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History of Flammable Refrigerants

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Why you should attend

- By analysing the history of the use of flammables this paper will give a comprehensive background to the when, why, how and where of their use.
- It explores their role in the emergence of mechanical refrigeration, how they have supported the implementation of the Montreal Protocol and how the range of applications is now expanding.
- It also explains how different flammability classifications and safety requirements have emerged.

Summary

Refrigeration history is interspersed with the use of flammable refrigerants. During the 19th century, many of the early inventions employed flammable refrigerants. Until the time when CFCs became commercialised in the 1930s about a quarter of smaller systems used a variety of different flammable refrigerants, including ethyl ether (R610), methyl chloride (R40), ethyl chloride (R160), methylene chloride (R30), methyl formate (R611) and isobutane (R600a) and the majority of industrial/commercial systems used ammonia (R717). Whilst most of the refrigerants for smaller systems became substituted with CFCs, this was primarily due to mitigation of toxicity hazards, rather than ignition risks. As the Montreal Protocol came into force there were numerous studies assessing alternatives, including flammable HFCs and HCs. Initially, the domestic appliance sector briefly opted for R134a, but following the Greenpeace “Greenfreeze” campaign, virtually all European manufacturers adopted R600a. From the early 1990s, HCs became used more widely in small commercial and intermittently in other subsectors. In parallel, refrigeration safety standards were revised and amended to reflect the use of this technology. A decade or two later, safety standards were modified again to include the 2L lower flammability safety classification, igniting the commercialisation of flammable HFCs; primarily the introduction of tetrafluoropropene (R1234yf) in car AC systems and then difluoromethane (R32) in air conditioners. This paper traces the use of flammable refrigerants through textbooks, technical articles and patents, from the middle of the 18th century to the present day, breaking it into four “eras”, mirroring the extent of use of flammables at the time.

1 Introduction

Refrigerants[1] – or “calorific media” (Siebel, 1918) – that are flammable[2] have interspersed refrigeration history. With the emergence of mechanical refrigeration, they were used simply because they were available and they worked well. Following the commercialisation of halocarbon refrigerants (chlorofluorocarbons, CFCs, hydrochlorofluorocarbons, HCFCs, etc.) they were set aside because they were less convenient; flammability of refrigerants was not a major issue, more of an inconvenience. Conversely, it was toxicity of many of the refrigerants – flammable and non – that posed the greatest concern. But as concerns over climate change/ global warming have become more prominent, the industry has little choice – by both environmental legislation but also chemistry – but to revert back to flammables for many applications. Furthermore it will be argued that whilst the use of a flammable refrigerants may instil resistance in some stakeholders, it is in principle a characteristic that is readily handled by good design and adherence to rules. Often exaggerated concerns and polarisation between refrigerant types, largely a hangover from earlier eras, is now complicating the wider use of flammable refrigerants.

Why should anyone be interested in the history of flammable refrigerants? Is the choice of refrigerant in the days of old of relevance today? It is hoped that a more intimate appreciation of the use and transition away

1 All refrigerants mentioned more than once are listed in Appendix: Table 4, along with safety and environmental data.

2 Throughout the literature, both terms “flammable” and “inflammable” (as well as “explosive”) are used. Clarification on the former terms is useful. “Flammable” and “inflammable” both mean "able to burn". Instead of the prefix “in“ denoting the negative, "inflammable" originates from the Latin “inflammare”, meaning "to cause to catch fire." Whereas "flammable" is from the Latin verb “flammare” meaning "to catch fire". Initially, “inflammable” was adopted into English during the early 1600s, whereas “flammable” from “flammare” was coined in the early 1800s. Consequently, there are two synonyms that appear to be antonyms. Hereafter, “flammable” will be used. (“Inexplosive” is always the antonym to “explosive”.)

from and back to flammable refrigerants will provide a more dispassionate acceptance of the technology. For this, the chronology of flammable refrigerants is divided into four “eras”:

- Unfolding of (flammables in) mechanical refrigeration – 1700s to 1930s
- The flammable interlude – 1930s to late 1980s
- Re-emergence of flammables – late 1980s to c. 2010
- The explosive era – c. 2010s onwards

These eras broadly reflect a level and extent of activity involving flammable refrigerants, but also the available (literary) sources, amount of information and degree of interest in such refrigerants. They are vaguely consistent with the “epochs” of Thévenot (1979) and the “generations” of Calm (2012).

As with any discussion on choice of refrigerants, it is apt to mention all the usual criteria: performance, cost, environmental impact, material suitability, etc. However, with a historical perspective, the author would also recommend the century-old equivalent in the article of Matthews (1920), which provides a entertaining “Benny-Hill-esque” overview of the various HC-based and other refrigerants. Regardless, the concluding statement is “Technically there are as many refrigerants, therefore, as there are different substances less one, some of which possess advantages over other, but none of which have all the advantages of the theoretically perfect refrigerant.” The essence of this is recurrent throughout almost all publications presently drawn upon, including the recent Guidance Note 37 (IOR, 2021).

2 Unfolding of (flammables in) mechanical refrigeration – 1700s to 1930s

The unfolding of refrigeration technology appeared to be fairly slow; the occasional invention or demonstration here or there. But the idea slowly gained pace towards the second half of the 1800s. Synthetic chemistry began in the mid-1800s, but because refrigeration was still an embryonic technology, the new chemists of the period would not have chosen to seek out new refrigerants as a matter of priority. Therefore, refrigeration impresarios (as they apparently were) had to rely on any fluids that were available and which worked (Calm, 2012), regardless of flammability or any other characteristics. Similarly, there were almost no books, no refrigeration technology journals or magazines from this time, so the only available information is from patents and the occasional report.

2.1 The first flammable refrigerant

It appears that the first refrigerant was in fact flammable – ethyl ether (R610) – which coincided with the first mechanical refrigeration system. This was demonstrated by the legendary William Cullen (1710 – 1790), born in Lanarkshire, Scotland. His training and career appeared fairly diverse; he attended arts classes, a medical apprenticeship, was a ship's surgeon, an apothecary, had a medical practice, lectured in medicine, was the Chair of Medicine and lectured on chemistry at Glasgow and Edinburgh Universities. He spent many years formulating his own theory of heat and combustion and was referred to as “the true commencer of the study of scientific chemistry in Great Britain”, although there seems to be considerable disagreement as to his contribution to the progression of chemistry as a science. For example, “Cullen wrote very little on chemistry and made no discovery” and his “hopes for drawing generalisations from a mass of miscellaneous information, were not novel” (Doyle, 2021).

Nevertheless, Cullen was surely remarkable in that at the University of Glasgow in 1748, he was the first to demonstrate artificial refrigeration. And it used a flammable refrigerant. In his demonstration, Cullen used a pump to create a small vacuum over a container of R610. When the R610 began to boil, it absorbed the heat from the container's surroundings, causing it to cool. This was recorded in his only published chemistry-related paper, “Of the Cold produced by Evaporating Fluids, and of some other Means of producing Cold”. At least from the perspective of anyone who relies upon artificial refrigeration, this was surely a major discovery!

Coincidentally, whilst philosophising on heat and combustion, Cullen made a significant contribution to extending the current (at the time) theory of flammability: phlogiston theory. Phlogiston theory originated in 1667 from the alchemist and physician J. J. Becher (later formalised by G. E. Stahl) and postulated the existence of a fire-like element called phlogiston. This was contained within combustible bodies and released during combustion. Cullen’s contribution was that of “mephitic air” that held out hopes for the physical isolation of phlogiston. The existence of phlogiston was based on empirical observations; the transfer and decomposition of phlogiston could be described by chemical explanation (Taylor, 2006). Although a number of chemists – notably Joseph Priestley, one of the discoverers of oxygen (“dephlogisticated air”) and incidentally who discovered R717 (“alkaline air”) – tried to retain some form of the phlogiston theory, by around 1800 it had been superseded by conventional combustion theory.

Cullen had a series of successors to (Nairne, Leslie, Vallance, etc.) who adapted and developed his ideas for mechanical refrigeration, often also using R610 (Thévenot, 1979).

2.2 Incendiary inventions

Over the 19th century there were a series of successive developments and inventions related to refrigeration technology, many of which utilised flammable refrigerants. These are widely described in books such as the legendary Thévenot (1979), Gantz (2015), Rees (2016) and the exuberant book of Wilson (1979).

In 1805, Oliver Evans (1755 – 1819; USA) designed a refrigeration machine, which was intended to use R610. Whilst he is often called the inventor of the refrigerator, he never actually built it. Apparently taking the ideas of Evans, Jacob Perkins (1766 –1849; USA/GB) obtained a patent in 1835 for “Improvements in the apparatus and means for producing ice and in cooling fluids”. In this patent it states “I chiefly recommend [ethyl] ether as the material to be evaporated” and “I would have it understood that I do not claim the cooling of fluids by the evaporation of [ethyl] ether, or other volatile fluids; neither do I confine myself to the use of [ethyl] ether, though I prefer that fluid both as to its cost and its property of evaporating at exceedingly low temperatures.” Such favourable views of flammable refrigerants run throughout the history of refrigeration.

About the same time, John Hague (1781 – 1857; GB) collaborated with Perkins to construct the machine, using R610. Apparently the first “compression expansion heat pump”, using R610 was built by Hague and Perkins (Grace’s, 2021), although there may be confusion over their hot water heating system.

A few years later in 1850, Alexander Twining (1801 – 1884; GB/USA) was granted a British patent for a commercial refrigeration machine for ice making (in the name of James Kingsford), which utilised R610 as the refrigerant. Moments later in 1855, James Harrison (1816 – 1893; GB/Australia) received a patent for a refrigeration system. The British patent 747 referred to R610, R717 or (ethyl) alcohol as the refrigerant. Daniel Siebe (1830 – 1866; GB) then opened a factory, achieving success in the 1860s and 70s with dimethyl ether (RE170) machines, based Harrison’s system (Pearson, 2018). Away from Europe, Daniel Holden (1837 – 1924; USA) began building ice machines in 1870s with “chimogene” (Roberts, 2015).

