Rising to the challenge

The introduction of new refrigerant gases with reduced global warming potential

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When Carl von Linde first used gases such as methyl chloride and ammonia as heat transfer fluids in his refrigeration systems, the selection of the ideal refrigerant gas was primarily based on system performance. Since that time, the sweet spot for selection of an ideal refrigerant gas in any application has been governed by factors such as the achievable operating temperature, energy efficiency, the cost of the refrigeration equipment, safety and environmental impact. Despite being both toxic and flammable, ammonia has survived as a refrigerant gas until the present day. Methyl chloride, on the other hand, was phased out alongside other CFC's due to the Montreal Protocol, in efforts to protect the Ozone layer.

The latest issue driving change in the refrigeration sector is the requirement to reduce the global warming potential (GWP) of refrigerant gases. In practical terms, this means that the current generation of HFC's is being phased down in favour of a group of refrigerant gases known as HFO's. Gases such as ammonia, carbon dioxide and propane are also finding favour as heat transfer fluids in modern refrigeration systems. The most sophisticated systems use multiple circuits, each containing a different refrigerant gas to cascade from cool to very cold temperatures and thereby maximise the overall system efficiency.

The challenges associated with production and handling of modern HFO refrigerants, many of which are flammable, are significantly different to the inert gases that were dominant in the past. This means that the introduction of the new generation of refrigerant gases is a monumental challenge which has consequences through the refrigerant gases value chain from molecule producers, to distributors and end-users.

Jumping the safety hurdles

For refrigerants distributors wishing to stay the course and introduce flammable HFO products, multiple investments have been taking place. Cylinder filling equipment must be upgraded to be compatible with flammable gases. Approvals must be secured from local regulators to handle and store the required inventories of flammable materials. New cylinder valves with a left-hand outlet thread must be purchased. Cylinders must be re-painted with a red shoulder colour to denote flammable contents. Numerous hurdles exist and not all participants have been fit enough to jump them.

The consequences in many European countries have been consolidation from a breadth of players with a range of technical capabilities to concentration towards fewer companies with the highest operational and safety performance. Compliance to standards is clearly essential to receive certification from local authorities and it goes beyond that because the ability to safely handle refrigerant gases is a deal breaker when the major producers are considering and selecting their distributor partners.

On this point, Matt Ritter, Global Business Director for Fluorocarbons at Arkema says that, "In Europe and Asia, we work with several channel partners to improve our access to the market. When we select a refrigerants distributor, the top two criteria on our list will be their safety record and the integrity of their product stewardship programme. This industry has transformed in recent decades and we are now so extremely focused on reducing product losses to atmosphere, which minimises our environmental impact, and so deeply concerned for safety when we handle flammable gases that there is simply no room for choosing anybody but the best. Put simply: our corporate responsibility culture comes first."

The squeeze-out

Safety regulations and high expectations from molecule suppliers have narrowed the field and driven up standards in the sector. There is, however one additional 'squeeze-out' that needs to take place. The elephant under the carpet in Europe at present is the issue of suspected illegal imports of refrigerant gases that are subject to quota restrictions such as the HFC R134a. Whilst few people really know what is going on in this undercover activity one mass-balance indicator suggests that illegal imports are abundant and widespread: the reduction in R134a sales volumes is not being matched by an equivalent increase in the sales of its main replacement: R1234yf.

R134a was used widely as an automotive air conditioning gas. All the major car makers in Europe now have made the switch to R1234yf for new models. But, car service garages are suspected to be the targets for illegally imported R134a which can easily be smuggled across borders in cylinders in the boot of a car. One of the clearest indicators of this illegal trade is the arrival of disposable cylinders in Europe...they are banned for refrigerants use in the EU so their presence is a tell-tale sign that gases are being illegally imported also. This kind of trade was also an issue during the phase out of CFC's in Europe 20 years ago.

The phasedown

The refrigerant gas of choice for much of the commercial refrigeration sector, or supermarket freezers as we might also refer to this segment, in recent years has been R410A. Fabrizio Codella, Refrigerants Technology and Product Specialist at Rivoira Refrigerants in Italy, now part of Nippon Gases, explains how customers are responding to the phasedown targets for this high GWP HFC blend in Europe. "We have received several enquiries for samples of R454A, R454C and R455A for commercial refrigeration applications. We believe that R454C will have a very good future because it satisfies the post 2022 target in this application for a GWP value below 150. It seems well suited to small-scale supermarkets where the higher cost and complexity of a cascade system using a fluorocarbon plus CO_2 would be too expensive."

"For air conditioning, there has been good uptake for R32 in the last few years. However, we can imagine that parts of that market in Europe will move towards R452B and R454B due to their lower GWP values and because they have a lower compressor discharge temperature which means that the refrigeration equipment can be more easily manufactured than that for use with R32. It is notable that all the gases that I have referred to up to now are flammable."

"Some of the blends that contain HFO chemicals blended with HFC's are also non-flammable. For example, R513A which is often selected as a replacement for large building air conditioning chillers in medium temperature applications. This product has only half the GWP of R134a, which it commonly replaces. Some of the replacements for R404A are also non-flammable blends. They include R448A, R449A and R452A. Whilst these products have the handling advantage of being non-flammable, they contain HFC's in the blend and all of them, therefore, have a GWP more than 1,000. It's just the way the chemistry works that the lower GWP products are more flammable."

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Getting to zero

To hit ultra-low GWP levels with fluorocarbons, we need to move to pure HFO's such as R1234yf and R1234ze, both of which have a GWP of less than 10. Finding the optimal solution is never easy. There are always trade-offs in this industry – there always have been, ever since Carl von Linde got us started. For example, to use R1234ze the refrigeration system must be designed with high capacity centrifugal compressors, which add to the capital cost of the equipment. But, despite this, there seems to be a bright future for this gas in new-build systems.

Moving beyond fluorocarbons, the industry can also opt for the so-called natural refrigerants ammonia and CO_2 (R744) that have zero GWP. The so-called 'not-in-kind' hydrocarbon refrigerant Propane (R290) has also become popular for domestic refrigerators and sits alongside some of the pure HFO gases and natural refrigerants with GWP values less than 10. Again, trade-offs are at play. Ammonia (R717) is toxic, flammable and has a pungent smell. Its properties have meant that it has firmly occupied a niche in large industrial refrigeration systems, for example in the chemicals industry, for many years. But since the arrival of alternatives, these attributes have become disadvantages in domestic refrigerators use.

No signs of shortages, yet

Despite the long hot summer in some European countries in 2018, there were no widespread shortages of refrigerants. One tell-tale product where the shortages could have occurred (or might yet occur) is R404A. On the one side of the supply versus demand balance, producers have reduced their production volumes and switched to alternative lower GWP products to meet their production quotas. To counteract the impact of reduced production, demand for R404A has also been suppressed due to the success of alternatives such as R448A and R449A. In addition, the use of in-situ refrigerant recycling equipment that removes some of the oil from an aged system is helping to avoid demand for virgin materials. All in all, the scales seem to have been evenly balanced and shortages have, thus far, been avoided. gw