

## Working towards more environmentally friendly Refrigerant Blends

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### ABSTRACT

This paper describes our ongoing work to identify azeotropic and near azeotropic mixtures with a normal boiling point of between -40 and -80°C. The aim was to match the saturated pressure-temperature characteristics and refrigerating capacity of R410A, whilst achieving higher critical temperatures. Thus, the intended outcome is an extended range of applicability and an improvement in potential energy efficiency. Of a large number of potential combinations, five azeotropic and four near azeotropic mixtures have been identified, all formed from natural refrigerants or synthetic chemicals with a global warming potential (GWP) of less than 150. These mixtures were subject to a variety of further analyses, including thermodynamic, performance and safety assessments, thereby providing a shortlist of the most suitable blends.

### 1. INTRODUCTION

The problem could not be simpler: cooling is the largest single demand on electrical consumption in the world and the synthetic refrigerants that are utilised by most cooling appliances add significantly to climatic change and ozone depletion.

Global energy demand is projected to increase by more than 25% in the period to 2015<sup>1</sup>. Building services will account for around 45% of this figure. This scenario is wholly unsustainable even without any increase in HFC use.

HFC control matters because of the very limited margin left before global warming becomes unstoppable due to positive feed back from the Earth's control mechanisms. Human induced climate change above 2°C would take us into this danger zone, but historic emissions already commit us to about 1.3°C. Up to 0.25°C temperature rise could be due to F-gases by the second half 21st Century, i.e. 36% of the remaining available global warming could be used up by HFCs!

The Global Warming Potentials (GWPs) of HFCs are being continually revised as the science improves. The table below compares the GWPs published in the IPCC's Third Assessment Report (2001)<sup>2</sup> with the 2006 United Nations Environment Programme (UNEP) assessment report<sup>3</sup>, which encompasses the latest data from the IPCC special report and the 2006 World Meteorological Organisation (WMO) Scientific Assessment. Note that in all cases, the values shown are direct GWPs (as opposed to indirect or net GWPs).

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<sup>1</sup> IEA World energy Outlook 2006

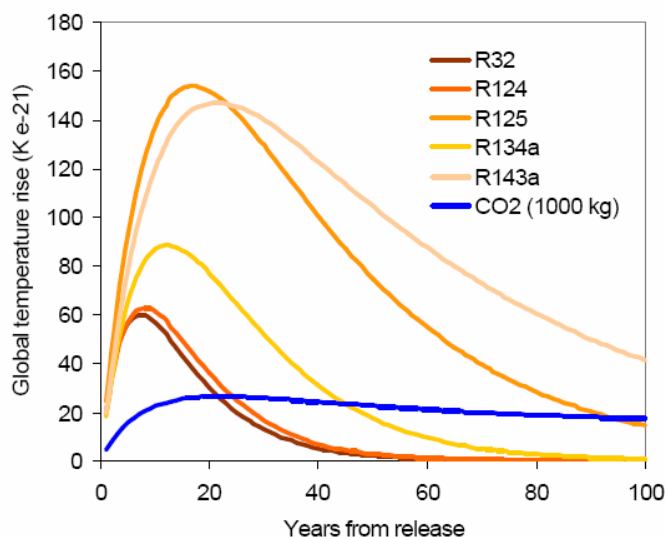
<sup>2</sup> Intergovernmental Panel on Climate Change, Climate Change 2001: The Scientific Basis. Summary for Policymakers (Cambridge, UK: Cambridge University Press, 2001).

<sup>3</sup> Report of the Refrigeration, Air conditioning and Heat Pumps Technical Options Committee, 2006 Assessment, UNEP, Nairobi, January 2007.