About the same time, developments were also progressing in Europe, where Ferdinand Carré (1824 – 1900; France), whilst known for his development of the R717-water absorption system, also developed an R610 compressor around 1857. Also, Charles Tellier (1828 – 1913; France) developed an RE170 compressor in the

1860s and refrigerating plants both for static applications (factories, breweries) and ships for the transportation of perishable foods. German engineer Carl von Linde (1842 – 1934; Germany), patented the process of liquifying gas in 1876. His first machine, using R40, was completed in 1874 and tests proved its efficiency was double that of other existing equipment. Linde also developed a compressor for RE170 and an "improved" R717 machine in 1877, whilst David Boyle (1837-1891; USA) also developed one of the first R717 compressors in 1873.

There were many other characters that made significant discoveries and/or obtained numerous patents in refrigeration and related fields. As with recent times, not all of the major events and discoveries during the era of the unfolding of mechanical refrigeration involved flammable refrigerants, although many of them did.

From the late 1890s, refrigeration began to play a more prominent part in society; not only for the industrial and food storage sector but also within domestic settings. In 1899, A. T. Marshall received a US patent for a refrigerator, which used R717. The novel features were its automatic controls (expansion valve, a thermostat, a motor cut-off and condenser water regulator). In addition to some non-flammable options, R40 was used alongside R600a. Across Europe and North America, refrigeration units were being produced with flammable refrigerant; Figure 1 and Figure 2 show some examples.

Figure 1: Zerozone R40 condensing unit from 1926 (Refrigeration Museum, Brighton, Michigan, USA)

Figure 2: Copeland R600a condensing unit from 1926 (Refrigeration Museum, Brighton, Michigan, USA)

Notably, during the early 1930s, Underwriters Laboratories (UL) produced a report examining the safety of various, including flammable, refrigerants (Nuckolls, 1933). Amongst other (non-flammables), it included R30, R40, bromomethane (R40B1), R160, ethyl bromide (R160B1), ethane (R170), propane (R290), butane (R600), methyl formate (R611), R717 and R1130(E). Not only does it provide flammability data such as ignition temperature, flammability limits, explosion pressure and flame propagation, it also describes toxicity of decomposition products. It concludes with comparative health hazards of refrigerants in the presence of flames and surfaces at high temperatures as well as fire and explosion hazards.

Despite many of the refrigerants in use towards the end of this era being flammable, the patents and later literature (trade journals, technical papers, textbooks) do not express concern (other than a philosophical context) or report on accidents due to flammability.

3 The flammable interlude – 1930s to late 1980s

During the interlude era, there is little discussion on the use of flammable refrigerants, except of course, for R717. As is well known, the use of many of the preceding fluids were substituted by the halocarbon refrigerants, so flammables faded from use in most applications. Arguably, the replacement halocarbons were not necessarily "better" refrigerants, but easier to use given there were fewer concerns to worry about. Indeed, it seems that the vast majority of accidents reported were related to the toxicity of various (flammable and non-flammable) refrigerants and not their flammability (Giunta, 2006). Regardless, as pointed out by McLinden and Huber (2020), the development and production of a fluid specifically for use as a refrigerant was undoubtedly a revolutionary development. Needless to say, it was found that this technology would ultimately have serious consequences (Kahlert, 2013). Although halocarbon refrigerants were commercialised in 1930s, most were initially discovered and synthesised between 1890s and 1920 by the Belgian chemist, Frédéric Swarts (1866 – 1940); he first prepared R12 in 1891 and many others followed (Banks and Tatlow, 1986; Kauffman, 1955).

3.1 Comburent textbooks

Very little of the literature covering this era refers to flammable refrigerants, so refrigeration textbooks have been studied to help form an impression. All of these textbooks introduce the choice of refrigerant in more or less the same way, offering the usual list of criteria to consider when selecting: performance parameters, non-corrosive, low toxicity, leaks should be easy to detect and locate and interestingly, while some state "definitely" non-flammable, they additionally say, but "preferably" non-explosive!

Throughout the interlude era there were many articles relating to thermophysical properties, heat transfer coefficient and pressure drop of fluids, including both HC and halogenated flammables, although none addressed application aspects.

Table 1: Flammable refrigerants mentioned in textbooks[3]

Source	Year	Methylene chloride (R30)	Methyl chloride (R40)	Ethyl chloride (R160)	Ethane (R170)	Propane (R290)	Butane (R600)	Isobutane (R600a)	Diethyl ether (R610)	Methyl formate (R611)	Ammonia (R717)	Dichloroethene (R1130(E))
Wallis-Tayler	1895								X		X	
Siebel	1918		X	X		X	X		X		X	
Hull	1927		X	X		X	X	X	X		X	
MacIntire	1928	X	X	X	(x)	(x)	(x)				X	
Moyer & Fittz	1932	X	X	X	X	X	X	X	X		X	X
Crawhill & Lentaigne	1934		X	X							X	
Althouse & Turnquist	1943		X					X		X	X	
Althouse & Turnquist	1944	X	X	X				X		X	X	
Lewis	1943		X	X				X		X	X	
Bäckström	1946		X	X				X			X	
Jordan & Priester	1948	X	X	X	(x)	(x)	(x)	X		X	X	X
Wostrel & Praetz	1948	X	X	(x)		(x)	(x)	X	(x)	X	X	(x)
BS1608	1949		X									
Collacott	1950		X								X	
BS 1725	1951		X								X	
Nelson	1953	X	X	(x)	X	X	X	X		(x)	X	
Sparks & DiLilio	1959										(x)	
Althouse & Turnquist	1960	X	X	X	(x)	(x)	(x)	X		X	X	
Breddy	1961		X								X	
Dossat	1961	X	X		X	X	X				X	
Fidler	1965		(x)								X	
Anderson & Herbert	1971		X								X	
Reed	1974		X								X	
Meacock	1979	(x)	X	(x)	X	X	X	(x)	(x)	(x)	X	(x)
Althouse et al.	1982		(x)	(x)	(x)	(x)	(x)	(x)		(x)	X	(x)
Gosney	1982		X		(x)	(x)					X	
Stoecker & Jones	1982		X		(x)	(x)					X	
Jones	1985										X	
Boast	1986										X	
Trott	1989										X	
Dossat	1991	(x)	(x)	(x)	(x)	(x)	(x)	(x)	(x)	(x)	X	(x)

(x) means listed but not discussed

Several interesting observations can be drawn from Table 1:

- R717 is consistently prominent from 1895 until the 1990s.
- Whilst R610 was pivotal to the development of refrigeration systems, it seems to have fallen from interest from the early 1930s onwards.
- Ethyl chloride (R160), R611, R30 and even R600a remained refrigerants of interest into the mid-1900s.

3 Books that give no mention of flammables have not been listed.

- Methyl chloride (R40)[4] drew much attention until the 1980s.
- Dichloroethene (R1130(E)), R600, propane (R290) and R170 seem to attract limited attention throughout the 100 years covered.

Hull (1927) mentions that of the approximately 500,000 domestic refrigerating machines in the USA, less than a quarter of them use flammables such as R40, R160, R600, R600a, R717, R290 and R610. It also states that R717 is used in more than 90 per cent of the larger or commercial refrigerating plants. R610 has some use in small hand operated machines which are manufactured in Europe and sold in the tropics. However, "a non-inflammable refrigerant is preferred in order to prevent danger in case of a gas leak in the refrigerating system in a home and also to prevent danger in case of fire." On R160, Hull remarks: "A certain quality of ethyl chloride has been produced in England which is claimed to be non-inflammable. This result is obtained by the addition of a certain amount of methyl bromide."

Bäckström (1946) estimates that R40 accounts for about 5% of refrigerant use in most sectors and R160 at about 2%, with R717 being about 10% across all sectors except industrial at 80%. The remaining are halocarbons. R600a was used in domestic refrigerators up until about 1933 (Jordan and Priester, 1948; Palm, 2018).

On R40, Lewis (1943) says "there is little danger of explosions, as with the amount used in an ordinary household refrigerator, if mixed with the air in the average kitchen would not make a mixture nearly strong enough to explode. It should be kept away from flames however." But "methyl formate is the refrigerant used by General Electric Co. in some of their refrigerators. … It is anaesthetic if inhaled, and, is highly inflammable." And R717 is "somewhat inflammable and with the proper mixture of air will form an explosive mixture." However, whilst there are two pages on R600a, there is not a single mention of its flammability. Conversely, Jordan and Priester (1948) are somewhat unique in that they write in quite some detail, expressing concern over use of flammable refrigerants.

Interestingly, Siebel (1918) uses some antiquated terms, such as referring to "chimogene" – possibly a variation of "cymnogene", used elsewhere – which is probably a blend of R290 and R600 or "very volatile liquids derived from petroleum". It also refers to "rhigolene" (apparently a mixture of HCs with a normal boiling point of -9°C) and "cryogene" which is probably a mixture rich in R170 and/or methane (R50).

In terms of information on flammable refrigerants, MacIntire (1928) is somewhat of an exception amongst most, in that a detailed table of flammability characteristics is included, covering flammability limits, explosion limits, AITs, range of maximum explosion pressures, time to develop explosion pressure and "rates of diffusion". Conversely, within Moyer and Fittz (1932), despite detailed sections on R290, R170 and R600, the topic of flammability is not even mentioned; any safety discussion is related only to toxicity. As with numerous authors, Siebel (1918) seems to have a serious affection for R717, particularly illustrated with the section entitled "Ammonia not explosive", where he goes on to explain that R717 is only as explosive as water (under pressure).

3.2 Fulgurating flammables

Once non-flammable, lower toxicity halocarbons became established across most parts of the industry, the use of flammable refrigerants dwindled. However, there appeared to be a few instances of their use, when commercialised refrigerants were not suited or unavailable.

