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ABSTRACT

The TEWI analysis of residential heat pumps shows that it is sensitive to refrigerant emissions and mainly dependent on the seasonal coefficient of performance of the heating unit. Otherwise for countries where electricity is mainly produced by a combination of nuclear-power and hydro-power, the direct emissions become not negligible compared to the indirect emissions.
Both direct and indirect emissions must then be considered. The selection of new refrigerant candidates will depend on climatic conditions, the refrigerant global warming potential, the refrigerant safety and many other criteria such as the COP, the volumetric capacity and system operating pressures and temperatures.
This paper presents a new method for the selection of refrigerant blends based on a series of selection criteria. The flammability analysis is based on experimental data of flammability limits and theoretical heat of combustion calculations. The chemical reactions are also introduced. The RF-number introduced by Kondo as an index for flammability classification is used. This method is applied to retrofit applications of air-to-water heat pumps installed for moderate temperatures hydronic heating systems (55°C-45°C). Alternative blends are compared to R-407C. A first general evaluation shows a few number of refrigerant blends with flammable and non flammable refrigerants. A second more restricted evaluation shows some other blends with slightly flammable candidates.

1. INTRODUCTION

Refrigerant choices have been radically changed by the Montreal Protocol, which is leading to a progressive and complete phase-out of chlorinated substances. Moreover, the application of the Kyoto Protocol – especially in Europe – leads to uncertainties on the refrigerant choices for the long term. Interest is increasing on the possible use of ‘moderately’ flammable refrigerants or refrigerant blends due to the lower GWP of molecules having lower fluorine content or higher hydrogen content. The phase-out of CFC and HCFC refrigerants led to the introduction of new refrigerants. The most common refrigerant used in heat pumps produced in Europe today is R-407C, although R-404A, R-134a, and at a lower extent R-290 are also used.

Several papers deal with refrigerant selection and refrigerant mixture alternatives to replace CFCs and HCFCs. Some authors propose a balance between the various factors, namely ODP, TEWI, toxicity, flammability, performance characteristics, and cost (Didion and Brown, 2000). A more recent study has focused on screening refrigerant blends in high temperature heat pumps for retrofit applications (Zehnder and Favrat, 2004) with a multi-objective optimization algorithm and a simple approach for calculating the lower flammability limit of refrigerant mixtures have been used, with targeted COPs and specific heat capacitys. Their results show that all the interesting solutions include flammable refrigerants.
The method presented in this paper allows the screening of refrigerants blends by superposing refrigerant selection criteria. The approach used for the flammability classification is detailed in the next section.

2. FLAMMABILITY CLASSIFICATION AND CALCULATIONS

HCs such as R-290 and HFCs such as R-32, and R-152a have been considered as alternative refrigerants for CFCs and HFCs because of their zero ODP and relatively low GWPs. However, their applications are limited because of their flammability. An understanding of their flammability and possible mitigation by non-flammable components is important for the development of new blends.

ASHRAE Standard 34 has been continuously updated for ten years to integrate both improved test methods and the use of new refrigerants and blends. The classification is based on the heat of combustion (HOC) of complete reaction of the refrigerant and on the measurement of the lower flammability limit (LFL). However, ASHRAE classification is not totally consistent and new indexes or physical properties have been introduced for the classification : the ignition probability *RF-number* (Kondo, 2002) and the burning velocity (Jabbour and Clodic 2004).

In the present paper, the RF-number is used as an index for flammability classification. The RF-number is calculated by:

$$RF = \frac{(UFL \times LFL)^{0.5} - LFL}{LFL} \times \frac{Q}{M} \qquad (1)$$

Where Q is the heat of combustion in KJ/mol and M the molecular weight.

The determination of flammability limits and of the heat of combustion of the refrigerant mixtures are necessary for the calculation of RF-number. The use of RF-numbers allows the classification of materials in more detail, those with RF-numbers less than 30 are classified to *moderately flammable*, and those higher than 30 are *strongly flammable*. The refrigerants that do not show flame propagation are considered non-flammable.

