A SYNTHETIC VIEW ON THE GWP OF REFRIGERANT FLUIDS, VERSUS THEIR COOLING CAPACITY AND FLAMMABILITY

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1. Introduction

The Kigali amendment to the Montreal Protocol and other regulations like the EU F-gas are controlling the use of some refrigerant fluids: elimination of the ODS's (Ozone Depleting substance) and restrictions on the use of HFC's. Alternative solutions include natural refrigerants, HFC's with lower GWP, new generation synthetic fluids such as HFO's, and a blends of the above. Some of these are flammable to a certain extent. Some regulations are already in force, but the regulatory context is still evolving. Per the Kigali amendment, individual countries have flexibility to adjust the ways to meet their obligations. In EU, the F-gas should be updated within a few years. In US, regulations are different depending on the states. Standards and codes about flammable refrigerants are still being discussed. There is also a growing awareness of the importance of energy consumption, resulting in more stringent energy efficiency regulations. All this generates some confusion. Therefore, it was felt useful to try to clarify some of the underlying issues.

In this paper, the main compounds used as refrigerants, pure or blended, are first presented, then the principles behind their blending to achieve desired properties, and eventually a synthetic view on the various solutions available, with emphasis on the trade-offs between the GWP of the fluid, their volumetric cooling capacity, the GWP and the energy efficiency.

To present the results, various fluids are spotted on a graph with the GWP on the vertical axis, and critical temperature on the horizontal axis. The reason for this choice is that the critical temperature T_C is a good proxy to the volumetric capacity of a fluid. Ranking them by T_C corresponds quite well with the ranking by volumetric capacity (Ref. 1).

2. Pure compounds

As aforementioned, ODS's now being out of scope, the pure compounds used are natural refrigerants, HFC's, and synthetic products of new generation. Emphasis here will be especially on synthetic fluids (HFC's, HFO's…), some of which are flammable, while some others are not.

Among the HFC's, are the non-flammable medium pressure R134a, and three high pressure HFC's: the non-flammable R125, and the flammable R143a and R32. The HFC's R227ea (class 1) and R152a (class 2) are also found in a few blends. Until recently, R134a was the only one being used pure; the high pressure ones were only used in blends. But with forthcoming restrictions on high GWP HFC's, R32 is now also increasingly used pure.

The new generation chemicals HFO's are medium or low pressure fluids. The medium pressure are R1234ze and R1234yf with physical properties close to R134a, but very low

GWP, and flammability class 2L. The low pressure ones are R1233zd and R1336mzz (E or Z). A new molecule was recently introduced with chemical formula CF_3I, with reference R13I1 per the ASHRAE classification. It is another high pressure fluid, non-flammable, also used as a fire suppressant.

3. Blends

3.1 Principles of the formulation of blends

Blends are formulated to achieve a desired compromise between cooling capacity, energy efficiency, flammability and GWP. It is known that pure compounds or blends with higher pressure tend to provide a higher volumetric capacity; but they also tend to have a lower energy efficiency (Ref. 1). The pure compounds used have various properties in terms of pressure, flammability and GWP. These properties are reflected in the blends in proportion to their contents. In addition, blending fluids with substantially different pressure levels tends to give a higher temperature glide, while blends of fluids with relatively close pressure levels give low glide, or gives more easily azeotropic blends.

In general, the first steps toward the formulation of a blend are first to target a level of volumetric cooling capacity, approximately reflected by the T_C and second, to decide if flammability is accepted or not. It is also desired to achieve as low a GWP as possible; yet, it is known that fluids with lower GWP also tend to be more flammable. Blends are generally formulated to be close to the borderline between two flammability classes. For instance, non-flammable blends are formulated to be close to the limit of flammability class 2L without crossing the border line, in order still to be in class 1, while achieving as low a GWP as possible. Likewise, blends of class 2L are formulated to be close to flammability class 2.

