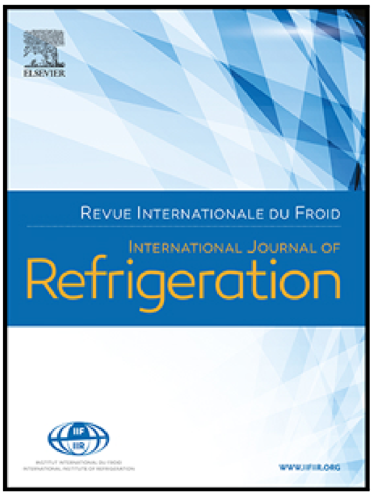

# A3 and A2 refrigerants: Border determination and hunt for A2 low-GWP blends

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# Title page

**Manuscript title:**

## A3 and A2 refrigerants: Border determination and hunt for A2 low-GWP blends.

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# A3 and A2 refrigerants: Border determination and hunt for A2 low-GWP blends

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## Abstract

The hunt for new refrigerant blends has been concentrated to locate A1 refrigerants. However, the investigation for A2 or A2L blends to replace hydrocarbons (A3) has not attracted attention yet, although these mixtures will allow to increase the maximum charge of refrigeration systems from 500 g to 1200 g. This paper extends Linteris' *et al.* work to define, for first time, the frontier between A3 and A2 ASHRAE safety classifications with an approach that can avoid large experimental campaigns. Then, using the methodology, it determines the composition limits of possible A2 binary blends with hydrocarbons that have a GWP below 150. Only mixtures of hydrocarbons with A2 or A2L components meet the criteria, and the composition of the least flammable fluid is predominant. Proposed hypothesis, developed theoretically, should be completed in the future with experimentation, to quantify the energy performance of found blends.

## Keywords

Hydrocarbons, R-152a, R-1234yf, R-1234ze(E), flammability

## Nomenclature

| | |
|---|---|
| C | Carbon atom |
| DME | Dimethyl ether |
| F | Fluorine atom |
| FP | Flame Propagation |
| GHG | Greenhouse Gases |
| GWP | Global Warming Potential |
| H | Hydrogen atom |
| HC | Hydrocarbon |
| $h_f$ | Enthalpy of formation, kJ·kmol$^{-1}$ |
| HFC | Hydrofluorocarbon |
| HFO | Hydrofluoroolefin |
| HOC | Heat Of Combustion, kJ·kg$^{-1}$ |
| IEC | International Electrotechnical Commission |
| LFL | Lower Flammability Limit, kg·m$^{-3}$ |
| NC | Nominal Composition |
| RH | Relative Humidity, % |
| $S_u$ | Burning velocity, cm·s$^{-1}$ |
| T | Temperature, ºC |
| WCF | Worst Case of Formulation for Flammability |
| WCFF | Worst Case of Fractionation for Flammability |
| $X_{H_2O}$ | molar proportion of water at 23ºC and 50% RH |

## Subscripts

| | |
|---|---|
| ad | Adiabatic |
| i | Initial |

## Greek symbols

| | |
|---|---|
| $\Delta$ | Increment |
| Ø | Fuel-air equivalence ratio |
| $\Gamma$ | Molar oxygen required for stoichiometric combustion |
| $\Pi$ | Flammability Angle |

# 1. Introduction

Accelerated Planet global warming, which main cause is anthropogenic, requires that all industrial sectors quickly reduce their emissions of greenhouse gases (GHG). Refrigeration sector, responsible for 7.8% of overall GHG in 2018 [1], accelerated the phase-down of high global warming potential (GWP) fluids due to the entry into force of the F-Gas Regulation [2] in Europe, which was extended globally through the Kigali Amendment to the Montreal Protocol [3]. These agreements and prohibitions pushed the scientific community to search for reduced GWP alternatives to the most common used refrigerants.

The first intensive search was performed by McLinden *et al.* [4], who analysed around 100 million known and unknown chemicals looking for low-GWP substances that could operate as refrigerants. They observed that only 62 pure substances had their critical temperature between 300-400 K, operating region of common refrigeration, air-conditioning and heat pumps. Following, McLinden *et al.* [5] and Domanski *et al.* [6] refined the search with screenings to find substitutes for R-410A and R-404A, concluding that there are few possible fluids and all of them are mildly flammable. Next, Bell *et al.* [7], using a similar approach, conducted an extensive search of blends up to four components (among HFOs, HFCs, $CO_2$) to find possible substitutes to R-134a. They identified 16 mixtures. However, they concluded that no mixture was a perfect substitute, since A1 mixtures with energy performance like R-134a were only able to reduce GWP by 54%, and blends with 99% GWP reduction showed flammability characteristics. Finally, Yu *et al.* [8] performed another theoretical search for low-GWP substitutes of R-410A for air-conditioning and heat pump applications considering blends from 12 pure fluids (among HFOs, HFCs, HCs, $CO_2$ and R13I1). They identified 34 low-GWP potential mixtures, all of them flammable, and concluded that only 4 mixtures matched R-410A vapour pressures but suffered from a COP decrease. The search for new refrigerant blends was taken a step forward by Calleja *et al.* [9], who established for the first time, a comprehensive screening to find alternative fluids to R-290 and R-600a. Through a vast thermodynamic screening limited by 150 GWP value and no flammability restrictions, they observed that there are 6 potential blends to substitute R-600a and 5 to replace R-290, all of them with flammable characteristics too.

The explorations for low-GWP substances indicate that stand-alone refrigeration systems (domestic and commercial), where the use of substances with a GWP value higher than 150 will be forbidden from 2022 on in Europe [2], unavoidably head towards a future based on flammable refrigerants. Although pure flammable fluids, especially R-290 and R-600a, have excellent thermodynamic properties and allow working with high COP values, they suffer from restrictions because their flammable characteristics. In fact, most of European countries have still the limit of 150 g as maximum refrigerant charge for A3, A2 and A2L refrigerants in a single circuit, although the update of the International Electrotechnical Standard has raised it to 1200 g for A2 and A2L refrigerants and 500 g for A3 ones [10]. In practice, this charge limit establishes the maximum capacity that a single cycle could satisfy. Attending to recent works devoted to minimizing the refrigerant charge (detailed in Table 1), it can be said that the maximum capacity of a single circuit using propane ranges from 1041 to 2200 W for a charge limit of 150 g, and when the IEC enters into force, it could be raised up to 3470 to 7350 W for a 500 g charge in a single circuit. For isobutane, the actual maximum capacity is between 213 to 328 W and soon from 710 to 1095 W. Although the needs of most domestic refrigeration requirements (with R-600a) could be generally satisfied using the maximum capacities detailed in Table 1, commercial refrigeration appliances, which standard refrigerant is propane, could not satisfy the cooling needs of all the equipment with a single circuit. For this equipment going to multiple circuits or using complex heat exchangers to minimize refrigerant charge, usually require an overrun that cannot be accommodated.

As mentioned, the recent version of the International Electrotechnical Standard [10], allows to use up to 1200 g of A2 or A2L refrigerants in a single circuit, therefore it creates a new opportunity for stand-alone refrigeration industry. If an A2 or A2L refrigerant with close thermodynamic properties to R-290 or R-600a is found, the range of capacity of systems that could be built with the maximum charge limit will rise.

However, up to the moment and to the knowledge of authors, no systematic search has been performed to found A2 or A2L refrigerants that can be replacements of the current used hydrocarbons.

