

REFRIGERANTS OF THE FUTURE

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Abstract; The high global warming potential of most HFC fluids is forcing a change to fluids with less environmental impact. The search for the ideal refrigerant is not new, but has been ongoing for one hundred years, even though the reason for the search has changed.

The paper gives a background to the present search for new refrigerants, discusses the criteria for the selection and gives some information on the status concerning introduction of new fluids.

In conclusion, there is only one new refrigerant close to be put on the market, HFO1234yf. Other closely related fluids, such as HFO1234ze may be alternatives in the future. Beside these new fluids, it is believed that natural refrigerants like hydrocarbons, ammonia and carbon dioxide, as well as the low GWP, but flammable, HFC152a, will all find a place in future refrigeration and heat pump systems.

Key Words: Refrigerants, HFO, R1234

1 INTRODUCTION

The selection of working fluid for vapor compression refrigeration and heat pump systems has been a hot topic at intervals during almost one hundred years. In the beginning of the 20th century, many different fluids were used, some flammable and some poisonous and/or having a strong smell. At the time, only open compressors were available, and small leakages from shaft seals were unavoidable. It is not surprising that the industry targeting the home market realized the need for a safe refrigerant, i.e. one which was neither flammable, poisonous or smelling. It is well known how Thomas Midgley and Albert Henne got the assignment of Frigidaire company to develop such a fluid. After only a short time they focused on halogenated hydrocarbons. The logic behind this is easy to see: Replacing hydrogen with halogen reduces flammability and makes the molecule more stable. A stable molecule does not easily react and therefore could be expected to be inert, not reacting with biological systems. After the demonstration at a meeting of the American Chemical Society in 1930, where Midgley inhaled the invented gas (R12) and blew out the gas over a lit candle, the world was convinced and the era of the CFCs began. It took another 50 years for us to realize that the stability of the halocarbon molecules made them ideal transporters of chlorine to the stratosphere, and to realize the influence of the chlorine release at these altitudes on the ozone layer. It took another 10 – 15 years to realize the effect on global warming of these substances.

During the 1980s the “Freons” were widely discussed, leading to the signing of the Montreal protocol in 1987. As a result, several research projects were initiated in the search for alternative refrigerants. In the US, NIST’s refrigerant program was substantially increased (McLinden 2008), leading to the development of Refprop, the *de facto* standard for calculating refrigerant properties. Another example of this interest was that the Swedish Energy Agency in the 1990s funded a three year research program named Alternative Refrigerants. The research and development during this period helped in the fast phase out of CFCs and thereby to a reduction of the emissions of chlorocarbons. This has resulted in the recovery of the ozone layer (NASA 2007).

The phase out concerned in most countries only the CFCs, and the change was partly to HCFC and partly to HFCs. However, at the same time, voices were raised that perhaps all substances not present in the natural environment should be avoided, in the sake of safety, as it seems impossible to foresee all possible effects of the refrigerants on the natural environment. One prominent voice in this choir was professor Gustaf Lorentzen, who, in a number of papers (e.g. Lorentzen 1994, 1995) spoke for the use of, primarily, carbon dioxide and ammonia as refrigerants. Another important event promoting the use of natural refrigerants was the presentation in 1992, by Greenpeace in cooperation with the small company Foron of a household refrigerator using isobutane as refrigerant, and cyclopentane as the blowing agent in the insulation (Lohbeck 2004). The success of this product on the market forced the large manufacturers of refrigerators and freezers for the home market to follow, and today almost all refrigerators sold in northern Europe, and many in e.g. Japan use isobutane as refrigerants, and several hundred million such units are in operation.

With the switch from CFCs (primarily R11 and R12) to HFCs the second threat posed by the halocarbon refrigerants to the environment, their contribution to global warming, was also reduced considerably, as the GWP of the substitutes are much lower. The contribution of halocarbon refrigerants to global warming should not be underestimated, as is clearly shown in Figure 1. This figure also shows that the ban on CFCs, caused by their ozone depletion potential, had a substantial influence also on the refrigerants' contribution to global warming. A positive, but at the time unintended, effect.