4 R40 was the fluid within counterfeit R134a that caused a series of explosions with reefer containers (UNEP, 2012)

One notable work was an ingenious invention of the seemingly eccentric German (residing in USA), Peter Schlumbohm (1897 – 1962). His concept was to use R290 in a "transitory cycle" for transport refrigeration, where it first passes through the evaporator and then as a motive fuel to the truck engine, shown in Figure 3 (Schlumbohm, 1939). Schlumbohm had exchanged the inheritance of his family's chemical company with funding of a lifelong education, although "the improvement of refrigeration through chemical, mechanical, and engineered processes was Schlumbohm's perennial interest throughout his working life"; he considered refrigeration to be one of the most important and necessary scientific fields (Anon, 1949). He had over 100 patents related to refrigeration, including the transitory R290 system (Schlumbohm, 1937).

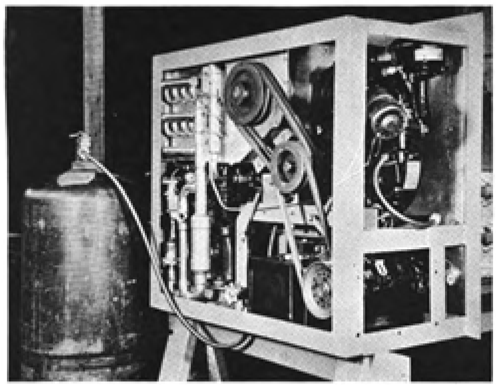

Figure 3: Photograph of R290-driven refrigerated truck and fuel system (Schlumbohm, 1939) (©ASHRAE www.ashrae.org Refrigerating Engineering, Economic Application of Air Conditioning and Refrigeration, Vol 37, No 4, Apr 1939)

From the middle of the 19th century, there was far less discussion on flammables. WWII had certain impacts on refrigerant use, though. Since in Europe at least, halocarbons were diverted for military use, it resulted in a return to the use of certain flammables in household refrigeration (Palm, 2018). Apparently, a major concern was that bombing could result in major releases of refrigerants, such as R40, R717 and some non-flammables, with catastrophic impacts on building occupants (McNally, 1943). Stonebanks (1949) reporting on the need to operate low temperature systems during WWII in absence of R22, detailed extensive successful trials carried out with R290. He remarks: "Under 'standard ton' conditions, propane compares favourably with other refrigerants in more common use." and "The main disadvantage is, of course, its inflammability and though in certain cases this might be a source of danger our experience, taking reasonable care, has been entirely without untoward incident".

In Fidler (1965), chapter author Webb was apparently besotted by halogenated refrigerants: "with the rapid increase in the use of the halogenated refrigerants, there has been a more or less complete falling off of carbon dioxide, sulphur dioxide and methyl chloride, due either to very high pressures involved or a low critical temperature, or to toxicity, methyl chloride being an anaesthetic." There is little mention of other flammables, but reluctantly adds "The other classic, ammonia, is still being widely used and is likely to be so for some time to come."

Still, for most industrial applications R717 played a pivotal part throughout this era (Stoeker, 1998). Similarly, despite R290 (and R1270) not being used for smaller applications, its was retained for chemical and industrial process systems globally (Perry, 1984), as well as for liquefied gas shipping. For example, Howdens, Stal, etc. continued to produce a range of R290 compressors for large systems.

Although infrequent, there are reports of interesting work with HC mixtures during this era. Carr (1949) trialled tertiary blends of R290, R600 and R601. Haselden and Klimek (1957) and Klimek (1959) report on experiments of HC blends for the purposes of energy saving in heat pumps (HP). Other studies from 1939 and 1947 are also cited. Another article also evidently ahead of its time, looked at amongst others, blends of R290/R601 and R600/R601 as options for industrial HPs (Schnitzer, 1983).

Although the interlude era was dominated by the halocarbons, flammables were used occasionally – often for their favourable performance characteristics – and when they were, ignition risk was not considered a major issue; appropriate design of equipment and handling was all that was required.

4 Re-emergence of flammables – late 1980s to c. 2010

The era of re-emergence of flammables covers events within (some of the author's) "working" memory, coincidentally, from around the time of ratification of the Montreal Protocol. The Montreal Protocol sparked off a series of events: extensive probing of possible alternatives to ozone depleting substances (ODS), the Greenpeace Greenfreeze campaign, adoption of HCs by domestic refrigerator manufacturers, proliferation of HC to other equipment and in parallel, revision of safety standards and stakeholder studies on alternatives.

4.1 The Montreal Protocol

Under the framework of the 1985 Vienna Convention for the Protection of the Ozone Layer, the Montreal Protocol on Substances that Deplete the Ozone Layer was adopted on 15 September 1987 and entered into force in 1989. It aimed to phase out both the production and consumption of ODSs, including CFCs and latterly HCFCs. With the looming phase-down, industry began to rummage around for replacements leading to a torrent of studies examining numerous substances as potential alternatives, many of which included flammables.

One of the earliest and perceptive studies, of McLinden and Didion (1987), took a "molecular approach" to screening for possible alternatives. Despite starting with "must be nonflammable", they conclude that "some compromise with the traditional criteria [including flammability] is inevitable." Soon afterwards, Kuijpers et al. (1988) appraised various flammables, including R152a, R161, RE170, cyclopropane (RC270), R290, R600a, propadiene (R2250) and propyne (R2250b); the latter two having two unsaturated bonds. Whilst it recommended R134a, secondary proposals were R152a, RE170, RC270 and a blend of R290 and R600a. Similarly, Jürgensen (1992) presented test results with domestic refrigerators, using not only R600a, but also R290, R600 and blends. Missenden et al. (1990) and Missenden and James (1992) reported an insightful study on R290 in refrigerators, covering comparative performance, combustion safety tests and deliberation of safety standards. Bodio et al. (1993) studied the performance of R290/R600 mixtures in domestic refrigerators and concluded that the performance is at least the same or better than R12. Also for domestic refrigeration, Snelson et al. (1991) found R152a to give considerably better performance than R12 and R134a, whilst Devotta and Gopichand (1992) favoured RC270 and R152a. Kuijpers et al. (1991) further reported extensively on tests with R152a and Shiflett et al. (1992) positively evaluated various flammable HFCs. Others (e.g., Sanvordenker, 1992) challenged the advantages of R152a, although Spatz (1991) stated that the flammability of R152a would either eliminate it from consideration or impact costs by requiring additional safety controls. Less familiar flammables such as blends of R290 and RC270 were found to yield lowest energy consumption (Camporese et al., 1991). Whilst R152a was looking like a promising option, it seemed to fade from interest.

Given the apparent interest in flammables, there were early risk assessments on domestic refrigerators (Pelto and Harris, 1990) and for wider application (Dierckx and Berghmans, 1993). Richard and Shankland (1991) published an impressively comprehensive study of ignition characteristics of numerous flammable refrigerants. It reported on flammable limits of more than 20 fluids, in many cases using a variety of ignition sources. There were even detailed studies examining the explosion risks of HCs in hermetic compressors (Zgliczynski and Sansalvadore, 1994).

Whilst domestic refrigeration seemed to be a major focus for alternatives at the time, flammable alternatives for HPs was also an area of notable interest at the time. For example, Kruse and Hesse (1988) proposed R142b and R152a for HPs, whilst Pannock et al. (1992) looked at a mixture of R32/RI52a. Bivens (1991) considered various flammables for HPs, including R290 and R32 but errs towards non-flammable R32 mixtures. Other applications were also considered for flammables. For transport refrigeration, Boldrin et al. (1991) examined several various refrigerants including R290, with regards system performance as well as toxicity, environmental impacts and costs; of course, R290 was found to provide highest efficiency. Treadwell (1991) favourably addressed safety aspects of R290 for a packaged AC unit and presented test results, identifying numerous cost, environmental, efficiency and performance benefits. In general, Kramer (1991) argued that whilst R290 is flammable, it is highly effective, readily available, compatible with standard lubricants and with proper precautions and approvals, can be substituted for R22 and R502.

Surprisingly, R32 seems not to have been considered as a single component (within the literature) until 1991. Before 1995, there were almost no studies looking at (pure) R32; only mixtures. Powell (1991) contemplated R32, but then erred towards mixing it with R134a to avoid flammability.

4.2 The "Greenfreeze" detonation

Whilst these various debates were ongoing, the domestic appliance sector decided upon R134a as the replacement for R12 – despite a GWP in the 1000s and numerous studies demonstrating other alternatives were more favourable. However, the environmental campaign network – Greenpeace – who had been involved in the earlier movement against ODSs, became concerned about substitution of R12 with R134a. In the early 1990s, after aerosols, the domestic refrigerator had become a symbol for CFCs. In order to address the CFC and subsequent HFC problem, Greenpeace (Germany) tried developing its own CFC-free refrigerators, such as with a Stirling engine. These were, however, all failures since efficiency was poor compared to existing CFC models. During this process, an associate from the Dortmund Hygiene Institute, Dr Preisendanz, reported on his effective use of HCs; he with Wolo Lohbeck and Harald Zindler of Greenpeace set about introducing HCs to domestic refrigeration.

Initially, the mainstream West German (at the time) manufacturers rejected HC alternatives. However, a struggling company in the former East German Democratic Republic (GDR), Deutsche Kälte- und Kraftmaschinen (DKK) Scharfenstein eventually expressed interest. (At their pinnacle in the 1980s, they had 5300 employees, producing >1 million appliances a year, being sold as discount products in the West and also across the Eastern Bloc.) Although, as with other manufacturers, they has also switched to R134a. From March 1992, Lohbeck, Zindler and Preisendanz visited DKK on several occasions to discuss the possibility of switching to HCs. (Interestingly, DKK found records that they had already worked with HCs in the 1930s.) Subsequently, Greenpeace concluded an agreement with the factory to build ten HC refrigerators and organised a press conference. In the meantime, the Treuhandanstalt (or "Trust agency") – an agency established by the West German government to oversee privatisation of East German enterprises – was planning to act upon DKK, which would have blocked any possibility to switch to HCs. The Treuhand director travelled to Scharfenstein to prohibit the press conference, which failed, because there were 150 journalists already present and as a consequence the Treuhand ended up guaranteeing continuation of DKK. The factory was renamed Foron in January 1993.

