Refrigerants – Part 2:

Past, present and future perspectives of refrigerants in air-conditioning applications

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Abstract

The second part of the refrigerant paper deals with the refrigerant development throughout the history, which took place due to different reasons, such as safety, stability, durability, economic or environmental issues, thus giving the boost to new research and equipment improvement in terms of safety and efficiency. Recent legislation worldwide and in the EU is still not quite completed concerning refrigerant issues. The delicate subject of refrigerants is widely discussed, viewpoints of different parties are opposite, depending on positions and interests, and compliance on that issue is not easy to achieve. The chance for "closing the circle" and return to natural refrigerants exists and should not be missed.

Historical overview of refrigerants' development

Beginnings of mechanical refrigeration, starting from early 19th century are characterized by use of natural refrigerants. Water and air were the first refrigerants considered for use in mechanical refrigeration systems. In 1834 Perkins proposed ethyl ether as the working fluid in his patent of the vapor - compression refrigeration system. Perkins system was a closed circuit comprising all the modern vapor-compression system components: the compressor, the condenser, the expansion device and the evaporator. By that time ammonia, sulfur dioxide and carbon dioxide had been isolated and were available for use as well. The first one who used methyl ether, which operated at higher pressure and thus reduced the risk of drawing air into the system and forming an explosive mixture within the machine was Tellier in 1863. First ammonia compressor for refrigerating purposes was designed and constructed by Boyle in 1872, and 4 years later Linde designed the first machine working with ammonia. In 1862 Lowe developed a carbon-dioxide refrigerating system. Carbon dioxide has very low toxicity but required high-pressure machinery and was difficult to use because of its low critical temperature (31,6°C) which does not allow for condensation in many situations. Methyl chloride was used for the first time as a refrigerant in 1878. Most of those early refrigerants were flammable, toxic or both [1,2]. **Table 1** shows properties (molecular weight M, normal boiling point NBP at pressure 1 bar, critical temperature CRT, critical pressure CRP, safety group according to ASHRAE standard 34, ozone depletion potential ODP and global warming potential GWP

Table 1. Properties of early refrigerants.

Substance	R number	Chemical formula	M kg/kmol	NBP °C	CRT °C	CRP bar	Safety group	ODP	GWP_{100}
Carbon dioxide	R-744	CO_2	44,01	-55,6[1]	31,6	73,77	A1	0	1
Ammonia	R-717	NH_3	17,03	-33,3	132,25	113,33	B2 (B2L[2])	0	0
Sulfur dioxide	R-764	SO_2	64,06	-10,0	157,49	78,84	B1	0	0
Ethylether	R-610	$C_4H_{10}O$	74,12	35	194,0	36	-	0	0
Dimethylether	E-170	C_2H_6O	46,07	-25	126,9	53,7	A3	0	0
Methyl chloride	R-40	CH_3Cl	50,49	-24,2	143,1	66,77	B2	0,02	16

[1] – tripple point

[2] – new class introduced since 2010

Table 2. Properties of CFC and HCFC refrigerants dominant in 20th century.

Substance	R number	Chemical formula	M kg/kmol	NBP °C	CRT °C	CRP bar	Safety group	ODP	GWP_{100}
Trichlorofluoromethane	R-11	CCl_3F	137,4	23,71	197,96	44,1	A1	1	4000
Dichlorodifluoromethane	R-12	CCl_2F_2	120,91	-29,75	111,97	41,4	A1	1	8500
Chlorotrifluoromethane	R-13	$CClF_3$	104,5	-81,3	29,2	39,2	A1	1	11700
chlorodifluoromethane	R-22	$CHClF_2$	86,47	-40,81	96,15	49,9	A1	0,055	1700
R22/R115	R-502	$CHClF_2$+ CF_3CClF_2	111,6	-45,3	80,73	40,2	A1	0,33	5600

based on 100 years) of practical refrigerants available for vapor compression cycles at the end of the 19th century.