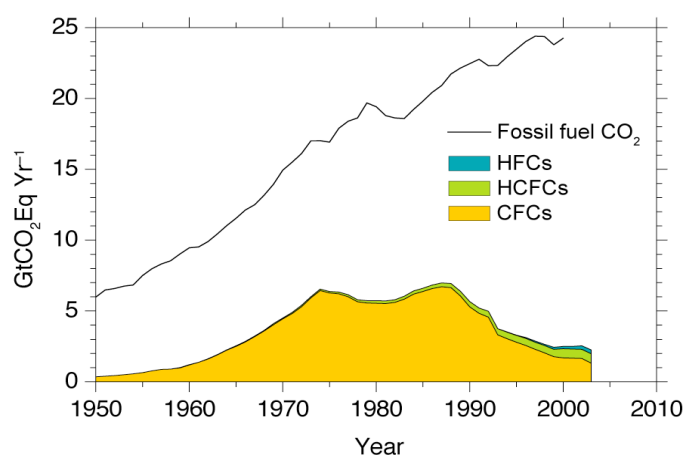


Figure 1: Contribution of halocarbons to global warming expressed as CO₂ equivalents. Source IPCC

After the phase-out of CFCs, and in some countries HCFCs, and the wide introduction of HFC refrigerants, there was a certain tiredness in the refrigeration industry, and perhaps a contentness among the authorities funding research in the area. At first, the fact that the problem of the high GWPs of the HFCs was not solved did not appear to be just as important as the ozone depletion.

Some years later, the authorities in Europe, through the MAC- directive (EU 2006) put a time limit to the use of fluids with GWP > 150 in automotive applications. To meet this demand, the chemical corporations and automotive industry, have been spending much effort on the development of new refrigerants and new car AC systems. In Europe this developed into a struggle between two technologies, one using CO₂ as refrigerant and the other using synthetic refrigerants, mainly HFO1234yf or mixtures, with this fluid as a main component.

With the demands on automotive industries to find solutions with low GWP, it is not far to expect similar solutions to be demanded also for other parts of the HVAC industry. It is

therefore not surprising that the search for new refrigerants has once again emerged as an important and relevant topic for the whole industry.

2 DEMANDS ON A REFRIGERANT

There are several demands to be met by a fluid to be suitable as a refrigerant. The most important ones are given in Table 1. When Midgley and Henning developed the Freons in the 1920s they were well aware of the requirements. They also concluded that substances suitable to be used as refrigerants must be composed of a very limited number of elements, all from the upper right hand corner of the periodic table, but not including the noble gases. The reason is that only these elements form covalent bonds, thereby forming compounds with liquid and vapor phases at reasonable temperatures, compounds which are stable and non-toxic (Midgley 1937). Since Midgley's days, there have been several other studies done in search of suitable substances for use as refrigerants. As concluded by many investigators (McLinden and Didion 1987, Calm and Didion 1998, Bivens and Minor 1998, Calm 2008, Cavallini et al. 2010), the probability of finding new fluids with ideal properties is very low. Each choice therefore is bound to be a compromise.

Table 1: Important requirements on a refrigerant

Chemical:

- Stable and inert

Health, safety and environmental:

- Non-toxic
- Non-flammable
- Slight smell
- Benign to the global physical and biological environment etc.