An additional advantage of DKK/Foron was that they also manufactured compressors; given the objections of the appliance manufacturers, it was unlikely that any compressor manufacturer would readily supply HC models for the project. A blend of R290 and R600a (named “Dortmunder Mischung” or Dortmund Mixture after the institute where it had been conceived) was chosen as the refrigerant so that minimal changes to the compressor would be required thus enabling rapid transition. This was crucial for the success of Greenfreeze. With all the bedlam surrounding DKK/Foron, instead of the ten test fridges, they directly prepared for mass production. The first series models of Greenfreeze Foron fridges were shown at Domotechnika in Cologne in February 1993 and the first series of Greenfreeze fridges (model KT135R) were completed on 15th March 1993 (Figure 4). In the meantime, having ceased their anti-HC campaign, the other leading manufacturers at the time also presented their first HC prototypes.

Figure 4: The first HC fridge from DKK/Foron (Sabine Vielmo/Greenpeace) (left) and on display (Manfred Scharnberg/ Greenpeace) (right)

As with today, the principal objection to using HCs was the flammability risk. Greenpeace and Foron were immediately attacked for the “explosion hazard” and the leading European manufacturers (AEG, Bauknecht, Bosch, Electrolux, Liebherr, Miele and Siemens) jointly wrote a letter in 1992 to the trade associations warning against a “new, allegedly CFC-free refrigerator”. This letter, being unlawful according to the anti-competition rules, led to the manufacturers having to retract their objections and apologise. Regardless, videos appeared showing “German” refrigerators exploding. Despite such activities, the product standard IEC 60335-2-24 (IEC 335-2-24 at the time) was revised in tandem to allow up to 150 g of flammable refrigerant to be used, provided potential ignition sources on the appliance were eliminated. Anecdotally, there was never an accident with these DKK/Foron refrigerators.

The existing standard (BS 3456-202.24: 1990 – the BSI implementation of IEC 335-2-24) did not prohibit flammables; in fact there were no requirements related to refrigerant safety. But for one exception: in Annex ZX, there were a list of special “national conditions” (deviations) and applicable to the UK only, it was stated: “The refrigerant shall present no more hazard than those listed in the following table, except that ammonia shall not be used in compression type appliances.” The list included R22, R12, R11, R115 and R502. The deviation was due to expire on 1st January 1991.

A standard that simply does not prohibit a flammable refrigerant is not as helpful as one that provides guidance, so for the fourth edition in 1997 it was revised and published, including a limit for the HC charge of 150 g[5] and associated measures for marking and safe electrical components. Revision of the standard was fundamental to success of R600a. Within a year or two, DKK/Foron, as did most European refrigerator manufacturers, switched to R600a. Hermetic compressor manufacturers also responded and Liebherr's "table top" fridge with an Aspera compressor was the first R600a product for 60 years.

It is evident that Greenfreeze opened up the possibility of extending the use of HCs to many other applications within the refrigeration, air conditioning and heat pump (RACHP) sector – today we see extensive use in commercial refrigeration, portable ACs, chillers and HPs. That R600a is used in more than one billion fridges (UNEP, 2018) gives confidence to other sectors. Not only was this an incredibly successful campaign for Greenpeace, but it paved the way for the wider introduction of HCs to other applications. Arguably, it may also have enabled a smoother introduction of flammable HFCs ("A2Ls"). Since HCs have negligible GWP, legislators saw HCs as viable alternatives to HFCs, so as legislation edged towards pushing for lower GWP, halocarbon producers developed more suitable alternatives and flammable HFCs were the most appropriate options on their table. Moreover, because HCs had become the flammability "punch-bag", it was not only easier to introduce A2Ls, but they could be offered as an antidote to "high flammability" HCs.

4.3 Greenfreeze babyboom

Undoubtedly, Greenfreeze generated a momentum for HC refrigerants. Globally (except in North America), more and more refrigerator manufacturers switched from CFCs or HFCs; by 2010 more than 50% of new production used R600a (UNEP, 2015). The initial conversions in Article 5 countries were carried out by implementing agencies, funded by the Montreal Protocol's Multilateral Fund. The first factory conversions, from R12 to R600a, was by GTZ (now GIZ) Proklima in China (Kelon and Haier) in 1994. This was followed by projects in India, Pakistan, even Cuba, and latterly Argentina and Brazil, again by GTZ, Infras and others. In a separate development, an Italian appliance manufacturer, De'Longhi, launched a range of portable and split ACs with R290 in 1994, as well as some Scandinavian and German HP manufacturers.

Correspondingly, numerous producers of HC refrigerants materialised worldwide: Ecozone, Elgas, Linde Gas, Musicool, Oz Technology, Settala Gas and Calor Gas, amongst (numerous) others, whilst Hychill/Esanty (Australia) in fact began even earlier in 1985. Some of these enterprises created significant impetus for the progression of HC refrigerants, working with refrigerator, commercial refrigeration, ACs and other manufacturers to extend application ranges.

There continued to be many studies focussing on HCs in various applications and with a surprisingly detailed treatment of safety aspects. Frehn (1993a and 1993b) argued that none of the leading options for HPs offer as many favourable characteristics as R290, as did Halozan (1994) and Eggen at al. (1994). Safety was further addressed by Granryd et al. (1994) including risk assessment approaches, whilst a more formalised quantitative risk assessment approach was described by van Gerwen and Jansen (1994).

Even Hickman (1993) posited that R290 and R717 are likely to receive fresh consideration in the turmoil created by changes. Maclaine-cross (1993; 1994) looked at the application of HCs to motor car air conditioning systems (MACS), concluding that HCs led to better efficiency and negligible flammability risk. At the same time, there

5 It is frequently asked "why 150 g?" The explanation is broadly, since a "typical European kitchen" is about 8 m^2 x 2.5 m high = 20 m^3 then using a 20% factor applied to the LFL of R600a gives: 20 × 0.2 × 43 = 172 g. Based on the charge that most manufacturers needed at the time for the majority of models, 150 g suited.

began widespread replacement of R12 (and latterly R134a) by HCs in MACS. Later, there were also studies looking at – and associated patents for – flammable refrigerants mixed with fluoroiodocarbons to inhibit flammability (e.g., Nimitz and Lankford, 1994). 25 years later this is being repeated in the form of mixtures such as R466A.

The attention on HCs prompted revision and drafting of further other standards, such as BS 4434:1995 and DIN 7003: 1995. With the wider interest in refrigerants such as HCs and R717, the International Institute of Refrigeration (IIF-IIR) held the first conference on natural refrigerants[6]. This was in Hannover in 1994 ("New Applications of Natural Working Fluids") and became the "Gustav Lorentzen Conference" at Oslo in 1998. Similarly, the trade association, Eurammon, which swiftly opted to encompass all natural refrigerants, was set up in 1996. "Market accelerator", Shecco began in 2000, later expanding their purview to also encourage faster adoption of flammables, R717 and HCs.

In 1998, the Greenfreeze campaign turned its attention to the major corporate sponsors of the 2000 Sydney Olympics – giant food and beverage companies such as Coca-Cola, McDonald's and Unilever, whose operations used millions of refrigeration systems worldwide. As the opening of the Sydney Olympics approached, Greenpeace took various initiatives to convince these sponsors to adhere to the "environmental guidelines" issued by the Olympic Committee. Subsequently, Coca-Cola, McDonald's and Unilever announced plans for a global phase-out of HFCs. This led to the Refrigerants, Naturally! Initiative, also encompassing other brands such as PepsiCo, Ikea, Heineken, Carlsberg and Red Bull (plus supporting participants, Greenpeace and UNEP). The momentum created by the global adoption of HCs (and CO_2) across these end users' millions of commercial refrigeration units led to wider acceptance of flammables in the retail sector. Manufacturers began large-scale production of hermetic R290 compressors and the global output of HC compressors outstripped that of R134a.

Beyond retail refrigeration appliances, numerous manufacturers were beginning to offer products with HCs: HPs, split and portable ACs, chillers, etc. However, whilst many system manufacturers were using R22 compressors, some prominent compressor producers were opposed to the use of flammables. With the entry into force of the European Pressure Equipment Directive (97/23/EC), this practice then became prohibitive; few compressor manufacturers offered HC-approved equivalents, thus the range of HC systems began to dwindle. Indeed, a further catastrophe for some AC manufacturers was the approval of the standard, IEC 60335-2-40 in 2003, specifying charge limits for flammables which effectively obstructed the use of HCs in many such systems (Colbourne et al., 2020). Whilst in Europe, the focus was more on new systems, a large retrofit/top-up market established throughout Asia/Australasia, North America and even the Middle East, particularly for the MACS sector. For instance, an analysis of samples taken from car AC systems in Thailand found about 25% contained HC only and a further 25% with R12 or R134a mixed with HC (UNDP, 2000). Maclaine-cross (2004) estimated in excess of 5 million cars using HCs in MACS, a number likely dwarfed by the numbers is China and other parts of Asia. Considering the astronomical number of "drop-ins" and the absence of reported incidents, in retrospect the scare stories (at the time) appear unjustified.

Although the use of HCs in RACHP equipment was in flux, there were numerous patents being filed (e.g., Lindgren, 2002), although similar mixtures were patented almost a century before (Seaman and Crawford, 1918). Not only were these patents originating from smaller companies, but also multinationals such as Exxon Mobil and even Du Pont (now Chemours) applied for HC refrigerant patents, presumably in anticipation of

6 The term "natural refrigerant" is apparently a contentious one. In the current context it is used to characterise fluids that are widely found in nature and which are regarded as sustainable. Principal natural refrigerants are hydrocarbons, ammonia, carbon dioxide, water and air.

increased acceptance and growth of HC refrigerants. Amongst these were several imaginative inventions such as a "hydraulic" refrigeration system where HC refrigerant is circulated with water, thus rendering a leak "non-flammable" (Rice et al., 1991), or adding an odorant such as orange blossom to provide a warning in the event of leakage. Indeed, later patents have included flammable unsaturated HFCs and HCs along with a variety of potential odorants: fresh lemon, cherry, cinnamon, peppermint, or orange peel (Minor, 2009).

