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Improving the performance of booster heat pumps using zeotropic mixtures

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Abstract

This study demonstrated an increase in the thermodynamic performance of a booster heat pump, which was achieved by choosing the working fluid among pure and mixed fluids. The booster heat pump was integrated in an ultra-low-temperature district heating network with a forward temperature of 40 °C to produce domestic hot water, by heating part of the forward stream to 60 °C, while cooling the remaining part to the return temperature of 25 °C. The screening of working fluids considered 18 pure working fluids and all possible binary mixtures of these fluids. The most promising solutions were analysed with respect to their performance under off-design conditions and their economic potential. The best-performing mixture showed a coefficient of performance (COP) of 9.0 and thereby outperformed R134a by 47 %. Although the mixed working fluids resulted in higher investment cost, the economic performance was comparable to the pure fluids. The mixtures showed similar performance as the pure fluids at off-design conditions. It was concluded that the mixtures 50 % Propylene / 50 % Butane and 50 % R1234yf / 50 % R1233zd(E) could considerably improve the thermodynamic performance of the overall heat supply system while being economically competitive to pure fluids.

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1 Introduction

District heating is expected to play a major role in sustainable energy systems of the future. Conventional district heating systems (DH) supply both space heating (SH) and domestic hot water (DHW) to the customer. The supply temperature of conventional district heating systems is constrained to exceed 60 °C by the minimum DHW temperature, while the heat required for floor heating could be supplied at lower temperatures. In order to be able to integrate renewable heat sources efficiently and minimize heat losses from the grid, a reduction of district heating temperatures has been proposed, e.g. [1]. It is proposed that district heating supply temperatures can be decreased to supply only the space heating requirements of the building directly from the grid, while the DHW is supplied by boosting the temperature of the district heating supply line with a booster heat pump.

The so-called ultra-low-temperature district heating (ULTDH) and the corresponding booster heat pumps have recently been the focus of many researchers. Ommen et al. [2] define a DH network as ULTDH when the supply temperature is below the temperature required to directly supply DHW (35 °C to 50 °C).

Different studies focused on the optimization of existing district heating grids by reducing the temperature levels and considering the possibility of booster heat pumps [2–4]. Studies have shown that the optimal supply and return temperatures of the grid and the economic feasibility of the integration of booster heat pumps are strongly dependent on the boundary conditions assumed. While the integration of booster heat pumps seems not economically viable for district heating systems with a high share of combined heat and power [3], it becomes more interesting with an increasing share of low temperature heat sources in the district heating network, such as industrial waste heat or centralised heat pumps [4]. Further issues when reducing temperatures in existing district heating networks can result from shifted requirements for heat exchangers and higher mass flow rates [3].

Several studies have conducted similar analyses that neglected the constraints imposed by existing networks and assumed the expected future composition of heat sources [2,3,5], factoring in the trend for an increasing share of renewables, and thus decreasing the share of combined heat and power in electricity production.

These studies show that the use of booster heat pumps allows significantly lower operation temperatures in the network and thereby provide a decrease in transmission losses and a more efficient use of heat sources, such as waste heat with and without using centralised heat pumps. Assuming the supply to originate from centralised heat pumps, the use of booster heat pumps results in an increase of 12 % in the overall performance compared to direct supply at above 60 °C [2]. This scenario becomes especially interesting for

1 newly constructed districts, where temperature requirements of existing district heating networks do not
2 constrain operation.

3 The overall performance and the economic feasibility from the consumer's perspective strongly depend on the
4 performance of the booster heat pump. Østergaard and Andersen [5] assumed a fixed Lorenz efficiency for the
5 heat pumps and reported a result which outperforms individual heat pump or boiler solutions. Zvingilaite et al.
6 [6] analysed different opportunities for integrating booster heat pumps with different working fluids in
7 different arrangements and compared it to conventional heat supply systems. They found the set-up in which
8 the booster heat pump uses the supply stream as sink and source to be economically and thermodynamically
9 superior to the ULTDH alternatives they investigated. Braber et al. [7] and Kleefkens et al. [8] analysed different
10 booster heat pump system configurations with respect to thermodynamic and economic performance, defined
11 recommendations for design and operation and highlighted the requirement for standardized testing
12 procedures. Elmegaard et al. [9] evaluated different booster heat pump substations according to their
13 exergetic and economic performance, based on consumer costs for heat supply. They reported that the
14 exergetic efficiency of the system using a booster heat pump with R134a and conservative assumptions is close
15 to the system performance of conventional district heating system at the lowest possible temperatures. The
16 results indicated that a moderate performance increase of the booster heat pump could improve the ultra-low-
17 temperature system to become competitive with conventional low temperature district heating systems.
18 The screening of state of the art technologies for the booster heat pump included simple heat pump cycles for
19 the refrigerants R134a, R600a (iso-butane), R290 (propane) and R744 (CO₂). Dependent on the boundary
20 conditions, a large share of the irreversibilities can result from heat transfer, since the sink and source are
21 typically single-phase fluids with a linear temperature profile during heat transfer, which does not match the
22 constant temperature of the working fluid during phase change well and thus, inevitably results in exergy
23 destruction.

24 Radermacher and Hwang [10] noted that zeotropic mixtures show a temperature glide during phase change,
25 which can potentially be matched with the temperature glide of sink and source and thus can contribute to
26 improved performance. Mohanraj et al. [11] conducted a comprehensive review of the different studies carried
27 out in this field. They concluded that the use of mixtures does not only result in an improved performance, but
28 also enlarges the range of a given set of fluids. This becomes especially interesting as established refrigerants
29 are phased out due to legislation by the Montreal protocol [12], the Kyoto protocol [13] and especially the
30 amendment to hydrofluorocarbons (HFCs) from Kigali [14].

Zühlsdorf et al. have shown in previous studies [15,16], that heat pumps with mixed working fluids constitute a competitive alternative that outperformed conventional heat pumps in terms of their thermodynamic and economic performance. It has been shown that the use of mixtures is especially beneficial in applications with a low temperature lift between thermodynamic average temperature of sink and source in combination with a relatively large temperature glide in sink and source and that they can result in performance increases of more than 25 % [15,17].

The present study analysed the performance of mixed working fluids in a booster heat pump application in an ultra-low-temperature district heating network. A comprehensive screening was conducted to determine the most promising mixtures. These selected solutions were analysed in more detail, which included the sizing of components, an economic analysis from the consumer point of view and a performance analysis under different operating conditions than the design criteria (off-design analysis). Finally the performance indicators obtained were reused in the models from Ommen et al. [2] to re-evaluate district heating network system performance.

2 Methods

2.1 Case Description

The present study focused on the development of a booster heat pump for an application, which is aligned to the EnergyLab Nordhavn project [18]. The booster heat pump is part of a DH substation, which is shown in Figure 1. The substation consists of a heat exchanger to supply the space heating demand, a booster heat pump with storage tank to supply domestic hot water and a second smaller heat pump to reheat the recirculated hot water in the building. The recirculation system is not the focus of the present work and is thus excluded from the drawing.

