundary condition.

Refrigerant	COP [-]	p_{ev} [bar]	p_{cd} [bar]	PR [-]	VHC [kJ/m^3]	η_{lor} [%]	Mode	IHX
R1234ze(Z)	4.64	12.1	44.6	4.68	8882	54.1	Transcritical	✓
R1233zd(E)	4.60	9.3	37.6	4.03	7295	53.7	Transcritical	✓
R1336Mzz(Z)	4.58	6.3	31.3	5.00	5322	53.4	Transcritical	✓
Acetone	4.50	3.27	18.35	5.62	3444	52.5	Subcritical	✓
Isopentane (R601a)	4.45	6.45	30.67	4.75	5218	51.9	Transcritical	✓

From Table 5 it can be observed that four out of the five best performing fluids are pure fluids operating in the transcritical region. With the top three being HFOs/HCFOs. R1234ze(Z) has, with a COP of 4.64 (η_{lor} =54.1%), the highest performance. The non-transcritical refrigerant acetone is highly flammable. When flammable fluids are not considered, water is, with a COP of 4.13, the best performing subcritical fluid. In this scenario, transcritical operation would allow for a COP increase of about 12%. Moreover, the HFOs/HCFOs and R601a have high VHCs, but they inherently induce high pressures. Because of the constant temperature at the heat source side, and strong temperature glide at the heat sink side, zeotropic mixtures are less interesting for optimal temperature matching in this scenario.

3.3 Generalization

Based on the large dataset, the results are generalized. The best performing operational modes and corresponding fluids for each scenario can be found in Table 6. When the best performing fluid is non-flammable or mildly flammable, no flammable fluids are reported. If the best performing fluid is flammable the most optimal non-flammable fluid is reported as well.

Table 6: Generalization of the best performing fluids and operational modes for each type of boundary condition.

<table>
<tr><td colspan="2" rowspan="2"></td><td colspan="2">Heat Source</td></tr>
<tr><td>Latent</td><td>Sensible</td></tr>
<tr><td rowspan="4">Heat Sink</td><td rowspan="2">Latent</td><td>Subcritical pure fluid
• Flammable: hydrocarbons
• Non-flammable: water</td><td rowspan="2">Zeotropic mixtures and pure fluid
• Flammable: water/acetone
• Non-flammable: pure water</td></tr>
<tr><td>(near-) azeotropic mixtures
• Flammable: water/acetone (azeotrope)
• Non-flammable: x</td></tr>
<tr><td rowspan="2">Sensible</td><td>Zeotropic mixtures and pure fluid (Medium ΔT_{sink})
• Flammable: mixtures of HCs
• Non-flammable: pure water</td><td rowspan="2">Zeotropic mixtures
• Flammable: acetone/toluene and acetone/water
• Non-flammable: water/ammonia</td></tr>
<tr><td>Transcritical cycles (Large ΔT_{sink})
• R1336Mzz(Z) or R1234ze(Z)</td></tr>
</table>

In event of a latent heat source and latent heat sink, pure working fluids with high critical temperatures (e.g. hydrocarbons or water) shows the best performance. Moreover, some binary mixtures with azeotropic points (e.g. water/acetone) shows good performance and operating conditions. In case of a sensible heat source and latent heat sink, the zeotropic mixture water/acetone shows the best performance, and pure water when flammable fluids are not allowed. For a latent heat source and a sensible heat sink, zeotropic mixtures of hydrocarbons, or pure water when flammable fluids are not allowed, shows the best performance in event of small glides at the heat sink. For large temperature glides, transcritical cycles of HFOs/HCFOs shows the best performance, with large VHCs. When both heat source and heat sink are of sensible nature zeotropic mixtures clearly shows the best performance and favorable operating conditions.

Overall, it is expected that zeotropic mixtures could show even better performance by introducing a mixture composition regulation technique between evaporator and condenser. In this way, the Lorentz cycle can be better approached [Xu et al., 2018]. Especially for scenarios where there is a great difference in temperature glide between heat sink and source, regulation of the composition can have a great influence.

4. Conclusion

The results show that matching temperature profiles is an effective approach for increasing the COP. Both subcritical and transcritical operation as zeotropic mixtures are suitable to achieve this temperature matching, depending nature of the boundary conditions. However, zeotropic mixtures and transcritical operation are currently not widely employed, with the exception of the transcritical CO_2 cycle at lower temperatures, while there is a clear potential for them. Furthermore, next to the increase in performance, mixing pure fluids allows for more feasible operating conditions. Therefore azeotropic mixtures could be advantageous for applications with no temperature glides. In addition, a mixture composition technique could be applied for zeotropic mixtures as such they could better approach the Lorentz cycle for a wide variety of boundary conditions. No fluids operating in the supercritical region are observed to perform well for the considered boundary conditions. Moreover, they would require high pressures.

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