Chillventa 2018 – the Baked Alaska of refrigerants business debate

By Stephen B. Harrison

Changes in refrigerant gases took centre stage at the biennial Chillventa exhibition last October (16th to 18th) in Nürnberg, Germany. The event was likened to a 'Baked Alaska' – the weather was stunningly warm and sunny outside as Bavaria enjoyed another golden autumn, but the talk inside was decidedly cold as refrigerant gases were the hot topic. And much of that talk centred on the pros and cons of fluorine-based chemistry for refrigerants.

From rock, they make refrigerants

Fluorspar is mined in locations such as Canada, Kenya and South Africa. From these rocks, the mineral calcium fluoride is extracted and processed with sulfuric acid to form hydrogen fluoride gas. And so, we have the first links in the chain for production of most modern refrigerant gases.

The chemistry of the fluorine atom is unique, and many industry participants believe it will feature in refrigerant gases for decades to come. According to Fabrizio Codella, Refrigerants Technology and Product Specialist at Rivoira (now part of Nippon Gases), "The introduction of alternatives such as ammonia, carbon dioxide and propane may penetrate up to 30% of the total global refrigeration market in the next few decades, but these gases simply do not offer the same performance, compatibility with installed refrigeration equipment, economics, ease of handling and safety as those that contain some amount of fluorine."

Sunburn and flame speeds

Fluorine has been in use in refrigerant gases for many decades. Initially it was combined with chlorine and carbon to produce CFC's, then came the second generation of HCFC's which evolved to the third generation of HFC's. These changes were implemented to reduce either the ozone depletion potential or the global warming potential (GWP) of the refrigerants. The most recent step has been the introduction of fourth generation HFO's.

HFO's molecules contain the same atoms as HFC's, but a carbon-carbon double bond is introduced. To explain how this helps, Codella said, "We want the molecules to break down in the upper atmosphere, in the presence of UV light from the sun, so that their GWP can be reduced. But, we can't have it both ways! If the molecule can be burned up by the sun's energy it is also likely to burn down here on earth. So, a feature of the latest generation of fluorine containing refrigerants, known as HFO's, is that they are classified as 'Mildly Flammable'."

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'Mildly Flammable' may sound like being 'a little bit pregnant' but the ASHRAE Standard 34 does indeed differentiate between propane as having 'Higher Flammability' with an A3 classification and the HFO gas R1234yf as being 'Mildly Flammable' with the designation A2L. Codella affirmed, "It all comes down to the flame speed and with a value of less than 10cm per second, the modern HFO refrigerant R1234yf, can be classified as AL2."

Hundreds of millions of dollars invested

The transition to HFO refrigerants has been underway for the past decade, with the auto industry now a major consumer of R1234yf, which has broadly replaced R134a for car air conditioning systems in Europe. Stationary refrigeration systems, which have historically relied on R404a, are also making the change to HFO-based products, such as Opteon™ XP40, which has the generic designation of R449A.

For end-users, the challenge has been to move from non-flammable gases to those that have some element of flammability. For the producers, the challenge has also been tremendous. According to Stefanie Kopchick, Global Market Manager for Opteon™ Stationary Refrigerants at The Chemours Company, her organisation has, "invested hundreds of millions of dollars in HFO production in recent years, with the latest major investment for new capacity coming on-stream in Chorpus Christi, Texas, at the end of this year (2018)."

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Moving down the periodic table

Chemours is not alone in the race to reduce GWP. According to Matthew Ritter of the fluorocarbon specialist Arkema, it also sees great potential in fluorine-based chemistry for refrigerants.

He added that, "Our business model is built on excellence in fluorocarbons. For this reason, when we observed the decline in the market share for fluorine molecules in the overall refrigeration sector and the emergence of so called 'natural refrigerants' such as ammonia or carbon dioxide (CO_2), we chose not to offer those gases in our range. We have, instead, focused on applying our core strength in fluorocarbon chemistry to other applications for these molecules, such as foam blowing and the electronics industry."

Honeywell sees the world differently. One of its innovations for 2018 was to commercialise a non-flammable R404a replacement, a refrigerant blend, marketed as Solstice® N41. Martin Orsag, Communications Director for Performance Materials and Technologies, said about this development, "The key feature of N41, that sets it apart from other R404a replacements for stationary refrigeration, is that it is non-flammable. We achieved this designation by using a blend which contains CF3I, a refrigerant molecule that contains Iodine. Iodine is in the same group of the periodic table as chlorine and fluorine."

Wrapping it all up

The packaging for refrigerant gases is also evolving. For several years, the use of disposable containers in Europe has been banned for most refrigerants. This has led to the search for lightweight alternatives.

Amtrol-Alpha has taken a bold step in this direction with the launch of its new Fourtis® cylinder. Arek Kubasik, Strategic Accounts Manager at Worthington Industries, explained, "We launched the Fourtis® at the LPG exhibition in Houston earlier this month. It is a Type IV fully recyclable composite cylinder. The 24-litre version has an un-valved weight of only 5kg, less than half the weight of an equivalent size steel cylinder."

Whilst composite cylinders are certainly in growth, the lion's share of refrigerants cylinders, in use today, are of a welded steel construction and the Czech company Vitkovice Milmet SA is a major manufacturer. Piotr Siudej, Sales Manager at Vitkovice, declared to **gas**world, "We make about 1,300,000 welded steel cylinders per year at our factory in Poland. About 200,000 of these are destined for the refrigeration sector and the remainder are used for LPG and chemical gases such as ammonia and sulfur dioxide. Our success is built on a combination of competitive pricing and attention to quality." gw