Besides these fundamentals, other criteria may be added like the compatibility with some families of oils, especially for blends intended for retrofits of existing systems. The discharge temperature is also an issue, especially for applications with high compression ratio, such as low temperature refrigeration, or A/C in high ambient temperatures. There are also commercial issues: various combinations of components are feasible to reach similar properties. Producers are competing to propose blends depending on their patents and ability to produce the components. There may also be some political considerations, as some thresholds can be perceived as politically sensitive, as limits between “low”, “medium”, “high” GWP, although these thresholds are more political than technical.

3.2 HFC blends

Since the mid 1990’s, and before concerns arose about the GWP of refrigerants, HFC’s were the most usual alternatives to ODS’s. Besides pure R134a, several HFC blends were proposed. The main ones were R410A, R404A, R507 and the R407 series. When these products were introduced, the GWP was not perceived as an issue, and there was no incentive to accept the constraints of flammability. So, all these products were formulated to be non-flammable; and at equivalent T_C, they tend to have a higher GWP than new generation products, as presented below. In this category, are also some HFC blends like 438A or the R422 series. These were designed to be potential retrofits to R22, and include a small amount (about 3%) of hydrocarbons to make them miscible with the oils used with R22, thereby avoiding oil changes in the retrofits.

3.3 HFO's and HFC/HFO blends

To reduce the GWP of fluids compared to the aforementioned HFC's and blends, the trend is now to include higher contents of components like HFO's with lower GWP in spite of their flammability, in as much as the targeted flammability class is still achieved. The blends is the study are shown in table 1. As seen on the graph of Figure 1, these HFC/HFO blends tend to align in two narrow bands, one for non-flammable, and one for 2L fluids.

3.4 Lower GWP or flammability products

A few products stand out as exceptions to the above. This is illustrated by two examples. The first one is the new blend R466A. In addition to the high pressure HFC components R32 and R125, it has a substantial amount (39.5%) of CF3I (R13I1) reducing its flammability. Thanks to this, although being non-flammable, it is located in the band of the other 2L blends composed of HFC's and HFO's only (see Fig. 1).

Another blend out of the typical "bands" is R455A (2L). Its GWP per AR4 is just 150, while other 2L, HFC/HFO blends of similar properties, have a GWP close to 600, like R447A (R32, 68%; R125, 3.5%; R1234ze, 28.5). The composition of R466A is R32 (21.5%), R1234yf (75.5%), and CO_2 (3%). CO_2 has very high pressure as is strongly non-flammable. Adding it compensates for the high content of R1234yf, in 2L class that provides the very low GWP, and lowers the low pressure. This allows this blend to reach the politically "magic" threshold of GWP 150. But technically, the price to pay is an extremely high temperature glide of 12.5°C, compared to values around 5°C for other typical blends in the same category.

4. Fluids in the study

The fluids in the study are listed in Table 1. They include some pure compounds and blends for a wide range of A/C and refrigeration applications, from low pressure fluids for centrifugal chillers, to high pressure fluids. This list is not exhaustive, but the sample is wide enough to illustrate the general conclusions derived. The fluids are listed by order of increasing T_C, with their GWP (AR4) and flammability class. They are classified in three columns. The first one includes HFC's and HCFC's. The second one, for HFO's and HFC/HFO blends; the third column includes the two blends R466A and R455A with a flammability depressant substance as aforementioned.