This work proposes a methodology (applied to binary mixtures but extendable to mixtures with more components) that determines the border between A3 and A2 ASHRAE 34 [11] safety classifications and then uses the proposed frontier, HOC and LFL parameters to determine the limit compositions of binary mixtures formed by propane, isobutane and propylene for building A2 refrigerant mixtures. It opens a new line of work, the hunt for A2/A2L refrigerants that could replace hydrocarbons having lower flammability.

## 2. A3/A2 flammability border location

Safety classification of a refrigerant is given by ASHRAE according to the Standard 34 [11]. If a blend, for a given nominal composition (NC), contains a flammable component, its classification is given by the worst case of formulation for flammability (WCF) and its worst case of fractionation for flammability (WCFF). First, for a mixture considering component tolerances, the worst case of formulation (WCF) is determined. Second, for this WCF, a fractionation analysis is done to evaluate the sensibility of the mixture to change its composition during leakages at different temperatures and in different conditions during the useful life. From that, the WCFF is determined, and it is which defines the safety classification of the nominal composition (NC) according to the following flammability terms (see Fig. 1):

- A1 (non-flammable): The blend does not show flame propagation (FP) at its NC, WCF, and WCFF.
- A2 (lower flammability): The blend shows FP, a Lower Flammability Limit (LFL) > 0.1 kg·m$^{-3}$ and Heat of Combustion (HOC) < 19000 kJ·kg$^{-1}$ at its NC, WCF and WCFF. If a mixture meets these requirements, optionally, a burning velocity ($S_u$) test shall be conducted. If the result at the NC, WCF and WCFF is lower than 10 cm·s$^{-1}$, the blend shall be assigned to A2L class (mildly flammable).
- A3 (higher flammability): The blend shows FP, a LFL < 0,1 kg·m$^{-3}$ or a HOC > 19000 kJ·kg$^{-1}$ at its NC, WCF or WCFF.

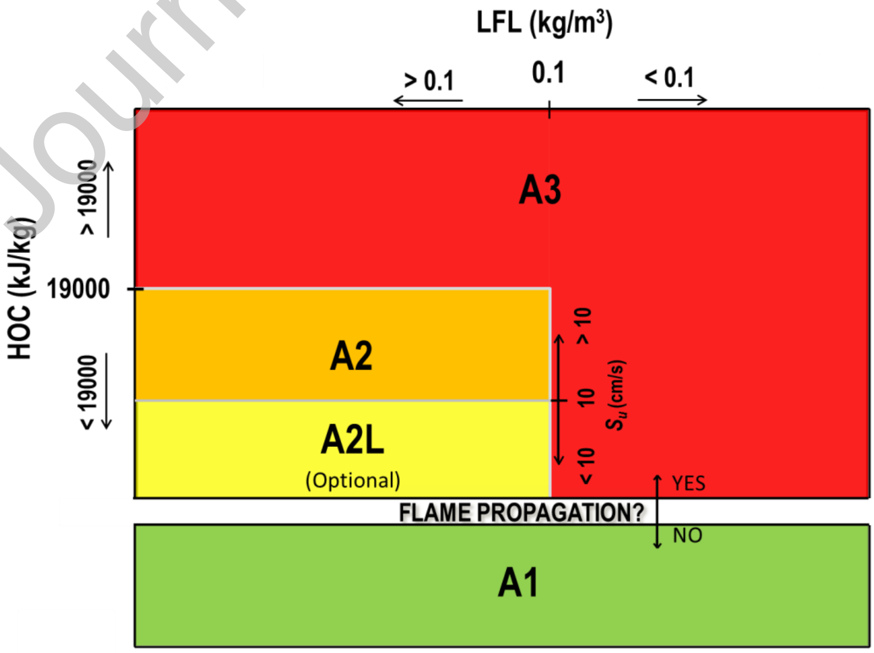

*Fig. 1. ASHRAE safety classifications according to HOC, LFL and burning velocity characteristics.*

Flammability classification depends on four parameters: FP, LFL, HOC and, optionally, burning velocity. Of all of them, only HOC can be calculated theoretically from the enthalpies of formation of reactants and products. However, the FP and LFL should be determined experimentally in accordance with ASTM E681 methodology [12] and burning velocity can be determined with the method summarized by Clodic & Jabbour [13]. Some authors have proposed formulas to calculate theoretically lower and upper flammability limits of some materials [14-17], but they generally cannot be extended to other substances. Also, for burning velocity new methods have been proposed [18, 19], but they need more comprehensive research to be extended to other substances. The summary is that for classifying the safety of a refrigerant a great number of experimental tests should be performed and a methodology could be able to save time an effort to hunt for A2 or A2L blends.

Linteris *et al.* proposed a method to identify if a refrigerant presents flammability and proposed the location of the frontier between A1 and A2L blends in 2019 [20]. They proposed to evaluate the adiabatic flame temperature ($T_{ad}$) and the fluorine substitution ratio ($^F/_{F+H}$) for a substance. To calculate $T_{ad}$, combustion reaction Eq. (*1*) is used with the software Cantera® [21] and Matlab®. Ø is the fuel-air equivalence ratio (<1 lean, >1 rich combustion), $Fuel$ is the blend composition multiplied by its molar mass and $\Gamma$ is the molar oxygen required for stoichiometric combustion. $X_{H_2O}$ is the molar proportion of water at 23 ºC and 50% RH (0.014 kmol·kmol$^{-1}$). $T_{ad}$ is calculated over a range of Ø between 0.5 and 2.0, from which the value that maximizes $\mathrm{T_{ad}}$ is taken. Fluorine substitution ratio is the molar ratio of F atoms to the sum of F and H atoms ($^F/_{F+H}$) in the reactants (consult reference [20] for further details).

$$\emptyset \cdot \mathrm{Fuel} + \Gamma\left[\mathrm{O_2} + 3.76\ \mathrm{N_2} + \frac{\mathrm{X_{H_2O}}}{(\frac{1.0}{4.76})(1-\mathrm{X_{H_2O}})}\mathrm{H_2O}\right] \tag{1}$$

Linteris et al. proposed an angle ($\Pi$) to sum up both variables, as expressed by Eq. (2).

$$\Pi = \mathrm{arctan2}\left\{\left[\frac{\mathrm{T_{ad}} - 1600}{2500 - 1600}\right], \left[\frac{\mathrm{F}}{\mathrm{F+H}}\right]\right\} \cdot \left(\frac{1800}{\pi}\right) \tag{2}$$

Fig. 2 represents the positions of nominal compositions of refrigerants and blends present in ASHRAE 34 standard (HFC, HFO, HC, $CO_2$ and DME and their mixtures). Origin is established at 0 fluorine substitution ratio and 1600 K, minimum adiabatic temperature observed for flammability. According to Linteris' et al., the angle defines different flammability regions. They identified 36º as the angle defining the border between A1-A2L regions ($\Pi_{A1-A2L} = 36º$). It was conservative, since some non-flammable mixtures are inside the A2L region, but no A2L blends appear in the A1 region. Authors performed fractionation analysis for these fluids, but no great scatter was produced near the A1-A2L border.

Also, Linteris's et al. proposed an angle of 60º to separate A2 and A2L regions, although they stated that more research is needed to determine it properly. However, they did not focus on the determination of the A3-A2 border, which is the first objective of this work.

