The state-of-the-art on Refrigerants

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Abstract. The two recent global emergencies (stratospheric ozone depletion and global warming) force refrigerating engineers and operators to face a new revolution on the choice of the working fluids for the different applications of refrigeration technology. Chemistry by now runs short of new synthetic products meeting within acceptable limits all the requirements asked for by the different refrigeration applications, and compromise solutions are more and more necessary, involving a limited use of few old-generation fluids, the new family of products HFO and an increased consideration for natural refrigerants. While dealing with these topics, this paper will show how basic thermodynamics can highlight important characteristics of a refrigerant.

1. Introduction

The American Jacob Perkins is accredited with the invention of the refrigeration machine using compression of a liquefiable gas, patented in London in 1834, and devised to use diethyl ether (then dubbed sulfuric ether) in a closed circuit as the refrigerant. According to some bibliographic sources, it seems that the first practical realisation of this machine, made in London in 1835 by John Hague, used instead caoutchoucin as the refrigerant, an inflammable, volatile, oily liquid hydrocarbon obtained by the destructive distillation of caoutchouc, of common use in the printing industry. Anyway, at the birth of mechanical refrigeration, all refrigerants were necessarily natural substances: almost any available chemical compound, which could grant a result, was used. A tentative chronological list of the main first generation refrigerants is the following: diethyl ether (C₂H₅OC₂H₅, R-610), dimethyl ether (CH₃OCH₃, E170), chemogene (a mixture of petrol ether and nafta); later on: carbon dioxide (CO₂, R-744), ammonia (NH₃, R-717), sulphur dioxide (SO₂, R-764), methyl chloride (CH₃Cl, R-40). After the turn of the century, from about 1920, also some hydrocarbons entered the use as refrigerants in mechanical compression refrigeration [1]. Almost all these substances are either flammable or toxic or both flammable and toxic; carbon dioxide CO₂ is an exception, but its thermodynamic properties were not favorable for the technology of that time (low critical temperature, high pressures).

Soon after world war one, summer climatisation began to take hold in public buildings (theatres, movie-theatres, department stores …) of the rich American cities, attracting a lot of patrons; it became imperative to find safer refrigerants for direct expansion air conditioning installations, benefitting also other applications of the fast growing refrigeration technology; at that time, chemistry was already able to create, by synthesis, new molecules foreign to nature. In 1931, at General Motors Research Corporation in the USA, the team led by Thomas Midgley, after concluding that a refrigerant molecule could only include atoms of eight elements, namely C, H, N, O, S, F, Cl, Br, first synthesized R-12 (F₂CCl₂) and then other fluids CFC (ChloroFluoroCarbons) like R-11 (FCCl₃) and R-115 (F₂ClCCF₃). After world war two, with the spreading of domestic air conditioning, also fluids of the HCFC family (HydroCloroFluorCarbons) joined the second generation of refrigerants, such as R-22 (F₂CCCl₂H). Only a few natural refrigerants survived this revolution: ammonia, thanks to its excellent thermodynamic properties, continued to be used, especially in Europe, in the applications of food preservation and brewery, while some hydrocarbons continued to be used in the petrochemical industry; even carbon dioxide experienced a rapid abandonment.
The second generation of refrigerants was the undisputed master of the market for almost sixty years; during this period, some fluids took over in specific main applications:

- CFC R-11 was the leading refrigerant for large capacity water chillers with centrifugal compressors. This fluid is classified as a low-pressure refrigerant (Normal Boiling Point \(NBP = +23.71\) °C): the consequent reduced value of the volumetric cooling effect allows reducing the cooling capacity produced by this type of machines without compromising energy efficiency with size reduction.
- CFC R-12 was the leading working fluid for domestic refrigeration, mobile air conditioning and water chillers with volumetric compressors: it is classified as a medium pressure refrigerant \((NBP = -29.75\) °C).
- HCFC R-22 was the leading refrigerant for compact air conditioning units, where a high value of the volumetric cooling effect is a premium. It can be classified as medium-high pressure refrigerant \((NBP = -40.81\) °C). When used in water-cooled centrifugal water chillers, this fluid could grant a refrigerating capacity exceeding 20 MW in a single unit.
- CFC/HCFC R-502, an azeotropie mixture of R-22 (48.8% by mass), and R-115 (51.2% by mass). This high-pressure fluid \((NBP = -45.26\) °C) was the leading refrigerant for medium and low temperature cooling in supermarket commercial refrigeration. It displays a volumetric cooling effect similar to R-22, but with a lower discharge temperature in single stage compression. This feature, obtained by the addition of R-115 to R-22, is very important for the safeguard of compressors used across high-pressure ratios, as it’s common in commercial applications.