With the growing adoption of HCs in certain applications, emotions flared. Whilst not clearly documented, there was a distinct polarisation of views between those backing flammable HCs and non-flammable HFCs. Meetings, symposia and conferences were often distinctly pro- or anti- or would have refrigerant evangelists spouting in favour of one or another. Once, after giving a presentation on flammables, an audience member looked the author in the eyes and exclaimed "You are trying to kill me, my wife and my children!"

5 Explosive era – c. 2010s onwards

From around 2010, there was an explosion in the study and use of flammable refrigerants, evidenced by the commercialisation of flammable HFCs. On one hand, R1234yf was beginning to become commonplace in MACS and soon R32 in static AC systems. On the other hand, a wide range of flammable HFCs and blends thereof were being developed and offered by refrigerant producers. Beyond domestic refrigeration, HCs became widely used in retail environments (and sporadically in large integral systems such as chillers), not only in Europe but also in North America, Asia, Southern Africa and Australasia. In particular, the decision under the Montreal Protocol in 2007 to accelerate HCFC phase-out heightened the need for suitable alternatives in Article 5 countries. Subsequently, there were numerous demonstration projects with a focus of natural refrigerants, executed by implementing agencies such as UNDP, UNIDO and GIZ Proklima. Example projects include HC chillers in Indonesia and R290 room ACs in China and India and commercial refrigeration using HCs in Southern Africa. One notable success was the introduction of R290 split ACs into India, by Godrej (Rajadhyaksha et al., 2015). The current output in excess of one million units. Indeed, it is curious that HCs have not been applied more widely for the split AC sector, given the (flammability) risk is hundreds of times lower than that of HC refrigerators (Colbourne and Suen, 2015).

5.1 The great inversion

Earliest mention of flammable HFCs seems to be around 1900 by Swarts (Kauffman, 1955) and unsaturated HFCs (fluorinated alkenes or hydrofluorooelfins, HFOs) around the 1940s; for example, Henne prepared R1234yf and R1132a in about 1945 (Sicard and Baker, 2020). McLinden and Huber (2020) provide a detailed description of the various research efforts during this period to identify viable molecules to address the ODS and GWP pressures. The possibility of commercialisation of unsaturated HFCs first appeared as a patent by Daikin for R1234yf and similar compounds ("fluids for heat transfer purposes") in 1990. This was closely followed by a Russian patent that included a greater number of unsaturated HFC molecules – R1216, R1225, R1243, R1252, R1261 as well as R1234 – and also mixtures with HCs (Nikolaevich et al., 1994). From there on, there are innumerable patents on such fluids, applied for by all the mainstream refrigerant producers. Despite decades of received wisdom that refrigerants shall not be flammable, environmental pressures largely forced the great inversion; gradually it was no longer heresy to view flammables as possible mainstream refrigerants.

In the early 2000s, preparatory work on the first European rules to control fluorocarbons, or "f-gases", began. With the anticipated MACS directive (2006/40/EC) likely to limit refrigerants to GWP<150, halocarbon producers were desperate to find a suitable alternative; MACS are a highly profitable application due to the huge numbers of systems and the high re-charge rate, representing more than a third of global refrigerant consumption. Numerous options were on the table including HCs, R744, R152a and several concoctions based around R1234yf. Eventually, pure R1234yf was opted for in the majority of instances and wider use progressed from the early 2010s. Extensive work and discussions is reflected by the industry projects, SAE CRP (2021). Whilst half of the debate revolved around performance, the other half was related to flammability issues (UBA, 2021), which – of all systems – seems irrational for MACS, given the extent of flammable fluids already used in cars (brake fluid, engine oil, petrol/LPG/LNG/hydrogen fuels, etc).

Another sector about to begin a shift to flammable HFCs was static air conditioning (ACs). Developments had been ongoing since the 1990s, but there were numerous studies assessing mixtures of R32 with non-flammable HFCs (such as R410A). From around 1993/1994, there were many studies looking at R32, the majority of which found significant improvements in performance with the pure substance (e.g., Yajima et al., 1994), so it is surprising that it was neglected for so long. The first R32 split AC was launched in 2012 (Daikin, 2021) and gradually more AC producers, initially from Japan but then other countries, followed suit.

Although, as implied above, the number of patents covering flammable refrigerants is mindboggling, a snapshot of them helps provide an impression of what portions of the industry is thinking with regards to the ongoing direction of flammable refrigerants. Patents cover both the fluid (molecule, production, etc.) and systems and components. Surprisingly, the number of patents associated with HC refrigerants is broadly comparable with those of fluorinated flammables. The study of NGBIPRI (2014) found that in Japan alone, of 810 patents, 619 are related to flammable HFC refrigerants and 284 for HCs. Internationally, of 1026 patent families (i.e., of the same invention but covering a number of countries), 780 are related to flammable HFCs and 395 to HCs. Many of these patents involving HCs were registered to halocarbon producers: DuPont (now Chemours), Arkema, Central Glass Co. (Ashahi Glass), Mexichem (Koura) and Honeywell. Of 426 patents for R1234yf alone, many are being disputed (in 2020) without a ruling (Booten et al., 2020; Anon, 2021). Roger (2015) uncovered 1370 patents relating to flammable refrigerants, of which nearly 1000 were for R32.

5.2 Flammability hazards in perspective

Of course, the introduction and commercialisation of flammable HFCs has involved discussion that has been to the detriment of higher flammability (HC) refrigerants, where HC flammability has been used to “cushion” the impact of lower flammability HFCs (e.g., EFCTC, 2021).

Nevertheless, it must be recognised that the flammability classification of refrigerants is not clear-cut, for instance, the well-known class A1 refrigerant (Table 2), R22 is flammable under pressure. Tsai et al. (2018) show that the explosion pressure can be up to 30 times that of the start pressure; ignition of R22-air mixture within a compressor at 10 bar can result in an overpressure of 300 bar. Indeed, many accidents have been reported, involving fatalities due to explosions of “non-flammable” and lower flammability refrigerants (e.g., Behera et al., 2017; Moga et al., 2021). These tend to happen during servicing (partly because air is more likely to be introduced into the system, but more so because persons are present in close proximity to the system), but such explosions have also been reported in absence of servicing. A simple search on the internet yields an extensive number of reported accidents – six examples found within a few moments of searching.[7]

7 https://www.youtube.com/watch?v=GxYJlR5Eajg

https://www.channelnewsasia.com/asia/man-killed-son-injured-air-con-compressor-explodes-seremban-881821; https://www.youtube.com/watch?v=iu4F8e1iJZ4; https://www.coolingpost.com/world-news/one-dead-two-injured-in-air-conditioning-explosion/; https://timesofindia.indiatimes.com/city/thane/thane-mechanic-dies-after-blast-in-ac-compressor/articleshow/62626750.cms; https://www.chiangmaicitylife.com/citynews/local/ac-explosion-led-severe-injuries/ ; https://www.coolingpost.com/world-news/second-man-dies-from-chiller-blast/

A study in Japan helped to elucidate the situation. Higashi et al. (2017) and Higashi et al. (2018) measured Diesel explosion pressure with refrigerant-air mixtures and various types of oils. They found that not only flammable refrigerants, R32 and R1234yf produced such explosions, but R410A and R22 as well. Depending upon the type of oil, the explosive range of R32 and R1234yf was up to between 1% to 50% in air. Thus, there is a large window of opportunity for creating an explosion when drawing an air-refrigerant mixture into the compressor. Conversely, measurements with R290 showed that under the same conditions, there was only a range of 0% to 2% where a Diesel explosion could occur, regardless of the oil type. In other words, the compressor needs to be drawing a 98% mixture of air with refrigerant for the possibility of ignition to occur; this is considerably more difficult. Thus, these severe accidents seen with non- or lower flammability refrigerants are almost impossible with HCs. Unfortunately, the ill-informed can easily jump to incorrect conclusions (Refcom, 2021). Further, whilst some external (to the system) ignition studies have found modest consequences with A2L refrigerants (Gandhi et al., 2017; Davis and Pagliaro, 2019), some experiments with A2L refrigerants and oil have shown surprising results that are seldom discussed (Kopylov et al., 2019).

Whilst HC refrigerants would undoubtedly lead to more severe consequences than A2L and A2 refrigerants, external to the system, this does not automatically mean that such consequences will regularly occur. Accidents have of course happened with HCs. Serious accidents have been very few and far between, but have invariably occurred as a result of people doing daft things; dropping HCs into very large systems (designed for A1s) without first eliminating sources of ignition (as safety standards demand) or carrying out brazing or electrical work in a confined, unventilated space. Small numbers of certain domestic refrigerator models exploded due to manufacturing faults, resulting in recalls and changes to the safety standard to avoid such problems with future models. However, national statistics demonstrate fire frequencies due to flammable refrigerants are minimal (DCLG, 2014), less than one-hundredth of accidents arising from electrical faults. Indeed, frequency of fires from refrigerators over the period that R600a supplanted R12 and R134a shows a gradual reduction (likely due to improvements in electrical components).

Over the preceding decade or so, flammable refrigerants had become more widespread and, in some sectors, prominent. Despite the often emotionally- or commercially-driven opposition to flammables, accidents are extremely rare and less frequent than electrical fires (in the same equipment) by orders of magnitude. Of course, as such events occur, safety standards are revisited and refined accordingly.

6 Safety standards and similar rules

Rules and regulations for handling flammable substances have been in place for decades and identification of requirements to enable safe application of flammable refrigerants is relatively easy (once one has become familiar with the principles and workings of these regulations). However, concluding upon practices specific to refrigeration systems, extracted from highly generic rules for any application of flammables relies upon subjective judgement. For this reason, industries prefer dedicated rules tailored and refined for their specific circumstances. Hence the evolution of safety standards.