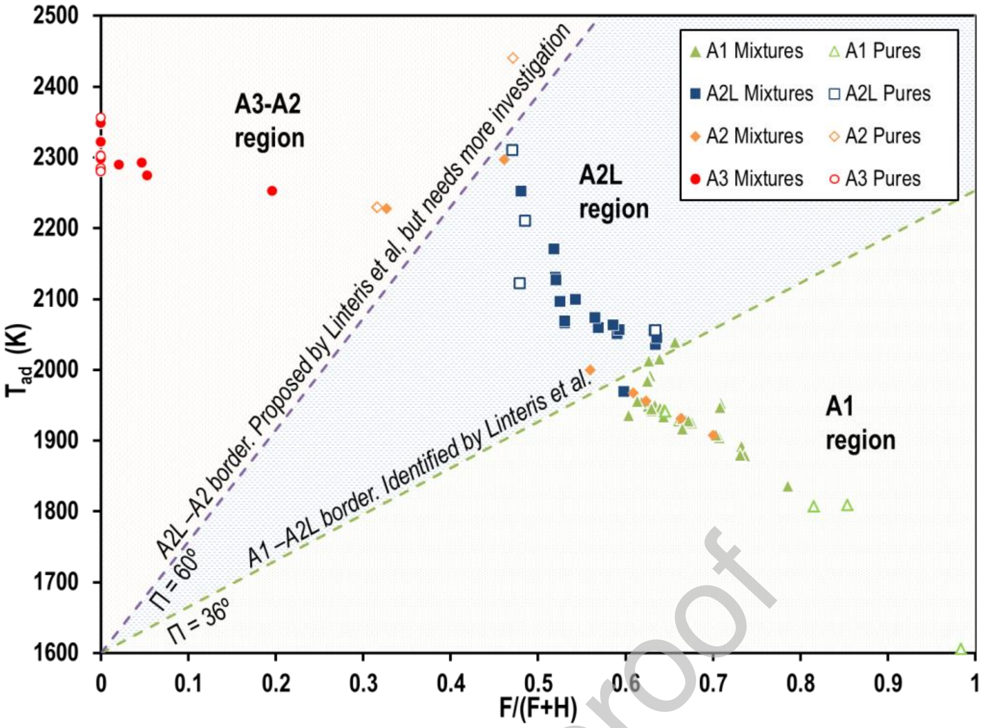

*Fig. 2. Application of Linteris' method to some ASHRAE 34 blends.*

## 2.1. Empirical determination (from classified refrigerant mixtures)

To locate the A2-A3 border, we applied Linteris' et al. method [20] to A2 and A3 pure fluids and blends classified in ASHRAE 34, results being presented in Fig. 3. All fluids onwards from R-439A to those included in the standard at the day of writing of this work (last is R-465A) were evaluated. Former fluids to R-439A were not considered, since the A2L classification still did not exist, and it is not possible to classify the blends into A2 or A2L groups. For each blend, we evaluated the properties for the NC (point to the right for each fluid) and for the different possibilities of fractionation. Fractionation analysis was performed using REFLEAK software [22] for all cases of WCF with the conditions defined in section B.2.4.1 and B.2.4.2 of Appendix B of the Standard 34. The WCFF is the point at the left for each fluid in Fig. 3.

To illustrate the calculation process, Table 2 summarizes the fractionation analysis of R-465A (R-32/R-290/R-1234yf; 21.0/7.9/71.1 $\%_{\text{mass}}$). Two WCF are possible [R-32/R-290/R-1234yf; 21.5/8.0/70.5 $\%_{\text{mass}}$ and R-32/R-290/R-1234yf; 19.9/8.0/72.1 $\%_{\text{mass}}$], to which the fractionation during leakage under the scenarios established by ASHRAE standard were performed. The composition changes under different scenarios, as well as the $T_{ad}$ and the ratio $\left({}^{F}/_{F+H}\right)$, are detailed in the table. For R-465A the WCFF, which establishes the safety classification of the blend, corresponds to the leak under storage/shipping conditions at -40 ºC. Final composition of the blend at the end of the leakage process results in (R-32/R-290/R-1234yf; 44.30/16.36/39.34 $\%_{\text{mass}}$). This WCFF has the highest angle, thus this is the most flammable fractionation condition.

Illustrated fractionation analysis was performed with A2 mixtures previously selected and to A3 mixtures containing HFC or HFO components, since for only-HC mixtures the fluorine substitution ratio is 0 and does not affect to the angle $\Pi$. Results are plotted in Fig. 3 (all data is presented in supporting information). Dispersion for a blend is smaller when it is composed with one main fluid and small proportions of others, such as R-512A, and broader when there is no dominant component, such as R-439A. Mixtures with a value of $\left({}^{F}/_{F+H}\right)$ close to zero also present small scatter, since having small presence of fluorides in the nominal composition, the variation of this parameter is small during fractionation. In any case, it can be observed that the fractionation is very important when classifying a mixture.

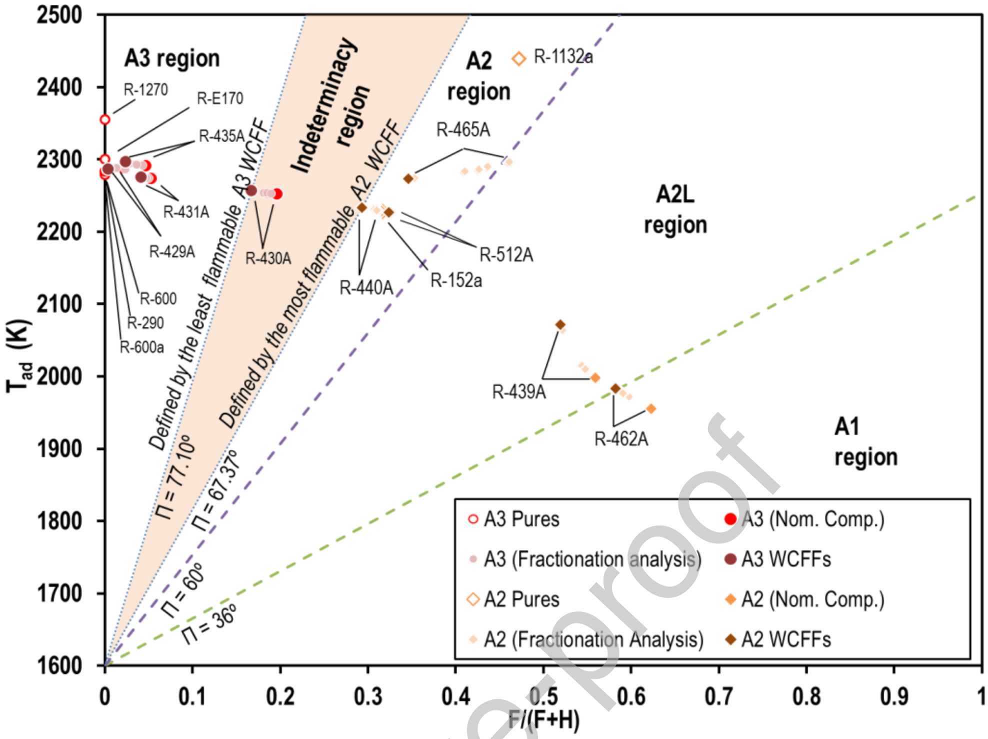

*Fig. 3. Application of Linteris' method to A2 and A3 ASHRAE 34 blends and their fractionation cases.*

Our empirical determination defines the boundary between A3 and A2 safety classifications between the most flammable A2 WCFF (R-440A) and the least flammable A3 WCFF (R-430A). Fractionation analysis for these blends is detailed in Table 3, where it can be inferred that the A3/A2 boundary is located between the angles of 67.37º and 77.10º, resulting in an indeterminacy region. While in A1/A2L border identification [20] there was high density of blends around the boundary and a clear division between A1 and A2L classes could be seen, this does not occurs for the A3/A2 classes, because the efforts of refrigeration industry have been focused on developing A1 and A2L blends with the lowest possible GWP.

