SCREENING FOR REFRIGERANT BLENDS IN HIGH-TEMPERATURE LIFT HEAT PUMPS FOR RETROFIT IN RESIDENTIAL HEATING

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ABSTRACT

Providing heat pumps for the retrofit of fuel based boilers in residential heating, is a short or medium term challenge and a major opportunity for a substantial reduction of greenhouse gas emissions. While effective solutions for improved high temperature lift, vapor compression heat pumps have been analyzed elsewhere, this paper specifically deals with the refrigerant selection aspects for alternative blends, using a multi-objective optimization algorithm. The objectives COP and specific heat output are calculated for arbitrarily mixed refrigerant blends, using 17 selected pure fluids. Seasonal mean operating conditions (ambient air 0°C, heating water 50°C) have been used to simulate the heat pump cycle. Blends with a saturation curve extending over the range of –20°C (normal boiling point) and 70°C (critical point) are considered.

Alternative blends are compared with the commercial mixture R-407C. The refrigerant mixture with the highest COP shows an improvement of 8% on the low capacity end of the Pareto-optimum curve. By maximizing the specific heat rate, a gain of 83% can be achieved. All the dominating solutions are composed of flammable refrigerants.

Key Words: ***heat pump, refrigerants, multi-objective optimization, retrofit application***

1 INTRODUCTION

Retrofitting oil or gas boiler heating systems with heat pumps represents a major market opportunity. While effective solutions of improved thermodynamic approaches for high temperature lift, vapor compression heat pumps have been extensively analyzed in another work (Zehnder 2004), the present paper focuses on the refrigerant selection for best efficiency and heat rate.

Many efforts in chemical engineering have been undertaken to find appropriate fluids for HVAC systems, considering in particular safety and stability issues. Since the introduction of the fluorinated refrigerants in 1930 (Midgley and Henne 1930), many different non-toxic and non-flammable refrigerants appeared on the market (for the different temperature ranges). In the late 1980's due to the accepted elimination of chlorinated refrigerants, several HFC refrigerants and (some selected mixtures) were identified as drop-in replacement of the fluids predominantly used at that time, like: HFC-134a for CFC-12, HFC-404A for R-502 and HFC-407C (and R-410A) for HCFC-22. A large number of publications related to the refrigerant selection and to the screening of new refrigerants replacing the CFC and HCFC refrigerants can be found in the literature, e.g. (Calm 1998, Didion 1999, Vorster and Meyer 2000). Other studies are focusing on natural refrigerants, especially the hydrocarbons (Ghodbane 1999, Granryd 2001). Only a few of the publications to our knowledge focus on higher temperature lift (Kazachki and Gage 1997) and

(Engler et al. 1999). In the latter, a comparison of 82 pure candidates has been done over a wide range of evaporation and condensation pressures, comparing their performance, pressure ratio and discharge temperature in a theoretical heat pump cycle. Their results show, that the best performing refrigerants are (unfortunately) all flammable (several hydrocarbons, ammonia and HFC-32).

2 SELECTION OF NEW REFRIGERANT CANDIDATES

In order to complement the above mentioned results, a systematic approach is made here to evaluate the best candidates among pure refrigerants or arbitrarily composed mixtures (up to 4 components). The approach is based on the use of an evolutionary multi objective optimization tool (MOO) developed by (Leyland 2002, Molyneaux et al. 2001). The algorithm is coupled with specially developed Matlab models, which rely on an adaptive fluid interface code, called FLINT, internally developed at LENI[1], allowing an easy communication with fluid properties programs like REFPROP (with version 7, (Lemmon et al. 2002). This software combination is used to perform the systematic evaluation of new high performance refrigerant mixtures.

Selection criteria and restrictions

The evaluation of heat pump working fluids has to consider different aspects, which are listed here below:

- **Thermodynamic properties**

  Normal boiling temperature <-20°C

  Critical temperature >70°C[2]

  Maximum system temperature: Is limited by the thermal stability of the lubricant. Limiting the maximum system temperatures will generally have a positive impact for the lifetime of the compressor. However, no limit has been set for the present evaluation process.

  Maximum pressure level: Has a direct impact on the fabrication costs of the heat pump. High pressure levels (>30 bar) require non standard elements (and consequently imply a price premium) for developments in the near future. In the optimization process, no limit has been imposed.

- **Compatibility with materials**

  For short term developments it is recommended to ensure compatibility with common materials of the refrigeration sector (mainly copper, steel and Teflon). Compatible materials are already available for most of the refrigerants considered in this work. One main exception is ammonia, which is not compatible with copper, and in combination with its high toxicity is not a major candidate for low cost systems. Ammonia is therefore excluded from the evaluation, but is kept for thermodynamic comparison in some of the figures.

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[1] LENI=Laboratoire d'Energétique Industrielle (Laboratory of Industrial Energy Systems) at the Swiss Federal Institute of Technology of Lausanne, Switzerland.