*Table 1: Comparison of GWP (100y ITH) estimates*

| Fluid    | Formula                          | Scientific GWP IPCC, 2001 | Scientific GWP UNEP, 2006 |
|----------|----------------------------------|---------------------------|---------------------------|
| HCFC-22  | CHClF <sub>2</sub>               | 1,700                     | 1,810                     |
| HFC-23   | CHF <sub>3</sub>                 | 12,000                    | 14,760                    |
| HFC-32   | CH <sub>2</sub> F <sub>2</sub>   | 550                       | 675                       |
| HFC-125  | CHF <sub>2</sub> CF <sub>3</sub> | 3,400                     | 3,500                     |
| HFC-134a | CH <sub>2</sub> FCF <sub>3</sub> | 1,300                     | 1,430                     |
| HFC-143a | CF <sub>3</sub> CH <sub>3</sub>  | 4,300                     | 4,470                     |
| HFC-152a | CH <sub>3</sub> CHF <sub>2</sub> | 120                       | 124                       |
| HFC-404A | -                                | 3,780                     | 3,900                     |
| HFC-407C | -                                | 1,600                     | 1,800                     |
| HFC-410A | -                                | 1,900                     | 2,100                     |

An alternative method of evaluating the impact of greenhouse gas emissions is the absolute global temperature potential (AGTP), which estimates the average global temperature rise associated with a release<sup>4</sup>. The figure below illustrates the global temperature rise over time resulting from a 1 kg emission of several HFCs, and a 1000 kg release of CO<sub>2</sub>. The HFCs show a rapid warming effect soon after the release but this typically fades well within a 100 year period; the highest impact after a release occurs between 5 – 25 years for most HFCs. Compared to the warming effect of HFCs, the profile of CO<sub>2</sub> is considerably flatter over the 100+ year period following an emission. This demonstrates that the effect of HFCs is significantly more serious than CO<sub>2</sub> in the short-term, so that HFCs play a greater role in the feedback mechanisms associated with the irreversibility of climate change. Integrating the warming impact of HFCs over an arbitrary 100 year period conveniently hides their more immediate and hazardous warming impact.



*Figure 1: Temperature rise potential of emissions of HFCs and CO<sub>2</sub>*

<sup>4</sup> Shine, K. P., Fuglestedt, J. S., Hailemariam, K., Stuber, N. Alternatives to the global warming potential for climate impacts of emissions of greenhouse gases. *Climatic Change*, Vol. 65, No. 4. 2004.

At its height, halocarbon emissions from all sources accounted for about 24% of man made global warming. Improved working practices and the switch from CFCs have resulted in a significant improvement in this figure. However, the improvement is not as great as many would believe. The most recent figures, just published in the IPCC Climate Change 2007 Report are:

|                  |       |
|------------------|-------|
| CO <sub>2</sub>  | 62.9% |
| CH <sub>4</sub>  | 18.2% |
| Halocarbons      | 12.9% |
| N <sub>2</sub> O | 6.1%  |

In 2001 the halocarbon figure was 14%, so despite the Montreal and Kyoto Protocols we have only managed to achieve a very modest 1.1% reduction in 6 years!

Emissions of HFCs are set to triple by 2015, according to a study by the IPCC in April 2005. The report stated that concentrations of HFCs are increasing by 13-17% per year respectively. It also warns that radiative forcing from HFCs could show "significant growth" beyond that date. Moreover, the bank of HFCs in equipment, foams and stockpiles is also set to increase markedly. The build-up of banks of relatively new applications of HFCs will - in the absence of additional bank management measures - also significantly determine post-2015 emissions, the report warns.