The district heating supply enters the substation at a temperature of 40 °C. While one part of the stream is used as the heat source in the evaporator and cooled down to approximately 25 °C, the other part is heated up to the design temperature of 60 °C and fed into the stratified hot water tank or directly used for heating up the DHW in the linked heat exchanger.

The outlet from the booster heat pump evaporator is mixed with either the return from the DHW heat exchanger or the cold outlet from the tank while charging (both approximately at 15 °C to 18 °C), before it is discharged into the district heating return line at approximately 21 °C. If the DHW storage tank is discharged, cold water is drawn from the DHW heat exchanger to fill up the tank from the bottom.

1 The booster heat pump analysed in this study is based on the dimensioning of a prototype, which was designed
2 within the framework of the EnergyLab Nordhavn project [18] to provide DHW for a multifamily building
3 including 15 flats. Following the Danish Standard DS439 for water supply installations [19] and the assumption
4 of 3 persons per flat with an average daily consumption of 46.2 l per person, the demand amounts to
5 2,079 l/day. To account for heat losses and a possible additional use, a daily consumption of in total 2,450 l/day
6 was considered. The storage temperature was chosen to be above 55 °C to avoid the growth of legionella
7 bacteria in the DHW distribution system inside the building [20]. The daily charging time of the prototype was
8 assumed as 4 h to increase the suitability for integration as a flexible unit in a smart grid. This defines the heat
9 supply load of the booster heat pump at design conditions to be 13.9 kW while heating 600 kg/h from 40 °C to
10 60 °C. Disregarding the possibility to benefit from flexible electricity consumption, the described booster heat
11 pump can as well be integrated in substations with larger storage tanks, covering larger demands at an
12 increased daily operation.

Figure 1: Flow sheet of the substation for supply of space heating and domestic hot water by the booster heat pump and a storage tank

2.2 Thermodynamic model

The first step consisted of a screening to identify the most promising fluids for the booster heat pump in terms of thermodynamic performance, represented by the coefficient of performance (COP). A thermodynamic model of the heat pump cycle was implemented, as shown in Figure 2.

Figure 2: Flow sheet of the thermodynamic model of the heat pump (left) with T - $\dot{Q}$ -diagram of an exemplary mixed working fluid (right)

The model consists of energy and mass balances and characterises the thermodynamic cycle by determining the state points of the working fluid. The working fluid is evaporated (6→7) and superheated (7→1) by receiving heat from the heat source at low pressure, before it is compressed (1→2) to reject the heat at higher pressure and temperature to the heat sink (2→5). The heat rejection can be separated into desuperheating (2→3), condensing (3→4) and subcooling (4→5). From (5→6) the fluid undergoes an isenthalpic throttling process, before it is heated again. All heat transfer processes were assumed to be isobaric. The pressure levels were defined by a minimum pinch point temperature difference of 2.5 K in the entire heat exchanger. The subcooling was chosen to end at the pinch point temperature difference for obtaining the maximum efficiency [21]. For some fluids with a high temperature glide during condensation, this may result in no subcooling. The superheating temperature difference was chosen to respect a minimum temperature difference between the dew line and the inlet and outlet of the compressor of 5 K. Since a higher potential for the use of mixtures can be expected, if this temperature difference is minimized [15], the screening was repeated with 0 K minimum superheating.

The compressor was modelled with an isentropic efficiency as described by Granryd et al. [22], defining the ratio of the power of an isentropic compression over the actual consumption. The promising solutions expected for these applications typically cover a limited range of pressure ratios, which justifies the choice of a specific non-pressure dependent isentropic efficiency during the screening process [22]. The isentropic efficiency used in the screening was assumed as 70 %. No additional heat losses from the compressor were considered. In the following more detailed analysis of the most promising solutions, those parameters were further analysed. A sensitivity analysis of the isentropic efficiency of the compressor between 50 % and 80 % revealed only minor influence with respect to the ranking of the different mixtures.

Table 1: Assumptions for thermodynamic model used in the screening process

Component	Assumptions
Evaporator	<ul style="list-style-type: none"> - Pinch point temperature difference: $\Delta T_{\text{pinch, evap}} = 2.5 \text{ K}$ - Minimum superheating temperature difference: <ul style="list-style-type: none"> - $\Delta T_{\text{SH}} \geq 0 \text{ K}$ (Mixtures) - $\Delta T_{\text{SH}} \geq 5 \text{ K}$ (Pure fluids) - No pressure drop
Condenser	<ul style="list-style-type: none"> - Pinch point temperature difference: $\Delta T_{\text{pinch, cond}} = 2.5 \text{ K}$ - Maximum subcooling to pinch point temperature difference: <ul style="list-style-type: none"> - $T_5 = T_{\text{sink, in}} + \Delta T_{\text{pinch, cond}}$ - No pressure drop
Compressor	<ul style="list-style-type: none"> - Isentropic compression (design-conditions): $\eta_{\text{is, comp}} = 70 \%$ - No heat loss to environment
Throttling Valve	<ul style="list-style-type: none"> - Isenthalpic expansion

The simulation results of the thermodynamic model can be analysed based on different performance indicators. The COP relates the supplied heat $\dot{Q}_{\text{Sink}}$ to the consumed electric power of the compressor $\dot{W}_{\text{Comp}}$.

$$\text{COP} = \frac{\dot{Q}_{\text{Sink}}}{\dot{W}_{\text{Comp}}} \quad (1)$$

The Lorenz efficiency η_{Lor} can be used to evaluate the performance with respect to the theoretical maximum performance. It relates the COP to the maximum achievable COP_{Lor} for finite heat reservoirs in terms of a Lorenz cycle [23] and therefore gives an indication about the improvement potentials.

$$\eta_{\text{Lor}} = \frac{\text{COP}}{\text{COP}_{\text{Lor}}} \quad (2)$$

1 COP_{Lor} is solely dependent on the thermodynamic average temperatures of sink $T_{Sink,av}$ and source $T_{Source,av}$,
 2 which can be defined as $T_{Sink,av} = (T_{Sink,out} - T_{Sink,in}) / \ln(T_{Sink,out}/T_{Sink,in})$ and $T_{Source,av} = (T_{Source,in} -$
 3 $T_{Source,out}) / \ln(T_{Source,in}/T_{Source,out})$ assuming a constant specific heat capacity.

$$COP_{Lor} = \frac{T_{Sink,av}}{T_{Sink,av} - T_{Source,av}} \quad (3)$$

4 The exergetic efficiency ε accounts for the exergy of the streams and is defined according to [24] considering a
 5 dead state at ambient conditions of $T_0 = 25^\circ\text{C}$ and $p_0 = 1$ bar.

$$\varepsilon = \frac{\dot{E}_{Sink,out} - \dot{E}_{Sink,in}}{\dot{E}_{Source,in} - \dot{E}_{Source,out} + \dot{W}_{Comp}} \quad (4)$$

6 The physical exergy of a stream $\dot{E}$ describes the maximum work, which can be obtained from a stream while it
 7 is brought from its initial state into thermodynamic equilibrium with the environment. At the initial state the
 8 working fluid has the specific enthalpy h and the specific entropy s , while the specific enthalpy $h = h(T_0, p_0)$ and
 9 the specific entropy $s = s(T_0, p_0)$ are defined by the ambient conditions T_0 and p_0 , when in equilibrium with the
 10 environment.

$$\dot{E} = \dot{m} (h - h_0 - T_0 (s - s_0)) \quad (5)$$

11 The results include furthermore variables, which give an indication of investment cost and technical feasibility.
 12 Such variables can be the absolute pressures for evaporation p_{evap} and condensation p_{cond} , the pressure ratio
 13 p_{cond}/p_{evap} , the mass flow rate of the circulated refrigerant $\dot{m}$ and the volume flow rate at the inlet of the
 14 compressor $\dot{V}_1$, which indicates the size and thereby the investment cost of the compressor.
 15 The model was implemented in Matlab [25] using Refprop [26] to calculate the medium properties using the
 16 recommended standard equation of state for each mixture.

