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RECENT DEVELOPMENTS ON REFRIGERANTS

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SUMMARY/ABSTRACT

The realization of the contribution of the synthetic HFC-refrigerants to global warming has resulted in a search for new, environmentally benign refrigerants. This paper intends to give a background to the present situation on the refrigerant market and to describe the presently ongoing development. It is believed that natural refrigerants, i.e. ammonia, hydrocarbons and carbon dioxide, will have a natural place in the refrigeration industry in the future. However, synthetic refrigerants with low or no flammability will continue to be used in many applications due to safety concerns. In the near future, the synthetic refrigerants which are most probable to be used are R1234yf, R1234ze(E), R32 and R152a, or blends with these refrigerants as constituents.

INTRODUCTION

Finding proper refrigerants has been a challenge ever since the vapour compression systems were first developed. The requirements on the refrigerants have in a general sense been the same over time: Ideally, they should be safe, give good efficiency of the system, be compatible with the preferred materials and be available at a reasonable cost. Safety, in this respect, should include the local environment, i.e. not being poisonous or flammable, not having a strong smell which may cause panic, not giving an excessively high pressure, as well as the global environment, i.e. not contributing to ozone depletion or global warming, or in any other way, directly or indirectly, influencing the global environment. Unfortunately, no refrigerant is ideal, so the choice is always a compromise.

During the last 20 years, the concern for global warming has resulted in a search for substitutes for the HFC refrigerants previously being considered as the most ideal choice for small to medium size applications. In general, the development has followed two paths: The first is a strive towards the use of natural refrigerants, i.e. fluids which are naturally present in the environment. The main argument for considering these fluids is that, as they are already present in the natural environment, we do not have to be concerned about any unexpected effects, like ozone depletion or global warming, at least as long as the release of refrigerants is small compared to the natural levels. The fluids considered are primarily hydrocarbons, carbon dioxide and ammonia. The second path is towards use of “new” synthetic refrigerants. The main argument here is that it may be possible to find synthetic refrigerants which are safer than the natural refrigerants (i.e. non-flammable, non-toxic) and do not constitute a threat to the global environment in any known way (i.e. no ozone depletion potential, ODP and low global warming potential, GWP). The present paper will give a brief outline of the history and the present development concerning the use of refrigerants.

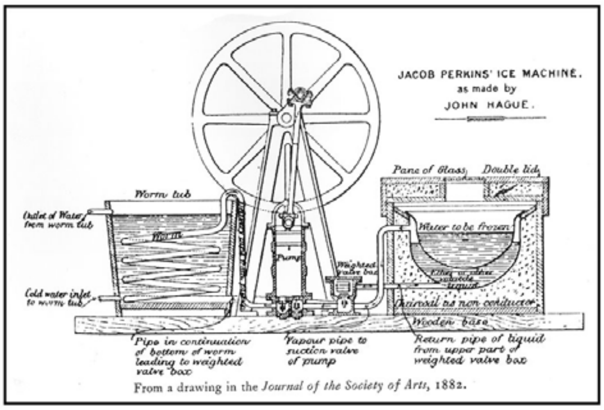


Figure 1: One of the first vapour compression machines, using ether as refrigerant

1 SHORT HISTORY

1.1 Early Developments

One of the first descriptions of a vapour compression system is from a patent by Jacob Perkins from 1834. The system has exactly the same main components as a modern system, and was suggested to use ether as the refrigerant. Up until the 1920s several refrigerants were used, e.g. ammonia, sulphur dioxide, carbon dioxide, methyl chloride and different simple hydrocarbons. At that time, some of the electric companies were trying to introduce electrically driven refrigerators for private use, and the companies realized the need for a safe refrigerant. The task of finding such a refrigerant was given to two prominent researchers, Thomas Midgley and Albert Henne. They started looking at the periodic table of the elements and realized that the elements to the left in the periodic table, i.e. the metals, would form ionic compounds which cannot be evaporated and condensed at conditions of interest for vapour compression systems. In the centre are a group of elements which will form unstable or toxic compounds. At the right edge of the periodic table are the inert gases, which do not form compounds at all, and which in the pure form would be supercritical at relevant temperatures. They concluded that only seven elements would be suitable as building blocks of molecules with properties which would make them useful as refrigerants. These elements are hydrogen, carbon, nitrogen, fluorine, sulphur, chlorine and bromine, all located next to the inert gases at the top right corner of the periodic table.