Thermal:

- High enough critical point and low enough freezing point for the application
- Reasonable saturation pressure at the temperatures of the application
- Pressure ratio
- Low viscosity
- High thermal conductivity

Other:

- Satisfactory oil solubility/miscibility
- High dielectric strength of vapor
- Easy leak detection
- Low cost

A few comments on the demands in the table may be of interest: Chemical stability is highly essential as the refrigerant must stay intact for many years inside the system, where the temperature at the high pressure side of the compressor may be well above 100°C, without decomposing or reacting with components in the system. Once outside the system, however, the atmospheric lifetime should preferably be short to assure that substances not naturally appearing in the environment disappears and are not concentrated anywhere in the biological chain. Low toxicity is important, both for the fluid and for decomposition products in case of fire or in reactions in the natural environment. Non-flammable substances are preferred, but it should be noted that there is a large difference between the risks and consequences of ignition of e.g. R152a or ammonia on one hand and that of propane or isobutane on the other. For ammonia, the risk of accidents is probably higher due to the strong smell than to the toxicity or flammability, as the smell may easily cause panic. Odorless refrigerants on the other hand may be dangerous due to the risk of suffocation if the refrigerant is released in a basement or inside the hull of a ship.

For the performance, high critical temperature (T_{cr}) is advantageous, as the process will then not be running close to the critical point. As discussed by McLinden (1987), if the condensing temperature is close to the critical point, the superheat of the refrigerant gas during compression will be excessive, and much of the liquid will evaporate during the expansion, thereby reducing the fraction of the heat of evaporation available for absorbing heat in the evaporator. However, the higher the critical temperature, the lower will be the system pressure at any specific operating temperature. High critical temperature of the fluid therefore means large necessary volume flow/compressor size for a specific cooling or heating capacity. Instead of considering the critical temperature, the normal boiling points (T_{nb}) can be compared, as the ratio T_{nb}/T_{cr} is in the range 0,6 to 0,7 for most fluids (McLinden and Didion 1987).

By tradition, refrigerants have been chosen for a given application to give system pressures in the range 1 to 25 bar in all parts of the system. With the introduction of R410A this tradition is broken, which opens up for use of other refrigerants with higher pressures. Higher pressure level decreases the pressure ratio, for given evaporation and condensation temperatures, and thereby, in most cases, increases the isentropic and volumetric efficiencies of the compressor.

Low viscosity favors low pressure drop, but more important for pressure drop is the pressure level, as high pressure means less volume flow of gas. Viscosity and thermal conductivity are both important for heat transfer.

High oil solubility facilitates the return of the oil to the compressor, but may also result in refrigerant being absorbed in the oil inside the compressor during standstill, which may lead to problems in terms of foaming at compressor startup.

High dielectric strength is important in hermetic systems where the compressor motor is cooled by the refrigerant.

3 COMPARING REFRIGERANTS

The expected performance of any refrigerant can be evaluated from the thermodynamic and transport properties of the fluid. A suggested basis for the comparison is to compare the performance of the basic cycle, i.e. the cycle without subcooling or superheat, and with isentropic compression. Only the expected evaporation and condensing temperatures have to be given for such a comparison. Based on these values, the coefficient of performance (for cooling) of the refrigerant, $COP_{2, ideal}$, the volumetric refrigerating effect and the volumetric compression work can be calculated. These values can be found tabulated for several refrigerants at several combinations of evaporation and condensation temperatures, for example in Granryd et al. (2006). This source also gives values for the % change in performance per degree of subcooling or superheating. All these values can easily be calculated based on refrigerant data.

Important in a comparison is also the thermal conductivity, directly influencing heat transfer, and the viscosity, determining the pressure drop of the fluid. As thermodynamic properties are also of influence to heat transfer and pressure drop, a method of comparing fluids is to use well established correlations to derive Figures of Merit (Palm 2008). In this way, it is possible to compare the performance of different refrigerants in a system with specific geometry, assuming the same cooling capacity.