[2] Trans-critical cycles (using e.g. CO_2 (R-744), Methane (HC-170)) are not considered in this work due to the important exergetic losses on the heating side, when the temperature glide in the heat distribution system is small. Transcritical cycles are more intensively considered in air-conditioning units for the automotive sector, where very compact systems are needed, or for hot water boilers, where a high temperature glide exists on the water side.

- **Safety properties**

  Flammability and toxicity for the fluid is a major concern in the design of heat pump units and will influence production costs. The resulting solutions will be post analyzed regarding these criteria.

- **Availability and price**

  The availability of new types of refrigerants and mixtures is the most restrictive aspect for the selection of appropriate fluids and the homologation process for new candidates can strongly delay their market introduction. Due to the worldwide relatively low market share of heat pumps and particularly in the retrofit sector, it might take a while for propositions of new mixtures, specially adapted for this application, to be considered in a large scale in the near future. Actual replacement candidates are limited to HFC blends, excluding flammable and highly toxic mixtures.

3 SIMULATION CONDITIONS

A semi theoretical approach has been chosen for the comparison of arbitrarily composed refrigerant blends. A heat pump cycle with suction line heat exchanger and pinch based heat exchanger models, has been simulated, using the following input parameters:

1. Adaptive air flow on the evaporator with fixed inlet and outlet temperatures of 0°C/-4°C.
2. Heating water on the condenser with fixed temperature glide (in/out) of 45°C/50°C.
3. Suction superheat (referred to the dew point saturation temperature) at compressor inlet of 6 K. In order to take the advantages of the temperature glide of zeotropic mixtures, all the superheat is assumed to be produced in the suction line heat exchanger.
4. The pressure levels of the heat pump are calculated to meet the minimal temperature difference (pinch) in the heat external flow exchangers, ΔT_{min}: evaporator 4 K, condenser 2 K.
5. The compression efficiency is fixed to the value of 60% (isentropic efficiency). The volumetric efficiency is set to an ideal value of 100%.

In the considered case of a high temperature lift heat pump, the extreme operating condition is set to 65°C heating water output temperature at the external inlet air temperature of -12°C. This point therefore corresponds to the most demanding point in terms of heat rate. However when considering the energy demand during the whole heating season, the most important heat requirements in function of the atmospheric temperature, are seen at more moderate operating conditions. For the example of the city of Zurich (Zehnder 2004), the dominating energy requirements are at 0°C, temperature at which this screening is applied to.

4 COMMERCIAL FLUIDS: PROPERTIES AND PERFORMANCE

Refrigerant candidates with thermodynamic properties, which fit to the aimed application, are listed in Table 1 and their respective calculated performance is plotted in Figure 1.

The refrigerants in Figures 1–3 are visually separated into 3 classes: bullets (red): **HC + ammonia**, diamonds (black): **(H)CFC** and squares (blue): **(H)FC**. The (H)CFC's have been maintained in this comparison for academic reasons, although they are already suppressed from most markets for new systems, due to their ozone depletion potential - ODP. For this reason their physical and safety properties have not been included in the table. HFCs are considered in industry as the *long term* replacement refrigerants, but several European countries are about to heavily reduce the use of these refrigerants having a high global warming potential (GWP, see Table 1). The non colored points on the Figure 1, represent the fluids which are only considered for the use in blends as their normal boiling point temperature is too high, >-20°C, for the air-water heat pump application. Fluids presenting a lower critical temperature than 70°C and therefore leading to trans-critical cycles have not been included in the optimization procedure.

In addition to the calculated performances, the pressure level and the discharge line temperature are plotted. These are representative indicators for potentially increased system cost and for reliability. In actual components, pressure levels of max. 30 bar (e.g. for the compressor housing) and temperatures < 120°C are common and should not be exceeded. Lower pressure ranges allow the heat exchangers to be designed with thinner walls, leading to slightly improved heat transfer performance. The maximum discharge temperature criterion is less critical, since several improved concepts of air-water heat pumps (in particular economizer or two-stage cycles) facilitate a drastic reduction of these values at the extreme operating conditions. Figures 2 and 3 however show that ammonia (R-717) and methylene fluoride (HFC-32) are completely out of range for at least one of these criteria and would be highly penalized by increased cost.

Table 1. Physical properties, flammability, and global warming potential of selected pure refrigerants
(Calm 1998)

Refrigerant	*Molar Mass g/mol*	*NBP °C*	*Tcrit °C*	*TLV-TWA PPM*	*LFL %-vol.*	*HOC MJ/kg*	*GWP 100 years*
HFC-32	52.02	-51.7	78.1	1000	14.4	9.4	550
HFC-125	120.02	-48.1	66.0	1000	none	-1.5	3400
R-1270	42.08	-47.7	92.4	600	2.0	-	~20
HFC-143a	84.04	-47.2	72.7	1000	7.0	10.3	4300
HC-290	44.1	-42.1	96.7	2500	2.1	50.3	~20
FC-218	188.02	-36.8	72.0	1000	none	-	8600
HC-C270	42.08	-33.5	125.2	-	2.4	49.4	-
R-717	17.03	-33.3	132.3	**25**	15.0	22.5	<1
HFC-134a	102.03	-26.1	101.1	1000	none	4.2	1300
HFC-152a	66.05	-24.0	113.3	1000	4.8	17.4	120
HFC-227ea	170.03	-16.4	101.7	1000	none	3.3	3500
R-600a	58.12	-11.7	134.7	800	1.7	49.4	~20
FC-C318	200.03	-6.0	115.2	1000	none	-	10000
HFC-236fa	152.04	-1.4	124.9	1000	none	-	9400
R-600	58.12	-0.6	152.0	800	1.5	49.5	~20
HFC-236ea	152.04	6.2	139.3	-	none	3.3	1200