Overall, the conclusion that is extracted from the empirical determination is that border between A3 and A2 classes is within angles of 67.37º and 77.10º, but to identify it with more precision other approaches are needed.

## 2.2. Determination with Heat Of Combustion (HOC) index

If the HOC of a blend is higher than 19000 kJ·kg$^{-1}$, its safety classification according to ASHRAE 34 standard is A3. The HOC, as specified in Appendix F of ASHRAE Standard 34, is calculated theoretically from a complete combustion of the refrigerants as the difference of the enthalpies of formation of the reactants (refrigerants and oxygen) minus the enthalpies of formation of the products according to Eq. (*3*) .

$$HOC = \sum \Delta h_{f,reactants} - \sum \Delta h_{f,products} \tag{3}$$

For a blend, the combustion reaction is evaluated as if the blend was a hypothetical molecule formed by the different atoms present in the components multiplied by the mole-fraction of each refrigerant ($x$, $y$, ...). Total oxygen required is given by the stoichiometric demands of each molecule ($\Gamma_1, \Gamma_2$, ...) multiplied by the molar fraction of each refrigerant. The hypothetical molecule formed for a general blend of two components is detailed by Eq. (*4*).

$$\begin{aligned} &\mathrm{x \cdot \left[C_i H_j F_k O_l + \Gamma_1 O_2\right] + \ y \cdot \left[C_m H_n F_p O_k + \Gamma_2 O_2\right]} \\ &\qquad \mathrm{\rightarrow C_{i\cdot x+m\cdot y} H_{j\cdot x+n\cdot y} F_{k\cdot x+p\cdot y} O_{l\cdot x+l\cdot y} + (x \cdot \Gamma_1 + y \cdot \Gamma_2) O_2} \end{aligned} \tag{4}$$

Stoichiometric combustion reaction, expressed in a general form by Eq. (*5*), can have as products HF, $COF_2$, $CO_2$ and $H_2O$. Rules to define which product is formed are: if there is not enough hydrogen available for HF and $H_2O$ formation, HF creation takes preference over $H_2O$ formation; if there is more fluorine than hydrogen, HF is created and the remaining fluorine forms $COF_2$, having preference of the carbon over $CO_2$.

$$\mathrm{C_\alpha H_\beta F_\gamma O_\delta + \Gamma \cdot O_2 = \zeta \cdot CO_2 + \eta \cdot COF_2 + \theta \cdot H_2O + \lambda \cdot HF} \tag{5}$$

We performed a wide screening of ternary mixtures to evaluate the limit composition of a blend that must be classified as A3 according to the HOC. Thirteen pure fluids were selected, including common components in blends (2 saturated HC, 1 unsaturated HC, 1 ether, 5 saturated HFC, 2 HFO, 1 FC, and 1 inorganic compound) with different flammability classifications (4 A3, 2 A2, 3 A2L and 4 A1). The screening included all possible combinations of three pure fluids (205 mixtures) with a molar composition step of 0.5% (20301 blends). Pure fluids, products, and their enthalpies of formation at 298 K are detailed in Table 4 (R-1234ze(E) was not included in the screening since the molecule is similar to R-1234yf).

The HOC was evaluated for each mixture and we selected the composition whose HOC was between 18990 and 19000 kJ·kg$^{-1}$ to be at the limit between A3 and A2 safety classifications. The screening identified 1419 mixtures. For these, $T_{ad}$ and ($^{F}/_{F+H}$) were calculated and represented in Fig. 4 (see supporting information for detailed data). In summary, 788 blends are composed by HFC-HFO-HC (grey dots), 473 with R-E170 as component (blue dots) and 158 with $CO_2$ presence (green dots). Mixtures of HFC-HC-HFO, organic compounds composed by C, H and F are concentrated around the same area. Blends with R-E170 and $CO_2$ present high scatter along the graph since their behaviour is quite different from the rest of substances: R-E170 presents an oxygen atom (boosts flammability) and $CO_2$ is a substance with a high power of inertization (limits flammability). Despite this, it has been observed that for molar quantities lower than 10% (of R-E170 and $CO_2$) and HOC between 18990 and 19000 kJ·kg$^{-1}$, those mixtures present similar location than to the HFC-HFO-HC ones. Therefore, a limit between A3 and A2 safety classifications is clearly identified, as observed in Fig. 4. This tentative limit (Fig. 4) is very close to 67.37°, which was the angle identified in Section 2.1. It must be highlighted that this angle is conservative, as probably some A2 mixtures may appear in the A3 region, but it is very unlikely to happen otherwise.

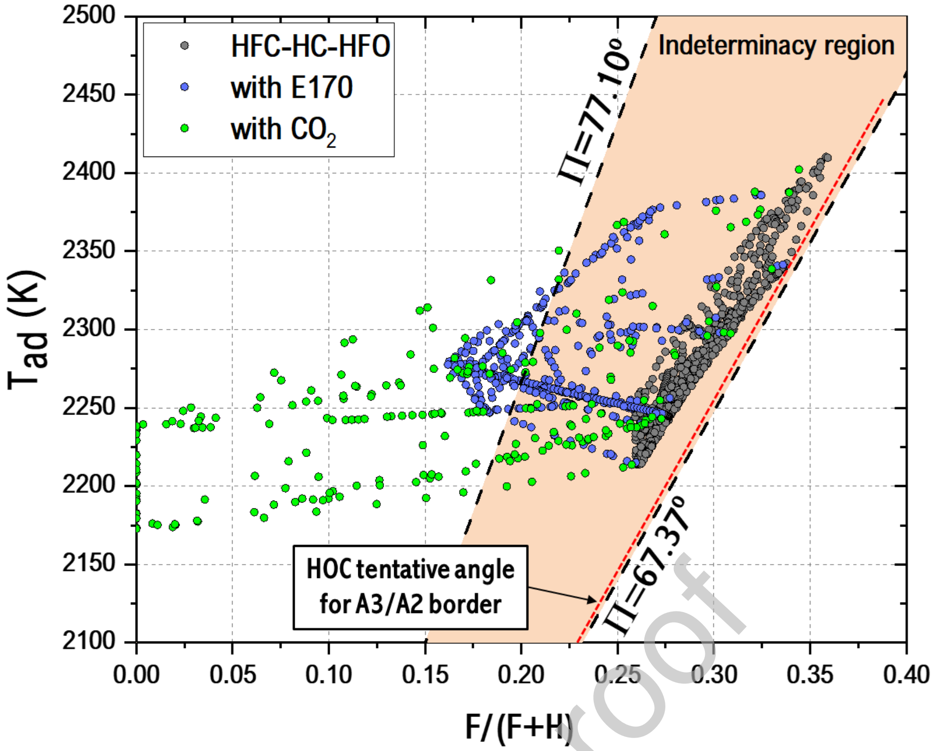

*Fig. 4.* $T_{ad}$ *and fluorine substitution ratio of blends with HOC between 18990 and 19000 kJ·kg*$^{-1}$

### 2.3. Definition of A3/A2 flammability border

Both empirical and HOC determinations coincide approximately in an angle of 67.37° as the frontier between A3 and A2 regions. Figure 4 shows that above grey dots A2 mixtures could not appear. However, it does not mean that below these points all mixtures will be A2, since ASHRAE Standard 34 also requires them to have a LFL below 0.1 kg·m$^{-3}$. Although HOC and LFL are parameters generally correlated, as indicated by Kazakov et al. [23], our screening cannot be extended to the LFL parameter, since it is determined experimentally and no generalization method has been found. However, as the empirical determination (based on ASHRAE experimentation, and determined by the most flammable A2 blend, R-440A) is slightly more restrictive than the HOC determination, it can be concluded that the frontier between both safety classifications at an angle of 67.37° is consistent and it can be generalized. This angle is conservative, as some A2 mixtures may appear at the A3 region (near the border in any case) but it is very unlike that it could happen otherwise.