The second generation of refrigerants, chlorofluorocarbons (CFCs) replaced classic refrigerants in early 20th century. Midgeley and his associates, in their research aimed to find for stable, but neither toxic nor flammable refrigerant in 1928, selected R-12, dichlorodifloromethane as a suitable compound for refrigeration applications [2]. The commercial production of R-12 began in 1931, followed by R-11 in 1932 and R-13 for low temperature applications in 1945. Chlorofluorocarbons (CFCs) and starting in 1950s hydrochlorofluorocarbons represented by R-22 and azeotropic mixture R-502 dominated the second generation of refrigerants. Those refrigerants dominated throughout the second half of 20th century. Ammonia was only natural refrigerant that still remained the most popular refrigerant in industrial applications. [1,2]

Present situation

Present situation is determined by use of refrigerants of zero ODP with no impact on ozone layer, according to demands of Montreal protocol (1987). In 1974 researchers Roland and Molina predicted that emissions of HFCs could damage Earth's atmosphere by the catalytic destruction of ozone in the stratosphere. The hypothesis has been proven in 1985 by measurements which have shown the destruction of the ozone layer over Antarctica. In 1987, the Montreal Protocol limits the production and consumption of CFCs. Between 1990 and the present emissions have decreased substantially as a result of the Montreal Protocol and its subsequent amendments and adjustments coming into force. By 2008, stratospheric chlorine abundances in the stratosphere were 10% lower than their peak values reached in the late 1990s and were continuing to decrease. January 2010 marked the end of global production of CFCs under the Protocol. In 2009 the Montreal Protocol was universally ratified by 196 nations [3]. European regulation concerning that issue is No. 2037/2000 of June 29, 2000 on substances that deplete the ozone layer.

The discontinuation of CFC (2006) and HCFC (2015) use brings us to the today's state of utilization of HFCs, the mixtures thereof and the natural refrigerants. In EU countries HCFC phase-out has been accelerated and those are not in use anymore. Today's refrigerants may not contain chlorine, they must ensure efficient performance and must have a low impact on global warming.

The commercially available refrigeration units mostly use R-134A for fresh produce and R-404A (or R-507A) for frozen produce. Natural refrigerant R-290 is in some countries used in refrigerated display cabinets at medium and low temperatures. R-404A is used in direct central refrigeration systems for low and medium refrigeration temperatures. It may also be used for both fresh and frozen produce. Natural refrigerant CO_2 is used as a refrigerant in the lower cascade of the cascade systems or in transcritical systems. It may also be used either as a heat transfer medium. R-134A dominates as the refrigerant in the home refrigeration units and some regions use the hydrocarbons (e.g. isobutane R-600a) as well [4].

Ammonia is still widely used in industrial systems and its previously decreasing utilization due to halogenated hydrocarbons use is on the increase again [4]. The modern-day refrigeration systems using ammonia are constructed with the tendency of decreasing ammonia charge in the system as much as possible for safety reasons. One way of doing that is to apply indirect systems with the heat transfer medium, so that the ammonia is kept in the refrigeration device, whereas the heat transfer medium flows through the distribution system.

Chillers are important part of HVAC installations. R-134a is used in large chillers equipped with centrifugal compressors and flooded evaporators. R-407C is used in direct expansion systems with counter flow heat exchangers. Recently, R-410A units became competitive with the R-407C units and almost fully replaced

Table 3. Some ozone friendly refrigerants (ODP = 0).