NBP=normal boiling point; Tcrit=critical temperature; GWP=global warming potential; TLV-TWA=ACGIH Threshold Limit Value - Time Weighted Average; HOC=heat of combustion; LFL=lower flammability limit

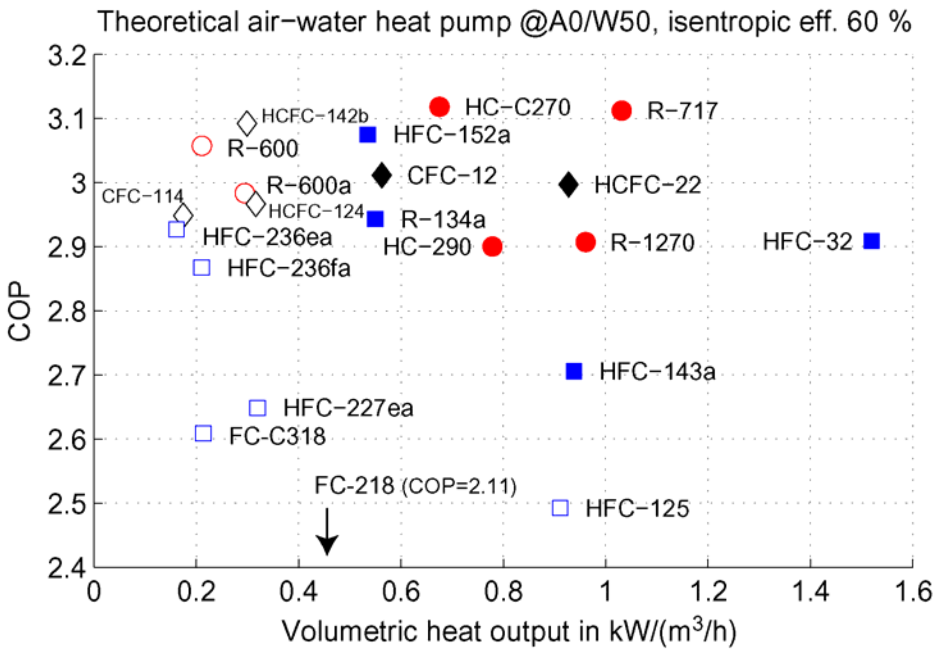


Fig. 1. Performance chart COP versus Heat output / displacement volume (theoretical heat pump at air=0°C/water=50°C), pure refrigerants. White colored markers indicate fluids, which can only be used in mixtures (NBP temperature out of range).

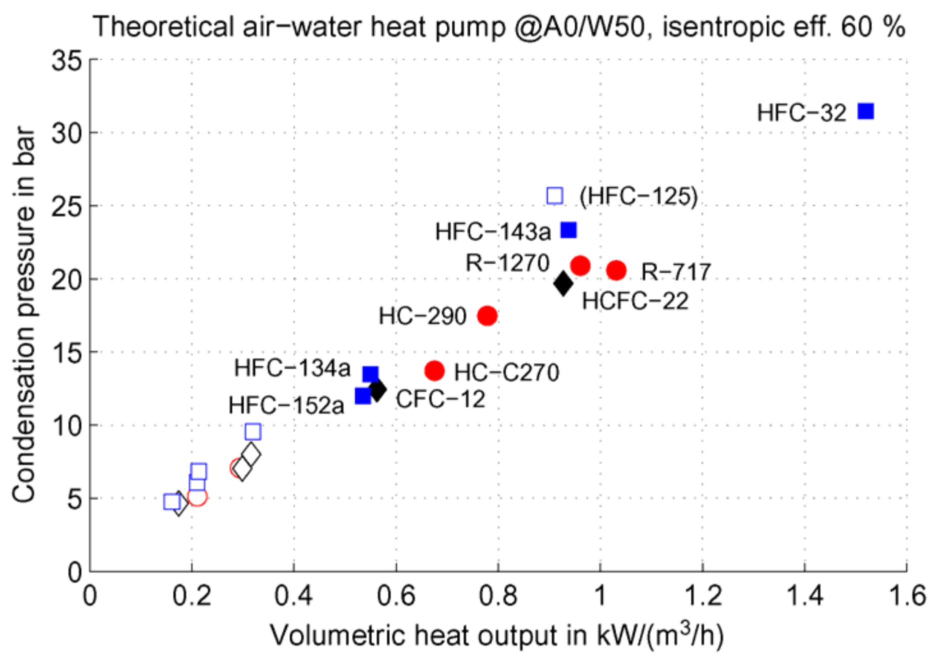


Fig. 2. Pressure level vs Heat output / displacement volume (theoretical heat pump at air=0°C/water=50°C), pure refrigerants. White colored markers indicate fluids, which can only be used in mixtures (NBP temperature out of range).