Towards the mid-eighties of the last century, the global environmental emergency broke out concerning the destruction of the ozone layer in the stratosphere. When it became evident that the reason was the release of synthetic chemical compounds containing chlorine (but also the other halogens bromine and iodine) in the atmosphere, it was necessary to run for cover by imposing, under general laws (Montreal protocol, 1987) and local laws, the gradual ban in the use of CFC and HCFC refrigerants. Then the third generation of synthetic refrigerants had to be created, soon identified in the family of products somewhat similar to the previous ones, but excluding the presence of chlorine in the molecule (fluorine has no destructive effect on stratospheric ozone): the HFC refrigerants were born (HydroFluoroCarbons). One should be aware that the presence of hydrogen atoms in the molecule, in comparison with completely halogenated products, has the positive effect of drastically reducing the lifetime of the product in the atmosphere, without necessarily compromising its stability in the refrigeration circuit; this is a serious drawback of CFC products.

At first, an attempt was made to develop drop-in fluids with respect to the refrigerants used up until then, meaning fluids which, by replacing the previous refrigerants in the same circuit (with minimal changes), provided very similar machine performances in terms of cooling capacity and required power. In the case of R-12 the drop-in substitute was immediately identified in HFC R-134a. In many other sectors of refrigeration, in order to find refrigerants with similar characteristics to those of the fluids to be replaced, it was necessary to use HFC mixtures (in some circumstances even containing in minimal quantities hydrocarbons, to provide compatibility with mineral lubricants). Alongside the azeotropic mixtures, zeotropic mixtures were also accepted, with temperature glides restricted to 7 - 8 K in the conditions of use. With the use of mixtures it was possible to make available refrigerants that are safe (non-flammable and of the lower toxicity class A) for the most important refrigeration sectors, while also using flammable components (HFCs such as R-32, or hydrocarbons in small quantities), whose flammability is suppressed by the presence of the other components in the mixture.

The third generation refrigerants that established themselves as the main substitutes for the leading working fluids of the previous generation highlighted above were:

- R-11 → HFC R-245fa (CHF₂CH₂CF₃). Where permitted: HCFC R-123 (CHCl₂CF₃), with destructive effect on the stratospheric ozone much lower than CFC R-11.
- R-12 → HFC R-134a, considered a drop-in substitute.
- R-22 → HFC zeotropic mixture R-407C (23% by mass R-32, 25% R-125 and 52% R-134a).
- R-502 → HFC zeotropic mixture R-404A (44% R-125, 4% R-134a and 52% R-134a), or the HFC azeotropic mixture R-507A (50% R-125 and 50% R-143a).

In the same period, a new fluid imposed itself due to its good thermodynamic characteristics associated with a higher volumetric cooling capacity compared to the other refrigerants available:

- HFC R-410A, a zeotropic mixture (with glide less than 0.2 K, sometimes dubbed quasi-azeotropic) of R-32 (50% by mass) and R-125 (50%); in the air conditioning sector it found application in residential unitary air-conditioners, heat pumps, light commercial chillers and in VRV/VRF systems.

It is classified as a high pressure refrigerant, with \(NBP\) (at normal pressure and quality 0.5) = -51.41 °C.
Third-generation refrigerants had a short life. In fact, in the first years of this century the environmental emergency about anthropogenic global warming broke out, and forced the enactment of legislative provisions at world level (Kigali amendment to the Montreal protocol, 2016), national or multinational levels (such as the EU directive 517/2014) necessary to drastically phase down the use of products that, if released into the atmosphere, would cause greenhouse effect. HFC products are effective greenhouse gases. Both the regulations mentioned reduce progressively the quantity of F-gas available on the market in terms of CO$_2$ equivalents (CO$_2$e; see below); although the EU F-gas regulation includes bans on using specific refrigerants in some specific applications, in principle no single HFC product is banned, provided that the total CO$_2$e limit is met.

The most common metric to evaluate the capability of a given compound to impact the climate is the parameter $GWP_{100}$, Greenhouse Warming Potential. It expresses the amount of greenhouse effect caused by the compound considered in comparison to that caused by the reference gas Carbon dioxide CO$_2$, on the basis of an equal mass released into the atmosphere, over a time horizon of 100 years (Kyoto Protocol’s choice). CO$_2$e is the product of the mass of refrigerant times its $GWP_{100}$.