Nonetheless, in Section 3, the LFL criterion, when available, is also checked in the evaluation of binary mixtures.

## 3. Low-GWP A2 binary blends determination

The second objective of this work is to identify the composition limits of binary blends with reduced flammability in relation to HCs (R-600a, R-290 and R-1270) having at the same time a GWP below 150. These blends, that will have an A2 safety classification, will be subjected to 1200 g of maximum charge instead of 500 g (for A3 fluids), and thus it will offer larger capacities for stand-alone refrigeration systems.

Methodology used to determine the blends is sketched in Fig. 5. For a blend of two components, first the WCFF is calculated. If experimental data of the LFL are available in literature, the WCFF is calculated setting the composition of the most flammable component to the limits established by ASHRAE for A2 classification (HOC or LFL); if data is not available the composition limit is calculated using an angle of 67.37º, as detailed in section 2. At this point, the WCFF that guarantees an A2 safety classification is obtained. The next step is to calculate the GWP of the WCFF. If GWP is higher than 150, it is not possible to obtain a WCF with a lower GWP, since the WCF is always going to have a higher presence of the component with a higher GWP. Therefore, no possible composition can meet the criteria. If the GWP of the WCFF is lower than 150, an iteration process with REFLEAK is performed to calculate the WCF that after fractionation will result in the previous WCFF. This process starts with low percentage of the most flammable component which is increased by 0.1%$_{mass}$ until the WCFF provided by REFLEAK coincides with the previous value. Considering that mass tolerances are neglected, WCF composition coincides with the NC of the blend that will be classified as A2.

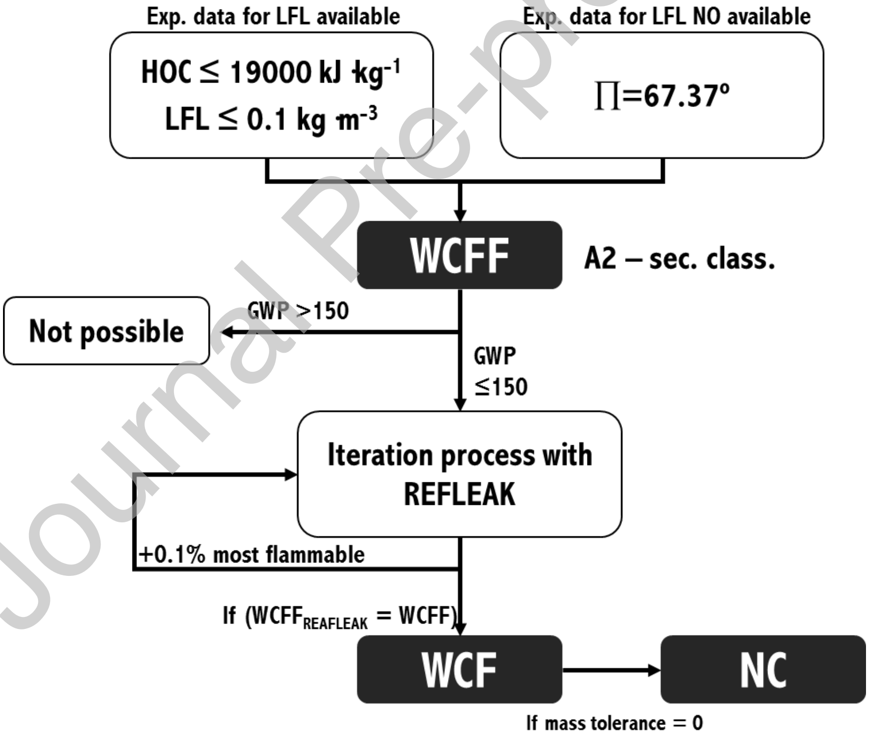

*Fig. 5. Method to determine composition limits for A2 blends with GWP < 150*

### 3.1. Limit composition results

This methodology is used to evaluate binary blends resulting from mixing the reference HC fluid with fluids belonging to A2, A2L and A1 to reduce the flammable characteristics of the blend. Table 5 reflects the pure fluids for the evaluation as well as their safety classification and GWP value.

Calculated nominal composition limits that guarantee an A2 classification and a GWP below 150 are summarized in Table 6 (right column), where the references used to calculate the LFL values and the ASHRAE leakage test that produces the WCFF are detailed.

For propane blends there are two sets of blends: mixtures of propane with A1 pure fluids, where to obtain an A2 classification the quantity of additive is too high that exceeds the GWP limit, therefore is not possible to formulate blends of propane with R-143a, R-125, R-134a and R-218 meeting the criteria. This also happens for isobutane and propylene; thus, they have not been included in the table. The exception is the blend with R-744, that will provide an A2 classification for $CO_2$ proportions from 95.4% on. The second set corresponds to mixtures with propane with A2 and A2L fluids. For all of them, except for R-32 whose proportion for flammability reduction exceeds the GWP limit, is possible to obtain A2 blends meeting the criteria. But as observed after the fractionation analysis, the proportion of the A2 or A2L component is predominant. Except for the blend with R-1234yf, for which the proportion to get an A2 classification is of 89.0%, the rest of mixtures need at least 95.0% of the least flammable component to meet the criteria after fractionation of the NC.

Similar results have been obtained for mixtures of isobutane and propylene with other fluids. No possible formulations have been found with A1 fluids, except with R-744, and the mixtures with A2 and A2L components result in high proportions of the A2 and A2L fluids in the mixture. Again, the component with highest percentage is R-1234yf.

Conclusion obtained from this section is that it is possible to formulate low-GWP mixtures with A2 classification blending pure HC components. To do this, high proportions of A2 or A2L fluids need to be added to the blend, because the fractionation of the NC results in a WCFF with a higher proportion of the A3 component.

## 4. Further considerations and future investigation

At this point, the angle 67.37º has been proposed as the frontier between A3 and A2 safety classifications and has been used to identify the flammability limits of binary mixtures when LFL data is not available. As seen, literature provides experimental LFL data or formulas that can be used for a more or less broad group of binary mixtures. However, the available data diminish considerably for ternary mixtures or mixtures with a larger number of components. It is then when this angle becomes of great importance, since it allows predicting flammability without an extensive experimentation.

The study of mixtures with three or more components has not been addressed in this work, but could be of great interest. As can be seen in Table 6, when performing fractionation analysis on binary mixtures, the amount of HC in the composition varies greatly between the NC and the WCFF. In addition, it has been possible to observe a relation between the difference in NBPs that exists between the fluids that form the binary mixture and the reduction in the amount of HC between the composition of the WCFF and the NC. An example of this is the R-600a/R-744 mixture, where the amount of HC decreases by 97.72% between the WCFF (limited by the LFL) and the NC. This fact greatly limits the possibilities of the A2 binary mixtures. However, fractionation in ternary mixtures has not been studied. The behavior of fractionation in mixtures of three or more components may be key to achieve a higher HC presence in the NC. Studying how fractionation affects ternary mixtures could mitigate the large gap between the composition in the NC and the WCFF of HCs and thus increase the chances of A2 mixtures containing hydrocarbons.