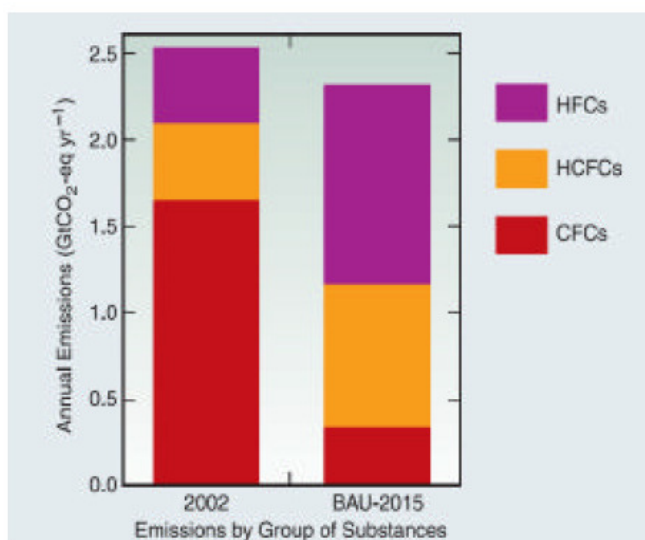


Figure 2: Forecast banks and emissions of F-gases

Over 50% of all HFC-134a ever produced has already been leaked into the atmosphere and the Norwegian Institute for Air Research (NILU) reports that Arctic atmospheric concentrations of HFC-134a doubled over the four year period 2001 – 2004. The Institute describes the increase in HFC concentrations as ‘substantial’. A graph published by the Institute reveals a steady straight line increase in atmospheric concentrations of HFC-134a, based on daily monitoring from the Zeppelin monitoring station at Svalbard.

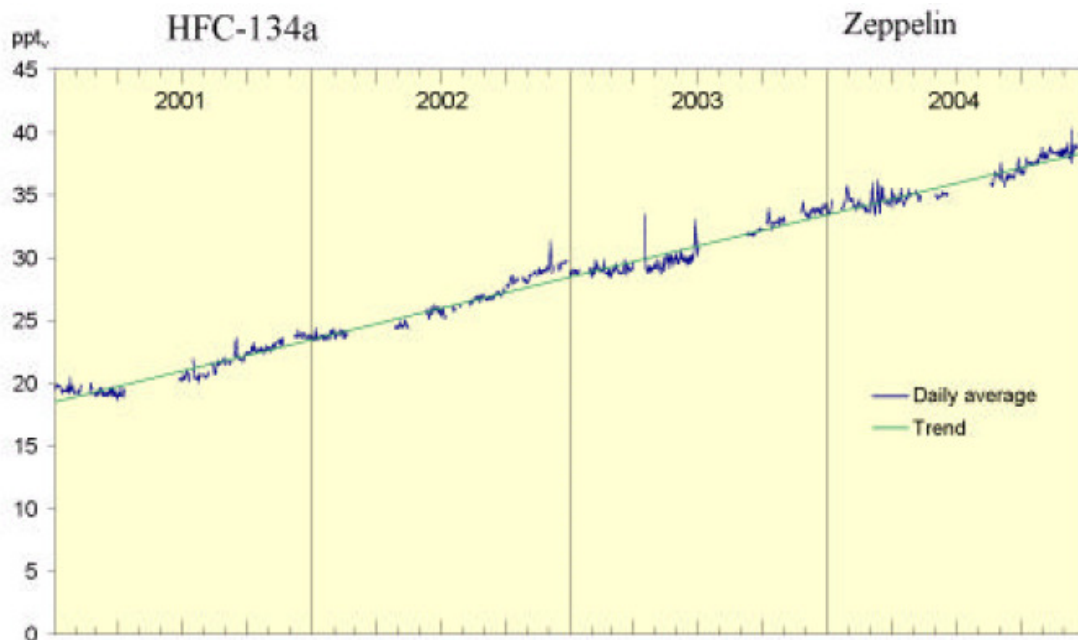


Figure 3: HFC-134a concentration levels over four years

The chart below demonstrates that refrigeration will remain a stubborn emitter under business as usual scenarios and that the EU Regulation on fluorinated gases will not prevent rapidly rising HFC emissions as refrigerant users seek to get out of HCFCs by 2010. With HCFCs increasingly becoming unacceptable, refrigerant users are on the threshold of embracing HCFC replacement technologies, and they needed to be persuaded to consider alternatives to HFCs as their preferred replacement but this opportunity is now being lost.