Although in many countries, safety standards are not necessarily legal requirements, they somehow seem to be pivotal for the application of flammable refrigerants. For example, in the UK, in principle, a system must comply with the relevant parts of the Supply of Machinery (Safety) Regulations 2008, Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR) and Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres Regulations 1996. However, this somehow presents difficulties, so the various rules must be interpreted and expressed as specific requirements for RACHP equipment. Nevertheless, safety standards somehow act as traffic lights to the use of flammable refrigerants; if a standard permits, the sector can adopt, if it prohibits (despite the regulation allowing), the industry shuns it.

Generally, major accidents have resulted in changes in rules (legislation, standards, etc.) so given the progress of time, this tightening of rules led to fewer accidents. As an illustration, as seen in Figure 5, the number of annual fatalities of employees reduced from about 5000 to 100 over the past century. Prior to 1974, health and safety (H&S) legislation was less inclusive (with regards to breadth of industries) and reporting less rigorous, thus the actual number of fatalities in earlier times was likely much higher. This demonstrates that the effectiveness of wider H&S legislation, rigour of enforcement and level of awareness greatly improved levels of safety over this period. This must similarly apply for safety standards RACHP to systems.

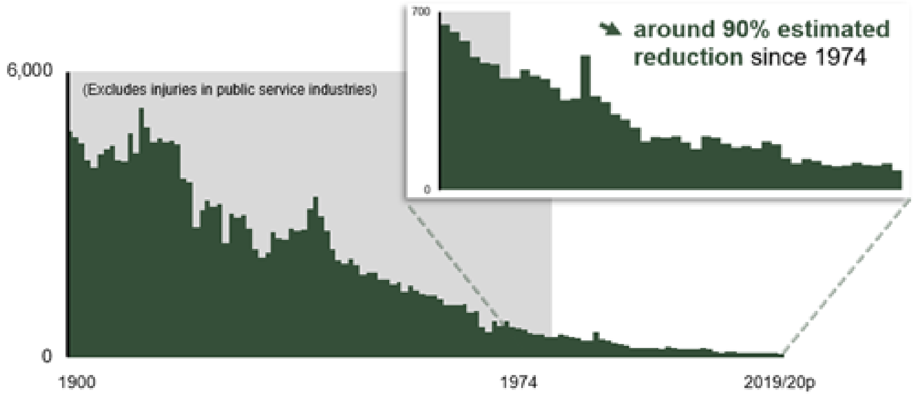

Figure 5: Number of fatal injuries to employees in Great Britain 1900-2019/20 (HSE, 2020)

In terms of flammability safety in general ("explosion protection"), the first notable contribution was made by Davy (1816), who developed an oil lamp for mines that prevented flame propagation by means of a close-meshed screen, which was also, incidentally, the first mechanical gas sensor. (Davy also reportedly was the first to discover R717 in 1807.) Later in 1884 the first "flameproof" enclosure, enclosing an electric switch, was patented by Theophilus Cad (British Patent 806). National rules seemed to lag these practical developments, though, with (one of) the first for explosion proof or "Ex" equipment being VDE 0170 in 1912 in Germany and BS 229 later in 1929 (Górny, 2013). Despite the not insignificant use of flammable refrigerants over this period, all of these developments were aimed at the mining industry. From the first Ex safety standard in 1957, the list has grown to nearly 50, reflecting the rise in knowledge and technologies applicable to explosion protection.

6.1 Safety classification

It is useful to consider fluid safety classifications. Most industries handling flammable gases use a system different to the alpha-numeric approach of the RACHP sector. Ex standards use three groups: I (firedamp), IIA, IIB, and IIC, which correspond to the maximum experimental safe gap (MESG; equivalent to the so-called "quenching distance") or the minimum ignition current (MIC) ratio of the gas. The current classifications are from IEC 79-1: 1971, whilst earlier ones originate from BS 229 (i.e., without consideration of MIC) or variation in other countries, although different systems were sometimes used, such as based on fluid flash point only (Grover and Wilson, 1960; Grove, 1968; Riddlestone, 1968). By contrast, the development of the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) began at the 1992 United Nations Rio Conference when various bodies agreed the need for a hazard classification system. This system simply identifies all flammable gases (liquified under pressure) as "Class 2.1".

An impression of the evolution of the safety classification used by RACHP sector are shown in Table 2. The earlier ASA, VBG and ASHRAE classes can be compared against the current ISO 817. Originally using three general classes ("benign", irritant and flammable), since 2014 there have been the eight classes used today. EN

378: 2000 represented a sort of transition, where the previous six classes were described, but (nonsensically) requirements were based on three groups, some of which combined higher flammability and toxicity. On one hand, this greater precision enables more specific system requirements to be formulated, on the other it increases complexity of the rules which could arguably result is errors. Whilst ISO/R 817 was first issued in 1968, it only contained refrigerant numbering; no safety classification and it was not until ISO 817: 2014 that it included safety classifications, as well as the new “2L”. Similarly, safety classifications were not part of ASHRAE 34 until 1978, although the 2L subclass was added in 2010 and then changed to a class of its own in 2013. The standard also toyed with further classifications to account for fractionation of blends.

Table 2: Various refrigerant safety classifications

Group/Class	ASA B9 (1919)	VBG 20 (1959)	ASHRAE 34: 1978	ISO 817: 2014
1	Not flammable or irritant	Non-flammable without any significant toxic effect on humans	Non-flammable and no death or injury to guinea pigs during 2 h at 2.5%	No flame propagation
2L	-	-	-	Flame propagation, LFL > 3,5%, HOC < 19 MJ/kg, FS ≤ 10 cm/s
2	Irritant: any which has irritating effect on eyes, nose, throat or lungs	Toxic or corrosive and with LFL of ≥3.5%	Death or injury to guinea pigs during 2 h at 2.5%	Flame propagation, LFL > 3,5%, HOC < 19 MJ/kg
3	Flammable: any which will burn in air	LFL of < 3.5%	Flammable and no death or injury to guinea pigs during 2 h at 2.5%	Flame propagation, LFL ≤ 3,5%, HOC ≥ 19 MJ/kg
A	-	-	-	Occupational exposure limit <400 ppm
B	-	-	-	Occupational exposure limit ≥400 ppm

A fascinating article from 1915 (“Ammonia Accidents”) appears to document the realisation that R717 is flammable. It refers to a meeting of the Berlin Refrigerating Society (Berliner Kaelte Verein) in 1914, where it was reported that an engineer working in an engine room “where much R717 has been lost” and “observed an advancing flame, ignited by an open light”; the engineer suffered burns to face and hands. Tests were conducted at the Technical High School in Karsruhe, which found that ignition (“with violence”) occurred in concentrations between 16.5% and 26.8% with air. Three other incidents were reported in Germany (between 1909 and 1914 in Elberg, Freiburg and Berlin), although it was contested that it was actually R717 that had resulted in an explosion. One specialist argued that R717 itself wasn’t flammable, but under high pressure and temperature it decomposed to hydrogen. It was concluded that pressure relief and safety valves should be used on all R717 compressors. Despite much to-ing and fro-ing, the conclusion seemed to be that R717 was in fact flammable and that regulations should be revised to prohibit open flames in engine rooms. A subsequent publication (ASRE, 1915) reported on a new regulation: “In all machinery rooms in which amounts of R717 or R160 is used, there shall be no flames, arc lights, gas jets or any apparatus employing flame”. Later, Lowenstein (1916) reported “The question as to whether ammonia will burn or not has been answered by experiments.” … “When an electrically-heated platinum wire is used, an explosion results when the percentage of ammonia gas is between 19.58 and 26”, validating his findings with “The author of this paper has made ammonia his life study.” Nonetheless, in an article on accidents in refrigerating plants from 1917 (Starr, 1917), ten types of accidents were classified. Two of these were fire-related "ruptures caused by fires or unusual heat from outside source" and "explosions due to testing with air (oil ignition mostly)". Despite the widespread use of flammable refrigerants at the time, there were no categories related to ignition of leaked refrigerant.

In fact, it was this issue of R717 flammability that brought about the formation of the International Institute of Refrigeration (IIAR). In 1970 there was a proposed change to the USA electrical safety rules that would have mandated Ex-type equipment for R717 machinery rooms. To help oppose such requirements, the North American R717 industry initiated the IIAR.

6.2 Mechanical requirements

The evolution of RACHP standards is a little less elusive. Unlike with Ex, RACHP safety standard have remained fairly low in number, but the depth and detail (number of pages) has grown significantly. They began around 1910, with ASRE-15 (now Ashare-15[8]), followed by other countries' national standards within the following couple of decades. The first such publication in the UK was BS CP 406 British code of practice for refrigeration safety, followed by various editions of BS 4434 from 1969. The international equivalent, ISO/R 1662 – the predecessor of ISO 5149 – was not published until 1971, then as a formal ISO 5149: 1993 and subsequently in 2014. Difficulties in achieving international consensus on such a wide scope of topics is reflected in the 20+ year cycle for each revision! Table 3 contains a selection of events related to RACHP safety standards.