The computation of $GWP_{100}$ for a particular gas present in the atmosphere requires various inputs and model calculations; the two basic input parameters are the atmospheric lifetime $LFT$ and the radiative efficiency $RE$ of the gas, both of them clearly affecting in a direct way the $GWP$ value. As regards atmospheric lifetime, we have already seen that a reduction factor is the presence of residual hydrogen atoms in the molecule; another drastic reduction factor is, for hydrocarbon derivatives, the presence of a double bond C=C (unsaturated products), provided that they retain stability in the refrigerating circuit. This is the case of the HydroFluoroOlefins (HFO), which, in the simplest molecules, have a volatility suitable to act as refrigerants.

Atmospheric lifetimes of synthesized refrigerants span from 1020 yr (CFC-115), 100 yr (CFC-12), 11.9 yr (HCFC-22), to 10.5 days (HFO-1234yf) and 4 days (HFO-1132a).

Regarding the radiative efficiency $RE$, all the common CFC, HCFC and HFC single refrigerants exhibit very similar values (0.30 - 0.10 W m$^{-2}$ ppb$^{-1}$), while the HFOs of possible use as refrigerants have values one order of magnitude lower.

2. Refrigerants of fourth generations

As discussed above, both atmospheric lifetime and radiative efficiency favour HFOs with very low $GWP$s; unfortunately the number of suitable HFO compounds is rather limited, and the reactivity associated to the double bond makes most of them mildly flammable (safety class A2L according to ASHRAE Standard 34, 2016), with some exceptions. The main HFO (HCFO) products considered as candidate new refrigerants (both as pure fluids or mixtures components) are indeed (in $NBP$ increasing order):

- R-1132a (CF$_2$=CH$_2$); $GWP_{100} < 1$; Safety Class A2; $NBP = -86.7$ °C
- R-1123 (CF$_2$=CHF) $GWP_{100} = 3$; $NBP = -59.09$ °C
- R-1234yf (CH$_2$=CF-CF$_3$); $GWP_{100} < 1$; Safety Class A2L; $NBP = -29.49$ °C
- R-1243zf (CH$_2$=CH-CF$_3$); $GWP_{100} < 1$; $NBP = -25.42$ °C
- R-1234ze(E) (trans CHF=CH-CF$_3$); $GWP_{100} < 1$; Safety Class A2L; $NBP = -18.97$ °C
- R-1234ze(Z) (cis CHF=CH-CF$_3$) $GWP_{100} < 1$; $NBP = +9.73$ °C
- (HCFO) R-1224yd(Z) (cis CF$_2$CF=CHCl); Safety Class A1; $NBP = +14.62$ °C
- (HCFO) R-1233zd(E) (trans CF$_3$CH=CHCl); Safety Class A1; $NBP = +18.26$ °C
- R-1336mzz(Z) (cis CF$_3$CH=CHCF$_3$) $GWP_{100} = 2$; Safety Class A1; $NBP = +33.45$ °C

(HCFO products display very low ozone depletion, again because of their very limited atmospheric lifetimes)

The low pressure fluids (characterized by high $NBP$ values) R1234ze(Z), R1234yd(Z), R-1233zd(E) and R-1336mzz(Z), all of them non-flammable, can find convenient application (both as single fluids or mixtures components) in high temperature heat pumps and centrifugal chillers.

The three medium pressure fluids listed above (R-1234yf, R-1243zf and R-1234ze(E)) are all mildly flammable. R-1234yf is considered a drop-in substitute for R-134a (and R-12). R-1234ze(E) is considered nonflammable in storage and transport, but its volumetric refrigerating capacity is lower than that of R-1234yf by more than 20%, and therefore its application is restricted to water chillers and high temperature heat pumps. These fluids can therefore be directly used as refrigerants in all middle
Table 1 – Characteristics of fourth generation substitute refrigerants (Thermodynamic data from RefProp10.0)

### FOURTH GENERATION SUBSTITUTES FOR REFRIGERANT R-123 [→CFC-11]

| ASHRAE NAME | BRAND NAME | HFC-32 (GWP=747) (A2) | HFC-125 (GWP=3130) (A2) | HFC-134a (GWP=1430) (A1) | R-123 (GWP=0.0) | SATURATION PRESSURE AT 0°C [bar] | SATURATION PRESSURE AT 0°C [bar] |
|-------------|------------|------------------------|--------------------------|---------------------------|----------------|-------------------------------|-------------------------------|
| R-123       |            | -                      | -                        | -                         | -              | 0.5254                        | 0.5254                        |
| R-124       |            | -                      | -                        | -                         | -              | -                             | -                             |
| R-514A XFP1 | -          | -                      | -                        | -                         | 74.7           | 25.3                          | 0.0089                        |
| R-1225mG7   | -          | -                      | -                        | -                         | 100            | 0.0011                        | 0.0011                        |
| R-1046mG8   | -          | -                      | 100                      | -                         | 0.0017         | 0.0017                        | 0.0017                        |