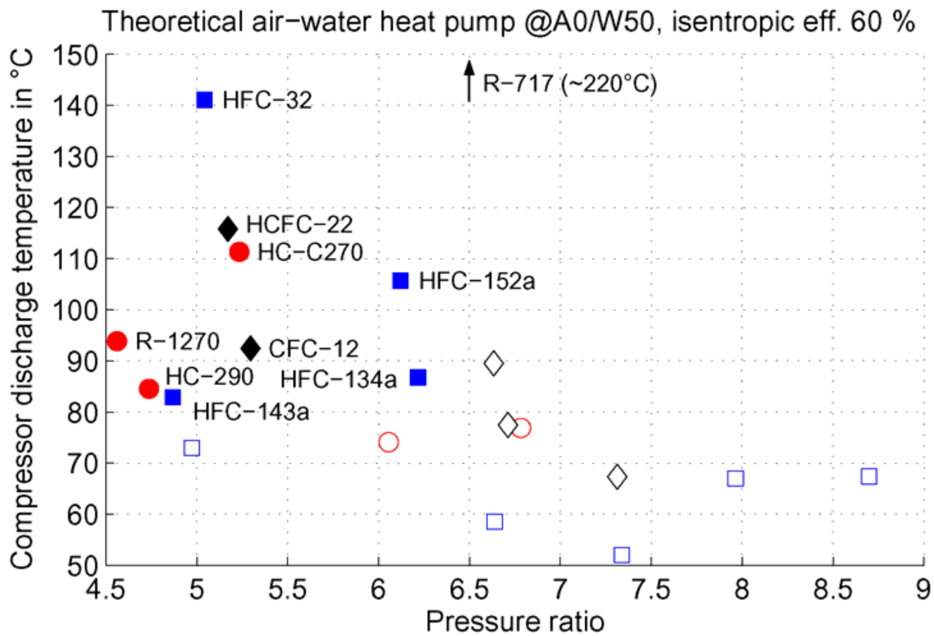


Fig. 3. Compressor discharge temperature vs pressure ratio. (Theoretical heat pump at air=0°C/water=50°C), pure refrigerants; white colored markers indicate fluids, which can only be used in mixtures (NBP temperature out of range.)

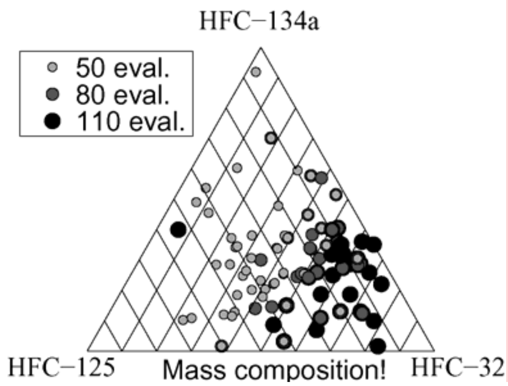
Due to either their flammability or their ozone depletion potential, most of the pure (H)CFC and HC fluids represented in Figures 1-3 have on the market specific replacement counterparts, which either are pure HFC alternatives, or especially designed mixtures, made of HFC and HC. Calculated performances of these (chlorine free) mixtures are summarized in Table 2.

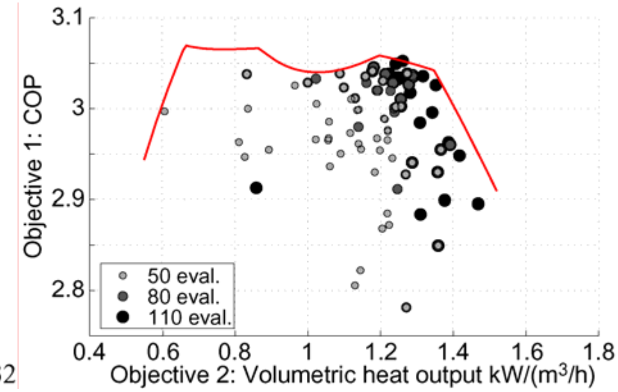
Table 2. Selected commercial refrigerant blends (HFC and HC), calculated performance data for heat pump at air=0°C/water=50°C

Refrigerant mixture name [by mass]	COP -	Heat output kW/(m^3/h)	T max. °C	P cond. bar	PR $P_{cd.}/P_{ev.}$
R-404A (HFC-125/143a/134a [44/52/4])	2.67	0.91	79.4	23.3	4.98
R-407C (HFC-32/125/134a [23/25/52])	3.00	0.95	98.6	21.2	5.30
R-407D (HFC-32/125/134a [15/15/70])	3.03	0.81	95.0	18.2	5.51
R-410A (HFC-32/125 [50/50])	2.81	1.35	107	30.7	5.00
R-413A (FC-218/HFC-134a/R-600a [9/88/3])	2.93	0.59	82.3	14.3	5.88
R-417A (HFC-125/134a/R-600 [46.6/50/3.4])	2.89	0.75	78.9	18.2	5.29
R-507A (HFC-125/143a [50/50])	2.63	0.91	78.6	23.9	4.96