17 2.3 Refrigerant screening

18 The above model was used to evaluate a wide range of pure and mixed working fluids. The mixtures considered
 19 were based on a list of pure fluids, from which the binary mixtures were generated and simulated for the range
 20 of possible mass fractions of the mixture. The list of fluids is shown in Table 2 and consists of different
 21 commonly used working fluids, supplemented with similar fluids, which might have a beneficial influence as a
 22 mixture component.

1 In order to ensure the sustainability of the chosen fluids, they were chosen in accordance with the current
2 conventions regarding the environmental impact of working fluids, represented by the Kigali amendment [14].
3 Due to the phase-out of HFCs with a GWP above 150, the remaining alternatives are natural refrigerants and
4 hydrofluoroolefins (HFO).

5 Natural working fluids and especially hydrocarbons (HC) are considered as promising alternatives with little
6 environmental impact. Due to their flammability, additional measures are required to ensure safe operation
7 [27,28]. The relevant European Standards for domestic heat pumps were being revised and updated at the
8 time of publication [28].

9 Table 2 shows that HFOs, which are unsaturated HFCs, have a comparably low environmental impact,
10 considering the ozone depletion potential (ODP) and GWP. To assess the overall emissions in terms of CO₂
11 emission equivalents, it is recommended to conduct an analysis of the total environmental warming impact
12 (TEWI) for each specific application, accounting for the entire life cycle from cradle to grave of the refrigerant
13 [29].

1 Table 2: List of fluids considered in the screening with characteristic properties [30–33]

No	Name of Fluid	Ref. No.:	Type	ODP, -	GWP, -	Normal Boiling Point, °C	Crit. Temp., °C	Crit. Pressure, bar	Safety Class
1	Methane	R50	HC	0	25	-161.5	-82.6	46.0	A3
2	Ethylene	R1250	HO	0	6.8	-103.8	9.2	50.4	A3
3	Ethane	R170	HC	0	2.9	-88.6	32.2	48.7	A3
4	CO ₂	R744		0	1.0	-	31.0	73.8	A1
5	Propylene	R1270	HO	0	3.1	-47.6	91.1	46.7	A3
6	Propane	R290	HC	0	3.0	-42.0	96.7	42.5	A3
7	Dimethyl ether (DME)	RE170	HC	0	1.0	-24.0	127.3	53.4	A3
8	Iso-Butane	R600a	HC	0	3.0	-11.7	134.7	36.3	A3
9	Butane	R600	HC	0	3.0	-0.5	152.0	38.0	A3
10	Iso-Pentane	R601a	HC	0	4.0	27.8	187.3	33.8	A3
11	Ethyl ether (DEE)	R610	HC	0	4.0	34.6	193.7	36.4	A3
12	Pentane	R601	HC	0	4.0	36.1	196.6	33.7	A3
13	Hexane		HC			68.7	234.5	30.3	
14	Heptane		HC			98.4	267.0	27.4	
15		R1234yf	HFO	0	4.0	-26.0	94.7	33.8	A2L
16		R1234ze(E)	HFO	0	7.0	-19.0	109.4	36.4	A2L
17		R1234ze(Z) ¹	HFO	0	<10.0	9.8	150.1	35.3	A2L
18		R1233zd(E)	HFO	0	4.5	17.9	166.5	36.2	A1

2 In two previous studies concerning the use of mixtures for heat pump applications ([13] and [14]) it was
3 observed that there is no strong correlation between any medium properties of the pure fluids and their
4 performance as mixture component in a heat pump. The list was therefore composed of fluids covering a broad
5 range of the typically influential medium properties, such as critical temperature and pressure. While most of
6 the working fluids show good miscibility with each other, there are some mixtures with a limited miscibility in
7 the liquid phase at low pressures and temperatures. If these combinations, e.g. one of the ethers with a
8 hydrocarbon, was among the most promising fluids, the miscibility was analysed in more detail.

9 2.4 Detailed engineering

10 Based on the screening of the working fluids and the identification of working fluids with promising
11 thermodynamic performance, selected solutions were analysed in more detail. This included the dimensioning
12 of the components, an estimation of the investment cost and an analysis of the performance in operating
13 conditions, which are deviating from the design specifications.

¹ Expected values according to [33] for ODP, GWP and safety class

2.4.1 Dimensioning and calculation of investment cost

Dimensioning of the components was performed as the basis for an investment cost calculation, which was then used for comparison purposes and for estimating the consumer heat cost in the system model. The total capital investment cost was determined based on the cost of the main components, which are the compressor and the two heat exchangers.

The determination of the heat exchanger areas requires the calculation of heat transfer coefficients for the working fluid and the secondary fluid side. These calculations are typically based on empirical correlations, which account for the fluid, the equipment and the operating conditions. For working fluid mixtures, no correlation was available that was valid for all considered fluids in plate heat exchangers at the expected operating conditions. Testing different correlations for various fluids showed that the results are highly dependent on the correlation, which is undesirable for this analysis. Based on this, it was concluded that the estimation of appropriate heat transfer coefficients would imply considerable inaccuracy, regardless of the method.

Considering the purpose of determining the heat exchanger area, it was found to be sufficient to assume fixed average heat transfer coefficients. Heat transfer coefficients as presented in Table 3 were estimated to be obtainable for pure fluids while accepting a reasonable pressure drop. For mixed working fluids, the heat transfer coefficients were assumed to be 25 % less during phase change to account for additional resistance due to mass transfer between the phases [34]. The assumptions were conservative and based on experience with the prototype system, to ensure a feasible solution. Nevertheless, optimizing the overall economic performance might yield a higher acceptable pressure drop and thus, higher heat transfer coefficients and smaller areas. These assumptions can therefore be considered to yield an estimation of the economic performance, which is feasible but might show improvement during optimization.

Table 3: Assumed heat transfer coefficients

Flow condition	Heat transfer coefficient, W/(m ² K)	
	Pure Fluid	Mixture
Evaporation	3,000	2,250
Condensation	2,400	1,800
Liquid	1,500	
Gaseous	1,200	

The types of components were chosen according to the prototype being tested in the EnergyLab Nordhavn project [18]. The heat exchangers were chosen from the C62 micro plate heat exchanger series from Danfoss.