McLinden and Didion (1987) presented a very interesting study where they related the thermophysical properties as well as flammability and toxicity to the structure of the molecule for halogenated hydrocarbons. At that time, the search was for substitutes for R11 and R12,

but the influence of the molecular structure on performance and other qualities are of course the same now in the search for substitutes for the common HFCs. Interestingly enough, they discarded at that time at an early stage the possibility of using molecules with double bonds due to the lower stability of these fluids. They also concluded that halocarbons with more than two carbon atoms are less favorable for the following reasons: 1) They “tend to have critical temperatures that are too high for most applications”, 2) they have high vapor specific heats, which may result in “wet” compression, 3) they are “much more difficult to manufacture than the smaller molecules”. The one- and two-carbon molecules are then compared based on the number of substituted fluorine and chlorine atoms, concerning toxicity and flammability. As shown in Figure 2, hydrogen increases flammability and decreases atmospheric life time. Chlorine increases the probability of toxicity. Chlorine-containing fluids would today not be considered due to their Ozone Depletion Potential (ODP).

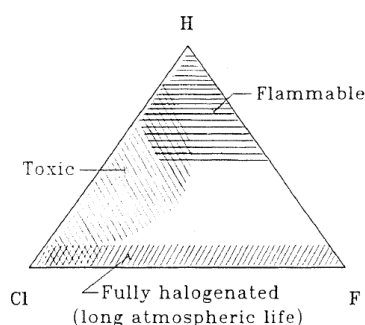


Figure 2: Toxicity and flammability of chlorinated and fluorinated hydrocarbons based on the number of each type of substituted atoms. From McLinden and Didion, 1987.

The environmental impact of the use of a specific refrigerant is dependent on direct effects, caused by the refrigerants when they reach the ambient, as well as indirect effects, caused during the production of the electricity necessary to run the system. Effects caused during production and destruction of the refrigerant should also be taken into account. Today, the impact on global warming is in focus, and a measure of this is the Total Equivalent Warming Impact (TEWI). It should be noted that the use of TEWI is not without problems. First, the origin of the electricity may be questioned, and thereby the size of the indirect contribution, second, the direct effect is highly dependent on the leakage rate, which is generally not known, and which will differ greatly between different applications. As an example, Cavallini (1996) estimated the direct effects to be only a few percent for household refrigerators and commercial chillers operating with HFC, while for automotive applications the direct effect was estimated to 70% and for commercial refrigeration to 55%. The high leakage rates for Mobile Air Conditioning (MAC) is of course the reason for the European legislation against future use of HFCs for this application. Obviously, TEWI is dependent on the application and the assumptions made in the calculation, it is not a property of the refrigerant. For comparing the refrigerants, the Global Warming Potential (GWP) and, perhaps, the atmospheric lifetime should be used.

Safety is another important issue in a comparison. Toxicity and flammability can be compared through the ASHRAE classification of the fluid. For flammability, the upper and lower flammability limits in air, burning velocity and heat of combustion are all important parameters in a comparison.

4 WHICH ARE THE REFRIGERANTS OF THE FUTURE?

When discussing refrigerants of the future it is impossible not to raise the issue of natural refrigerants vs new synthetic refrigerants. It is simple to reject the natural refrigerants as being flammable (HC), poisonous (NH₃) or having extremely high pressures (CO₂). As already noted, however, we cannot expect to find an ideal refrigerant. Therefore, the advantages and disadvantages of each type of refrigerant have to be considered for each specific application. Among the natural refrigerants, isobutane has already proven to be a good refrigerant for home appliances, used in hundreds of millions of units. As the charge is typically less than 100g, the risk of accidents if the refrigerant is released in a kitchen is very small. However, all precautions must be made in the design to avoid possible leaks inside the cabinet, or the possibility of ignition by electric sparks inside. Hydrocarbons are also used in domestic heat pumps, small AC equipment and in commercial refrigeration with secondary loops. With good design, location in ventilated areas, gas sensors and proper maintenance these systems can be made safe. The greatest obstacle hindering wider use of hydrocarbons is the lack of clear regulations. Additionally, there is a lack of compressors within a certain size range approved for use with hydrocarbons.