5 RESEARCH OF NEW SUBSTITUTION BLENDS FOR HIGH TEMPERATURE AIR-WATER HEAT PUMPS

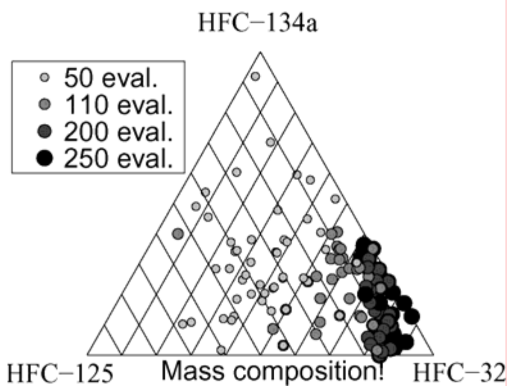
For the screening of the best combinations of known refrigerants, two distinct objectives are chosen to run in the optimization routine: **COP and volumetric heat output (which corresponds to the ratio of heat output to the displacement of the compressor)**. This trade off has been set in order to reasonably choose between size of the components and efficiency. Observing the envelope of a saturation curve it can be shown, that the two objectives are in opposition. The best COP is reached for cycles far from the critical point as well as having reduced throttling losses and the highest heat output is obtained at higher pressures and densities, therefore when the operating conditions approach the critical point.

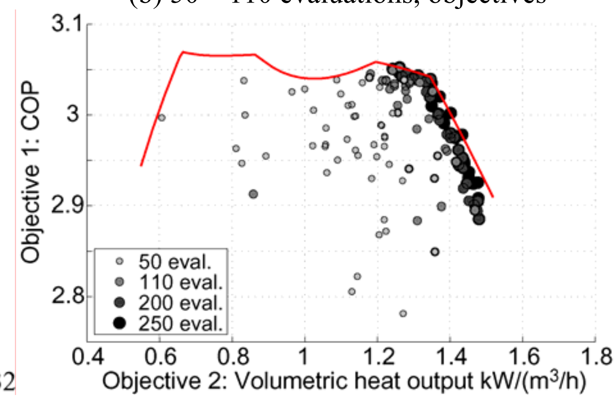




(a) 50 – 110 evaluations, mass comp.

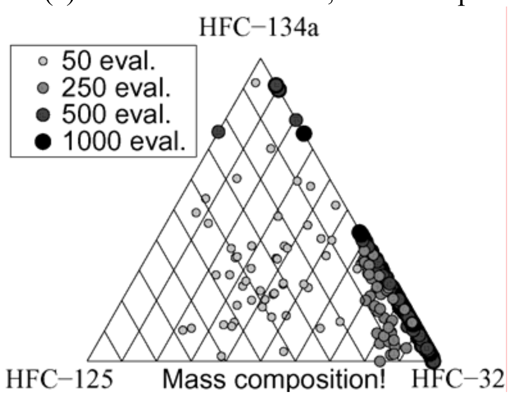
(b) 50 – 110 evaluations, objectives

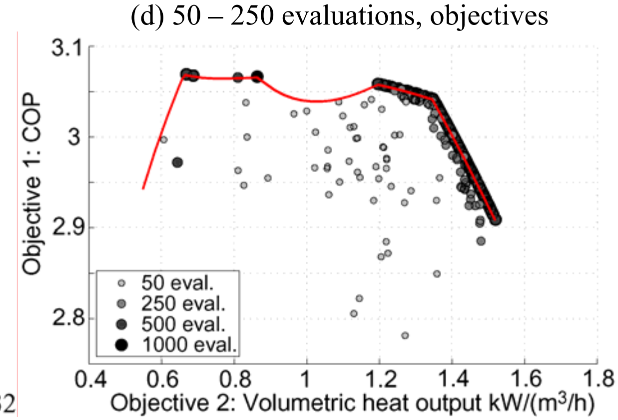




(c) 50 – 250 evaluations, mass comp.

(d) 50 – 250 evaluations, objectives





(e) 50 – 1000 evaluations, mass comp.

(f) 50 – 1000 evaluations, objectives

Figure 4. Example of a two-objective optimization (on COP and volumetric heat output of a heat pump at A0/W50) for the three component blend HFC-32/125/134a using MOO (Leyland 2002). Graphs a +b and c+d represent intermediate results, e +f includes the final population. The line in the graphs of objectives represents the binary mixing from pure HFC-32 to pure HFC-134a and corresponds to the attended limiting curve for the optimization problem.