Table 3: Timeline and momentous events for RACHP safety rules

Year	Source	Refrigerant classification or system requirements or events
1919	ASA B9 (→ASHRAE 15)	First edition
1933	AS/NZS 1677	First published (as AS CB3-1933)
1952	BS CP 406	First edition of British code of practice for refrigeration safety
1956	VBG20 (Germany)	First issue
1957	DIN 8975	Early edition
1969	BS4434	Successor to BS CP 406
1971	ISO/R 1662	Predecessor of ISO 5149
1978	ASHRAE 34	First edition
1997	IEC 60335-2-24	Revised to included 150 g charge limit for flammables
1995	DIN 7003	Specifically covering requirements for A3 refrigerants (including HCs)
1995	BS4434 (UK)	Revised to include sensible requirements for flammables
1998	AS/NZS 1677	Published, permitting flammables
2000	SNI 6500 (Indonesia)	Published, permitting flammables
2000	EN 378	First edition
2001	NPR 7600 (Netherlands)	Safety aspects for flammable refrigerants
2002	IEC 60335-2-89	First edition, included 150 g charge limit (copy from IEC 60335-2-24)
2003	IEC 60335-2-40	Revised to include requirements for flammables
2010/13	ASHRAE 34	Inclusion of A2L classification
2014	ISO 817	Inclusion of A2L classification
2014	ISO 5149	Revised to permit flammables similar to EN 378
2018	IEC 60335-2-40	Revised to permit substantially greater quantities of A2Ls
2019	IEC 60335-2-89	Revised to include 13xLFL charge limit for flammables
2020	CDV for IEC 60335-2-40	FDIS to include better rules for flammables; to be voted on in 2022

8 A comprehensive description of the history of ASHRAE 15 can be found in Reindl (2014) and McLinden and Huber (2020) provide a description of the safety classifications from ASHRAE 15 and ASHRAE 34.

Some earlier editions of the various safety standards were less discriminatory with flammable refrigerants. For instance, early editions of DIN 8975 and VBG 20 limit flammable refrigerants to 10 kg only if occupancy exceeds one person per 8 m^2 of floor space, otherwise the limit would be 50 kg. For AC systems, they simply say that refrigerants must be prevented from entering the rooms in quantities that would be harmful. BS4434 on the other hand did not permit flammables in institutional, public or residential occupancies. Whilst ASHRAE 15 was similarly less discriminatory in the early editions, it soon moved to similarly prohibit flammables from occupied spaces. ISO 5149: 1993, was equally as restrictive, prohibiting flammable refrigerants from any situation except laboratories up to 2.5 kg and industrial "special cases".

However, with the Montreal Protocol and the re-adoption of flammables for certain sectors, various safety standards were revised, not necessarily to permit flammables, but to provide a more robust framework for their application. Thus, national standards such as BS4434, AS/NZS1677, SNI 6500, NPR 7600 and DIN 7003 (specifically for A3 refrigerants) and the first edition of EN 378 were all (re)published within a few years of each other, permitting certain quantities of flammables in all applications and occupancy types. Such requirements, including those for safety devices, safe electrical equipment, gas detection, etc., were mostly identical.

Soon after, a draft IEC 60335-2-40 was issued with extensive requirements for flammables. Various national committees objected, especially since an electrical standard (IEC 60335-) should not be so focussed on mechanical requirements, so it was agreed to have a joint working group between the responsible committee and also that for ISO 5149. The intention was to develop a consistent set of rules which could be temporarily used in IEC 60335-2-40, but then taken out and referenced in the mechanical standard ISO 5149, once it was published. (Unfortunately, this sensible intention fell afoul of the lackadaisical rate of ISO 5149 revision; by the time it was published a decade or so later, IEC 60335-2-40 had moved on further and enacting such a switch was no longer viable.) Tragically, the requirements drafted and pushed through were highly obstructive to the use of HCs and contributed to the withdrawal of otherwise safe products from the market and prevented further introduction of HC ACs for many years. A decade later, as the new 2L classification was being established, a new working group was set up to develop improved requirements based on A2L. Apart from increasing upper charge limits from about 8 kg to 80 kg and additional means of extended allow charge limits, by means of ventilation, gas detection, system tightness, etc., simplified version of Ex-type protection concepts for electrical equipment were also included. This subsequent edition was published in 2018.

The other product standard, IEC 60335-2-89, had included the 150 g limit for flammables since the first edition in 2002, despite at least one attempt to raise it a few years later. In 2014 the BSI mirror committee submitted a proposal to increase the charge limit and include additional requirements for flammables. A working group was established and eventually in 2019 the draft was submitted for final vote. Initially it seemed that the draft had failed, but once it was realised that certain countries had incorrectly submitted their votes, IEC corrected the result to approval of the standard. Whilst the recent IEC 60335-2-40, EN 378 and ISO 5149 had opened up the rules significantly for A2L refrigerants, the approval of IEC 60335-2-89 represented the first fortuity for HCs in two decades.

With the publication of EN 378, conflicting national standards had to be withdrawn. This had a nasty sting in the tail for flammables, as a single line stated they shall not be used in direct systems be permitted for "air conditioning and heating for human comfort"; the origin of this requirement is unclear. A revision of EN 378 was issued in 2008 and – despite efforts to introduce improvements – it was effectively similar to the 2000 version and the prohibition for flammables in comfort cooling was replaced with the atrocious charge limits from IEC 60335-2-40. The latest, EN 378: 2016 was not better for HCs, but did include extensive requirements for A2L refrigerants, consistent with those in IEC 60335-2-40: 2018. Again, efforts to include enhancements for HCs were unsuccessful. The slightly earlier release of ISO 5149: 2016 was similar to EN 378: 2018, both in structure and requirements for flammables. The next revision of EN 378 is expected in 2024 and will likely contain substantially improved requirements for HCs and A2Ls alike.

It is noteworthy that within the governing rules for flammables – ATEX directives or DSEAR and EPS in UK – they make no reference to limiting quantities of flammable material, just that the mitigation measures should be proportionate to the quantity and circumstances.

Until the era of re-emergence, safety standards appear to have been fairly ambivalent in their dealings with flammables. However, once it became apparent that HCs posed a threat to halogenated refrigerants' market dominance, elements of the establishment worked towards ensuring obstructive safety standards were in place, acting as a barrier (Frost, 2002; Parliament, 2004; Brown and Collins, 2002). This strategy worked phenomenally well. During the explosive era, use of flammable HFCs had to be facilitated and safety standards were revised such that they could be applied to the same extent of non-flammable refrigerants, without adverse impact on cost. However, increased interest of system manufacturers in HCs and their frustration with illogical safety standards has resulted in renewed participation in standards development, likely with an incrementally positive outcome. As is observed with general improvements in H&S as rules improved, the same must also apply to RACHP systems, including for those with flammable refrigerants. Indeed, in the earlier eras textbooks and other literature implied that whilst flammability was a concern, it was not regarded in the demonic light as it has been by some in recent times. Accordingly, the advancements in both RACHP and Ex safety standard strongly suggest systems moved from "fairly safe" to "extremely safe".

7 Reflections and outlook

7.1 Fulminating debates

The first ever refrigerant was flammable and it is likely that that most of the "last" refrigerants will also be flammable (before magnetic refrigeration or another technology takes over). Whilst nearly every book or technical articles stresses that a refrigerant "ought not", "should not" or "must not" be flammable, these refrigerants have nevertheless been, and are again, widely used on account of their thermophysical and chemical merits (good performance, material compatibility, lesser environmental impact, lower cost, etc.).

It was frequently claimed that halocarbons were commercialised in the 1930s to address the negative safety implication of the existing fluids. However, although this was evidently the case for some of the higher toxicity refrigerants, detrimental impacts of flammability are not supported by the literature (e.g., evidenced by the celebrated "propane safety refrigerant" advertisement). Furthermore, initial commercialisation of CFCs was at least partly to provide a domestic refrigerator manufacturer with a commercial (marketing) advantage over competitors. Giunta (2006) provides a comprehensive and vivid description of the events and deliberations preceding the commercialisation of halocarbon refrigerants, describing the vying of established refrigerant (R40) producers and public entities.

Due to the Montreal Protocol terminating use of CFCs and Greenpeace's Greenfreeze campaign eventually leading to the use of HCs in most of the world's domestic fridges – today, over one billion – it appears that the flammability scare-stories of yesteryear are most probably exaggerated. Whilst a notable proportion of large systems have continually used R717 since the advent of refrigeration, there has similarly been a steady growth in its use even for commercial applications.

The current renaissance of flammables, adoption and continued use of HCs, surely stems from the Greenfreeze campaign. Perversely, it is likely also to have paved the way for the need and acceptability of flammable (A2L) HFCs. Since HCs and R717 have negligible GWP, legislators saw them (and other naturals) as viable alternatives. So as regulations have edged towards low GWP, halocarbon producers were forced to find more suitable alternatives, with flammable HFCs being one of the only options on their table. Moreover, because HCs had been the "flammability punch-bag" for 25 years, it was not only easy to introduce A2Ls, but they were even offered as an antidote to high flammability HCs.

Polarisation of the topic since the Montreal Protocol was a fact. On numerous occasions, when discussing HCs, colleagues from various sectors reiterated "never", "unacceptable", "not in your wildest dreams", etc. will the industry accept flammables. Somehow vested interests managed to fire-up the emotive fear of equipment manufacturers too. In some quarters this generated hardened opposition to HCs – and more recently even to A2Ls to an extent. At times fiercely anti-HC articles were regularly found in trade literature (e.g., Anon., 2008; Anon., 2009; Anon., 2010; although far more entertaining material can be found on internet discussion forums). Presumably, reflecting on their possible hypercriticism, many commentators who were previously outspoken against HCs, have similarly opposed A2Ls. More sober sources, such as IIF-IIR (2017) should be viewed for a balanced overview of the important flammability considerations.

7.2 Candescent risks and mitigations

Experience has shown that the risk associated with the use of flammable refrigerants can be negligible and it is only with daft acts that problems arise. Of course, just as accidents involving electricity, pressurised systems and brazing/welding equipment, this is anticipated and the appropriate mitigations put in place. Improvements, such better system tightness, have undoubtedly helped, but they are incremental and not high-tech, revolutionary engineering approaches. Safely applying flammables simply requires engineers to do what they always do – design and control machinery to account for undesirable characteristics and "noise factors".

Somehow, safety standards, despite being subservient to regulations, have attained a demigod-like status, dictating "go" or "no-go" for a given fluid. Functional requirements of safety standards will likely continue to be the key to successful adoption of flammable refrigerants. Leak detection technology will most probably become a pivotal for the extended use of flammables. Mechanical gas sensors were first invented around 1800 (biological detectors being used prior to that), with the first "modern" catalytic sensors in 1926 (Halder and Chatterjee, 2019). Since then, numerous technologies have evolved and it is likely that others will further emerge.