The compressor was sized according to the volume flow rate and chosen from the MLZ scroll compressor series from Danfoss, assuming a volumetric efficiency of $\eta_{vol,comp} = 90\%$, which is mostly exceeded in design conditions. The purchased equipment costs PEC describe the cost for acquisition of the main components and were calculated by using the area for the heat exchangers A_{evap} and A_{cond} in the Equation 6 and the volume flow rate at the suction port for the compressor $\dot{V}_1$ in Equation 7. The heat exchanger areas were determined by employing the heat transfer coefficients from Table 3 and mean temperature differences. The evaporator and the condenser were therefore discretized into 25 volumes of equal transferred heat. The remaining heat exchangers were discretized into five volumes.

The general cost functions are described e.g. by [16,17] and were fitted to current catalogue prices from [17,35] while considering experiences from component acquisition for the test rig construction. An addition of 20 % ($f_{flammability} = 1.2$) on the compressor cost was assumed to cover expenses for the required safety measures [35], if the fluid or one component of the mixture was a flammable refrigerant. The parameters for the estimation of the purchased equipment cost are summarized in Table 4.

Table 4: Parameters used to calculate the purchased equipment cost and the investment cost

Heat exchangers	
$C_{1,hx}$	126.9 €
$C_{2,hx}$	106.4 €/m ²
Compressor	
$C_{1,comp}$	2805.0 €
$\dot{V}_{ref,comp}$	21.9 m ³ /h
$f_{flammability}$	1.2 -
β_{comp}	0.8 -
$\eta_{vol,comp}$	0.9 -
Total capital investment	
f_{TCI}	4 -

$$PEC_{hx} = C_{1,hx} + C_{2,hx} \cdot A_{hx} \quad (6)$$

$$PEC_{comp} = C_{1,comp} \cdot f_{flammability} \left(\frac{\dot{V}_1}{\eta_{vol,comp} \cdot \dot{V}_{ref,comp}} \right)^{\beta_{comp}} \quad (7)$$

The sum of the purchased equipment cost of the main components yields the total purchased equipment cost PEC_{total} :

$$PEC_{total} = PEC_{evap} + PEC_{cond} + PEC_{comp} \quad (8)$$

The total capital investment TCI includes additional equipment, such as the throttling valve, piping, instrumentation, control system and remaining positions, and the cost for assembly and manufacturer margins can be estimated based on the PEC_{total} [24]. Based on pre-studies with the prototype, this cost is estimated as 400 % of the equipment cost of the main components. Apart from the increased purchased equipment cost for the compressor, no extra cost for safety measures were added when flammable refrigerants were used, since the cost of required measures [31] would be dependent on the circumstances under which the heat pump will be installed.

$$TCI = f_{TCI} PEC_{total} \quad (9)$$

To compare and evaluate the economic performance of the booster heat pump, the investment cost was discounted and summed up with the annual cash flows for heat and electricity consumption. The investment cost was discounted with the capital recovery factor [24], assuming a lifetime of 20 years and an effective interest rate of 5 %. It is expected that the booster heat pump will be rather economically promising, when operating with more daily operating hours than assumed for the dimensioning of the prototype. The yearly operation time was therefore assumed to be 3000 h/a constituting a case with a more extensive use of the heat pump than in the design case. The cost for electricity was aligned to the expectations of the Danish Energy Agency for 2040 [36] and fixed as 100 €/MWh.

The main purpose of the economic analysis was the comparison of the different booster heat pump solutions. However, we included a comparison to an alternative solution, which assumes that the heat is supplied directly at 60 °C to the customer, which eliminates the need for a booster heat pump station and thereby the additional investment cost. While the customer does not have any cost related to amortization of the investment cost or electricity consumption in case of direct heat supply from DH at 60 °C, the cost for heat consumption are typically higher at higher temperatures. The cost of heat supplied by DH at 60 °C was set to 80 €/MWh, which corresponds to experiences with existing DH networks. The cost for DH at 40 °C was assumed to be 70 €/MWh, since a decrease in the forward temperatures of the DH network will allow the central heat pumps to operate at higher COPs and with decreased heat losses from the network, which may correspond to a decrease of approximately 10 €/MWh of supplied heat in operating cost.

It may be noted, that current and future costs for heat and electricity underlie large variations and uncertainties depending on the actual DH network and future developments on the energy markets. The

assumed costs should therefore be seen as an exemplary scenario, which we expect to be realistic based on an analysis of current DH costs [37,38] and studies analysing the feasibility of the different technologies in different future scenarios [39]. In order to analyse the results for different scenarios, the annual cash flows for heat and electricity consumption may be scaled linearly with respect to the assumed specific energy cost.

Table 5: Assumptions for economic assessment

Lifetime:	20 a
Yearly operation hours:	3000 h/a
Effective interest rate:	5 %
DH supply > 60 °C:	80 €/MWh
DH supply at 40 °C:	70 €/MWh
Electricity:	100 €/MWh

2.4.2 Off design analysis

While the supply temperature of the district heating network can deviate from the assumed 40 °C due to seasonal variations, special circumstances or when the network piping is used as a capacity buffer, the heat sink outlet temperature of 60 °C must be maintained. This makes it necessary to analyse the off design behaviour of the booster heat pump and the complete supply system. As the setup of the booster heat pump allows for controlling the district heating return temperature [2], two operation strategies for changed supply conditions were considered. The first approach maintains the return temperature at the design point (25 °C), which implies changed operating conditions for the booster heat pump compared to the design point. As the second option, it was assumed to maintain the temperature glide in the booster heat pump evaporator at 15 K with a changed return temperature accordingly. In this case, the heat pump operates as closely to the design specifications as possible, which implies that the changed operation is shifted towards the remaining system components.

The cases considered for the off-design analysis were a district heating supply temperature of 35 °C, 45 °C and 50 °C with either a constant source glide temperature of 15 K or a constant return temperature of 25 °C.

In this section, the focus is on the off design performance of the booster heat pump, while it is related to the system context in section 2.5.

For the analysis of the off design performance of the booster heat pump the thermal conductance of the heat exchangers for sink and source were calculated at the design point and kept constant when simulating the off design conditions. This implies the assumption that the heat transfer coefficients vary only negligibly within the variation of the operating conditions.

The estimation of the isentropic efficiency of the compressor was performed analogously to the cost estimation based on the hermetic MLZ scroll compressor series from Danfoss. Such compressors have an isentropic efficiency including the electric motor of up to 74 % in the design point. It was assumed that a scroll compressor with a conservative isentropic efficiency of 70 % could be found for any working fluid at the design point of the heat pump.

The performance of scroll compressors is mainly dependent on the pressure ratio. The influence of changed isentropic efficiency related to the changed pressure ratio between design point and off design operation was estimated by using the correlation presented in [22]. The built in volume ratio was fitted to yield optimal performance in the design condition, which resulted in a slight decrease in isentropic efficiency for deviating pressure ratios. The volume flow rate at the compressor inlet was kept constant during off design analysis, with any changes in heat pump capacity to be covered by changed operating time.

2.5 Analysis of influence on system performance

As an integrated part of the system architecture, any improved performance of the booster heat pump may influence the overall benefit of utilising ULTDH. Ommen et al. [2] introduced a methodology to analyse the system performance in which they summarized the contributions in terms of work in the different sections of the network to supply the heat to the customer.