R number	Chemical formula / composition	M kg/kmol	NBP [°C]	CT [°C]	CP bar	Temp. glide [°C]	Safety group	GWP_{100}
R-32	CH_2F_2	-52,02	-51,65	78,11	57,8	0	A2L[1]	580
R-134A	CH_2FCF_3	102,03	-26,07	101,06	40,6	0	A1	1300
R-404A	R143A/125/134A (52/44/4)	97,6	-46,6	72,14	37,4	0,46	A1	3800
R-407C	R32/125/134A (23/25/52)	86,2	-43,8	86,05	46,3	5,59	A1	1600
R-410A	R32/125 (50/50)	72,59	-51,6	70,17	47,7	0,1	A1	1900
R-507	R143A/125 (50/50)	98,86	-47,1	70,75	37,2	0	A1	4000
R-508A	R23/116 (39/61)	100,1	-87,4	11,01	37,0	0	A1	13000
R-717 ammonia	NH_3	17,03	-33,3	132,25	113,33	0	B2L[1]	0
R-744 Carbon dioxide	CO_2	44,01	-55,6	31,6	73,77	0	A1	1
R-600A isobutane	$CH(CH_3)_3$	58,12	-11,6	134,66	36,29	0	A3	20
R-290 propane	C_3H_8	44,1	-42,11	96,74	42,51	0	A3	20
R-1270 propylene	C_3H_6	42,08	-47,62	91,06	45,55	0	A3	20

[1] – new safety classes introduced since 2010

Table 4. Today's refrigerant alternatives [5]

Traditional Service Refrigerants		Medium and Long-Term Alternative Refrigerants					
HCFC/HFC Partly chlorinated		HFS Chlorine fee		Low GWP refrigerants		Halogen free natural	
Single substances	Blends	Single substances	Blends	Single substances	Blends	Single substances	Blends
R-22 R-123 R-124 R-142B	Predominantly R-22 based	R-134A R-125 R-32 R-143A R-152A	R-404A R-507A R-407 serie R-410A R-417A7B7 R-422A/D R-427A	HFO-1234yf HFO 1234ze	HFO-1234yf/HFO 1234ze/HFC	R-717 R-290 R-1270 R-600A R-170 R-744	R-600A/R290 R-290/R-170 R-723

them in use. Design of micro channel heat exchangers was initiated by development of R-410A equipment. CO_2 is not usually used in chillers, mostly due to low energy efficiency of the process. CO_2 heat pumps for water heating started selling in Japan in 2001. They can heat the domestic water up to 70-80°C. The capacity of those chillers goes up to 100 kW. A transcritical cycle operated VRF systems have also been available on the market in recent years, but problems with lower efficiency and construction of high pressure refrigerant piping never allowed wide application. In recent years Japanese producers have pushed hard R-32 as a suitable refrigerant for VRF systems. New safety class A2L as defined by ASHRAE standard 34 discussed in previous paper (Part 1) comprises R-32 as well and one of arguments for R-32 application is the lower burning velocity as described in class A2L definition. The market share of ammonia chillers is still very small due to important issues as safety, charge reduction and first cost. Recently increased research focused on charge reduction (and thus safety) and energy efficiency of those chillers can give boost to wider use of ammonia chillers in HVAC, besides traditional industrial, food processing and beverage applications. Hydrocarbon chillers production is very low. Refrigerants are R1270, R290 and propane and ethane mixtures. The typical performance ranges from 20 to 300 kW and the amount of the refrigerant from 3 to 34 kilograms [4].

Replacement of R-22 in existing refrigeration systems is still actual. There is a significant number of chillers with high performance, built for a longer operational period, and those chillers are potential candidates for that operation called "retrofit". Retrofit basically means adaptation of the refrigeration system to the new refrigerant with changed safety and control equipment and instrumentation within the system, and with changed system performance. That adaptation is not so simple, especially in the case when transition from mineral oil lubricated systems (HCFCs) to synthetic oil lubricated systems (HFCs) is necessary. A lot of research is ongoing presently in order to find suitable, so called "drop-in" replacement for R22. Experience with previous retrofit of R12 systems using replacement R-134A do not give boost to any enthusiastic expectations. Cost of such an operation should carefully be analyzed, and experience shows that equipment replacement is much more likely to occur instead of retrofit.