2.1 The Flammability Limits estimation (LFL And UFL)

It is possible to determine the flammability limits (LFL and UFL) of mixtures of several flammable gases using 'Le Chatelier' rule. However, for gas mixtures containing both flammable and non-flammable components, it is not easy to accurately predict those limits. These values have rather to be measured experimentally.
In this paper, the approach presented by Yang Zhao (Zhao, 2004) is used for *estimating the flammability limits of refrigerant mixtures*. The model proposed in this reference is based on experimental data of the binary mixtures involved, composed of one flammable component and one non-flammable component, and can be applied to any mixtures, with no limitations to the number of flammable and non-flammable components.
For mixtures of three components composed of *one flammable and two non-flammable* or *two flammable and one non-flammable components*, a *critical flammable line* will result separating a ternary composition diagram in two zone: flammable zone and non-flammable zone. Experimental results for lower flammability limit and upper flammability limit of binary mixtures, as a function of the ratio of non flammable to flammable gas, are fitted with polynomial equations and are used in the method of choice.

2.2 The Heat Of Combustion calculation (HOC)

The heat of combustion *(HOC)* for the involved chemical reactions is also introduced. The heat of combustion is the enthalpy of formation of the reactants minus the enthalpy of formation of the products of reaction. Values for heats of formation are tabulated in several handbooks and databases of chemical and physical properties. Calculated values shall be based on the complete combustion of one mole of refrigerant with the oxygen volume necessary for a stoichiometric reaction.
The heat of combustion calculation requires the knowledge of the stoichiometric reactions. If more than one substance is part of the combustion process with the oxidant, regardless of whether this substance is flammable or not, it is assumed that all these substances contribute to the blend fuel.
All pure refrigerants selected for this study have their molecules composed of H, F and C atoms. The complete, stoichiometric equation of combustion reaction of refrigerant blends of $C_nH_mF_p$ refrigerant molecular structure, depends on the ratio of the number of atom H to the number of atom F in the molecule of the reactants.

As indicated by Takizawa (Takizawa, 2005), the reactants and the combustion products shall be assumed to be in the gas phase. The combustion products shall be HF, CO_2 and HCl, if there is enough hydrogen in the molecule. Excess

H shall be assumed to be converted to H_2O. If there is insufficient hydrogen available for the formation of HF and HCl but sufficient to form HF, then the formation of HF takes preference over the formation of HCl. If there is insufficient hydrogen available for the formation of HF, then the remaining F produces COF_2 or CF_4 in preference to the formation of CO_2. The remaining Cl produces Cl_2.

- *for H/F of less than 1, the reaction produces CO_2, HF, COF_2, CF_4 and N_2.*
- for H/F of more than 1, the reaction produces CO_2, HF, H_2O and N_2.

The stoichiometric reaction of a mixture composed of ***A*** ($C_{n1}H_{m1}F_{p1}$), ***B*** ($C_{n2}H_{m2}F_{p2}$), ***C*** ($C_{n3}H_{m3}F_{p3}$) and CO_2 can be expressed by:

$$V_1 .\ C_{n1}H_{m1}F_{p1} + V_2 .\ C_{n2}H_{m2}F_{p2} + V_3 .\ C_{n3}H_{m3}F_{p3} + V_4 .\ CO2 + D.\ (O2 + 3{,}76\ N2) \rightarrow a.\ CO2 + b.\ HF + c.\ CF4 + d.\ COF2 + e.\ H2O + f.\ N2$$

In the present paper, *Microsoft Excel Solver*[1] coupled to the method of choice tool is used to determine reaction products and reaction coefficients of the combustion of refrigerant mixtures. The heat of combustion is then calculated using the heat of formation of the reactants and products.

3. DESCRIPTION OF THE REFRIGERANT SELECTION METHOD

A new method of selection and optimization of refrigerant mixture choice has been developed aiming at finding new candidates, non-flammable or moderately flammable and non toxic. This method allows, starting from a certain number of pure refrigerants, the calculation of all the possible mixtures (up to 4 pure components), and allows the organization of the various mixtures obtained in groups according to the selection criteria.

Conventional one-stage and Economizer two-stage heat pump cycles are introduced in this method for the calculation of performances. Simulation conditions for air and water entering or leaving the evaporator and condenser are fixed and pinch-based heat exchanger models are used. The compressor efficiency values can be either constant or fitted with polynomial regressions.

The method is programmed in Visual Basic language under Microsoft Excel sheets to allow a simple and fast communication with the fluid properties program REFPROP version 7.