To complete the search for alternative fluids to A3 refrigerants (R-290, R-600a and R-1270), composition limits detailed in this work (Table 6) can be used as reference, but this search must be supplemented with energy analysis. If any A2 blend, as defined in this work, can equal or has closer energy performance to the base fluids, then it could allow increasing the refrigerant charge limit and thus enhance the capacity that can be provided using a single circuit. Authors invite other researchers to perform theoretical and experimental analysis of the proposed mixtures with refrigeration systems to complete the hypothesis launched in this work

## 5. Conclusions

Maximum allowed refrigerant charge with flammable refrigerants that can be used in a single circuit limits the capacity of the systems that can be built. A3 refrigerants are limited to 500 g and A2/A2L to 1200 g. Since most of stand-alone systems rely on pure HC refrigerants, belonging to an A3 safety classification, it is important to find new blends that, having close properties to the HC fluids, present at least an A2 safety classification.

This work has extended Linteris' et al. method to locate the border between A3 and A2 refrigerants as function of the fluorine substitution ratio and the adiabatic flame temperature. Border search has been performed using an empirical approach, from existing refrigerants in ASHRAE Standard 34, and has been completed with a wide screening based on the HOC index. It has been concluded that all the mixtures with an angle higher than 67.37º belong to an A3 safety classification.

The developed method has been used to determine blends of HC refrigerants (R-600a, R-290 and R-1270) with A1, A2 and A2L components that meet A2 safety classification and a GWP below 150. To find them out, the method determined the WCFF and with an iterative process using REFLEAK the NC of the blends that after fractionation result in the WCFF. It has been concluded that no blend with A1 fluids meet the criteria, because for inertization the quantity of A1 component makes the GWP value to exceed 150, and it is possible to create A2 blends mixing with A2 and A2L components. However, to decrease the flammability, the amount of A2 or A2L component is predominant, what limits the possibilities of the mixtures.

The work has established the NC of mixtures that will belong to an A2 security classification. However, in order to find substitutes to pure HC refrigerants, the energy performance of determined mixtures should be explored. Authors invite researchers to consider this possibility and perform experimental evaluations to validate the possibilities raised in this work.

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## Supporting information

In order to complete the information, supplementary material can be found attached to this paper. An excel file is available with the following data:

- Data of the fractionation analysis of the A3 and A2 ASHRAE 34 mixtures (see Fig. 3). Initial temperature and initial volumetric quality, as well as the details of the most unfavourable condition can be seen.
- Data with the results of the HOC screening (see Fig. 4). Mixtures obtained, HOC, F/F+H ratio, $T_{ad}$, and angle $\Pi$ can be seen.

## Author contribution statements

D. C. developed idea and methods, performed simulations, and wrote the manuscript. R. Ll. developed the idea and supervised the work. D.S. helped to develop methods and supervised work. L. N. helped to develop the method and made final proofreading. R.C. helped to get funds.

## References

1. International Institute of Refrigeration, *The Role of Refrigeration in the Global Economy (2019), 38th Note on Refrigeration Technologies.* 2019, International Institute of Refrigeration.
2. European Commission, *Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated greenhouse gases and repealing Regulation (EC) No 842/2006.*, E. Commission, Editor. 2014: Official Journal of the European Union.
3. UNEP, *Report of the Twenty-Eighth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer*. 2016: Kigali, Rwanda.
4. McLinden, M.O., et al., *A thermodynamic analysis of refrigerants: Possibilities and tradeoffs for Low-GWP refrigerants.* International Journal of Refrigeration, 2014. **38**(1): p. 80-92 DOI: 10.1016/j.ijrefrig.2013.09.032.
5. McLinden, M.O., et al., *Limited options for low-global-warming-potential refrigerants.* Nat Commun, 2017. **8**: p. 14476 DOI: 10.1038/ncomms14476.
6. Domanski, P.A., et al., *Low-GWP refrigerants for medium and high-pressure applications.* International Journal of Refrigeration, 2017. **84**: p. 198-209 DOI: 10.1016/j.ijrefrig.2017.08.019.
7. Bell, I., et al., *The hunt for nonflammable refrigerant blends to replace R-134a.* International Journal of Refrigeration, 2019. **104**: p. 484-495 DOI: 10.1016/j.ijrefrig.2019.05.035.
8. Yu, B., et al., *Evaluation of low-GWP and mildly flammable mixtures as new alternatives for R410A in air-conditioning and heat pump system.* International Journal of Refrigeration, 2021. **121**: p. 95-104 DOI: 10.1016/j.ijrefrig.2020.09.018.
9. Calleja-Anta, D., et al., *Thermodynamic screening of alternative refrigerants for R290 and R600a.* Results in Engineering, 2020. **5** DOI: 10.1016/j.rineng.2019.100081.
10. International Electrotechnical Commission., *IEC 60335-2-89:2019. Household and similar electrical appliances - Safety - Part 2-89: Particular requirements for commercial refrigerating appliances and ice-makers with an incorporated or remote refrigerant unit or motor-compressor.* 2019.
11. ASHRAE, *ANSI/ASHRAE Standard 34-2019. Designation and safety classification of refrigerants*. 2019, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.: Atlanta, USA.
12. International, A., *E681 - 09(2015) Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)*. 2015.
13. Clodic, D. and T. Jabbour, *Method of test for burning velocity measurement of flammable gases and results.* HVAC&R Research, 2011. **17**(1): p. 51-75 DOI: 10.1080/10789669.2011.543252.
14. Chen, C.-C., C.-P. Lai, and Y.-C. Guo, *A novel model for predicting lower flammability limits using Quantitative Structure Activity Relationship approach.* Journal of Loss Prevention in the Process Industries, 2017. **49**: p. 240-247 DOI: 10.1016/j.jlp.2017.07.007.
15. Li, Z., et al., *Flammability limits of refrigerant mixtures with 1,1,2,2-tetrafluoroethane.* Experimental Thermal and Fluid Science, 2011. **35**(6): p. 1209-1213 DOI: 10.1016/J.EXPTHERMFLUSCI.2011.04.008.
16. Zhang, K., X. Meng, and J. Wu, *Flammability limits of binary mixtures of dimethyl ether with five diluent gases.* Journal of Loss Prevention in the Process Industries, 2014. **29**: p. 138-143 DOI: 10.1016/j.jlp.2014.02.008.
17. Kondo, S., et al., *Flammability limits of five selected compounds each mixed with HFC-125.* Fire Safety Journal, 2009. **44**(2): p. 192-197 DOI: 10.1016/j.firesaf.2008.06.001.