Ammonia is known to be a very good refrigerant, giving high performance of the systems, due to good heat transfer and pressure drop characteristics, a high critical pressure, low molecular mass and high heat of evaporation. It is typically used in large industrial systems. The strong smell requires special design considerations so that no leaks can appear in public areas. Even though it is flammable, concentrations need to be high for ignition, ignition energy is high and the combustion energy is limited. Application in direct expansion systems has been rare due to the problem of oil return. As ammonia is not miscible in most oils, it will collect in the evaporator and deteriorate heat transfer. Oil managing arrangements will add an extra cost which may be prohibitive for small systems. However, new miscible oils are now available, and in a future where oil free compressors may be available, the interest for ammonia may well increase and the use spread to smaller systems. Additionally, introduction of highly efficient minichannel heat exchangers may reduce the necessary charge, allowing a wider application of ammonia and hydrocarbons.

Carbon dioxide is already used extensively for certain applications. In Europe, and to a lesser extent in other parts of the world, it is used both as a secondary fluid in low temperature systems and as refrigerant in the low temperature stage of two-stage systems. It is also used in supermarket refrigeration in trans-critical cycles, as the critical temperature is low, only 31°C. The performance in this case is more dependent on ambient temperature than sub-critical systems with other refrigerants, but for less hot climates this may be a good solution. A completely different application of carbon dioxide is in heat pumps for heating of sanitary hot water. This seems to be an ideal application for CO₂ due to the large temperature change of the water being heated. This change can be made to match the temperature in the gas cooler in the trans-critical CO₂ process. This type of unit, known in Japan as Eco Cute, have been sold in more than 2 million units, and the target is 20 million units by 2020 (IIR 2011).

When CO₂-systems were first introduced, there was a lack of components, such as compressors, heat exchangers, valves and pumps, but the situation is changing rapidly and with components now on the market it is possible to design CO₂ systems with good performance for several different applications.

As a conclusion, the natural fluids, hydrocarbons, ammonia and carbon dioxide, are all "refrigerants of the future". They are all well established for certain applications and there is no indication that their use will decrease. However, for some applications there will be a demand for fluids which are non-flammable (or less flammable), non-poisonous and without smell. It should be pointed out that there is a clear difference between different markets concerning the acceptance of natural refrigerants, with the important US market being most

reluctant to accept these fluids. The reason usually given is the higher risk of legal claims in case of an accident in US compared to other countries.

Because of the high leakage rates, the mobile air conditioning systems (MAC) have been the target of legislation against the use of high GWP refrigerants in Europe. New models put on the market from 2011 are not allowed to use fluids with GWP higher than 150 (EU 2006). It seems that this level was selected to allow the use of R152a as refrigerant. As cars are manufactured for a global market, the European legislation has a direct impact on the selection of refrigerants for the global MAC market. For several years, there was a parallel development of CO₂ systems, and systems with new hydro fluoro olefin (HFO) fluids. The important German automotive association (VDA) in 2007 took the decision to use CO₂ systems, but recently, in May 2010, there was a change in policy and it was announced that HFO1234yf would be used in new cars from 2011. Still, the argument is not settled, and to the author's best knowledge there are no cars sold with HFO1234yf yet. GM has announced a first introduction in 2013 (SAE 2010a). An important factor is that this refrigerant is still scarce and extremely expensive, as there are still no large scale production units in operation.

One important benefit of HFO1234yf is that its properties are very close to those of R134a. The vapor pressure curve is very close, the volumetric refrigeration effect is very close and it can be used with PAG oils. This means that the systems will be very similar to the ones used today. It may even be possible to run a HFO1234yf-system on R134a, or even to mix the fluids. However, as the price, according to the US EPA is expected to be at least 15 times higher than for R134a, there is an obvious risk that topping up may be done with R134a, thereby reducing the effect of the legislation (SAE 2010b).