### FOURTH GENERATION SUBSTITUTES FOR REFRIGERANT R-134a [→CFC-12]

| ASHRAE NAME | BRAND NAME | HFC-32 (GWP=747) (A2) | HFC-125 (GWP=3130) (A2) | HFC-134a (GWP=1430) (A1) | R-134a (GWP=1140) (A1) | SATURATION PRESSURE AT 0°C [bar] | SATURATION PRESSURE AT 0°C [bar] |
|-------------|------------|------------------------|--------------------------|---------------------------|---------------------------|-------------------------------|-------------------------------|
| R-12        |            | -                      | -                        | -                         | -                          | -                             | -                             |
| R-236      |            | -                      | -                        | -                         | 42                        | 58                            | 2.55                          |
| R-513A XFP10 | -       | -                      | -                        | -                         | 42                        | 58                            | 2.55                          |
| R-450A RT14 | -          | -                      | -                        | -                         | 42                        | 58                            | 2.55                          |
| R-424a N-13 | -          | -                      | -                        | -                         | 100                       | 5                            | 0.0018                        |
| R-424b N-13 | -          | -                      | -                        | -                         | 100                       | 5                            | 0.0018                        |
| R-424c N-13 | -          | -                      | -                        | -                         | 100                       | 5                            | 0.0018                        |
| R-290        | Propylene | -                      | -                        | -                         | 100                       | 5                            | 0.0018                        |
| R-424a RT-13 | -       | -                      | -                        | -                         | 100                       | 5                            | 0.0018                        |
| R-424c RT-13 | -       | -                      | -                        | -                         | 100                       | 5                            | 0.0018                        |

### FOURTH GENERATION SUBSTITUTES FOR REFRIGERANT R-407C [→HFC-122]

| ASHRAE NAME | BRAND NAME | HFC-32 (GWP=747) (A2) | HFC-125 (GWP=3130) (A2) | HFC-134a (GWP=1430) (A1) | R-123 (GWP=0.0) | SATURATION PRESSURE AT 0°C [bar] | SATURATION PRESSURE AT 0°C [bar] |
|-------------|------------|------------------------|--------------------------|---------------------------|----------------|-------------------------------|-------------------------------|
| R-488C      | DR-68      | 20                      | 20                       | 20                        | 51             | 5.22                          | 5.62                          |
| R-488C      | DR-68      | 20                      | 20                       | 20                        | 51             | 5.22                          | 5.62                          |
| R-488C      | DR-68      | 20                      | 20                       | 20                        | 51             | 5.22                          | 5.62                          |
| R-488C      | DR-68      | 20                      | 20                       | 20                        | 51             | 5.22                          | 5.62                          |
| R-448a      | L-204a     | 41.5                    | 41.5                     | 41.5                      | 10             | 5.17                          | 9.23                          |
| R-448a      | L-204a     | 41.5                    | 41.5                     | 41.5                      | 10             | 5.17                          | 9.23                          |
| R-448a      | L-204a     | 41.5                    | 41.5                     | 41.5                      | 10             | 5.17                          | 9.23                          |
| R-448a      | L-204a     | 41.5                    | 41.5                     | 41.5                      | 10             | 5.17                          | 9.23                          |
| R-454c      | DR-3       | 21.5                    | 21.5                     | 21.5                      | 10             | 5.17                          | 7.70                          |
| R-454c      | DR-3       | 21.5                    | 21.5                     | 21.5                      | 10             | 5.17                          | 7.70                          |
| R-454c      | DR-3       | 21.5                    | 21.5                     | 21.5                      | 10             | 5.17                          | 7.70                          |
| R-454c      | DR-3       | 21.5                    | 21.5                     | 21.5                      | 10             | 5.17                          | 7.70                          |
| R-454c      | DR-3       | 21.5                    | 21.5                     | 21.5                      | 10             | 5.17                          | 7.70                          |

### FOURTH GENERATION SUBSTITUTES FOR REFRIGERANT R-410A

| ASHRAE NAME | BRAND NAME | HFC-32 (GWP=747) (A2) | HFC-125 (GWP=3130) (A2) | HFC-134a (GWP=1430) (A1) | R-123 (GWP=0.0) | SATURATION PRESSURE AT 0°C [bar] | SATURATION PRESSURE AT 0°C [bar] |
|-------------|------------|------------------------|--------------------------|---------------------------|----------------|-------------------------------|-------------------------------|
| R-410A       |            | 60                      | 60                       | 60                        | 60             | 10.68                         | 10.68                         |
| R-410A       |            | 60                      | 60                       | 60                        | 60             | 10.68                         | 10.68                         |
| R-410A       |            | 60                      | 60                       | 60                        | 60             | 10.68                         | 10.68                         |
| R-410A       |            | 60                      | 60                       | 60                        | 60             | 10.68                         | 10.68                         |
| R-410A       |            | 60                      | 60                       | 60                        | 60             | 10.68                         | 10.68                         |