18. Linteris, G. and V. Babushok, *Laminar burning velocity predictions for C1 and C2 hydrofluorocarbon refrigerants with air.* Journal of Fluorine Chemistry, 2020. **230** DOI: 10.1016/j.jfluchem.2019.05.002.
19. Takizawa, K., et al., *On simple method for predicting burning velocities for lower flammability refrigerants using quenching distance measurement.* International Journal of Refrigeration, 2020. **120**: p. 370-377 DOI: 10.1016/j.ijrefrig.2020.08.027.
20. Linteris, G.T., I.H. Bell, and M.O. McLinden, *An empirical model for refrigerant flammability based on molecular structure and thermodynamics.* International Journal of Refrigeration, 2019. **104**: p. 144-150 DOI: 10.1016/j.ijrefrig.2019.05.006.
21. Goodwin, D.G.S., R. L., H.K. Moffat, and B.W. Weber, *Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes.* . 2021.
22. Brown, J.S. and P.A. Domanski, *REFLEAK: NIST Leak/Recharge Simulation Model for Refrigerant Blends Version 5.1; User's Guide.* 2018 DOI: 10.6028/nist.Nsrds.73-2018.
23. Kazakov, A., M.O. McLinden, and M. Frenkel, *Computational Design of New Refrigerant Fluids Based on Environmental, Safety, and Thermodynamic Characteristics.* Industrial & Engineering Chemistry Research, 2012. **51**(38): p. 12537-12548 DOI: 10.1021/ie3016126.
24. Zhou, W. and Z. Gan, *A potential approach for reducing the R290 charge in air conditioners and heat pumps.* International Journal of Refrigeration, 2019. **101**: p. 47-55 DOI: 10.1016/j.ijrefrig.2019.02.030.
25. Pisano, A., et al., *Optimal design of a light commercial freezer through the analysis of the combined effects of capillary tube diameter and refrigerant charge on the performance.* International Journal of Refrigeration, 2015. **52**: p. 1-10 DOI: 10.1016/j.ijrefrig.2014.12.023.
26. Cho, W., et al., *Refrigerant charge reduction in R600a domestic refrigerator-freezer by optimizing hot-wall condenser geometry.* International Journal of Refrigeration, 2020. **117**: p. 295-306 DOI: 10.1016/j.ijrefrig.2020.05.012.
27. Zhou, W., X. Bi, and Z. Gan, *Performance investigation of a domestic freezer with micro-bare-tube evaporators.* Applied Thermal Engineering, 2020. **174** DOI: 10.1016/j.applthermaleng.2020.115306.
28. Afeefy, H.Y., J.F. Liebman, and S.E. Stein, *Neutral Thermochemical Data*, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*. National Institute of Standards and Technology DOI: 10.18434/T4D303.
29. Burcat, A. and B. Ruscic, *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables*. 2005.
30. Joback, K.G. and R.C. Reid, *Estimation of Pure-Component Properties from Group-Contributions.* Chemical Engineering Communications, 2007. **57**(1-6): p. 233-243 DOI: 10.1080/00986448708960487.
31. IPCC, ed. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.* 2013.

32. Kondo, S., et al., *A study on flammability limits of fuel mixtures.* Journal of Hazardous Materials, 2008. **155**(3): p. 440-448 DOI: 10.1016/j.jhazmat.2007.11.085.
33. Kondo, S., et al., *Extended Le Chatelier's formula for carbon dioxide dilution effect on flammability limits.* Journal of Hazardous Materials, 2006. **138**(1): p. 1-8 DOI: 10.1016/j.jhazmat.2006.05.035.
34. Kondo, S., et al., *Flammability limits of isobutane and its mixtures with various gases.* Journal of Hazardous Materials, 2007. **148**(3): p. 640-647 DOI: 10.1016/j.jhazmat.2007.03.021.

## TABLES

*Table 1. Investigations to reduce refrigerant charge and achieved capacity vs. charge ratios.*

| Reference | Refrigerant | System | Ratio capacity vs. charge ($W \cdot g^{-1}$) | Capacity with 150 g (W) | Capacity with 500 g (W) |
|---|---|---|---|---|---|
| Zhou & Gan [24] | R-290 | Split air conditioning with micro bare-tube heat exchangers | 14.70 | 2200 | 7350 |
| Pisano et al. [25] | R-290 | Commercial freezer with finned-tube evaporator and tubeless condenser | 6.94 | 1041 | 3470 |
| Cho et al. [26] | R-600a | Domestic refrigerator-freezer with hot-wall condenser and finned-tube evaporators | 2.19 | 328 | 1095 |
| Zhou et al. [27] | R-600a | Domestic freezer with micro-bare-tube evaporators and wired-tube condenser | 1.42 | 213 | 710 |

*Table 2. Fractionation analysis of the refrigerant mixture R-465A.*

| R-465A | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Components in the blend | Nominal Composition (mass %) | Tolerances (mass %) | WCF 1 (mass %) | WCFF 1 (mass %) | | | | | WCF 2 (mass %) | WCFF 2 (mass %) | | | |
| | | | | WCFF 1 leak storage ($T_i$= 54.4ºC) | **WCFF 1* leak storage ($T_i$= -40ºC)** | WCFF 1 leak equipment ($T_i$= -40 ºC) | WCFF 1 leak equipment ($T_i$= 10 ºC) | WCFF 1 leak/ recharge ($T_i$= 23 ºC) | | WCFF 2 leak storage ($T_i$= 54.4 ºC) | WCFF 2 leak storage $T_i$= -40 ºC) | WCFF 2 leak equipment ($T_i$= -40 ºC) | WCFF 2 leak equipment ($T_i$= 10 ºC) | WCFF 2 leak/ recharge ($T_i$= 23 ºC) |
| R-32 | 21.0 | (+0.5/-1.5) | 21.5 | 31.35 | **44.30** | 43.50 | 34.01 | 27.39 | 19.9 | 29.68 | 42.96 | 42.09 | 32.25 | 25.66 |
| R-290 | 7.9 | (+0.1/-0.9) | 8.0 | 9.88 | **16.36** | 15.86 | 11.02 | 9.36 | 8.0 | 9.90 | 16.24 | 15.76 | 11.03 | 9.4 |
| R-1234yf | 71.1 | (±1.0) | 70.5 | 58.76 | **39.34** | 40.64 | 54.97 | 63.25 | 72.1 | 60.42 | 40.80 | 42.15 | 56.72 | 64.95 |
| | | | | | | | | | | | | | | |
| F/F+H | 0.462 | | 0.460 | 0.425 | **0.346** | 0.351 | 0.409 | 0.436 | 0.461 | 0.427 | 0.348 | 0.353 | 0.411 | 0.437 |
| $T_{ad}$ (K) | 2295.26 | | 2294.7 | 2284.5 | **2272.5** | 2273.1 | 2281.7 | 2288.3 | 2296.1 | 2285.9 | 2273.5 | 2274.2 | 2283.1 | 2289.7 |
| $\Pi$ | 59.15 | | 59.23 | 60.78 | **65.14** | 64.83 | 61.62 | 60.34 | 59.19 | 60.76 | 65.05 | 64.75 | 61.58 | 60.32 |

* Worst-Case Fractionated Formulation

*Table 3. Flammability characteristics of R-440A (most flammable A2 blend) and R-430A (lest flammable A3 blend) at the NC and at the WCFF*

| | Composition (by mass %) | | $\left({}^{F}/_{F+H}\right)$ | $T_{ad}$ (K) | Π (°) |
|---|---|---|---|---|---|
| **R-440A** | Nom. Comp. | R-290/R-134a/R-152a<br>(0.6/1.6/97.8) | 0.316 | 2228.2 | 65.66 |
| | WCFF | R-290/R-134a/R-152a<br>(4.0/0.9/95.1) | 0.293 | 2233.1 | 67.37 |
| **R-430A** | Nom. Comp. | R-152a/R-600a<br>(76.0/24.0) | 0.196 | 2252.1 | 74.88 |
| | WCFF | R-152a/R-600a<br>(68.6/31.4) | 0.167 | 2256.9 | 77.10 |