All the locally best solutions (e.g. no better COP at one volumetric heat output and vice-versa), can be represented on a **Pareto-optimal frontier**, see (Leyland 2002). If we hypothetically limit the search to pure fluids (even if rigorously no optimization has been performed yet, but a simple selection), the Pareto-optimal frontier is composed by HC-C270, R-717 and HFC-32 (see Figure 1), followed on the second level (when the first Pareto-optimal points are removed) by HFC-142b, HFC-152a, HCFC-22 and R-1270. All of these fluids are classified as flammable according to the standard safety classification (ASHRAE 2001), with the exception of HCFC-22, which is on the way to be phased out (ODP > 0).

The multi objective and multi-modal algorithm of the selected optimization tool uses the Pareto-optimal frontier to rank new evaluated points (solutions) in relation to the existing population. Optimal points are kept and new points are generated by cross-over among couples of existing solutions and then evaluated (type of genetic algorithm). By this approach the Pareto-optimal curve evolves rapidly to a set of optimal solutions or clusters of optimal solutions depending on the setting of the problem. A major attribute of the MOO optimizer, and distinguishing it from many other tools, is the ability to treat multi variable systems with a high degree of discontinuities (such is the case, when the algorithm changes the constituents of the mixture). By the nature of this approach it is impossible to know if (all) the optimal solutions have been identified. Nevertheless selecting a large randomly composed initial population, increases the part explored in the space of the solutions and reliable repetitive results have been obtained.

Figure 4 visualizes an **example of three component blends, multi objective optimization restricting the components to the three common refrigerants, which are: HFC-125, HFC-134a and HFC-32**. Before running the optimization problem, a look on the performance chart in Figure 1, already indicated that the two refrigerants HFC-134a and HFC-32 were clearly better performing (closer to the imagined Pareto-optimal curve) than HFC-125. It was therefore very likely, that the solution space would converge to a set of binary mixtures of the first two fluids. The line in the graphs of values for the objectives represents the location of this couple with variable composition, including the limits of pure HFC-134a and pure HFC-32. This line is coinciding with the points found on the final Pareto-optimal frontier, as has been expected before. The rise of COP, comparing to the pure fluids, can be explained with the adaptation of the saturation temperature glide of the non-azeotropic blend with the external flows. In the central part of this mixing line the COP is slightly lowered, when these temperature glides are becoming too important.

When observing the final set of solutions, the best COP is at 3.07 (corresponding to the mixture composition HFC-32/134a [9/91 by mass]) and the heat output is equivalent to 0.67 kW per m^3/h displacement. Close to a doubling of the heat rate can be delivered with a mixture HFC-32/134a [76/24], at a quite similar COP level (3.04 with 1.35 kW/(m^3/h)). This increase of the heating performance has to be paid with an important increase of the condensing pressure level (from 15 bar to 26 bar) and of the discharge temperature (90°C to 125°C). And the latter of these two mixtures is considered as flammable. The limit of flammability is given at max 42% of HFC-32 at 60°C, see (Didion 1999). The recommended mixture, taking into account of all these considerations, is represented at the point (COP=3.07, volumetric heat output = 0.86 kW/(m^3/h)), given by the mixture HFC-32/134a [25/75]. Compared the commercial R-407C (HFC-32/125/134a [23/25/52]) this represents a gain of 2% on the COP and a reduction of 9% on the heat output. Looking to the existing standard mixtures for these components, the most similar blend is R-407D (COP=3.03, volumetric heat output=0.81 kW/(m^3/h)).

The next step was an **optimization applied for the total of the 17 following pure fluids**: HC-170, HC-C270, HC-290, R-600, R-600a, HC-1270, HFC-32, HFC-125, HFC-134a, HFC-143a, HFC-152a, HFC-227ea, HFC-236ea, HFC-236fa, HFC-245fa, FC-218 and FC-C318. All CFC and HCFC fluids were not considered in these calculations. Ammonia (R-717) was also disregarded, due to its combination of negative attributes: toxicity, flammability and incompatibility with copper. The thermodynamic properties of all these fluids are available in the refrigerant's properties calculation software, Refprop, Version 7 (Lemmon et al., 2002) in which many binary interaction parameters for the constitution of the blends are defined. The mixing parameters for the missing pairs are calculated based on an appropriate estimation, which is set by the software itself.

Several optimization runs were performed with up to 10'000 evaluations, for each problem. A **first run of the optimization problem has been initialized to study the optimal configurations** of mixtures with up to 4 components. As most of the high performance fluids are flammable, a **second evaluation has been started to show the impact of a limitation of the flammability of quaternary blends**. To deal with this issue a very simple approach for calculating the lower flammability limit (LFL) of an arbitrary mixture has been applied, using the molar composition of the blend and the flammability values attributed to each component according to Table 1.

$$LFL_{mix} = \sum_i \varphi_i \ LFL_i \quad \text{with } \varphi_i = \text{molar fraction of component i} \qquad \text{Eq. 1}$$

The lower flammability limit of non flammable refrigerants has been set to 100%.