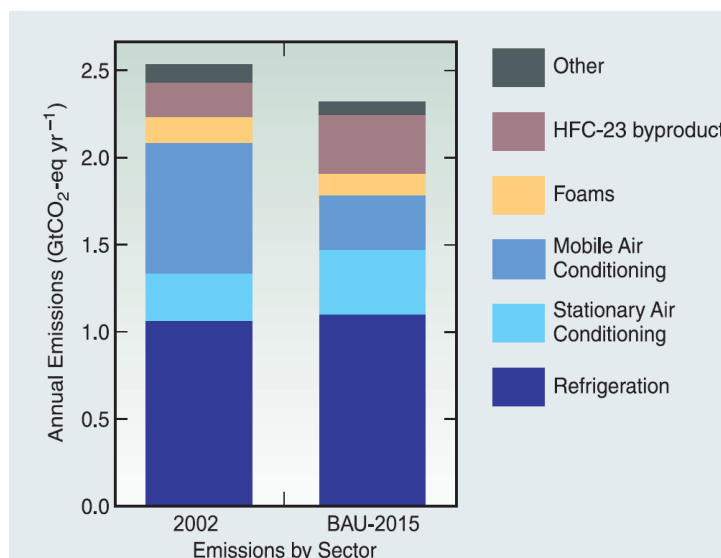


Figure 4: Fluorocarbon emissions by product sector

The environmental problems associated with HFCs extend beyond global warming. HFCs are a source of acid rain. Nor are HFCs genuinely ozone friendly, as the production of HFCs uses the very same CFCs and HCFCs that they were intended to replace, and emissions during manufacturing are inevitable. HFCs also have adverse effects on humans. Not only are they asphyxiants, but they also have toxic side effects. HFC experimentation on human subjects at USAF Patersen was terminated for

safety reasons following unexpected and uncontrollable rapid rises in pulse rate during inhalation exposure. HFCs may have been associated with a number of plane crashes in Australia. It is believed that HFCs are absorbed into the blood stream and break down to produce toxic TFA. BOC's R410a safety data sheet states, "In high concentrations may cause asphyxiation. May produce irregular heart beat and nervous symptoms". The Personal Protection Exposure limit LTEL is set to: 1000ppm, however the Institute of Naval Medicine recommends a continuous exposure limit for R134a of only 250ppm. It might be prudent for hotel bedrooms air conditioned with HFC refrigerants to have a sign warning guests with pacemakers to sleep with the window open.

The UK programme on Climate change was presented to Parliament on 17<sup>th</sup> November 2000. It contained the key elements of the Government's position on HFCs:

- HFCs should only be used where other safe, technically feasible, cost-effective and more environmentally acceptable alternatives do not exist
- HFCs are not sustainable in the long term - the government believes that continued technological developments will mean that HFCs may eventually be able to be replaced in the applications where they are used
- HFC emissions will not be allowed to rise unchecked

This was reinforced on 6<sup>th</sup> October 2004 when Environment Minister Elliot Morley announced stricter purchasing and estate management targets to ensure that government departments do not use hydrofluorocarbons (HFCs) where safe, cost-effective and feasible alternatives are available.

The Chartered Institute of Building Services Engineers, CIBSE, states, "HFCs have global warming potentials similar to most CFCs and HCFCs and as a result use alternative refrigerants with zero or low GWP such as ammonia and hydrocarbons"<sup>5</sup>

The Building Research Establishment's (BRE's) Environmental Assessment Method (BREEAM) 2005 awards an additional point for refrigerants with a GWP below 5 and states that "Hydrocarbons and Ammonia are now widely available and are valid alternatives to HFCs in all buildings"<sup>6</sup>.