Already during the phase out of R12, there was much research done on zeotropic refrigerant mixtures, i.e. mixtures with glide. By mixing refrigerants, it may be possible to find blends that mimic the vapor pressure curve, and thereby the performance, of pure fluids being phased out. Some hopes were also raised that the temperature glides in the evaporator and the condenser, if matched to the temperature change of the heat source and heat sink fluids, would allow increased performance. However, it has been found that fluids with larger glides than about 7-10K are less practical due to the risk of concentration shifts, within different parts of the system or in the system as a whole in case the system needs to be topped up. Cavallini (1996) concluded that larger glides would be necessary for glide matching to be a substantial benefit to the performance. He also noted that large glides will have the additional disadvantage of introducing mass transfer resistances in the heat exchangers, and that the transport properties of the mixtures usually are worse than the interpolated average of the values for the pure fluids, both factors which will deteriorate the performance of the system. The fact that only one mixture with a glide larger than 2K (R407C with a glide of 5 to 7K), have been successful on the market, in spite of the research done during 20 years, is an indication also for the future use of refrigerant mixtures.

Due to the difficulty of finding fluids which are both non-flammable and have a low GWP, it has been suggested to use mixtures which are non-flammable but with lower GWP than the HFC refrigerants. The flammability limits of several such mixtures, containing R1234yf, R32, R125 and R134a was presented recently by Yamada et al. (2010). Particularly, they conclude that a mixture of 40% R134a and 60% R1234yf is non-flammable and virtually without glide. The GWP of this mixture is comparatively low, 574 (100 years integration time).

The reason for the low GWP of HFO1234yf is that it has a very short atmospheric lifetime. This is because of the fact that the molecule has a double bond in the carbon "skeleton", which makes the molecule more reactive. This refrigerant belongs to a family of closely related fluids with three carbon atoms and one double bond. All are thus fluorine substituted propene-derivates. As mentioned, this group of fluids has previously been rejected as

refrigerants due to concerns for the long term stability of the fluids inside the system (McLinden and Didion 1987). In the open literature, there is no information about the stability of these new fluids, but the manufacturers promoting the use indicate that stability is satisfactory. Increasing the number of carbon atoms in the skeleton of the molecule increases the number of possible ways to substitute halocarbon atoms. Introducing a double bond increases the number of options even more. Figure 3 below shows this carbon skeleton. With six hydrogen atoms attached, this would be a propene (propylene) molecule, with the refrigerant number R1270. Substituting one hydrogen for a fluorine atom would give R1261 and substituting additional fluorine atoms gives R1252, R1243, R1234, R1225 and R1216. Depending on where on the skeleton the fluorine atoms are substituted, additional letters are added to the number, as determined by the ASHRAE standard 34 (ASHRAE 2007). It is easy to understand that the number of possible combinations is large. Only for R1234 there are seven isomers, including two pairs of (cis/trans-) stereoisomers, with different properties. This also points to the difficulty in production of any specific fluid, and the cause for the expected high cost. In this group of fluids, only R1234yf is expected to be available in commercial quantities in a near future. The automotive industry, together with the chemical companies preparing to manufacture the fluid, have had large scale investigations to determine the properties, environmental risks, health risks, compatibility with materials, flammability issues etc. of this fluid. More information is accessible through the SAE web page (SAE 2011).

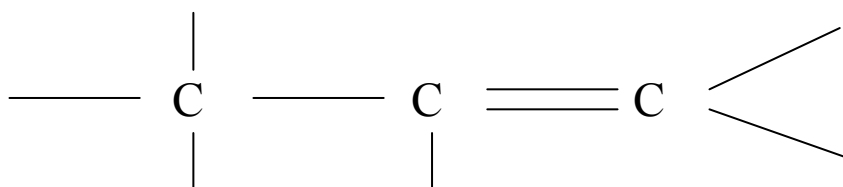


Figure 3: Carbon skeleton for propene, HFO1234yf, HFO1234ze and some other fluids considered as future refrigerants.