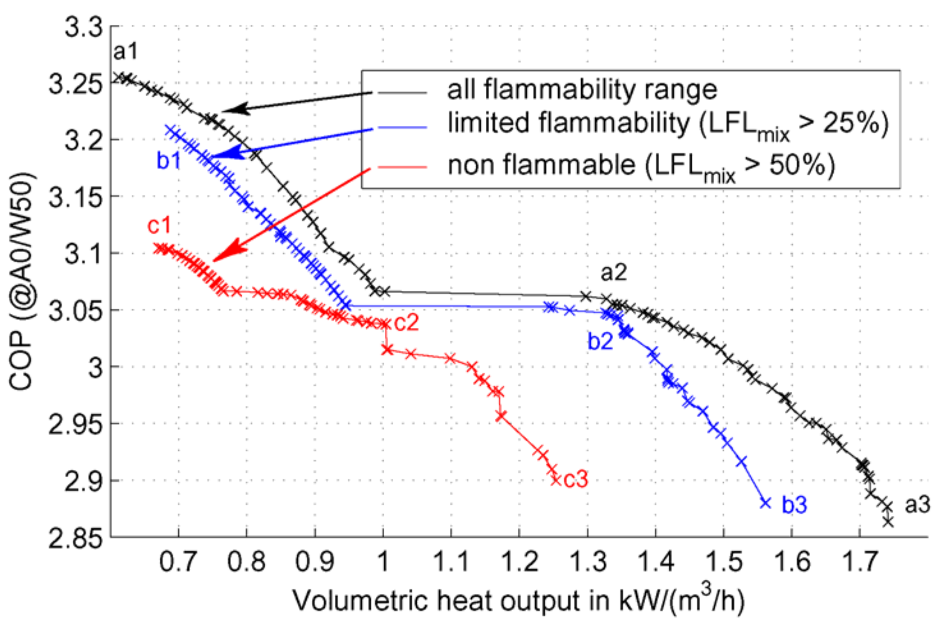


Fig. 5. Pareto-optimal frontier for a two objective optimization (COP and volumetric heat output, heat pump@A0/W50) of arbitrary refrigerant mixtures (max. 4 components, 17 selected pure fluids, using REFPROP 7). Frontiers for mixtures at distinct flammability degrees indicated.

Figure 5 with the extracted data in Table 3 shows the **importance of accounting for the flammability limit as a parameter**. In the **third optimization run, a minimum flammability limit of 50% (curve c1-c2-c3) for the mixture is set, using Eq. 1**. These fluids are considered to be non-flammable. The maximum attainable COP is at 3.10, which corresponds to a relative improvement of 3% compared to the reference fluid R-407C. The heat output is however sensibly reduced. Point c2 corresponds to the mixture HFC-32/134a, with the same mass concentrations, as in the run before. Performances of this mixture are very similar to R-407C. The other end of the Pareto-optimal curve corresponds to a ternary mixture with a higher heat output but a reduced COP.

The end points of the Pareto-optimal frontiers represent the best solutions in COP and in heat output, respecting the required saturation temperature range. The highest COP of 3.26 (+8% compared to R-407C) is given at the point a1. In this region all the solutions are mainly composed of the highly flammable hydrocarbon **cyclopropane (HC-C270)**, which has already been considered in some comparative studies before, see (Ghodbane 1999, Granryd 2001), in the context of automotive air-conditioning systems. Measured efficiency comparisons including cyclopropane are published by (Kim et al. 1993), showing improved efficiency of 6% - 7% compared to CFC-12 in a domestic refrigerator. The very low volumetric heat outputs of these mixtures require an increased size of the component, which is a major problem for designing systems with high safety requirements. On the opposing end of the performance graph, the major component of the mixtures identified is **HFC-32**. The operation conditions end up in the upper pressure range leading to increased wall thickness in the heat exchangers, which might have a slightly negative impact on heat transfer characteristics.

Table 3. Refrigerant mixture composition (mass percentage) for the solutions selected in Fig. 5.

	Refrigerants	Composition	COP	Heat in kW/(m³/h)
a1	HC-C270/600	85/15	3.26	0.61
a2	HFC-32/134a/152a	3/80/17	3.06	1.32
a3	HFC-32/HC-1270/HFC-134a	82/15/3	2.88	1.74
b1	HC-C270/HFC-134a/245fa	55/18/27	3.21	0.69
b2	HFC-32/134a	76/24	3.04	1.35
b3	HFC-32/125/HC-1270/HFC-134a	60/20/10/10	2.88	1.56
c1	HFC-125/HC-C270/HFC-134a/152a	16/6/47/31	3.10	0.67
c2	HFC-32/134a	40/60	3.04	1.00
c3	HFC-32/125/236ea	37/58/5	2.90	1.26

This evaluation of new refrigerant mixtures for air-water heat pumps in residential applications shows the potential of improvement of the performances (COP and heat output) compared to standard refrigerants. The research of alternative mixtures is also motivated by the environmental aspect, in order to reduce the **total equipment warming impact (TEWI)** of the chosen heating system, (Fischer et al. 1992). This warming impact is attributed in general for a minor part to the equipment and refrigerant leakage, and for a major part to the related energy consumption, depending on the production mix of the electricity grid. For completeness it is important to mention that, in order to enforce a reduction of the environmental impacts of refrigerants policy makers in several countries are committing to the use of natural refrigerants. This fact goes beyond the scope of this study as it considerably restricts the choice of refrigerants to only a few hydrocarbons and their mixtures, ammonia and CO_2.