### FOURTH GENERATION SUBSTITUTES FOR REFRIGERANTS R-404A & R-507A

| ASHRAE NAME | BRAND NAME | HFC-32 (GWP=747) (A2) | HFC-125 (GWP=3130) (A2) | HFC-134a (GWP=1430) (A1) | R-123 (GWP=0.0) | SATURATION PRESSURE AT 0°C [bar] | SATURATION PRESSURE AT 0°C [bar] |
|-------------|------------|------------------------|--------------------------|---------------------------|----------------|-------------------------------|-------------------------------|
| R-404A      |            | -                      | 20                       | 40                        | 40             | 5.82                          | 5.82                          |
| R-404A      |            | -                      | 20                       | 40                        | 40             | 5.82                          | 5.82                          |
| R-404A      |            | -                      | 20                       | 40                        | 40             | 5.82                          | 5.82                          |
| R-404A      |            | -                      | 20                       | 40                        | 40             | 5.82                          | 5.82                          |
| R-404A      |            | -                      | 20                       | 40                        | 40             | 5.82                          | 5.82                          |

### Footnotes:

* For zeotropic blends the saturation pressure is calculated at quality q = 0.5. Glysides relate to the same pressure.
** GWP200 values not included in IPCC AR5. Taken from a different source.
*** HC-290 Propane: GWP200 = 3, Safety class A3. CF34 (R-1331) Trifluoroiodomethane: GWP200 = 1; Safety class A1.
pressure applications when mild flammability is not an issue. Otherwise, they are proposed as components in mixture with HFC products: the contribution of the HFO is the reduction in the \( GWP_{100} \) of the mixture, whereas the contribution of the HFC(s) is the suppression of flammability.

Both the two high-pressure HFO products listed above (R-1132a and R-1123) have not found application as refrigerants so far; R-1223 because chemically unstable, and R-1132a because flammable (Safety Class A2); it might be considered in the future in new refrigerant blends for high pressure applications.

For the time being the synthesized fourth generation substitute refrigerants for medium-high and high pressure applications present on the market are zeotropic blends all based on HFC R-32 mixed with other HFCs (mainly R125 and R-134a) and with HFOs (mainly R-1234yf and R-1234ze(E)). The composition must be such to approximately match the pressure level required by the specific applications, while the content of R125 can suppress the flammability of R-32 and of the HFO component(s), but contributes to the increase of the greenhouse effect; mixtures with a low or no percentage of R-125 (as all the blends at present marketed as substitutes for R-410A) are unavoidably mildly flammable. Another effect of the different components mixed with R-32 is the containment of the discharge temperature, an important issue to safeguard compressors and lubricants in single stage high-pressure-ratio applications.

Table 1 illustrates the present market situation with the fourth generation refrigerants relative to the main applications of refrigeration technology; refrigerant R-466A, mentioned as a candidate substitute for R-410A, is not a viable refrigerant at this point; it will be dealt with at the end of this presentation.

Increasing average global temperature due to climate change, economic growth and urbanisation are expected to lead to a greater demand for cooling, both for air conditioning and for the strengthening of the cold chain to reduce food waste; besides, in the future there will be an increased use of heat pumps to reduce GHG emissions from heating systems. Consequently, the future will bring about a drastic increase in the demand for refrigerants, even if slightly slowed down by attempts to reduce the charge of equipment, for example through miniaturization of heat transfer surfaces (minichannel technology).

Based on a demand growth rate of 2%, recently Cohr Pachai et al. [3] calculated for the EU countries an average value of \( GWP_{100} \) around 310 for the refrigerants put on the market in 2030. Considering the \( GWP_{100} \) values reported in Table 1 for the substitute refrigerants in medium-high and high pressure applications, it must be concluded that either there will be a drastic surge on the application of natural refrigerants or most of the fourth generation refrigerants now available are to be considered as interim working fluids, and new solutions must be devised. An increased use of flammable or mildly flammable products seems anyway unavoidable.