No other newly developed refrigerant has been investigated as well as this fluid. However, properties of some other members of the same family, primarily R1234ze, have been presented in the literature, e.g. by Brown et al. (2009), Brown et al. (2010), Clodic (2010), Higashi (2010), Kondo et al. (2009).

An interesting refrigerant which was discussed already during the phase-out of the CFCs 15 years ago is the HFC R152a. At that time, it was discarded as it is flammable, even though not as flammable as ordinary hydrocarbons. The fluid was used before the ban of the CFCs in combination with R12, forming the mixture known as R500. It has a GWP just below 150, and as noted above, the EU-legislation on future MAC-refrigerants was most certainly set to allow the use of this fluid. However, it has been considered as too flammable to have in a direct AC-system in a car. Systems with secondary loops on the cold side have been designed and tested with good results. For applications where hydrocarbons are otherwise considered, this fluid may be a safer alternative, even though it does not have the advantage of being a natural refrigerant.

DATA FOR SOME REFRIGERANTS

In the table below, several properties of some of the fluids discussed above are compared to R134a. Notably, CO₂ is excluded from the comparison, as it would be in a supercritical state at 40°C and as a cycle comparison would not be correct at the conditions chosen in the table. It can be noted that R152a and R1234yf have normal boiling points close to that of R134a, indicating the similar vapor pressures. Notable is also the relatively large difference in normal

boiling point between R1234yf and R1234ze(E). Other properties are also quite different between these two closely related fluids.

Table 2: Comparison of some traditional and suggested future refrigerants

	Refrigerant properties at 40°C					
	R134a	R290	R717	R152a	R1234yf	R1234ze(E)
Chemical composition	CF ₃ -CH ₂ F	CH ₃ -CH ₂ -CH ₃	NH ₃	CH ₃ -CHF ₂	CH ₂ =CF-CF ₃	CHF=CH-CF ₃
M, kg/kmol	102	44	17	66	114	114
T _{nbp} °C	-26,1	-42,1	-33,3	-24,0	-29,4	-19,0
h _{fg} kJ/kg	163	307	1099	260	132	155
ρ _l kg/m ³	1147	467	579	860	1033	1111
ρ _v kg/m ³	50,1	30,2	12,0	28,3	57,7	40,7
T _{tr} °C	-103,3	-187,7	-77,7	-118,6	-53,2	-104,5
T _{cr} °C	101,1	96,7	132,2	113,3	94,7	109,4
P _{cr} MPa	4,06	4,25	11,3	4,52	3,38	3,63
Source: Refprop						
	Cycle performance properties, -20/+40°C					
	R134a	R290	R717	R152a	R1234yf	R1234ze(E)
p ₁ /p ₂ @ +40/-20	7,66	5,60	8,18	7,53	6,73	7,92
q _v @ +40/-20°C, kJ/m ³	883	1345	1679	882	818	626
ε _{is} , @ +40/-20 kJ/kg	42,5	81,0	319	68,0	33,7	38,3
COP _{2,ideal} @-20/+40	3,06	3,01	3,28	3,26	2,79	2,99
η _{Carnot} @ -20/+40	0,73	0,71	0,78	0,77	0,66	0,71
T _{1c,is} °C	48,6	48,2	135,5	62,11	40	40
Source: Refprop						
	Transport properties at 40°C					
	R134a	R290	R717	R152a	R1234yf	R1234ze(E)
k _l mW/(m K)	74,7	86,8	443,5	91,7	63,0	
k _v mW/(m K)	15,4	21,5	28,4	16,7	17,7	
μ _l μNs/m ²	161,5	82,6	114,0	137,1	129,9	
μ _v μNs/m ²	12,37	8,89	10,33	10,66	13,15	
Source: Refprop						
	Flammability and safety, environment					
	R134a	R290	R717	R152a	R1234yf	R1234ze(E)
GWP	1430	3	<1 [^]	140 [^]	4	6
ASHRAE class	A1 ⁺	A3 ⁺	B2 ⁺	A2 ⁺	A2L	
LFL/UFL, %	N/A	2,5/10,0	15/28	4,6/16,9	6,2/12,3	6/13 [*]
Burning velocity cm/s	N/A	46	7,2	23	1,5	
Minimum ignition energy, mJ	N/A	0,25	100	0,38	5000	
Heat of combustion, MJ/kg	N/A	46,3	18,6	17,4	10,7	
Sources: Clodic 2010, except *, ^, + * Kondo et al. 2009 ^ Granryd et al. 2006 + ASHRAE 2008						