A calculation example shows the importance of the highlighted parameters, on the evaluation of the TEWI indicator.

$$TEWI = GWP\ \dot{L}\ n_{years} + GWP\ M_{refr}\left(1-\alpha_{rec}\right) + n_{years}\ E_{el,ann}\ \beta_{em} \qquad \text{Eq. 2}$$

The first two terms of Equation 2 are direct contributions (leakage and recovery losses), while the third term on the right hand side is an indirect contribution, related to the CO_2 emission linked to electricity production.

A residential heating application with an annual heat demand of $E_{th,ann}$ = 20'000 kWh, implementing a heat pump system characterized by a seasonal COP of 2.5, a refrigerant charge M_{refr} of 5 kg[3] and with a life time n_{years} of 20 years, is assumed. Annual leakage rate is set to L = 1% of the refrigerant charge[4] and refrigerant recovery is about α_{rec}= 90%. With these assumptions, about 30% of the initial refrigerant charge is lost in the running period of the heat pump unit.

The CO_2 equivalent emission contributions of three refrigerants with distinct GWP100 values are compared in Table 4 ($GWP_{R\text{-}407C}$ = 1520 $CO_{2,eq.}$; $GWP_{Mix\ Point\ b1}$[5] = 500 $CO_{2,eq.}$; $GWP_{HC\text{-}290}$ = ~20 $CO_{2,eq.}$). This theoretical evaluation shows the approximate COP gains, which should be achieved to reduce the equivalent CO_2 emissions. For entirely fossil fuel based power production or for the European power mix, the direct emissions caused by refrigerant losses, are negligible compared to the indirect emission from the power plants. Only for countries like Switzerland, where electricity is mainly made of a

[3] For residential heating air-water heat pumps, the typical refrigerant charge is about 0.5 kg/kWth, see (WPZ 1993-2003).
[4] Ranging from 0.6% to 1.9%, see study CH4 in (Gilli et al. 1999).
[5] Composition of this mixture, see Table 3.

combination of nuclear-power (0.025 kg CO_2/kWh) and hydro-power (0.04 kg CO_2/kWh), the direct contributions are significant for all HFC refrigerants. In the latter case natural refrigerants contribute to a significant reduction of the equivalent CO_2 reductions.

Table 4. Direct and indirect CO_2 contributions for small size heat pump, assuming 1.5 kg of non-recovered refrigerant, an annual electricity consumption 8'000 kWh with β_{em} = 0.8 kg CO_2/kWh (fossil power plant), 0.5 kg CO_2/kWh (European electricity mix), 0.025 kg CO_2/kWh (nuclear power).

Considered time period 20 years.

$TEWI_{direct/indirect}$	with β_{em} = 0.8 kg CO_2/kWh	0.5 kg CO_2/kWh	0.025 kg CO_2/kWh
R-407C	2%/98%	3%/97%	36%/64%
Mix (Point b1)	<1%/99%	~1%/99%	16%/84%
HC-290	0%/100%	0%/100%	<1%/99%
$TEWI_{total}$	in T $CO_{2,eq.}$	T $CO_{2,eq.}$	T $CO_{2,eq.}$
R-407C	130	82	6.28
Mix (Point b1)	129	81	4.75
HC-290	128	80	4.03

6 CONCLUSIONS

The optimization approach used to evaluate new refrigerant compositions in high temperature lift air-water heat pumps for the residential sector, has demonstrated the performance increase potential on a semi theoretical simulation. The following conclusions can be formulated:

- **Rise in COP**

  An important elevation of the COP (+8% compared to R-407C) has been calculated at the operating point A0/W50. This improvement can be achieved mainly when using the highly flammable, but thermodynamically favorable cyclopropane (HC-C270). The heat output intensity is however reduced by an important factor (-36% compared to R-407C). The mixture identified and corresponding to this calculated optimum is exclusively composed of hydrocarbons and results in a very low direct global warming impact. Reducing the flammability tolerance, then the mixtures found with high COP, have higher GWP values (point b1: GWP_{mix} = 500, c1: GWP_{mix} = 1200), which are typical values for HFC refrigerants.

- **Rise in heat output**

  Compact systems with a high volumetric heat output are obtained with the mixtures containing mainly HFC-32 (highest heat output + 83% compared to R-407C). Flammability, lower COP and higher operating pressures are the major drawbacks to using such refrigerants.

- **Global warming impact**

  Residential heat pumps are in general compact systems with refrigerant leakage range tending to zero. The equipment global warming impact, calculated for several refrigerant combination is only marginally sensitive to refrigerant losses and is essentially dependant on the seasonal coefficient of performance of the heating unit. One exception to this is the case of heating systems, which are predominantly based on 'CO_2 free' electricity (produced by nuclear or hydro, wind and solar power plants).

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