3.1 The refrigerant selection method applied to residential heat pumps

Two-stage heat pumps used with a moderate temperature hydronic heating system (55 °C / 45 °C) allows a substantial gain of seasonal performance due to the absence of the supplement electrical heating resistances needed at the peak demand period. A two-stage reversible air-to-water heat pump for combined space heating and domestic hot water production has been developed and tested at the *CEP*[2] (Rahhal and Clodic, 2005). R-407C is first used and the new heat pump has shown high performances and substantial reduction of greenhouse gas emissions compared to conventional one-stage heat pump, and gas and fuel boilers. The refrigerant selection method is then used for screening the best appropriate refrigerants for this application.

3.2 Aspects and constraints

The pressure level and the discharge temperature are indicators for potentially increased system cost and for reliability. Maximum system pressure has a direct impact on the manufacturing costs of heat pumps. High pressure levels require non standard elements. In addition, maximum system temperature is limited by the thermal stability of the lubricant. Limiting the maximum system temperatures will generally have a positive impact on the compressor lifetime.
Compatibility with materials, safety properties, availability and prices are also other aspects that must be considered for the evaluation of new refrigerant candidates. Table 1 presents the constraints and the simulation conditions for the selected application under French cold climatic conditions. The criteria and restrictions can be chosen with reference to a selected refrigerant performances or to some technical and economical constraints.

[1] Microsoft Excel Solver is a complementary Macro to calculate solutions for scenarios of simulation on the basis of constraints
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Table 1 . Constraints and simulation conditions of the selected application (Cold France climate)

Air-water heat pump for space heating application	Constraints and simulation conditions	Descriptions and comments
Water at condenser, Water supply temperature	Water : moderate Heat curve [a] (-15°C/55°C, +15°C/28°C)	Hot water demand conditions
Air temperature at the evaporator Inlet and Outlet	Air: 5 °C / 0 °C	Most important heat requirements conditions
Flammability	Non-flammable or moderately flammable	Safety
GWP	GWP < GWP R-407C (1653)	Direct CO_2 emissions
Maximum system pressure	< 3 MPa (@ 55 °C)	Impact on system cost
Lowest pressure at evaporator	@Air (-15°C / -20 °C) > 0.1 MPa	Aspiration constraint
Compression ratio	1.5 < CR < 6.5	Impact on system performance
Maximum system temperature	< 130°C	Impact on lubricant thermal stability and compressor lifetime
Coefficient of performance (COP)	≥ COP R-407C	Impact on energy cost and indirect CO_2 emissions
Volumetric heat capacity [b]	≥ Vol. Heat capacity R-407C	Impact on system cost and size

a- The heat curve, is characterizing the required temperature by the heating system to the circulating heating water
b- The volumetric heat capacity corresponds to the ratio of heat capacity to the displacement of the compressor

3.3 Selection of pure refrigerants

All pure refrigerants selected in this study are chlorine free and non toxic refrigerants. Ammonia is excluded from the evaluation due to its high toxicity and incompatibility with copper. CO_2 (R-744) is only introduced for the evaluation of refrigerant blends (trans-critical cycles are not considered in this work). Refrigerant candidates that fit the application are listed in Table 2 from the lowest to the highest GWP value and their respective calculated performances are plotted in Figure 1 and Figure 2.

Table 2 . Selected characteristics of pure refrigerants

Refrigerant Number		Chemical Name	MW [g/mol]	Tcrit [°C]	Pcrit [kPa]	NBP [°C]	GWP [100 years]
CO_2	**R-744**	carbon dioxide	44.00	30.97	7104.15	-78.40	1
HC	**R-290**	propane	44.09	96.67	3973.94	-42.09	20
HC	**R-1270**	propylene	42.08	92.42	4391.45	-47.69	20
HFC	**R-152a**	1,1-difluoroethane	66.05	113.26	4243.60	-24.02	120
HFC	**R-32**	difluoromethane	52.02	78.10	5508.85	-51.65	550
HFC	**R-245ca**	1,1,2,2,3-pentafluoropropane	134.04	174.42	3651.85	25.13	640
HFC	**R-236ea**	1,1,1,2,3,3-hexafluoropropane	152.03	139.29	3228.83	6.19	1200
HFC	**R-134a**	1,1,1,2-tetrafluoroethane	102.03	101.06	3786.13	-26.07	1300
HFC	**R-125**	pentafluoroethane	120.02	66.02	3344.55	-48.09	3400
HFC	**R-227ea**	1,1,1,2,3,3,3-heptafluoropropane	170.02	101.65	2652.85	-16.45	3500