Analogously to the heat pumps, the performance was evaluated by introducing the coefficient of system performance (COSP), which was used to compare the investigated systems. It includes all the various requirements for supplying the heat demand. The indicator is defined as

$$\text{COSP}_{\text{demand,elec}} = \frac{\dot{Q}_{\text{HeatSupply}} + \sum \dot{Q}_{\text{BoosterHP}} - \dot{Q}_{\text{DH,loss}}}{\dot{W}_{\text{HeatSupply}} + \sum \dot{W}_{\text{BoosterHP}} + \dot{W}_{\text{pump}}} = \frac{\dot{Q}_{\text{Demand}}}{\sum \dot{W}} \quad (10)$$

Where the heat supplied from the central heat pumps ($\dot{Q}_{\text{HeatSupply}}$) to the network, the heat loss ($\dot{Q}_{\text{DH,loss}}$) and the heat from the booster heat pumps ($\sum \dot{Q}_{\text{BoosterHP}}$) jointly supplies the heat demand of the network ($\dot{Q}_{\text{Demand}}$). In the specific case analysed here, where the DH system is used as the heat source for the booster heat pumps, no additional heat ($\sum \dot{Q}_{\text{BoosterHP}}$) is supplied to the network, apart from the electricity consumption ($\sum \dot{W}_{\text{BoosterHP}}$), in which case they are equal [40].

In Ommen et al. [2], the ULTDH network supplied by central heat pumps was evaluated to result in COSPs in the range of 3.9 to 4.2 for booster heat pumps using R134a. The central heat pumps were using R717 (Ammonia) as working fluid, since it was considered as the most promising solution in terms of thermodynamic

and economic performance for large scale heat pumps and with the smallest risk to be affected by future legislation. The calculation of COSP for ULTDH assumed realistic component efficiencies and effectiveness for heat pumps, as well as other relevant parameters such as utility units and network pressure and heat losses. The simplified layout of the network is presented in Figure 3. The benefit of this supply scheme, compared to a corresponding LTDH network, was an increase of between 7 % and 24 %. The analysis was also performed for extraction type combined heat and power (CHP) plants, for which ULTDH was found to result in decreased performance compared to LTDH.

Figure 3: Layout of considered ULTDH system for evaluation of system performance

The employed method for conducting the analysis, as well as assumptions for the demand and the network structure, follows that of the previous analysis [2], except for the booster heat pumps used for supplying the DHW which follow the method described in detail in sections 2.2-2.4 above.

3 Results

3.1 Refrigerant Screening

Figure 4 shows an overview of the screening results. The diagrams show the COP for all binary mixtures generated from Table 2 over the composition of the higher index medium on the abscissa for 5 K (left) and 0 K minimum superheating (right). Selected well performing mixtures are shown in colour while the remaining mixtures are shown in grey to represent the entire solution space.

Figure 4: Overview of screening results: COP over composition of component 2 for minimum superheating temperature difference of 5 K (left) and 0 K (right) with selected mixtures coloured and remaining in grey

The COP of the pure fluids (composition 0 and 1) reaches values between 6.0 and 6.2 and is higher for a minimum superheating of 5 K. While the entire range of mixtures offers a large range of solutions, specific mixtures perform better than the pure fluids with $\text{COP} \approx 8.0$ for a minimum superheating of 5 K, while the performance increases to $\text{COP} \approx 9.0$ for no minimum superheating.

The relation between the working fluid components, the composition and the performance is highly non-linear. The presented COPs for the fluids are based on given minimum temperature differences in the heat exchangers. This means that the pressure in both condenser and evaporator varies considerably between different compositions of the same fluid mixture. Accordingly, different effects such as the pressure ratio, the absolute pressure difference, or the temperature glide matching during heat transfer contribute to the efficiency being non-ideal by irreversibilities during expansion, compression and heat transfer. These effects superimpose each other and can cause that the performance has different shapes when plotted over the composition and e.g. shows one or two peaks.

Table 6 summarizes relevant performance parameters for the best performing fluids. In terms of thermodynamic performance, R134a was considered as the reference fluid for the booster heat pump and included for comparison purposes. Due to its high GWP of 1430 it is affected by the phase out and therefore not considered as a feasible alternative for future applications.

While the state of the art working fluids R134a and propane give COPs of 6.11 and 6.01, respectively, the fluids R1234ze(Z) and R1233zd(E) show the highest COP of 6.24 and 6.11 among the pure fluids. Nevertheless, the HFO cycles have higher pressure ratios and higher volume flow rates, which incur a higher investment cost.

The mixtures show increased performance and reach COPs of 9.01 for 50 % Iso-Butane - 50 % Pentane. While a mixture of Iso-butane and pentane is flammable, the HFO mixture 50 % R1234yf – 50 % R1233zd(E) is expected to be mildly flammable and shows a competitive COP of 8.87 at a moderate pressure ratio and volume flow rate.

Considering R134a as the reference heat pump cycle, the use of 50 % Iso-Butane - 50 % Pentane as working fluid results in a relative performance increase of 47 % in COP and an absolute increase from 41.9 % to 58.1 % in exergetic efficiency ε for a minimum superheating of 0 K. Under the assumption that the minimum required superheating cannot be reduced to less than 5 K, the best performing mixtures show a COP of 8, which corresponds to a performance increase of 31 % in COP.

Table 6: Summary of key performance parameters for best performing fluids, pure fluids were simulated with 5 K and mixed fluids with 0 K minimum superheating. Solutions with sub atmospheric evaporation pressure were neglected

Working Fluid	COP	p_{evap}	p_{cond}	$\frac{p_{\text{cond}}}{p_{\text{evap}}}$	$\dot{m}$	$\dot{V}_1$	ε	η_{Lor}
	-	bar	bar	-	kg/s	m ³ /h	%	%
R134a	6.11	6.17	16.97	2.75	0.075	9.2	41.9	33.0
Propane	6.01	10.84	21.28	2.38	0.039	7.6	41.3	32.5
DME	6.19	5.49	14.60	2.66	0.032	10.2	42.3	33.5
Butane	6.15	2.25	6.64	2.95	0.036	23.1	42.1	33.2
R1234yf	5.99	6.36	16.79	2.64	0.093	9.8	41.1	32.4
R1234ze(E)	6.08	4.62	13.11	2.84	0.080	12.1	41.7	32.9
R1234ze(Z)	6.24	1.63	5.32	3.27	0.063	28.5	42.7	33.7
R1233zd(E)	6.21	1.19	4.07	3.43	0.068	37.7	42.5	33.6
50 % Iso-Butane – 50 % Pentane	9.01	1.93	4.08	2.12	0.038	26.7	58.1	48.7
50 % Propylene – 50 % Butane	8.85	6.29	11.83	1.88	0.037	9.9	57.3	47.8
50 % Iso-Butane – 50 % DEE	8.87	2.27	4.81	2.12	0.039	23.0	57.4	48.0
50 % R1234yf – 50 % R1233zd(E)	8.87	3.67	7.54	2.06	0.080	15.0	57.4	47.9
30 % Propane – 70 % R1234ze(Z)	8.76	4.84	9.60	1.98	0.055	12.0	56.8	47.4

Figure 5 presents temperature-heat diagrams for R134a (left) and for 50 % Iso-Butane – 50 % Pentane (right).

