WHAT COULD BE THE NEXT R410A?

Apart from mobile air conditioning systems, a number of heat pump and refrigeration applications are still missing good low-GWP refrigerant, which is capable to replace high-GWP ones used today. In this article we review the efforts in development of new low-GWP refrigerants with focus on refrigerant mixtures.

Theoretically, there are more than one thousand molecules with properties good enough to become low-GWP pure refrigerants [1]. Unfortunately, only few of them are well known and can to be successfully used in refrigeration equipment or in heat pumps. The list of such refrigerant includes some synthetic (HFO-1234yf, HFO-1234ze(E), HFC-152a), and natural refrigerants (HCs, CO_2 and etc.). However, the properties of these refrigerants do not allow them to be efficiently used in every application.

The demand for low-GWP refrigerants is growing as more industries are willing to decrease their environmental footprint. Mixtures of pure refrigerants are seen to be capable to become replacements to high-GWP refrigerants, which are in use today. Similar situation has been observed few decades ago, when transition to ozone-free refrigerants has been done. Then, a set of refrigerant mixtures has been proposed to replace the ozone depleting R-12 and R-22. R-410A is an example of such mixture, composed of equal parts of R-32 and R-125, which was invented by Honeywell and is actively used today as refrigerant for various air-conditioning and heat pump units. The list complements with R-404A, R-407C and other refrigerant mixtures.

Manufacturers are interested to secure a place on low-GWP market

Six chemical manufacturers has been willing to supply their refrigerants to Air-Conditioning, Heating, and Refrigeration Institute (AHRI) in order to independently evaluate their characteristics within the AHRI Low-GWP Alternative Refrigerants Evaluation Program. The evaluation results have been partially presented a while ago [2], but the evaluation is not finished yet. ARM-32a, DR-5, L-42b, LTR6A are just a few of the new blends of the entire low-GWP refrigerant candidates list under evaluation. The entire list is presented in the Table 1, where the refrigerants, both pure and in mixtures, are grouped based on their safety and baseline refrigerant they are aiming to replace.

Table 1 - Alternative refrigerants for testing and evaluation [2]

Baseline Refrigerants	**Alternative Refrigerant Candidates Classifications according to ASHRAE Standard 34**			**Others**
	A1	**A2L**	**A3**	
R-134a	AC5X, ARM-41a, D4Y, N-13a, N-13b, Opteon XP10	AC5, R-1234yf, R-1234ze(E), ARM-42a	R290+R600a (40%+60%), R-600a	
R-404A	ARM-32a, N-40a, N-40b, DR-33	ARM-31a, ARM-30a, D2Y-65, L-40, R-32, R-32+R-134a (95%+5%), DR-7	R-290	R-744
R-410A		R-32, ARM-70a, D2Y-60, DR-5, HPR1A, L-41a, L-41b, R-32+R-134a (95%+5%), R-32+R-152a (95%+5%)		R-744
R-22/R-407C	ARM-32a, LTR4X, N-20	D52Y, L-20, LTR6A	R-290	R-1270, R-717

As one can expects, extensive testing should be done to fully evaluate every refrigerant candidate, listed in Table 1.

Refrigeration composition gets undisclosed

The composition of many of the low-GWP refrigerant blends was kept undisclosed until recently, when AHRI have reported partial results of their testing [3] [4]. The composition of 28 low-GWP refrigerant mixtures is listed in the Table 2

Table 2 - List of low-GWP refrigerant blends, their composition and respective GWP value [3] [4]