The future

GWP of HFCs is another issue addressed by Kyoto protocol (1997). The European Parliament has issued a directive (No. 842/2006) banning the use of HFCs whose GWP is higher than 150 (the "F Gas" Directive) in air-conditioning units of newer cars from 2011 and of all new cars from 2017. Directive also requires periodic leakage check-ups of stationary systems containing HFCs. Changes may be expected in the direction of the ban on HFCs with high GWP use in stationary systems. Review of the F-gas Regulation started in 2010. The European Commission proposal is to broaden the scope of the regulation to refrigerated transport, to modify the frequency of leakage checks based on the CO_2 equivalents of the HFCs used and to modify the obligations regarding training and certification of personnel. A gradual phase-down of HFCs is also proposed using the 2008-2011 total quantity of HFCs in EU as a baseline. The document proposes a freeze by 2015 and a gradual reduction ending with 21% of baseline quantity by 2030. This proposal also includes a ban on HFCs in domestic, hermetically sealed commercial systems and movable air-condi-

Table 5. Possible directions of future development of refrigerants [2]

Refrigerants	**Remarks**
Natural refrigerants (NH_3, CO_2, hydrocarbons HCs, H_2O, air)	Efficiency; flammability for NH_3 and HCs
HFCs with low GWP (R-32, R-152a, R-161...)	Flammability, most of the ones that are subject to the ban have a high GWP
Hydrofluoroethers HFEs	Disappointing thus far, still?
Ethers (HEs) (RE170 – dimethyl ether)	Flammability
Olefins – unsaturated alkenes (R1234yf)	Short atmospheric lifetime and therefore low GWP. Flammability? Toxicity? Compatibility?
HFICs and FICs (R-31I1 (CH2FI), R-13I1 (CF3I)...)	Expensive, ODP>0, but not subject to the Montreal Protocol. Some are toxic. Compatibility?
Fluorinated alcohols (-OH) and ketones [-(C=O)-]	Efficiency? Flammability? Toxicity? Compatibility?
Other	??? - no ideal refrigerant

tioners by January 1st 2015. Refrigerators and freezers for commercial use (hermetically sealed systems) will be prohibited by January 1st 2017 for HFCs with a GWP of 2500 or more and by January 1st 2020 for HFCs with a GWP of 150 or more. Movable room air-conditioning appliances (hermetically sealed) using HFCs with a GWP of 150 or more will be prohibited by January 1st 2020. Industry and trade organizations agree on a phase-down of HFCs but with a less ambitious goals and some modifications. The approval of the proposed action is necessary within the European Council. Then the proposal shall be discussed at the level of the European Parliament. A new regulation cannot enter into force before 2014 and it is very likely that modifications will be adopted during the approval process. However, a phase-down of HFCs will certainly take place in Europe in the near future [6].

Possible future development of refrigerants is not easy to predict. Interesting projection is presented in Calm's paper [2] and the summary is repeated in **Table 5**.

Natural refrigerants

From the viewpoint of the author of this article, natural refrigerants, especially ammonia are presently available, and long experience exists with their application dating far into the beginning of mechanical refrigeration. The "circle" is now somehow closed, we already returned to natural refrigerants, but now with new technologies and with a lot of experience behind us.

Ammonia has no ozone depletion potential (ODP = 0) and no direct global warming potential (GWP = 0). Due to high energy efficiency of refrigerating equipment operating with ammonia, its contribution to the indirect global warming potential is also low. Ammonia is flammable. However, its ignition energy is 50 times higher than that of natural gas and ammonia will not burn without a supporting flame. Due to the high affinity of ammonia towards (air) humidity it is rated as "hardly flammable". Ammonia is toxic, but has a characteristic, sharp smell which makes a warning below concentrations of 3 mg/m^3 ammonia in air possible. This means that ammonia is evident at levels far below those which endanger health. Furthermore ammonia is lighter than air and therefore rises quickly into the atmosphere [7]. New experience shows that with proper care ammonia can be used efficiently and in a secure manner even in HVAC systems. The market opportunity produced by R-22 phase-out should not be missed by ammonia chiller producers. The major obstacles are legal demands in some countries as well as high initial costs as the consequence of present production in small series. Experience shows also that reasonless fear is connected with security of ammonia application and that should be overcome by adequate addressing to technical as well as to general public.