The left diagram is representative for the pure fluids, while most of the most promising mixtures show characteristics similar to those in the right figure, such as a low degree of superheating after evaporation, desuperheating before condensation and subcooling. This means that most of the heat transfer for the mixed working fluids occurs during phase change of the fluid.

The areas between the temperature profiles of the refrigerant and sink/source streams represent the irreversibilities or exergy destruction due to heat transfer, respectively. These areas, and thus the irreversibilities, are higher for the pure fluids, which contributes to a comparatively lower performance.

Figure 5: Temperature-heat diagram of R134a (left) and 50 % IsoButane – 50 % Pentane (right)

3.2 Economic Analysis of the Booster Heat Pump

Table 7 shows a summary of the dimensions of the main components, such as the heat exchangers and the compressor, as well as the purchased equipment cost (PEC). The table also shows the total capital investment cost (TCI), which includes an additional cost for the remaining components, assembly and overhead.

Table 7: Summary of key parameters in economic calculations

Working Fluid	COP	A_{evap} m ²	A_{cond} m ²	$\dot{V}_{\text{comp}}$ m ³ /h	PEC _{evap} €	PEC _{cond} €	PEC _{comp} €	PEC _{total} €	TCI €
R134a	6.11	1.52	2.11	9.21	289	350	1,525	2,165	8,662
Propane	6.01	1.52	2.13	7.56	288	353	1,564	2,206	8,825
R1234ze(Z)	6.24	1.53	1.96	28.47	289	335	3,764	4,389	17,558
50 % Iso-Butane – 50 % Pentane	9.01	4.83	4.37	26.69	641	591	4,290	5,522	22,091
50 % Propylene – 50 % Butane	8.85	5.09	4.28	9.92	668	582	1,943	3,193	12,774
50 % Iso-Butane – 50 % DEE	8.86	4.09	4.72	23.05	562	628	3,815	5,005	20,023
50 % R1234yf – 50 % R1233zd(E)	8.86	4.58	4.80	14.97	614	637	2,251	3,502	14,010
30 % Propane – 70 % R1234ze(Z)	8.76	4.41	4.62	12.00	596	618	2,263	3,478	13,912

It should be noted that the cost of the cheapest heat pump using a mixture is almost 50 % higher than the expected investment cost for the heat pump using R134a. While the volume flow rate of 50 % Propylene / 50 % Butane is similar to R134a, an increased PEC_{total} results from the assumed safety margin for the refrigerant being flammable and from the heat exchangers, which have approximately double the size as for R134a. The larger heat transfer area is mainly caused by the lower average temperature difference between the fluids, but the lower heat transfer coefficient of the mixture also has an impact.

1 A comparison of the investment costs shows a dominating influence from the volume flow rate at the
 2 compressor inlet compared to the cost for additional heat exchanger area. The volume flow rate depends on
 3 density at the compressor inlet and the enthalpy of vaporization of the fluid. This is independent of whether
 4 the substance is a pure fluid or a mixture.
 5 The reported investment cost of almost 9,000 € for the heat pumps using R134a and propane for supplying
 6 heat for a 15 apartment building is consistent with the values reported in [41]. The demonstration project
 7 estimated a market price of 660 € for a booster heat pump supplying heat to a one family building,
 8 corresponding to a slightly higher specific investment cost for smaller capacities.

Figure 6: Annual cash flows for consumed heat at 40 °C (70 €/MWh) and electricity (100 €/MWh) and discounted investment cost for selected working fluids as well as the cost for consumed heat directly supplied by DH above 60 °C without a booster heat pump (80 €/MWh)

9 Figure 6 shows the economic performance as the sum of the annual cash flows for the chosen candidates
 10 compared to the annual expenses when an alternative heat supply is used.
 11 The figure shows, that the economic performance of the best mixture (50 % Propylene / 50 % Butane) is similar
 12 to the performance of R134a and Propane, while 50 % R1234yf / 50 % R1233zd(E) and 30 % Propane / 70 %
 13 R1234ze(Z) also perform competitively. Especially the two last-named seem promising, considering that the
 14 HFO mixture is not flammable and the decreased flammability of the hydrocarbon mixed with a HFO.

Comparing the annual cash flows for R134a and the best performing mixtures, shows furthermore that the total annual cash flows are similar, meaning that the increased investment cost of 47 % for 50 % Propylene / 50 % Butane and 62 % for 50 % R1234yf / 50 % R1233zd(E) can be compensated to a large extent by the lower operational cost.

The best performing fluids show annual operating cost which are approximately 500 €/a higher than for the solution in which the DH is supplied at minimum 60 °C without a booster heat pump. It can be expected that a larger difference in cost for the consumed heat from DH as well as lower electricity prices will favour the booster HP scenario, while smaller differences in cost for heat consumption from DH at different temperatures will favour supplying the heat directly at 60 °C or higher.

An decrease of the cost for DH at 40 °C of 10 €/MWh or an increase of 10 €/MWh for DH at 60 °C will result the LTDH solution and the best performing booster heat pump solutions to operate with the same economic performance.

The booster HPs will furthermore increase their economic potential at lower electricity prices, and in applications with an increased utilization factor, meaning more operation hours than 8 hours per day.

Considering the possibility of benefitting from lower electricity prices by operating the heat pump flexibly, it is expected to have an opposing influence on the amount of daily operation hours, which would require a case specific assessment.

3.3 Off design analysis

Table 8 presents an overview of the heat pump performance for selected working fluids at different operating conditions. While it was assumed that the district heating supply temperature can vary between 35 °C and 50 °C, either the return temperature of 25 °C or the temperature glide in the source of 15 K was kept constant. The condenser outlet temperature of 60 °C was maintained in all scenarios. The table shows the COP for each working fluid at each point of operation and the relative deviation when compared to the COP at design conditions.