MW : Molecular Weight ; Tcrit : critical temperature ; Pcrit : critical pressure ;NBP : Normal Boiling Point ; GWP : Global Warming Potential

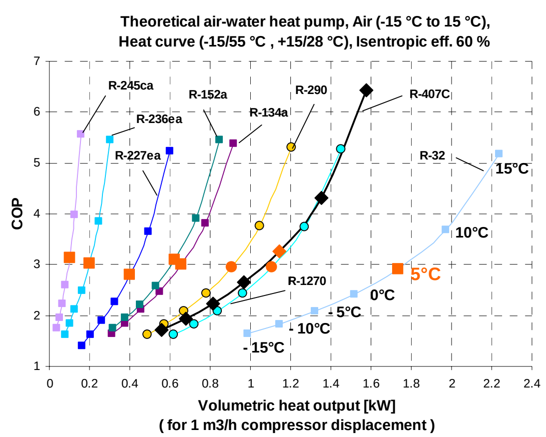

Figure 1 : Performance chart COP vs Volumetric Heat Capacity, pure refrigerants.

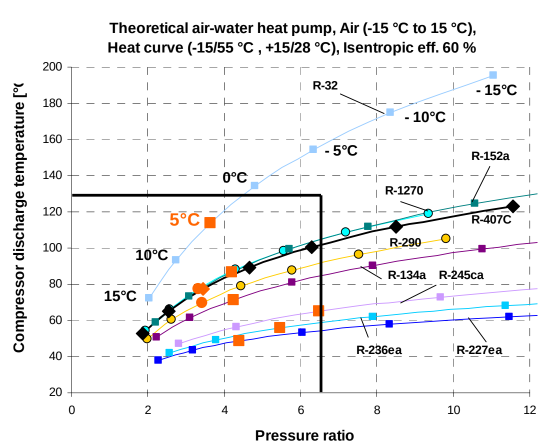

Figure 2 : Compressor discharge temperature vs pressure ratio, pure refrigerants.

R-407C shows better performance than pure refrigerants. The COP increase (Figure 1) can be explained by the adaptation of the saturation temperature glide of the non-azeotropic blend to the external flows.
When considering the energy demand during the whole heating season, the most important heat requirements according to the outdoor temperature, are seen at moderate operating conditions. For a French cold climate (such as in NANCY), the most frequent temperatures are close to 5°C (50 % for the interval 1°C to 7°C). This temperature has bee chosen for the new mixture screening.
When observing Figure 2, all refrigerants, with the exception of R-32, have acceptable discharge temperatures; some show very high compression ratio with respect to the outdoor air temperature (R-236ea, R-245ca). The two black lines plotted show the maximum acceptable values for the compressor discharge temperature and pressure ratio and therefore define when the two-stage heat pump cycles are needed.

4. RESULTS AND DISCUSSIONS

4.1 A first general evaluation without flammability classification

In this first evaluation, having the objective to identify candidates likely to replace R-407C, the water supply temperature is fixed to 55°C. This choice of the water supply temperature allows a first evaluation of the pressure level at the condenser without influencing too much the classification of the COP and of the volumetric heat capacity compared to the reference fluid R-407C. Figure 3 shows the application scheme where the classification at the level of the volumetric heat capacity and the COP is made with reference to R-407C. Each of the final groups ***(G1 to G16)*** contains the list of mixtures verifying the defined criteria. For example, ***G1*** group contains the highest efficiency blends.