3. Thermodynamic characteristics of refrigerants

Many important thermodynamic features of a substance employed as a refrigerant in vapour compression refrigeration can be gained by simple basic analyses. To this end, it’s necessary to consider a reference ideal cycle: in the following, the reference will be a simple subcritical refrigerating cycle, with isobaric condensation and evaporation at saturation temperatures \( t_c=40 ^\circ \text{C} \) \( (T_c=313.15 \text{ K}) \) and \( t_e=0 ^\circ \text{C} \) \( (T_e=273.15 \text{ K}) \) respectively, isentropic compression and isoenthalpic throttling, with no superheating at compressor suction and no subcooling at condenser exit. For zeotropic mixtures, \( T_c \) and \( T_e \) are the temperatures at middle quality of the condensation and evaporation processes (quality \( x=0.5 \) in the condenser), as in AHRI Standard 540. These temperatures may be considered representative of the working design conditions of an AC water-cooled chiller in temperate countries; different ideal cycles can be considered as references for other refrigeration applications and similar qualitative results will be obtained.

In this context, for zeotropic blends the normal boiling temperature is intended as the saturation temperature at normal pressure \( p=101.325 \text{ kPa} \) and quality \( x = 0.5 \); similarly a temperature-pressure saturation curve refers to the intermediate quality value \( x = 0.5 \).

The coefficient of performance \( \text{COP} \) and the volumetric cooling capacity \( \dot{Q}_v \) (the refrigeration effect per unit volume of the refrigerant vapor evaluated at compressor suction conditions) are the main performance metrics in vapor compression refrigeration technology. \( \text{COP} \) determines the energy efficiency of the equipment and therefore its operating cost, while \( \dot{Q}_v \), especially when volumetric compressors are involved, influences the physical size of the equipment, with implication on the plant cost. For the ideal reference cycle described above, one can plot both \( \text{COP} \) and \( \dot{Q}_v \) versus the saturation
pressure of the refrigerant \( p_c \) at condensation temperature \( T_c \), as shown in figure 1. The set of refrigerants considered in figure 1 includes all the synthetic fluids classified in ASHRAE Standard 34 (2016) (both pure compounds and azeotropic/zeotropic blends, plus ammonia and some hydrocarbons (propane, n-butane, isobutane, propylene)).

Figure 1 highlights the close correlation existing between the volumetric cooling capacity and the compressor suction pressure, which one can generally observe regardless of the operating conditions. A similar strict correlation exists even when plotting the volumetric cooling capacity vs. the normal boiling point of the refrigerant, again in a wide range of operating conditions. All substitute refrigerants for a previous generation working fluid must have normal boiling point similar to the one of the replaced refrigerant; all drop-in refrigerants have almost overlapping saturation \( T - p \) curves.

As to the Coefficient of Performance \( COP \), figure 1 shows a correlation versus suction saturation pressure of the refrigerant: high-pressure refrigerants are less energy efficient than low-pressure refrigerants. This depends on the fact that usually high-pressure refrigerants work closer to their critical temperature than low-pressure refrigerants, and this intrinsically means higher theoretical cycle losses, as shown in figure 2. This figure highlights the dependence of the theoretical reference cycle \( COP \) on the proximity of the condensation temperature to the refrigerant critical temperature.

One should consider that, in in-tube flow, the condensation and evaporation characteristics of high-pressure refrigerants (combining both heat transfer coefficients and associated pressure drops) are better than low-pressure refrigerants', and this helps in improving energy efficiency of an equipment in real operations. The thermodynamic analysis of the ideal refrigeration cycle cannot of course highlight this fact.

Quite a few intrinsic thermodynamic characteristics of a working fluid are displayed by a simple exergy analysis of the basic theoretical cycle. Exergy is a powerful tool for studying thermodynamic processes in the light of both the first and the second principle of thermodynamics.
The basic reference refrigerating cycle between $T_c$ and $T_e$ considered above and referring to a pure fluid or an azeotropic mixture can be plotted in a $T-s$ (absolute temperature – specific entropy) diagram as shown in figure 3. Since one wants to evaluate the intrinsic ability of the particular working fluid in producing mechanical cold, one can take the value of the ambient temperature in the definition of the exergy function coincident with the condensation temperature.

One can identify two sources of loss, where the reference refrigeration cycle differs from the ideal cycle (of Carnot) with the same refrigerating effect:

- **Specific desuperheating exergy loss** at the condenser inlet

$$\Pi_{des} = h_2 - h_5 - T_c(s_2 - s_5);$$

$h$ is the specific enthalpy and $s$ the specific entropy of the refrigerant.

- **Specific throttling exergy loss** at the expansion valve

$$\Pi_{thr} = T_c(s_3 - s_4).$$

Gustav Lorentzen dubbed this loss the hemorrhage of the refrigeration cycle. It negatively affects energy efficiency in two aspects: primarily, it does not recover the work that an isentropic expansion would make available. Secondly, it reduces the cooling effect of the cycle compared to an isentropic expansion.