Table 8: Performance of heat pump with equipment designed for operating conditions (bold) at different DH supply temperatures for either constant source outlet temperature or constant source temperature glide in terms of COP and relative deviation from performance at design conditions (dev)

	$T_{\text{supply}} = T_{\text{sink,in}}$ $T_{\text{return}} = T_{\text{source,out}}$	35 °C		40 °C	45 °C		50 °C		UA-Value	
		20 °C	25 °C	25 °C	30 °C	35 °C	25 °C	25 °C	Source, W/K	Sink, W/K
R134a	COP, - dev, %	5.78 -5.5	6.25 2.3	6.11 0.0	6.39 4.5	5.89 -3.6	6.59 7.8	5.60 -8.4	1511.7	1806.5
R290	COP, - dev, %	5.67 -5.6	6.15 2.3	6.01 0.0	6.31 5.0	5.79 -3.7	6.55 9.0	5.50 -8.5	1506.8	1823.5
R1234ze(Z)	COP, - dev, %	5.88 -5.8	6.35 1.7	6.24 0.0	6.52 4.5	6.06 -2.9	6.71 7.5	5.81 -6.8	1516.8	1719.3
50 % IsoButane – 50 % Pentane	COP, - dev, %	8.14 -9.7	8.59 -4.7	9.01 0.0	9.65 7.2	8.68 -3.6	10.06 11.7	7.79 -13.5	4350.7	3560.2
50 % Propylene – 50 % Butane	COP, - dev, %	8.03 -9.3	8.52 -3.8	8.85 0.0	9.51 7.4	8.45 -4.6	9.95 12.4	7.53 -15.0	4581.2	3468.6
50 % IsoButane – 50 % DEE	COP, - dev, %	8.01 -9.6	8.38 -5.3	8.86 0.0	9.54 7.7	8.59 -3.0	10.01 13.0	7.76 -12.3	3683.3	3837.9
50 % R1234yf – 50 % R1233zd(E)	COP, - dev, %	8.04 -9.3	8.46 -4.6	8.86 0.0	9.47 6.8	8.53 -3.7	9.85 11.2	7.66 -13.6	4125.6	3899.5
30 % Propane – 70 % R1234ze(Z)	COP, - dev, %	7.97 -9.0	8.37 -4.5	8.76 0.0	9.35 6.7	8.49 -3.1	9.75 11.2	7.71 -12.0	3972.0	3746.0

For a decreased supply temperature, the COPs decrease in general more for the mixtures than for the pure fluids, while they still perform better in absolute terms. The pure fluids perform even better for a decreased supply temperature when the return temperature is maintained at 25 °C.

For increased supply temperatures and a constant temperature glide in the source the performance increase compared to the operation at design conditions is higher for mixtures than for pure fluids.

For increased supply temperatures and constant return temperatures, the performance decreases for all fluids. While the relative decrease is comparable among the fluids at a supply temperature of 40 °C, the mixtures decrease the performance more than the pure fluids do at a supply temperature of 50 °C.

3.4 System Performance

Table 9 presents an overview of the system performance (COSP) for the combined ULTDH system, in case the booster heat pump for DHW was chosen according to the applicable working fluids from Table 8. Temperatures of supply and return are following the same parametric variation as shown in Table 8. Besides the COSP for the

design and off design operation conditions, the table further shows the relative deviation when compared to the COSP at design ULTDH conditions.

Table 9: Performance of considered DH system with equipment designed for operating conditions (bold) at different DH supply temperatures for either constant source outlet temperature or constant source temperature glide in terms of COSP and relative deviation from performance at design conditions (dev)

	$T_{\text{supply}} = T_{\text{sink,in}}$ $T_{\text{return}} = T_{\text{source,out}}$	35 °C		40 °C	45 °C		50 °C	
		20 °C	25 °C	25 °C	30 °C	25 °C	35 °C	25 °C
R134a	COSP, -	3.87	3.65	4.18	4.18	4.18	4.09	4.07
	dev, %	-7.2	-12.6	0.0	0.1	0.1	-2.0	-2.6
R290	COSP, -	3.87	3.64	4.17	4.18	4.17	4.09	4.06
	dev, %	-7.3	-12.6	0.0	0.1	0.1	-1.9	-2.6
R1234ze(Z)	COSP, -	3.88	3.65	4.18	4.18	4.19	4.09	4.07
	dev, %	-7.2	-12.7	0.0	0.0	0.1	-2.2	-2.6
50 % IsoButane – 50 % Pentane	COSP, -	3.99	3.72	4.30	4.27	4.27	4.15	4.12
	dev, %	-7.1	-13.3	0.0	-0.6	-0.5	-3.5	-4.1
50 % Propylene – 50 % Butane	COSP, -	3.99	3.72	4.29	4.27	4.27	4.15	4.12
	dev, %	-7.1	-13.3	0.0	-0.6	-0.5	-3.4	-4.1
50 % IsoButane – 50 % DEE	COSP, -	3.99	3.72	4.29	4.27	4.27	4.15	4.12
	dev, %	-7.1	-13.3	0.0	-0.6	-0.4	-3.4	-4.0
50 % R1234yf – 50 % R1233zd(E)	COSP, -	3.99	3.00	4.29	4.27	4.27	4.14	4.12
	dev, %	-7.1	3.7	0.0	-0.6	-0.5	-3.4	-4.0
30 % Propane – 70 % R1234ze(Z)	COSP, -	3.99	3.72	4.29	4.26	4.27	4.14	4.12
	dev, %	-7.1	-13.3	0.0	-0.6	-0.4	-3.4	-3.9

From the results presented in Table 9, it is possible to draw several important findings for the operation of ULTDH using mixtures in the booster heat pump for DHW. Firstly, it was found, that when using one of the proposed mixed working fluid designs, the COSP may be higher than for configurations with pure fluids, although the improvement is rather low, as the COSP for the best performing mixture compared to the reference R134a corresponds to an improvement of approximately 3 %. The corresponding improvement of COP was approximately 47 % according to Table 8. Secondly, it was noticed that the reduction in performance for off-design operation is larger than for pure fluids, but the absolute value of COSP is still larger for mixed working fluids in off design than for the reference fluid, or alternative pure working fluid heat pumps. For all three considered cases for changed supply temperature, and all the considered pure and mixed working fluids, the highest COSP was found to be for a constant heat source temperature glide of 15 K. Figure 7 presents an overview of the COSP including the different contributions of Equation 10 for various LTDH and ULTDH schemes using heat pumps as the central utility unit. The configurations with LTDH (COSP = 3.68)

and ULTDH (COSP = 4.18) correspond to the results presented in [2]. The result of ULTDH (COSP = 4.29) corresponds to a system utilising the best mixed working fluids heat pump candidate from Figure 6. Two additional scenarios are presented for LTDH and ULTDH systems utilising mixtures for the central heat pump unit of the network. The method for calculation of the performance of the central heat pump units correspond to the method presented in sections 2.3 and 3.1. These results indicate the performance improvement potential for the LTDH and ULTDH systems, when the approach of using mixed working fluids is additionally applied in the central heat pump units. The COSPs reach 4.16 for LTDH and 5.09 for ULTDH systems. This evaluation does not take into account the changed cost of the considered heat pump designs.

Figure 7: Electricity consumption of different system components per 1 MWh supplied heat for different system configurations

4 Discussion

The present study analysed the thermodynamic and economic performance of different pure and mixed working fluids. While the economic performance was found to be comparable for the best pure and mixed working fluids, the thermodynamic performance was considerably better for the mixed working fluids. The comparisons assumed that the mixed working fluids could operate without any required superheating temperature difference, which is an important step to obtain even higher performance increase from the use

of mixtures. The mixtures show a temperature glide during evaporation and therefore offer the possibility to determine the outlet quality by measuring pressure and temperature as independent variables, even in the two phase zone. This possibility might contribute to a more stable control of the superheat. Nevertheless, the realization of minimized superheat would require additional measures to balance and limit the varying liquid content at the outlet of the evaporator.