*Table 4. Pure fluids considered for the screening and products of combustion reaction. Enthalpy of formation at 298 K.*

| Reactants | | |
|---|---|---|
| Component | $\Delta h_f$ (kJ·kmol$^{-1}$) | Reference |
| R-290 | -104.70 | [28] |
| R-1270 | 20.41 | [28] |
| R-600a | -134.20 | [28] |
| R-E170 | -184.10 | [28] |
| R-152a | -497.00 | [28] |
| R-1132a | -344.00 | [28] |
| R-32 | -452.21 | [28] |
| R-143a | -748.70 | [28] |
| R-1234yf | -813.20 | [29] |
| R-1234ze(E) | -781.82 | [30] (estimated) |
| R-134a | -877.80 | [30] (estimated) |
| R-125 | -1120.00 | [29] |
| R-218 | -1784.70 | [28] |
| R-744 ($CO_2$) | -393.51 | [28] |

| Products | | |
|---|---|---|
| Component | $\Delta h_f$ (kJ·kmol$^{-1}$) | Reference |
| HF | -273.30 | [28] |
| $COF_2$ | -638.90 | [28] |
| $H_2O$ | -241.83 | [28] |
| R-744 ($CO_2$) | -393.51 | [28] |

*Table 5. Pure components used to determine A2 blends. GWP on a 100-year horizon value in brackets [31]*

| **A3 base component** | | **A2 pure fluids** | | **A2L pure fluids** | | **A1 pure fluids** | |
|---|---|---|---|---|---|---|---|
| R-1270 | (2) | R-1132a | (1) | R-1234yf | (1) | R-744 | (1) |
| R-600a | (3) | R-152a | (138) | R-1234ze(E) | (1) | R-134a | (1300) |
| R-290 | (3) | | | R-32 | (677) | R-125 | (3170) |
| | | | | R-143a | (4800) | R-218 | (8900) |

*Table 6. Composition limits of HC blends with A2, A2L and A1 fluids, resulting in A2 safety classification and GWP lower than 150*

| | **Environmental criteria** | **Flammability criteria** | | | | | | **Composition limit** (% mass) |
|---|---|---|---|---|---|---|---|---|
| **Binary blend** | **GWP < 150** | **WCFF** | | | | **WCF** | | **NC (A2 & GWP < 150) (Neglecting tolerances in composition)** |
| | | HOC=19000 $kJ \cdot kg^{-1}$ (% mass) | LFL=0.1 $kg \cdot m^{-3}$ (% mass) | LFL reference | $\Pi = 67.37º$ (% mass) | WCF | Limiting leakage test | |
| **Propane blends** | | | | | | | | |
| **R-290/R-152a** | n.e. | 8.9 / 91.1 | 12.3 / 87.8 | [32] | n.n. | 1.6 / 98.4 | a | **1.6 / 98.4** |
| **R-290/R-1132a** | n.e. | 11.4 / 88.6 | 12.4 / 87.6 | [32] | n.n. | 0.7 / 99.3 | b | **0.7 / 99.3** |
| R-290/R-32 | 78.3 / 21.7 | 26.0 / 74.0 | - | n.a. | n.n. | n.n. | - | n.p. |
| R-290/R-143a | 97.0 / 3.0 | 24.3 / 75.7 | - | n.a. | n.n. | n.n. | - | n.p. |
| **R-290/R-1234yf** | n.e. | 23.3 / 76.7 | - | n.a. | 21.2 / 78.8 | 11.0 / 89.0 | a | **11.0 / 89.0** |
| **R-290/R-1234ze(E)** | n.e. | 22.7 / 77.3 | - | n.a. | 21.2 / 78.8 | 5.0 / 95.0 | a | **5.0 / 95.0** |
| R-290/R-125 | 95.4 / 4.6 | 34.5 / 65.5 | - | n.n. | n.n. | n.n. | - | n.p. |
| R-290/R-134a | 88.7 / 11.3 | 29.6 / 70.4 | - | n.n. | n.n. | n.n. | - | n.p. |
| R-290/R-218 | 98.4 / 1.6 | 36.5 / 63.5 | - | n.a. | n.n. | n.n. | - | n.p. |
| **R-290/R-744** | n.e. | 41.0 / 59.0 | 40.0 / 60.0 | [33] | n.n. | 4.6 / 95.4 | b | **4.6 / 95.4** |
| **Isobutane blends** | | | | | | | | |
| **R-600a/R-152a** | n.e. | 9.1 / 90.9 | 13.7 / 86.3 | [32] | n.n. | 4.7 / 95.3 | a | **4.7 / 95.3** |
| **R-600a/R-1132a** | n.e. | 11.7 / 88.3 | 13.5 / 86.5 | [32] | n.n. | 0.3 / 99.7 | b | **0.3 / 99.7** |
| **R-600a/R-1234yf** | n.e. | 23.8 / 76.2 | - | n.a. | 22.1 / 77.9 | 8.4 / 91.6 | c | **8.4 / 91.6** |
| **R-600a/R-1234ze(E)** | n.e. | 23.2 / 76.8 | - | n.a. | 22.1 / 77.9 | 17.6 / 82.4 | b | **17.6 / 82.4** |
| **R-600a/R-744** | n.e. | 41.6 / 58.4 | 39.5 / 60.5 | [34] | n.n. | 0.9 / 99.1 | d | **0.9 / 99.1** |
| **Propylene blends** | | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **R1270/R-152a** | n.e. | 9.0 / 91.0 | 13.7 / 86.3 | [32] | n.n. | 1.8 / 98.2 | a | **1.8 / 98.2** |
| **R1270/R-1132a** | n.e. | 11.6 / 88.4 | 15.7 / 84.3 | [32] | n.n. | 1.0 / 99.0 | b | **1.0 / 99.0** |
| **R1270/R-1234yf** | n.e. | 23.6 / 76.4 | - | n.a. | 23.0 / 77.0 | 10.0 / 90.0 | a | **10.0 / 90.0** |
| **R1270/R-1234ze(E)** | n.e. | 23.0 / 77.0 | - | n.a. | 23.0 / 77.0 | 4.7 / 95.3 | a | **4.7 / 95.3** |
| **R1270/R-744** | n.e. | 41.5 / 58.5 | 48.9 / 51.1 | [33] | n.n. | 4.2 / 95.8 | b | **4.2 / 95.8** |

Notes about Table 6:

- Table 6 presents the nominal composition (NC) of refrigerant blends that would be classified at least A2 by ASHRAE standard 34 according to the methodology presented in this paper. Any blend with a mass proportion of hydrocarbon less than the value specified in 'Composition limit' would be classified as A2 or with a lower flammability class. Furthermore, any blend included in this table will present a GWP below 150.
- Compositions in column 'Composition limit' coincide with compositions of column 'WCF' which corresponds to the worst case of formulation for flammability. They coincide because this work omits tolerances in the blend manufacturing.
- Values in column 'WCF' are obtained considering the most flammable composition in column 'WCFF'. Composition identified in 'WCFF' has been evaluated using REFLEAK under the different leak conditions stablished by ASHRAE standard 34. Compositions in column 'WCF' are the results of the fractionation of 'WCFF' compositions under the most restrictive leak test (a, b, c or d). The most restrictive leakage test is also identified.

n.e.: limit non existing.

n.n.: calculation not needed.

n.a.: data not available.

n.p.: not possible A2 blend with GWP<150.

a: leak under storage/shipping conditions. Vapor 2% leakage.

b: leak under storage/shipping conditions. Liquid 95% leakage.

c: leak from equipment. Liquid 95% leakage.

d: leak from equipment. Liquid 84.2% leakage.

**Manuscript: '**## A3 and A2 refrigerants: Border determination and hunt for A2 low-GWP blends**'**

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**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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