Refrigerant	Supplier	Composition	Glide, C	GWP_{100}
AC5	Mexichem	R-32/R-152a/R-1234ze(E) (12/5/83)		92
AC5X	Mexichem	R-32/R-134a/R-1234ze(E) (7/40/53)		622
ARM-30a	Arkema	R-32/R-1234yf (29/71)		199
ARM-31a	Arkema	R-32/R-134a/R-1234yf (28/21/51)		491
ARM-32a	Arkema	R-32/R-125//R-134a/R-1234yf (25/30/25/20)	4.1 F	1577
ARM-41a	Arkema	R-32/R-134a/R-1234yf (6/63/31)		861
ARM-42a	Arkema	R-134a/R-152a/R-1234yf (7/11/82)		117
ARM-70a	Arkema	R-32/R-134a/R-1234yf (50/10/40)		482
D2Y-60	Daikin	R-32/R-1234yf (40/60)		272
D2Y-65	Daikin	R-32/R-1234yf (35/65)		239
D-4Y	Daikin	R-134a/R-1234yf (40/60)		574
D52Y	Daikin	R-32/R-125/R-1234yf (15/25/60)	8.5 F	979
DR-33	DuPont	R-32/R-125/R-134a/R-1234yf (24/25/26/25)		1410
DR-5	DuPont	R-32/R-1234yf (72.5/27.5)	10 F	490
DR-7	DuPont	R-32/R-1234yf (36/64)	5.4 F	246
HPR1D	Mexichem	R-32/R-744/R-1234ze(E) (60/6/34)		407
L-20	Honeywell	R-32/R-152a/R-1234ze(E) (45/20/35)	9.4 F	331
L-40	Honeywell	R-32/R-152a/R-1234yf/R-1234ze(E) (40/10/20/30)		285
L-41a	Honeywell	R-32/R-1234yf/R-1234ze(E) (73/15/12)		943
L-41b	Honeywell	R-32/R-1234ze(E) (73/27)		494
LTR4X	Mexichem	R-32/R-125/R-134a/R-1234ze(E) (28/25/16/31)	7.9 F	1577
LTR6A	Mexichem	R-32/R-744/R-1234ze(E) (30/7/63)	23.9-25 F F	206
N-13a	Honeywell	R-134a/R-1234yf/R-1234ze(E) (42/18/40)	1 F	604
N-13b	Honeywell	R-134a/R-1234ze(E) (42/58)	1 F	604
N-20	Honeywell	R-32/R-125/R-134a/R-1234yf/R-1234ze(E) (12.5/12.5/31.5 /13.5/30)		975
N-40a	Honeywell	R-32/R-125/R-134a/R-1234yf/R-1234ze(E) (25/25/21/9/20)		1346
N-40b	Honeywell	R-32/R-125/R-134a/R-1234yf (25/25/20/30)		1331
OpteonTM XP10	DuPont	R-134a/R-1234yf (44/56)	0	631

The companies behind the refrigerant blends

Among the companies, which are interested in creating low-GWP blends are Arkema, Daikin, Mexichem, Honeywell, DuPont and National Refrigerants. Among them, Honeywell and DuPont are two USA-based companies, who are known to be the ones behind the development of R-1234yf. Arkema, is another global chemical manufacturer with headquarters in France. Arkema is known for its conflicts with Honeywell and DuPont around the question of R-1234yf production. Arkema has expressed its will and possibility to produce R-1234yf in industrial quantities [5], but later was stopped of doing so due to patents which DuPont and Honeywell hold.

Balancing the properties

As we can see from the Table 1 and the Table 2 the companies have offered a range of low-GWP alternatives to baseline R-134a, R-404A, R-410A and R-407C. Looking at composition of the proposed mixtures one can see that companies are trying to balance the performance, flammability and GWP values by selecting components for the mixture. R-32, for instance, has very good properties and moderate GWP of 675 and thus used in every mixture to replace baseline R404A, R407C, R410A. Other components in mixtures with R-32 are seems to be used to suppress its flammability and adjust properties in order to match that of the baseline refrigerant.

Flammability is an issue around low-GWP refrigerants. It was not possible to find nonflammable alternative to R-410A, where as for other baseline refrigerants such options are available, but their GWP are not among the lowest (ranging within 622-943 for nonflammable replacements of R-134a; 1331-1577 for R-404A; and 975-1577 for R-407C/R-22). Thus, the majority of proposed refrigerant blends lies into A2L ASHRAE safety category. It is worth to mention, that the ASHRAE safety classes are estimated and not officially assigned by ASHRAE for majority of refrigerants listed in the Table 1.

AHRI, by their project, is not willing to prioritize one refrigerant over another. Instead, it evaluates refrigerant characteristics and presents results in consistent manner in order to make transition to low-GWP refrigerants predictable, smooth and informed. It is no doubt interesting to see how capable the proposed refrigerant mixtures to replace their high GWP baselines. We are leaving this task for the reader, and will come out with our own analysis in one of the upcoming Kyla+.

References

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