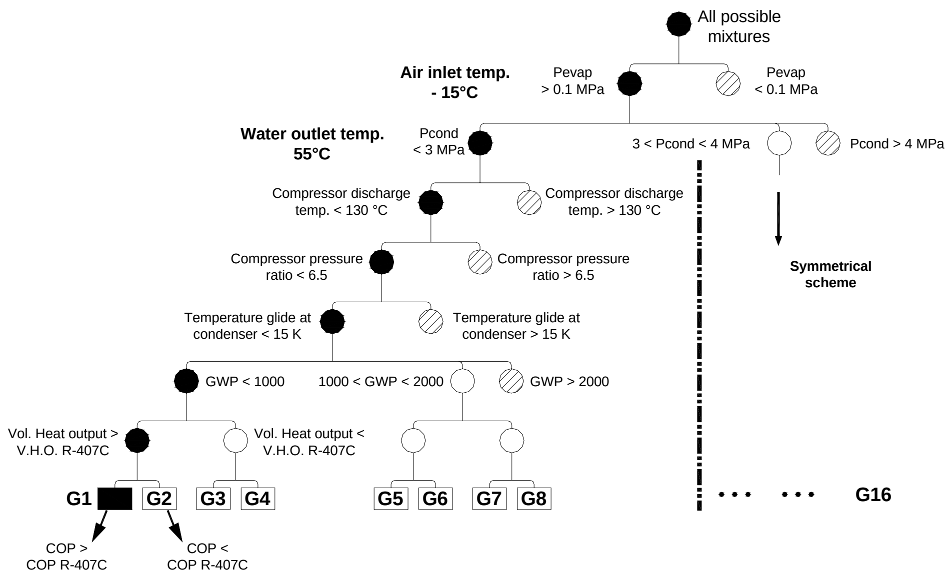

Figure 3 : An example scheme of the choice method of refrigerant mixtures

Among the classified mixtures, 74 % have pressures at the condenser lower than 3 MPa and 26 % have pressures between 3 MPa and 4 MPa. Only 0.64 % are classified in G1 group and are mainly composed of flammable refrigerants. For a water supply temperature of more than 75°C, the number of mixtures verifying the way of G1 group tends to zero. A very limited number of mixtures verifies the criterion of the condensing pressures higher than 3 MPa, and a COP and volumetric heat capacity higher to those of R-407C. Tables 3 to 6 present the selected mixtures according to the pressure level.

Table 3 . Optimized mixtures as a function of COP, Vol. Heat Cap. and GWP ***(Pcond < 3 MPa, groups G1 to G8)***

Mixtures		**Molar composition**	**COP (% gain R407C)**	**Vol. heat capacity (% gain R-407C)**	**GWP**
R-32 / R-152a / R-236ea / R-245ca	**(Max COP)**	6.6 / 88.5 / 2.3 / 2.6	(8.60 %)	(-38.26 %)	221
R-32 / R-125 / R-152a / R-227ea	**(Max Vol. heat cap.)**	70.1 / 5.1 / 23.0 / 1.8	(3.11 %)	(28.73 %)	875
R-744 / R-1270	**(Min GWP)**	4.8 / 95.2	(-3.06 %)	(12.82 %)	19

Table 4 . Optimized mixtures as a function of COP, Vol. Heat Cap. and GWP ***(3 < P cond < 4 MPa, groups G9 to G16)***

Mixtures		**Molar composition**	**COP (% gain R407C)**	**Vol. heat capacity (% gain R-407C)**	**GWP**
R-32 / R-125 / R-134a / R-152a	**(Max COP)**	71.3 / 2.6 / 12.1 / 14.0	(3.14 %)	(28.96 %)	778
R-744 / R-32 / R-125 / R-227ea	**(Max Vol. heat cap.)**	7.2 / 79.2 / 7.9 / 5.7	(-4.75 %)	(57.73 %)	1392
R-744 / R-1270	**(Min GWP)**	14.4 / 85.6	(-9.64 %)	(34.85 %)	17

Table 5 . Optimized mixtures as a function of COP, Vol. Heat Out. and GWP ***(group G1)***

Mixtures		**Molar composition**	**COP (% gain R407C)**	**Vol. heat capacity (% gain R-407C)**	**GWP**
R-32 / R-134a /R-152a	**(Max COP)**	46.6 / 2.9 / 50.5	(5.84 %)	(0.28 %)	351
R-32 / R-125 / R-152a / R-227ea	**(Max Vol. heat cap.)**	70.1 / 5.1 / 23.0 / 1.8	(3.11 %)	(28.73 %)	875
R-32 / R-1270 / R-152a	**(Min GWP)**	4.9 / 55.7 / 39.4	(0.18 %)	(2.96 %)	96

Table 6 . Optimized binary and ternary mixtures as a function of COP ***(group G1)***