In the current iteration of safety standards, A2Ls are given considerably more tolerance than A2s and HCs (and of course, R717 doesn't get much of a look-in anyway). For instance, maximum charge of HCs indoors is 1 kg, whereas A2Ls are permitted to reach around 100 kg (depending upon LFL). This is equivalent to a ten times larger flammable mixture, 25 times more released energy in the event of combustion and infinitely more toxic decomposition products. (Not to mention the greater likelihood and severity of explosions from adiabatic compression.) In theory, equanimity is needed, although achieving this is unlikely.

Due to the fluctuations in technology interests, RACHP safety standards have become muddled and unwieldly, with various standards spiralling off in different directions. Whilst the refrigeration system is essentially the same, substantially different rules apply depending upon the aesthetics of the housing. Unfortunately, the further these standards diverge, the more difficult it becomes to unify them.

Whilst the aforementioned discussions are almost entirely on flammability, it must not be forgotten that there are numerous other hazards associated with refrigerants that are always pertinent (Calm, 1994).

7.3 Thermogenesis

Observation of an industry "litmus paper" helps indicate the direction of things to come. Since 2015, there have been about 150 articles on the topic of safety of flammable refrigerants (as listed in IIF-IIR's FRIDOC[9]), corresponding to about 30 per year. For the preceding 20 years there were about five per year. Such a trend in research activities infers a flare up of interest. Many sectors are now accepting flammables; about 15% of the MACS sector is now using R1234yf (about 170 million cars), whilst a few million are using HCs as drop-ins. About 40 million split ACs use R32 and well over one million use R290. Dwarfing these numbers are the billion or so domestic refrigerators with R600a. Booten et al. (2020) states that HCs account for 6-7% of the global refrigerant market, R32, currently accounts for about 10% (although partly as a component in R410A) and both R717 and R1234yf about 5%. Data for Australasia/SE Asia shows sales of HC refrigerants have been doubling every 5 – 6 years. Today, some 60% of global small compressor production is for HCs, in excess of 100 million per year. Production of R1234yf compressors began around 2010, mainly for Japan, but growth for these and for other A2L blends is expected by manufacturers. Insightfully, a leading halocarbon refrigerant producer stated they expect some 30% of the refrigerant market would eventually be taken by natural refrigerants (Manzer, 1990). Considering the blends registered in ISO 817, nearly one-third are flammable as with two-thirds that have been registered over the past 10 – 15 years, most of which are primarily HFC-based.

It may be apt to make some philosophical projections about the future, based on these past eras and current conditions. Unlike for most of the time that refrigeration technology has been in existence, there presently appears to be a critical need to minimise environmental impact. Obviously the most apparent is global warming, but there are other impacts related to release of apparently indigestible compounds into the wild (Behringer et al., 2021). Previously, the refrigeration society had some degree of freedom to choose the most convenient options. But now it is increasingly evident that if we want to use refrigeration systems, it will have to be with flammables. Having said that, it is also useful to observe that there is a divergence between the drivers to adopt the different types of flammables, HCs and HFCs. The uptake in HC domestic and commercial refrigerators was (initially) driven by consumer desire for "green". With R1234yf it was legislation and with R32, manufacturer preference (reflecting a compromise between environmental impact, product cost and perceived risk). Unlike with domestic appliances in 1990s and supermarkets in the 2000s, today, refrigerant type is probably a minor criterion amongst many others for consumers of cars and ACs, considering the bombardment of current purchasing factors; refrigerant choice is lost in the fog. It is possible that for many types of equipment, refrigerant type will hold even less weight for the discerning customer. Notwithstanding, recent elevated concerns over GWP and reluctance of manufacturers to go through yet another refrigerant transition raises interest in HCs, R717 and other natural refrigerants, since they are regarded as "future proof".

My prediction is that all "smallish" systems and self-contained equipment (including big chillers) will asymptote towards flammable, negligible GWP and possibly halogen-free. For larger, distributed systems, compromise options will be used, based on the conditions (dictating temperature lift). As the industry becomes more tolerant or even accepting of flammables, they will inevitably take a larger portion. There is an approximate correlation between lower GWP, system compactness (lower cost), desirable performance and increasing flammability. Although seldom discussed, an increasing number of future options are class A2 refrigerants, so as to satisfy this compromise.

9 https://iifiir.org/en/fridoc

Soon, the "not flammable" mantra will itself become phased out, or at least phased down. Not only in the mindset of younger technicians to minimise climate impact, but familiarisation with flammables will lead to a new generation of technicians more tolerant and experienced with handling flammables. System manufacturers will become far less hesitant and even comfortable with all flammable refrigerants.

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Appendix Table 4: Characteristics of flammable refrigerants

Refrigerant	Name	Chemical formula	"Discovered"	Mol mass (kg/kmol)	NBP (°C)	Safety class	LFL (% vol.)	HOC (MJ/kg)	AIT (°C)	MIE (mJ)	FS (cm/s)	ODP (R12=1)	GWP (100 y)
R30	Methylene chloride	CH_2Cl_2	1839	84.9	39.6	B2	14.1	5.7	662	10000	n/k	n/k	11.2
R32	Methylene fluoride	CH_2F_2	c. 1930	52.0	-51.7	A2L	14.4	9.5	645	n/k	6.7	0	771
R40	Methyl chloride	CH_3Cl	1835	50.5	-24.2	B2	10.7	12.8	632	n/k	n/k	0.015	5.5
R41	Methyl fluoride	CH_3F	1835	34.0	-79.0	(A2)	7.1	19.6	n/k	n/k	28	0	135
R50	Methane	CH_4	1777	16.0	-161.5	A3	5.0	50.0	645	0.29	40	0	27.9
R141b	1,1-Dichloro-1-fluoroethane	CH_3CCl_2F	c. 1930	117.0	32.1	(B2)	7.6	8.0	532	n/k	n/k	0.10	860
R142b	1-Chloro-1,1-difluoroethane	$C_2H_3ClF_2$	c. 1930	100.5	-10.0	A2	8.0	8.9	750	n/k	4.6	0.065	2300
R143a	1,1,1-Trifluoroethane	CH_3CF_3	1948	84.0	-47.2	A2L	8.2	10.3	750	n/k	7.1	0	5810
R152a	1,1-Difluoroethane	CH_3CHF_2	c. 1900	66.0	-24.0	A2	4.8	16.3	455	n/k	23	0	164
R160	Ethyl chloride	C_2H_5Cl	1759	64.5	11.8	(B3)	3.7	19.9	507	2.37	n/k	n/k	0.5
R161	Ethyl fluoride	CH_3CH_2F	c. 1900	48.1	-37.6	(A3)	3.9	n/k	n/k	n/k	n/k	0	5
R170	Ethane	C_2H_6	1834	30.0	-88.6	A3	3.1	47.5	515	0.26	47	0	0.4
RE170	Dimethyl ether	CH_3OCH_3	1275	46.1	-24.4	A3	3.0	28.8	235	0.32	54	0	<1
RC270	Cyclopropane	C_3H_6	n/k	42.1	-32.9	(A3)	2.4	20.9	498	0.17	52	0	<1
R290	Propane	C_3H_8	1857	44.1	-42.1	A3	2.1	46.3	470	0.25	45	0	0.02
R600	Butane	C_4H_{10}	1849	58.1	-0.5	A3	1.6	45.7	365	0.25	45	0	0.006
R600a	Isobutane	C_4H_{10}	1866	58.1	-11.7	A3	1.8	45.6	460	0.25	37	0	0.006
R601	Pentane	C_5H_{12}	n/k	72.2	36.1	A3	1.45	44.8	264	0.22	43	0	<1
R601a	Isopentane	C_5H_{12}	n/k	72.2	27.9	A3	1.4	44.9	420	0.21	36.6	0	<1
R610	Ethyl ether	C_4H_{100}	<1540	74.1	34.9	(A3)	1.9	33.8	180	0.20	33.8	0	0.01
R611	Methyl formate	$C_2H_4O_2$	1671	60.1	31.8	B2	5.0	15.3	459	0.4	0.5	0	"low"
R717	Ammonia	NH_3	<1774	17.0	-33.0	B2L	16.7	18.6	630	680	7.2	0	0
R1270	Propene	C_3H_6	c. 1850	42.1	-47.6	A3	2.7	45.8	457	0.26	48	0	0.02
R1150	Ethylene	C_2H_4	1795	30.0	-103.8	A3	2.7	47.2	470	0.10	71	0	<1
R1130(E)	Trans-1,2-dichloroethene	$C_2H_2Cl_2$	< 1933	96.9	47.6	B2	5.6	10.0	460	n/k	n/k	0	"low"
R1132a	1,1-Difluoroethylene	CF_2CH_2	< 1943	64.0	-83.0	A2	5.0	15.6	n/k	n/k	n/k	0	0.05
R1234yf	2,3,3,3-Tetrafluoropropene	$C_3H_2F_4$	1945	114.0	-29.4	A2L	6.2	10.7	n/k	n/k	1.5	0	0.05

"n/k" means not known, "discovered" or first synthesised dates are very approximate, safety classifications in parentheses () are assumed by the author, references (in order of priority): ISO 817: 2014; EN 378: 2016; Smith et al., 2021; WMO, 2018; UNEP, 2019; Woodward, 1998; Haase, 1977; Internet, 2021

Nomenclature. NBP – normal boiling point (at standard atmospheric pressure) (°C), Safety class – refrigerant safety classification according to ISO 817, LFL – lower flammability limit (% vol.), HOC – heat of combustion (MJ/kg), AIT – Auto-ignition temperature (°C), MIE – Minimum ignition energy (mJ), FS – laminar flame speed (cm/s), ODP – Ozone depletion potential, with the reference R12=1 (-), GWP – global warming potential based on 100-year time horizon ($kgCO_2$-eq)