Carbon dioxide has low critical temperature and condensation is not possible at supercritical temperatures.

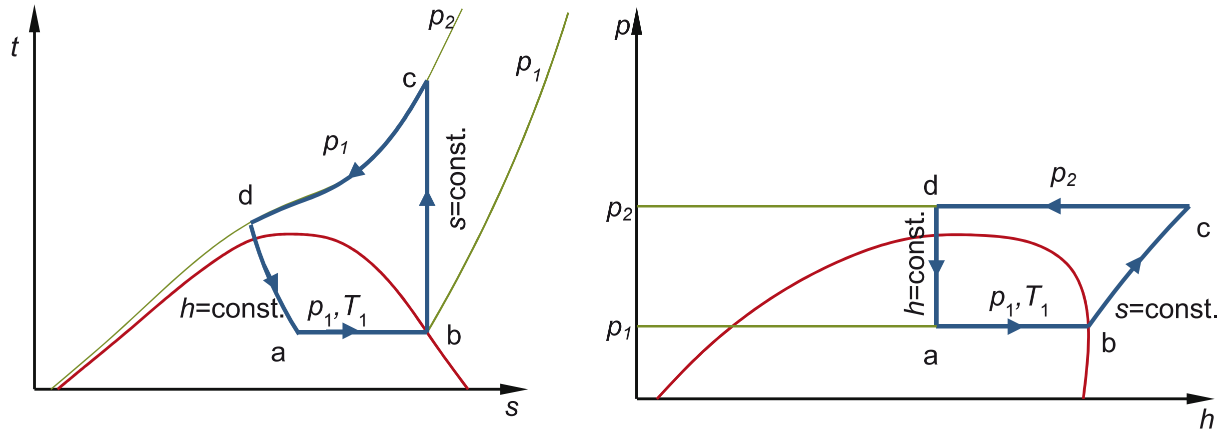

Figure 1. Single-stage vapor - compression transcritical process with R-744 (CO_2) in temperature - entropy t,s- and pressure – enthalpy p,h- diagrams

In that case transcritical process presented in **Figure 1** can be used. Refrigerant cooling down with significant temperature glide at a constant pressure p_1 takes place in a gas cooler (without the phase change) instead in the condenser. Pressure p_1 is not temperature-dependent as in subcritical processes. Temperature glide makes such a process more suitable for countercurrent domestic hot water heating than for application within heating systems with circulation. Internal heat exchange between condensed liquid and suction vapor refrigerant can increase process efficiency. Recent research activities have focused particularly on optimizing plant engineering, and more effective refrigeration plants are being developed to benefit from its extraordinary properties [7].

Hydrocarbons like propane (R290, C_3H_8), propylene (R1270, C_3H_6) or isobutane (R600a, C_4H_{10}) have been used in refrigeration plants all over the world for many years. Hydrocarbons are colorless and nearly odorless gases that liquefy under pressure, and have neither ozone depletion potential (ODP=0) nor significant direct global warming potential (GWP < 3). Thanks to their thermodynamic characteristics, hydrocarbons make particularly energy efficient refrigerants. Hydrocarbons are flammable, however, with current safety regulations, refrigerant losses can be maintained near zero. Hydrocarbons are available cheaply all over the world; thanks to their ideal refrigerant characteristics they are commonly used in small plants with low refrigerant charges [7].

Conclusion

In the future we may expect further research, regulation changes, the design of new systems suitable for the use of newly developed and natural refrigerants, the optimization of the system in the sense of compensating the lower efficiency of some refrigerants, but with keeping cost within acceptable limits. Conclusion is always the same: “No ideal refrigerant”, but proper applications suitable for different refrigerants can be found. The chance for “closing the circle” and return to natural refrigerants at a new, high technology level exists and should not be missed. ■

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