Mixtures		**Molar composition**	**COP (% gain R407C)**	**Vol. heat capacity (% gain R-407C)**	**GWP**
Binary mixtures					
R-32 / R-134a	**(Max COP)**	56.7 / 43.3	(3.13 %)	(10.16 %)	1000
Ternary mixtures					
R-32 / R-134a / R-152a	**(Max COP)**	46.6 / 2.9 / 50.5	(5.84 %)	(0.28 %)	351
R-32 / R-290 / R-152a	**(Max COP)**	44.8 / 6.6 / 48.6	(1.29 %)	(4.79 %)	287
R-32 / R-125 / R-152a	**(Max COP)**	46.8 / 2.5 / 50.7	(5.38 %)	(2.17 %)	456
R-32 / R-1270 / R-152a	**(Max COP)**	5.1 / 50.5 / 44.4	(1.68 %)	(1.53 %)	101
R-32 / R-152a / R-227ea	**(Max COP)**	52.4 / 45.8 / 1.8	(4.89 %)	(4.58 %)	482
R-32 / R-134a / R-236ea	**(Max COP)**	71.3 / 26.5 / 2.2	(2.97 %)	(24.7 %)	882

The highest COP, with a relative improvement of 8.6 %, is observed with a quaternary mixture composed of R-32, R-152a, R-236ea, and R-245ca. The heat capacity is however reduced of 38.2 % compared to the reference fluid R-407C (Table 3). A maximum gain on the heat capacity of 57.7 % is observed with the mixture (R-744/R-32/R-125/R-227ea). This corresponds to a decrease of the COP of 4.7 %, a GWP of 1392 and a pressure level at the condenser higher than 3 MPa (Table 4). For the most optimized G1 group (Table 5), the mixture (R-32/R-134a/R-152a) presents the highest value of COP with an improvement of 5.8 %. For this group, the lowest GWP blends are mainly composed of the highly flammable hydrocarbon propylene (R-1270). For GWP values lower than 1000, other binary and ternary mixtures composed mainly of R-32 and R-152a, and showing a gain on the COP and on the heat capacity, are listed in Table 6. In next section, these mixtures are analyzed in a restricted evaluation including flammability classification.

4.2 A second restricted evaluation with flammability classification

As most of the high performance fluids contain flammable components, a second more restricted evaluation has been performed to study the impact of the flammability classification on some potential ternary mixtures.
The selection method allows the determination of iso-properties concentrations for COP, volumetric heat capacity, GWP and of pressure level at condenser. These lines are plotted on a same diagram of composition compared to R-407C (Figures 4). The intersection between the various zones of gain allos the identification of the optimal compositions.

➢ ***R-407 blends (R-32/R-125/R134a)***

The shaded zone (Figure 4-a) corresponds to a GWP lower than the R-407C one, a gain on the heat capacity, a higher COP and an acceptable pressure level. Binary mixtures composed of R-32 and R-134a can then be optimized to satisfy the selection criteria.
As an example, the non-flammable mixture "Mix1t[3]" (R-32/R134a) = (32.5/67.5) is characterized by:

- a temperature glide > 0.3 K compared to R-407C,
- an equal volumetric heat capacity,
- a lower discharge pressure compared to the system with R-407C,
- a gain of the COP of 4.1 %.

[3] "t" denotes blends having close heat capacity similar to the one of R-407C

Table 7 . Optimization of R-407 blends (R-32/R-125/R134a) optimization

Mixtures		Molar composition Mass composition	COP (5/38°C) (% gain R407C)	Vol. Heat capacity (5/38°C) (% gain R-407C)	GWP	RF number	*Pcond
R-32 / R-134a	**Mix1t***	48.6/51.4 32.5/67.5	4.11 (2.86 %)	1.11 (-1.48 %)	1056	0	2.33
R-32 / R-134a	**Mix2**	76.5/23.5 62.5/37.5	4.06 (1.62 %)	1.43 (26.51 %)	831	1.77	2.98

***Pcond** corresponds to a water supply temperature of 55°C, **"t"** denotes blends having close heat capacity close to the R-407C one

Other slightly flammable mixtures (RF-number = 1.77) like "Mix2" (R 32/R134a) = (62.5/37.5) having a GWP of 831 can be selected to reduce system cost and size. Comparing to the R-407C, this represents an significant gain of 26 % on the heat capacity. With conventional technologies of scroll compressors, water supply temperatures higher than 75°C are acceptable only in a very limited zone of the diagram. This zone presents high compositions of R-134a and considerable reductions of the heat capacity and the COP. When comparing R-407 blends, R-407C can be considered as a quite acceptable fluid for air-water heat pumps in residential applications since the surface of the zone of gain compared to R-407C is relatively small.