On the 1<sup>st</sup> March 2007, senior representatives of ASDA, M&S, Sainsbury's, Somerfield, Tesco and Waitrose said the long-term viability of synthetic HFC refrigerants was undermined by their high global warming potential. This was incompatible with increasing concern over Climate Change, and the legislative uncertainty created by the forthcoming F-Gas review. Continued large scale reliance on HFCs was also inconsistent with their high profile policies on environmental responsibility. As a result, they are investing in new technologies that run on natural refrigerants, such as carbon dioxide and hydrocarbons.

The effectiveness of the F-gas Regulation will be assessed in 2011, and additional applications for F-gas restrictions will be identified. The most likely outcome of this will be a 2017 phase out date for new refrigeration, air conditioning and heat pump applications. Effectively this is the beginning of the end for HFCs. So the crucial question becomes the availability or otherwise of effective alternatives to HFCs.

## 2. OUR PROJECT

Most HFCs can be replaced by natural refrigerants, with the possible exception of the higher pressure HFC, R410A. There is commercial potential for a natural R410A substitute but our research suggests that there is no single component direct natural substitute for R410A. R170, ethane and R744, carbon

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<sup>5</sup> CIBSE, Guide B4 Refrigeration and Heat Rejection, section 4.4.1 Refrigerant selection & section 3.4.2 Greenhouse gases

<sup>6</sup> BREAAAM 02/03/05 v.1.1 P04: Refrigerant ODP / GWP

dioxide, both have potential, but their higher pressure and lower critical temperature limit their suitability as R410A substitutes, particularly in air conditioning applications.

We tested both R410a and the semi synthetic blend of R32/ R600a (90/10) as recommended in published literature (Calm and Domanskii, 2004). This blend has a slightly higher pressure than R410A. It offers higher efficiency, and a reduced GWP of 603, an improvement on R410A with a GWP of 2060, but still well above the EU target of 150. It is flammable (though not as flammable as pure hydrocarbons). It appears to be compatible with mineral oil in addition to synthetic lubricants. This gave us our reference data.

### 3. HYDROCARBONS

P.J. van der Weyde of Philadelphia first used hydrocarbon refrigerants in 1866; please remember that this is not new technology!

The greatest success of hydrocarbons has been the application of R600a to domestic refrigerators. Since 1992, over 120 million such refrigerators have been produced worldwide and I am not aware of a single accident due to the flammability of the refrigerant. Domestic refrigerators using isobutane are at least as safe as those using halocarbons; they are more efficient and quieter. Hydrocarbons have now been used in equipment covering the whole spectrum of commercial refrigeration and air conditioning equipment.

The excellent performance of hydrocarbons refrigerants can be attributed to the following parameters:

Lower compression ratio (due to higher suction pressures and lower discharge pressures at specific operating temperatures)

Improved heat transfer in heat exchangers (as a result of more favourable fluid thermal and transport properties)

Reduced system pressure losses (from lower refrigerant density and viscosity)<sup>7</sup>.

Hydrocarbons outperform traditional halocarbon refrigerants in all aspects other than that of flammability. It is this one single issue which has to date prevented their widespread adoption.

We tested hydrocarbon blends. The two graphs (Fig. 1) show evaporating pressure (at -6°C and -30°C) against volumetric refrigerating capacity (+35°C condensing). The data points are for R410A, an R290/R170 mix and R1270/R170 mix. The data-points for the HCs are for a composition ranging from 0.70/0.30 to 0.90/0.10 for each mix.