Table 1: list of fluids in the study

ASHRAE R-N°	Tc °C	GWP AR4	Flamm. class	HCFC & HFC	HFO & HFC+HFO	+C02 or R13I1
507A	70.6	4300	1	x		
410A	71.3	2088	1	x		
422A	71.7	2979	1	x		
404A	72.1	4200	1	x		
452A	74.9	2100	1		x	
452C	75.8	2200	1		x	
32	78.1	704	2L	x		
422D	79.6	2279	1	x		
452B	79.7	710	2L		x	
454B	80.9	490	2L		x	
447B	81.3	750	2L		x	
459A	81.5	480	2L		x	
449A	81.5	1400	1		x	
448A	81.6	1400	1		x	
407A	82.3	2100	1	x		
454C	82.4	2899	2L	x		
407F	82.6	1800	1	x		
447A	82.6	602	2L		x	
455A	82.8	150	2L			x
466A	83.8	734	1			x
438A	83.8	2264	1	x		
449B	84.2	1400	1		x	
446A	84.2	480	2L		x	
427A	85.3	1696	1	x		
407C	86.0	1781	1	x		
449C	86.1	1200	1		x	
454A	86.2	250	2L	x		
453A	88.0	1700	1	x		
454C	88.5	152	2L		x	
417A	89.9	2346	1	x		
458A	92.0	1600	1	x		
444B	92.1	305	2L		x	
457A	92.6	150	2L		x	
1234yf	94.8	4	2L		x	
513B	95.5	560	1		x	
22	96.1	1810	1	x		
513A	97.7	630	1		x	
516A	99.3	140	2L		x	
407G	99.5	1700	1	x		
134a	101	1430	1	x		
227ea	101.8	3220	1	x		
456A	102.4	650	1		x	
450A	106	601	1		x	
515A	109	380	1		x	
1234zeE	109	1	2L		x	
152a	113	124	2	x		
1336mzz(E)	138	32	1		x	
245fa	153	1030	1	x		
1233zdE	166	1	1		x	
1336mzz(Z)	171	1	1		x	
123	184	77	1	x		
514A	197	1	1		x	

5. Graph and comments

Figure 1 shows the GWP of refrigerants versus their critical temperature T_C. The fluids with GWP higher than 2400 are not represented, to improve the visibility on the more interesting lower GWP's. On the right of the graph are low pressure fluids for centrifugal compressors, in the category of the HCFC R123. On the left side are the high pressure fluids like R410A or R32. In between are fluids at intermediate pressure, in the category of R134a or R22.

For the low pressure fluids, non-flammable alternatives with near-zero GWP are available. In the high pressure category, prior to the introduction of R466A, all the alternatives to R410A (R32 or HP blends) were flammable (2L). In the intermediate pressure range, three different zones are noticed. A narrow orange band includes the flammable (2L) HFC/HFO blends. A second narrow band, in light green, includes the non-flammable HFC/HFO blends. At equivalent T_C, the difference in GWP between these two bands is about 800, meaning that the GWP of a 2L fluid is lower than that of an equivalent fluid, by about 800. The slope of these bands also illustrates the known trend, that high pressure fluids (low T_C) have a higher GWP than low pressure ones. Above the green band is a cluster of HFC's and HFC blends (plus R22). They have higher GWP, as they were introduced as alternatives to CFC's and HCFC's, before the GWP was a concern.

Exceptions to these rules are R466A and R455A. R466A in non-flammable, but with a lower GWP, similar to that of 2L fluids of equivalent properties; this is achieved by using the new molecule CF3I that had not been used in refrigerants before. R455A is 2L, but with substantially lower GWP than other fluids of similar T_C; this is achieved by using some CO_2 in the formulation; but the counterpart is an extremely high temperature glide.