➢ ***Other potential candidates***

Other identified binary mixtures "Mix3", which flammability is close to that of R-152a, corresponds to the highest value of COP with an improvement of 5.1 % compared to R-407C (Figure 4-b). The shaded zone corresponds to a GWP lower than 500, a greater heat capacity and a higher COP compared to the reference fluid R-407C.
The mixtures composed of (R-32/R-134a/R-152a) present strong interests in term of COP and GWP values. For compositions verifying equal heat capacity compared to R-407C; Mix4t, Mix5t, and Mix6t show the influence of decreasing GWP on the flammability classification degree.

Table 8 . Other potential candidates

Mixtures		Molar composition Mass composition	COP (5/38°C) (% gain R407C)	Vol. Heat capacity (5/38°C) (% gain R-407C)	GWP	RF number	*Pcond
R-32 / R-152a	**Mix3**	18.3/81.7 15.0/85.0	4.20 (5.12 %)	0.79 (-30.36 %)	184	13.35	1.64
R-32 / R-134a / R-152a	**Mix4t***	51.9/37.1/11.0 37.5/52.5/10.0	4.10 (2.74 %)	1.14 (0.94 %)	900	0	2.37
R-32 / R-134a / R-152a	**Mix5t***	56.1/9.0/34.9 47.5/15.0/37.5	4.06 (1.56 %)	1.16 (2.36 %)	501	7.43	2.40
R-32 / R-152a	**Mix6t***	53.4/46.5 47.5/52.5	4.06 (1.66 %)	1.13 (-0.51 %)	324	9.56	2.33

***Pcond** corresponds to a water supply temperature of 55°C, **"t"** denotes blends having heat capacity close to the R-407C one

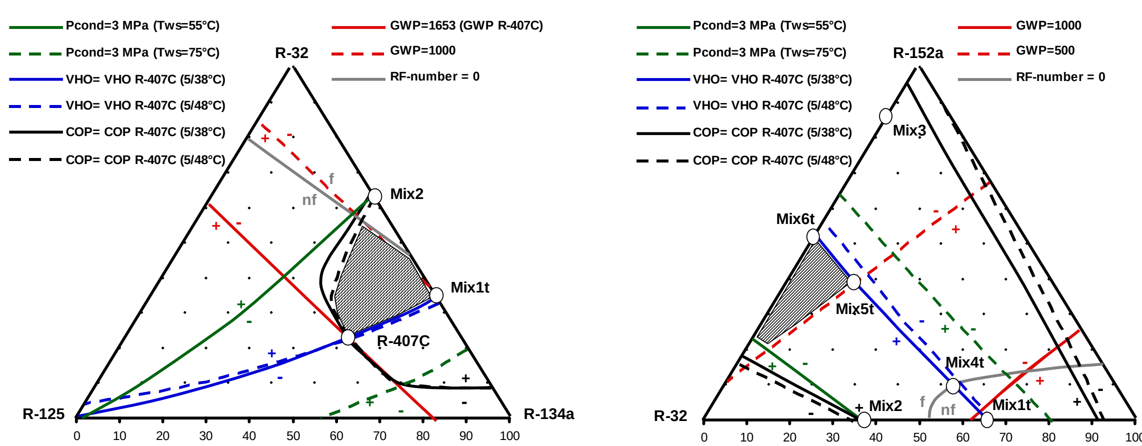

Fig. 4-a **Fig. 4-b**

Figure 4 : Mass composition diagram vs selection criteria of some ternary mixtures

5. CONCLUSIONS

The method of choice applied to refrigerant blends adapted to air-to-water hydronic heat pumps show a significant COP increase with mixtures mainly composed of R-32 and R-152a. Non-flammable or moderately flammable mixtures presenting equal R-407C heat capacity are proposed and classified as a function of their degree of flammability for fast and economical market introduction: Mix1t, Mix4t, Mix5t and Mix6t (GWP = 1056, 900, 501, 324; RF-number = 0, 0, 7.4, 9.6; COP (% gain R-407C) = 2.9, 2.7, 1.6, 1.7).

The total equivalent warming impact (TEWI) can be used as a selection criterion in the method of choice. Although, its introduction is not applied due to the large number of assumptions needed, related to refrigerant charges, refrigerant losses, refrigerant recovery, electricity production energy mix, GWP, and COP.
In a general way, the choice of refrigerants can be performed according to the COP and the volumetric heat capacity.

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