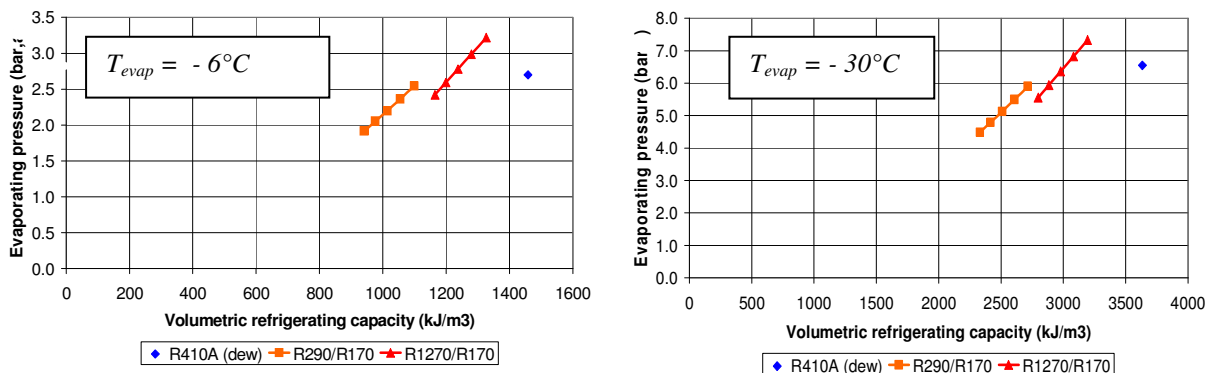


Figure 5. Evaporating pressure against volumetric refrigerating capacity

<sup>7</sup> www.care-refrigerants.co.uk-CARE Technical File-Design Resources--Performance Test Data

We noted that whilst R1270/R170 can achieve the desired pressure, the volumetric refrigerating capacity is much lower. In other words, if the blend is selected for the same evaporating pressure, the cooling capacity will be about 15% less than R410A. We also noted the temperature glide of up to 15K, which could be detrimental.

#### **4. CARBON DIOXIDE**

CO<sub>2</sub> (NIK744) has been called the forgotten refrigerant; used as a refrigerant since 1862, until the advent of halocarbons in the 1930s led to its abandonment, CO<sub>2</sub> finally went out of use in the 1950s. Recent developments suggest that the time is now right for its reapplication with modern technology.

It is important to remember that CO<sub>2</sub> is certainly not "safer" than ammonia and HCs. On the contrary, the pressure and physiological characteristics of CO<sub>2</sub> are such that it must be treated with at least as much respect as the others. Carbon dioxide is not just a simple asphyxiant like nitrogen; it has a toxic/narcotic effect at much lower concentrations. It causes unconsciousness at concentrations above 10% in air. At much lower concentrations than for a simple asphyxiant like nitrogen where you need about 50-60 % (to reduce the O<sub>2</sub> level below 10%) to have a similar effect.

Nevertheless, as well as being environmentally friendly, CO<sub>2</sub> has perceived advantages over both ammonia and the hydrocarbons. It is inexpensive and compatible with normal equipment and lubricants. Its relatively high pressure is well suited to modern equipment design and gives a dramatic reduction in compressor volumes and pipe dimensions. It possesses excellent heat transfer characteristics at high pressure.

The commercialization of CO<sub>2</sub> is proving difficult, not only due to the high pressures, but in heat pumps, CO<sub>2</sub> needs to glide down to very low temperatures making it suitable for domestic hot water 75c / 15c, but not for central heating 65c / 45c applications. The relatively low critical temperature and relatively high triple point hinder its application, and cause super-critical operation at high ambient temperatures and possible solidification when the refrigerant undergoes rapid reduction of pressure towards atmospheric.

#### **5. AMMONIA**

The dominant characteristics of ammonia are its penetrating smell and its acute toxicity. Despite these defects, ammonia has been widely used for well over 100 years and has a good safety record. This is perhaps partly due to the unpleasant and penetrating smell, which ensures that leaks are not tolerated.

Ammonia is the only one of the original refrigerants that has continued to be used on a widespread basis since the advent of halocarbons. It has been used for decades in industrial refrigeration plants and its continued popularity throughout the CFC era amply demonstrates its unique benefits. It has no ozone depletion potential and no global warming potential. Its energy efficiency is at least as good as, and in most applications better than, HCFC22.