In the $T-s$ diagrams, these losses can be viewed as areas, as shown in figure 3 for refrigerants consisting of pure fluids or azeotropic mixtures. For zeotropic mixtures the representation is that shown in figure 4, approximated for $\Pi_{thr}$, for which an alternative equivalent representation has been used.

In order to compare different refrigerants in the same reference cycle, one must normalize the exergy losses by division by the specific work $W = (h_2 - h_3)$, thus obtaining the so-called efficiency defects:

**Desuperheating efficiency defect** $\delta_{des} = \frac{\Pi_{des}}{W}$,

**Throttling efficiency defect** $\delta_{thr} = \frac{\Pi_{thr}}{W}$,

**Total efficiency defect** $\delta_T = \frac{\Pi_{des} + \Pi_{thr}}{W} = \frac{\Pi_T}{W}$.

The cycle exergy efficiency is defined as $\eta_{ex} = \text{COP}/\text{COP}_{\text{Carnot}}$, where $\text{COP}_{\text{Carnot}} = T_e/(T_c - T_e)$.

It turns out then:

$$\eta_{ex} + \delta_{des} + \delta_{thr} = 1$$

The molecular structure of the new refrigerants is generally more complex than that of the older generations’ refrigerants, and this translates into a higher value of the specific molar heat at constant pressure of the vapour phase. The greater complexity of the molecule changes the general shape of the area of saturated vapours in the $T-s$ diagrams representation, approaching the intermediate part of the dry saturated vapour curve to the vertical. An isentropic compression starting from dry saturated vapor in this zone can at least partly take place in the area of wet saturated vapours, without or with minimal overheating at the compressor outlet. Of course, in the actual compressions in refrigeration machines, superheating at the compressor outlet is enhanced by the fact that usually the refrigerant is already weakly superheated at the compressor inlet, and by the fact that compression takes place with an increase in entropy.

Figure 5 shows the efficiency defects (desuperheating and throttling) plotted against the constant pressure molar heat capacity of saturated vapour at 0 °C. This plot refers to the same full set of
refrigerants with the exclusion of those with depletion potential of stratospheric ozone, and to the same ideal reference cycle considered above.

Figure 5 clearly shows that the throttling losses are generally much higher than the desuperheating losses; only for the very simple ammonia molecule, the two basic losses are of similar value. This same plot highlights that, at increasing molecular complexity, the desuperheating loss tends to decrease going to zero, while the throttling loss tends to increase. It is evident also that the total exergy loss tends to increase along with the increase in molecular complexity.

The refrigerants with higher desuperheating losses tend to give high discharge compressor temperatures. They are therefore unsuitable to operate, without mitigation measures (water-cooled compressors, multi-stage compression with inter-refrigeration, liquid injection) with high-pressure ratios or in compressors oil reservoir on the high-pressure side. On the other hand, these refrigerants are more suitable for cooling units with partial heat recovery (the desuperheating loss turns out to be an opportunity).

Throttling losses can clearly be decreased by subcooling the liquid condensate at the evaporator exit, before entering the throttling device. This can be done with a heat exchanger in countercurrent with the vapour coming out of the evaporator: cycle with heat exchanger between the liquid line and the suction line (LL / SL-HX). In this way, the loss due to desuperheating increases and a new factor of thermodynamic loss due to the regenerative heat transfer in the exchanger is also introduced. This cycle configuration is energetically convenient only with refrigerants with low or no desuperheating losses in the base reference cycle. Figure 6 refers to the fourth generation refrigerant R-1234yf in a refrigerating cycle with LL/SL-HX, isobaric condensation at $T_c=40$ °C and isobaric evaporation at $T_e=0$ °C. It shows how the thermodynamic losses (desuperheating, heat transfer, throttling efficiency defects) vary as the degree of subcooling of the liquid in the heat exchanger increases, up to the its possible limit value (unitary efficiency of the exchanger). This cycle configuration is not even theoretically convenient with refrigerants with relatively high exergy losses due to desuperheating in the base reference cycle (R-717, R-32, R-410A …).
A two-stage process with flash vapour extraction can drastically reduce throttling losses. One can achieve this situation with the two-stage compression and two-stage throttling refrigeration cycle with intermediate separator, or more simply with the two-stage flash economizer cycle, possible with compressors equipped with an intermediate suction port (screw, scroll); any losses of exergy due to desuperheating are also reduced in this way.