The economic evaluation was only done for selected fluids. The selection was based on the thermodynamic performance in terms of COP, which means that the economically best performing fluids may not have been identified because the investment is relatively higher for the mixtures because of the better temperature match. While the thermodynamic performance, and especially the ranking of working fluids according to their thermodynamic performance shows little sensitivity to the input parameters, the ranking of the solutions according to their economic performance is strongly dependent on the boundary conditions. The economic performance is very dependent on the cost of heat and electricity, which may be different depending on the location. This may prove even more uncertain for future scenarios with changes to the cost of fuels and taxes. Lund et al. [39] have analysed different technologies for different future scenarios and concluded that the ULTDH scenario with booster heat pumps is only competitive to alternative heat supply at above 60 °C in favourable business cases, which would mean a large cost difference between heat supply at 40 °C and above 60 °C. This study assumed a cost of 80 €/MWh for DH at above 60 °C, which is close to current prices in Copenhagen with similar supply temperatures [37], and a cost of DH at 40 °C of 70 €/MWh. The results have furthermore indicated, that the ULTDH systems are competitive with LTDH systems, if the difference in cost for DH increases to about 20 €/MWh. As indicated by Lund et al. [39] and Elmegaard et al. [9], such boundary conditions are indispensable for the economic feasibility of ULTDH systems with booster heat pumps and might be conceivable in e.g. DH networks with a large share of industrial excess heat between 40 °C and 60 °C [42] or in networks which offer district heating and cooling.

It may furthermore be noted that the annual cost flows were compared to alternative heat supply by district heating at a minimum supply temperature of 60 °C. This assumption implies that the actual supply temperature of these cases will be between 65 °C and 70 °C, which might contribute to an enlarged difference between the cost for DH at 40 °C and respectively above 60 °C.

The study is additionally based on assumptions of interest rate and technical lifetime, which might be different if, for example, the booster heat pump was to be operated by the district heating company. In that case, the economic feasibility would need to be evaluated for the entire system. Changes in these assumptions might change the preference for or against investment intensive solutions.

An additional uncertainty stems from the estimation of the total capital investment cost, which was considered as a fixed multiple of the cost for the main components, even though, e.g. additional plates in a heat exchanger could be realized without any additional cost for auxiliary equipment or assembly. This may have resulted in the cost for the solutions of mixed working fluids being overestimated. The estimation of the heat pump cost did furthermore neglect the possibility of discounted component costs, in case of e.g. in-house acquisition. The goal was to suggest solutions that were sustainable, with a special focus on the choice of the refrigerants. The list of fluids included hydrocarbons, which are indeed flammable but acknowledged as environmentally friendly and HFOs, which are mostly non-flammable but might have a negative impact on organisms. While solutions exist to handle flammable refrigerants, any possible environmental impact will have to be further analysed.

The HFOs decompose to large extent into trifluoroacetic acid (TFA), which is moderately toxic. Recent studies [43–45] analysed the environmental impact of TFA and determine the concentrations to be below the lowest levels that have a measurable impact on organisms, using simulation studies and measurements in Switzerland that were based on the TFA emissions of HFCs with similar impact. However, the studies assumed that the use of HFO-1234yf would be limited to mobile air conditioners, which might require a reassessment if the range of applications of HFOs is enlarged. Furthermore, the fact that there is an environmental impact, regardless of whether its influence is currently measurable or not, raises the possibility that HFOs might be affected by future legislative restrictions.

Follow-up studies should focus on the design and operation of a prototype to analyse operational issues and on a more detailed determination of the investment cost.

5 Conclusion

The analysis demonstrated the potential increase in thermodynamic performance that could be achieved by employing a mixed working fluid instead of R134a or propane. The increase in COP was found to be 31 % for a required minimum superheating of 5 K for the mixtures and 47 % in case the required superheating can be reduced to 0 K. The best performing mixture at design conditions and operating without superheating was 50 % Iso-Butane - 50 % Pentane with a COP of 9.01. The behaviour of the mixture was comparable to pure fluids while operating under off design conditions.

Despite the considerably better thermodynamic performance of mixtures, the economic analysis yields a comparable performance of the best performing pure and mixed working fluids. Both solutions can only under

very favourable economic boundary conditions compete in terms of economics with LTDH, which supplies heat directly at a temperature above 60 °C.

If the use of mixtures as working fluids is applied additionally in the central heat pumps, the COSP of LTDH increases from 3.68 to 4.16 while the COSP of ULTDH increases from 4.18 to 5.09 in case the booster heat pump and the central heat pump are both using a mixture. The improvement in COSP between ULTDH and LTDH increases from 13 % to 22 % when mixed working fluids are utilised in both the central and the booster heat pump units.

In summary, it can be noted that a booster heat pump using the suggested mixed working fluids constitutes a sustainable, promising and effective solution for elevating the temperature of ULTDH to 60 °C. Extending the approach of using zeotropic working fluid mixtures to the central heat pump units, the performance of ULTDH systems can be improved even more.

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Nomenclature

Abbreviations:

CHP	Combined heat and power
COP	Coefficient of performance
DH	District heating
DHW	Domestic hot water
DHWC	Domestic hot water circulation
GWP	Global warming potential
HC	Hydrocarbon
HFC	Hydrofluorocarbon
HFO	Hydrofluoroolefine
HP	Heat pump
HO	Hydroolefine
LTDH	Low-temperature district heating
ODP	Ozone depletion potential
SH	Space heating
TFA	Trifluoroacetic acid
ULTDH	Ultra-low-temperature district heating

Latin Symbols:

A	Area, m^2
C	Parameter for estimation of equipment cost, unit as in Table 4
COP	Coefficient of Performance, -
COSP	Coefficient of System Performance, -
dev	Relative deviation, %
$\dot{E}$	Exergy flow rate, W
f	Factor cost estimation, -
h	Specific enthalpy, kJ/kg
$\dot{m}$	Mass flow rate, kg/s
PEC	Purchased Equipment Cost, €

1	$\dot{Q}$	Heat flow rate, W
2	s	Specific entropy, kJ/(kg K)
3	T	Temperature, °C or K
4	TCI	Total Capital Investment, €
5	$\dot{V}$	Volume flow rate, m ³ /h
6	$\dot{W}$	Work, W

7 **Greek Symbols:**

8	θ	Scaling factor, -
9	Δ	Difference, -
10	ε	Exergetic efficiency, -
11	η	Efficiency, -

12 **Subscripts and superscripts:**

13	av	average
14	BoosterHP	Booster heat pump
15	comp	Compressor
16	cond	Condenser
17	elec	Electric
18	evap	Evaporator
19	hx	Heat exchanger
20	is	Isentropic
21	Lor	Lorenz efficiency
22	pinch	Pinch point temperature difference
23	ref	Reference value
24	SH	Superheating
25	Sink	Sink stream
26	Source	Source stream
27	total	Total system
28	vol	Volumetric
29	0	Dead state

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Highlights:

- Zeotropic working fluid mixtures can improve the COP of a booster HP by 31 %
- The improvement can be up to 47 % if the min. superheating can be reduced to 0 K
- The improved performance of mixtures can compensate the higher investment cost
- The off-design behavior of mixtures is similar to pure fluids
- ULTDH systems using HPs with mixtures outperform LTDH w.r.t. energy performance