There are, however, a number of drawbacks. Ammonia is not compatible with conventional lubricants and with trace quantities of water is highly corrosive to copper (also zinc, tin, cadmium, rubber and some plastics). It cannot therefore be used with hermetic or semi-hermetic compressors unless aluminium windings are used. Leakage from shaft seals is difficult to eliminate. Ammonia is flammable in air at concentrations of 16 to 27% by volume, although the ignition temperature of ammonia is high at 650°C. Ammonia is not a cumulative poison but it is toxic at high levels. Inhalation can be lethal but it has a pungent smell, which will warn personnel of leakage even at very small concentrations - typically 5ppm or below. The thresholds for permissible exposures are 25ppm long term and 35ppm for short-term exposure. Exposure at short-term concentrations up to 200ppm will cause mucous membrane and eye irritation but will have no lasting consequences.

It has a relatively high NBP (i.e. higher than the desired application temperature), low evaporating temperatures lead to sub-atmospheric operation which can cause air to leak into the system, and very high compressor discharge temperatures, often necessitating an additional stage of compression with inter-stage cooling.

## 6. CONCLUDING REMARKS

We conclude that there is a need for an azeotropic or near azeotropic (i.e. glide of 2K or less) mixture with similar pressure characteristics to R410A.

Since azeotropic forecasts from experimental data are expensive and time-consuming, the availability of theoretical predictions for azeotropic behaviour not only reduces costs, but also saves time by narrowing the experimental search field. A new viewpoint for the prediction of azeotrope formation between components in a mixture that does not require vapour-liquid equilibrium calculations has been developed. The method employs neural networks and global phase diagram approach to correlate azeotropic data for binary mixtures based only on critical properties of the individual components in the refrigerant blend.

The thermophysical properties of various mixtures were evaluated with respect to critical point, saturation pressure-temperature, triple point, temperature glide, and other properties such as densities, enthalpies and viscosities. It was then determined whether chemical interactions are likely to take place between the component fluids, with compressor oils, common contaminants such as air and moisture, and with common system construction materials including metals, plastics, elastomers and compressor oils. At this stage, other factors such as the mixing characteristics of the substances identified, and their flammability and toxicity were also considered.

Next, consideration was given as to the likely safety classification of such mixtures. This was accomplished by calculating, from currently available safety information (toxicity, flammability), the resultant ISO 817 classification, for both the intended mixture and fractions thereof. Whilst it is important to strive for improved potential efficiency, there are also significant advantages associated with a “lower” (i.e. less hazardous) safety classification. Finally, the environmental characteristics of the proposed blends were considered. Of primary interest in this regard, is the evaluation of mixture GWP and ODP, but consideration was also given to other environmental factors (such as the potential for photochemical ozone creation, and bio-accumulation) in the hope that future legislation to control such factors will not affect the chosen blends.

Once preferred mixtures were determined, consideration was then given to their performance within the intended refrigeration systems. This was initially carried out by system performance simulations, and latterly by experimental evaluation. In addition to checking that minimum performance criteria are met, the simulated and experimental exercises are additionally used to determine the mixture composition that provides an improved efficiency across the range of likely equipment. Consideration was also given as to the performance of possible blends in existing components and systems that have been designed for already commercialised refrigerants, since the application of new refrigerants is simplified if components are already available

These new blends offer notable advantages over existing refrigerants. In particular these blends exhibit:

- zero ODP;
- a low (below 150) GWP;
- improved thermodynamic properties (such as critical temperature and temperature glide) over similar existing refrigerants;
- good solubility with oils;
- low toxicity; and

reduced flammability.

In addition, these blends comprise of predominately environmentally benign substances and as such are more environmentally friendly than some existing refrigerants, and have well known and understood chemical and material compatibility. We are extending our work to identify New Low Environmental Impact Azeotropic Refrigerant Blend replacements for a wide range of practical applications.

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