The heat of evaporation differs considerably between ammonia and the rest of the fluids, and generally decreases with increasing molecular weight, as may be expected. The critical

pressure is notably higher for ammonia, and lowest for the two HFOs. This can generally be expected to influence the performance negatively for the HFOs.

Looking at the cycle performance assuming a process operating between -20°C and $+40^{\circ}\text{C}$, without subcooling or superheating, and with isentropic compression, we see that the pressure ratio of the synthetic fluids are quite similar, while for ammonia it is higher and for propane a bit lower due to the higher vapour pressure (lower normal boiling point) of this fluid. Similarly, the volumetric refrigerating effect is very similar for the four synthetic fluids, while it is higher for ammonia and propane, for propane because of higher pressure.

Comparing the COP for cooling of this ideal process, we note that ammonia and R152a have about 10% higher, and R1234yf about 7% lower value than the other three refrigerants. The same result can be expressed in terms of the Carnot efficiency of the processes.

The temperature after isentropic compression differs widely, with ammonia giving very high values, while for the two HFOs, the temperature is at the saturation, indicating wet compression.

Looking at the transport properties, the liquid thermal conductivity is most important for heat transfer. This value is much higher for ammonia than for the other fluids, and slightly lower for R1234yf. For R234ze(E) no values for transport properties have been found. For the liquid viscosities, the two natural fluids have lower values than the synthetics. In general, the transport properties of the natural fluids are better, while R1234yf does not deviate too much from the other synthetics.

As already discussed, the global warming potential is negligible for the HFOs and the natural refrigerants. The value for R152a may be acceptable, being about 10% of that of R134a.

Of the listed fluids, only ammonia is judged as poisonous according to the ASHRAE classification. However, due to the strong smell, the risk of poisoning is low, and other risks, mainly panic, for ammonia, and suffocation for non-smelling fluids, should be considered when making risk assessments with different refrigerants. An additional concern which has been much in focus in the media in Germany is the possible formation of hydrofluoric acid during combustion of HFO (Die Zeit 2011).

The differences in flammability are clearly seen from the tabulated values. All data for R1234ze(E) is not available, but should not deviate much from that of R1234yf. From the values, it is clear that the new HFOs are much less flammable than ammonia and R152a.

CONCLUSIONS

In conclusion, it seems that there is only one new refrigerant expected to be commercially available in the near future, and that is HFO1234yf. This fluid has the advantage of being non-poisonous and of having very low flammability. Its properties are very close to those of R134a, which facilitates its introduction on the market. Based only on thermodynamic and transport properties, the performance in a system can be expected to be slightly lower than for R134a. The cost of the fluid has been predicted to be very much higher than for R134a. Other fluids in the same family, particularly HFO1234ze(E) and HFO1234ze(Z) are also being discussed. To the author's knowledge no large scale production is presently planned.

As for the refrigerants of the future, we will have to accept that there are no ideal fluids. Therefore, we can expect to see a range of natural and synthetic fluids being used, all finding their niche applications. This range of fluids will most probably include hydrocarbons,

ammonia, carbon dioxide, R152a and some new HFO-refrigerants. To fit different applications, near azeotropic mixtures may be developed.

Independently of the type of refrigerants, for safety reasons or for cost reasons, it will be necessary to decrease the leakage rates, and to actively work towards decreasing the refrigerant charge. However, charge reduction must always be done keeping the energy efficiency of the system in mind.

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