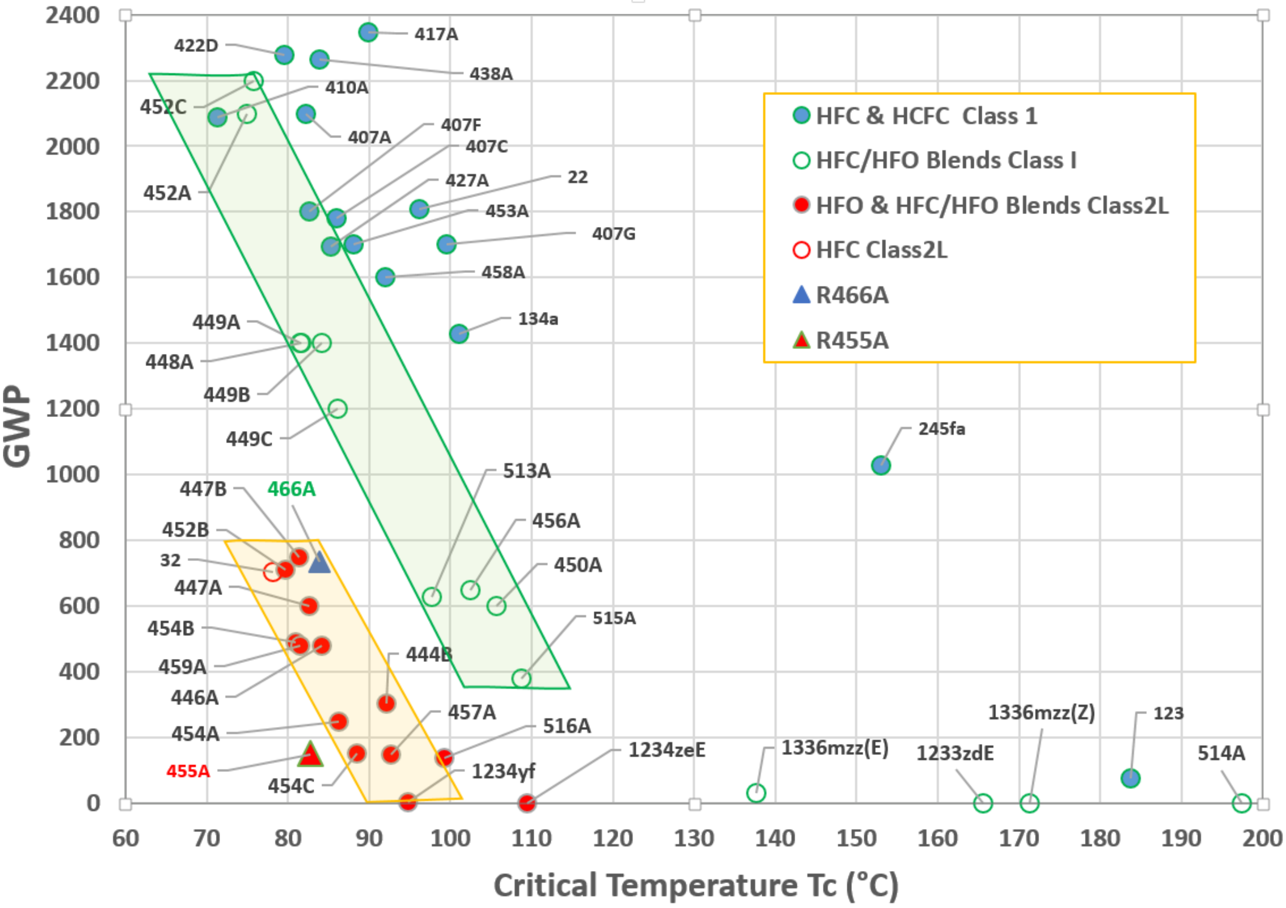

Figure 1: GWP versus Critical Temperature of fluids

6. Conclusions

It is known that high pressure fluids tend to have a higher GWP than low pressure ones, but lower GWP is feasible by including HFO's in the blends instead of blending HFC's only. Other components like CO2 or CF3I can also be added to reduce the flammability. The graph as presented shows the trade-offs between capacity, flammability and GWP. Incidentally, it also shows that it make little sense to try to define absolute categories of GWP such as "low", "medium", high" etc, or use targets of "average" GWP values common to all applications. Whatever the limit chosen, it might be impossible to reach for some applications, or be pleaded as an excuse to using sub-optimal solutions in other cases.

References

(&) de Larminat & Wang: "Overview of Fluids for A/C Applications", parts 1 and 2. ASHRAE Journal, February and July 2017.