Clearly all refrigerants benefit in terms of cycle energy performance from the adoption of two-stage throttling with flash vapour extraction. Moreover, the greatest benefit is obtained with refrigerants with a low value of the critical temperature $T_k$ (high pressure refrigerants), as highlighted in figure 7. This figure shows the increase factor of the exergetic efficiency (or of the coefficient of performance $COP$) obtained with the two-stage flash economizer cycle as compared to the analogous value of the basic ideal cycle. Condensation and evaporation temperatures are $T_c = 40 \, ^\circ C$ and $T_e = 0 \, ^\circ C$; the refrigerants considered are limited to pure fluids and azeotropic blends. Zeotropic blends are not included, because fractionation effects caused by the separator may be problematic. The intermediate flash pressure considered is the optimal one, which maximizes the energy efficiency of the two-stage flash economizer cycle. This value is always very close to the value of the refrigerant saturation pressure at the intermediate temperature between $T_c$ and $T_e$.

It is worth remembering that the recovery of throttling losses by means of mechanical expanders has been the subject of research for a long time, without reaching at present practical application possibilities; instead, the use of ejectors, although with low efficiency, is now common practice in commercial sector refrigeration systems operating with carbon dioxide.

4. New atoms in a refrigerant molecule?

In a most valued publication [4], Mc Linden and co-workers searched for single-component replacement refrigerants by applying screening criteria to a comprehensive chemical database comprised of over 60 million chemical structures. Their conclusion was that only a few pure fluids possess the combination of chemical, environmental, thermodynamic and safety properties necessary for a refrigerant, and that most of these fluids are at least moderately flammable. The great majority of these fluids are already considered as alternative refrigerants, both as pure-component working fluids or as components of refrigerant blends.

The conclusion from the above is that, in our search for synthesised replacement refrigerants, we’re now scraping the bottom of the barrel, and that it is very unlikely that the future will offer a fifth generation of refrigerants.

In their research work, Mc Linden and co-workers limited their search to molecules comprising only the elements C, H, F, Cl, Br, O, N or S, in line with Midgley’s belief back in 1931.

In contrast to this conclusion long considered well established, last June 2018, US Honeywell has unveiled a new refrigerant as a non-flammable substitute for R-410A, provisionally designated by ASHRAE as R-466A (see Table 1), with a preliminary A1 safety categorization. It is a quasi-azeotropic mixture comprised of R-32 (49 % by mass), R-125 (11.5 %) and the new product (in the refrigeration sector) CF3I (R-13I1, 39.5 %). This last iodine compound is a powerful fire suppressant, used in aircrafts for fuel inerting and for firefighting, already considered in the past as a refrigerant, but never put on the market. It has a very short atmospheric lifetime (1≈6 days), because of the weak C-I bond.
Table 2 provides a comparison among the thermodynamic properties of R-410A, R-32 and R-466A.

|               | R-410A | R-32  | R-466A |
|---------------|--------|-------|--------|
| Critical Temperature, °C | 71.34  | 78.11 | 84.52  |
| Critical pressure, bar     | 49.01  | 57.82 | 65.02  |
| Normal Boiling Point, °C   | -51.41 | -51.65| -53.95 |
| Saturation pressure at 0 °C, bar | 7.99  | 8.13  | 8.59   |
| Coefficient of Performance COP * | 5.13  | 5.34  | 5.21   |
| Volumetric Cooling Effect*, MJ/m³ | 4.73  | 5.29  | 5.17   |
| Compression Discharge Temperature*, °C | 57.28 | 70.35 | 62.00  |
| Evaporation / Condensation Temperature Glaides*, °C | 0.08 / 0.12 | 0 / 0 | 0.04 / 0.15 |

|**Table 2**
Thermodynamic properties of R-410A, R-32 and R-466A

R-466A is still under ASHRAE scrutiny. Honeywell intends to start commercialisation in Fall 2019; the main issues are chemical stability and material compatibility.

Should R-466A obtain ASHRAE classification as a refrigerant, this might open the way to new non-flammable refrigerant mixtures or even new iodine-containing compounds to be considered as working fluids in refrigeration technology.

5. References

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[3] Cohr Pachai A, Kuijpers L and Vonsild A 2018 Reviewing new refrigerant options for industrial refrigeration systems *Proc. 13th IIR Gustav Lorentzen Conference on Natural Refrigerants*, (Valencia, Spain)
[4] Mc Linden M O, Brown J S, Brignoli R, Kazakov A F and Domanski P A 2017 Limited options for low-global-warming-potential refrigerants *Nat. Commun.* 8 14436

**Postscript:** Following the presentation of this key-note paper at the UIT 2019 Conference, on November 19 2019 ASHRAE released the addendum to ANSI/ASHRAE Standard 34-2019, which adds R-466A to the list of refrigerant blends, with the following data: Average Molecular Mass 80.7 g/mol, Normal Bubble Point -51.7 °C; Normal Dew Point -51.0 °C; Safety Group A1.