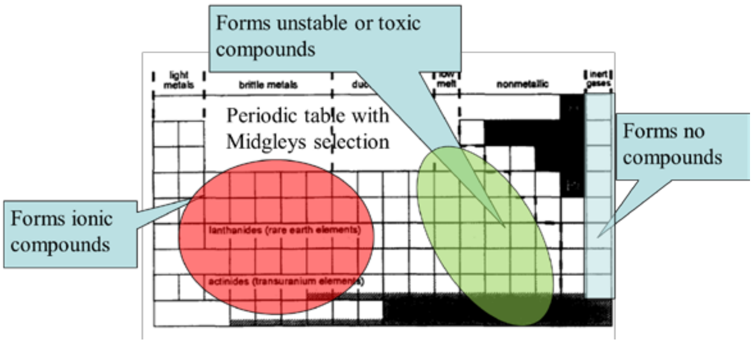


Figure 2: Periodic table indicating the reasoning of Midgley and Henne in the search of a good refrigerant.

The natural backbone of such a molecule would be carbon. It was widely known that the atoms attached to the carbon backbone influences the properties of the compound: Hydrogen increases the flammability of the compound. Oxygen, nitrogen and sulphur decreases stability and increase the risk of the compound being toxic. Fluorine, chlorine and bromine, i.e. the halides, increase stability and decrease the flammability. Based on this reasoning, Midgley and Henne suggested to use chloro-fluoro-carbons, CFC, as refrigerants, and after only a few weeks they had synthesized the first batch of fluid. The invention was announced at a congress with the American Chemical Society in 1930 [Giunta, 2006] where they demonstrated the safety of the new refrigerant (R12, $C\,Cl_2\,F_2$) by inhaling the gas and blowing it out over a candle, thereby proving it was neither poisonous nor flammable. By this, the world was convinced of the CFCs, and particularly R12, being the perfect refrigerant and these fluids became generally known as the Safety Refrigerants. For many years, CFCs, and some Hydro Chloro Fluoro Carbons (HCFCs) were dominating the market for small and medium size refrigeration systems.

1.2 The natural alternatives

Even though the CFCs and HCFCs were dominating for small and medium size systems, the natural refrigerants were used in parallel for certain applications. Ammonia was used in large industrial systems, as this refrigerant has good thermodynamic and transport properties and has low cost. Carbon dioxide was used within the shipping industry. Hydrocarbons have also been used, mainly for certain industrial applications.

1.3 Global threats

The CFC-fluids were used also for other applications than as refrigerants. One of these was as propellants in spray bottles. In the 1970s there were growing concerns for the CFCs and HCFCs depleting the ozone layer. The reason for these fluids having this effect is that they act as transporters of chlorine to the higher atmosphere, where it is acting as a catalyst for the breakdown of ozone. Chlorine from other sources is easily washed out of the atmosphere by the rain, but the CFCs and

HCFCs are extremely stable and are not broken down in the atmosphere until they reach high altitude, where they are broken down by the ultra violet radiation from the sun. This is the part of the atmosphere where ozone is acting as a shield to UV radiation, and thus, the CFCs and HCFCs act as transporters of chlorine from the lower levels of the atmosphere to the altitude of the ozone layer. By what may be seen as the first global agreement on an environmental issue, CFCs were banned by the Montreal Protocol, signed in 1987.

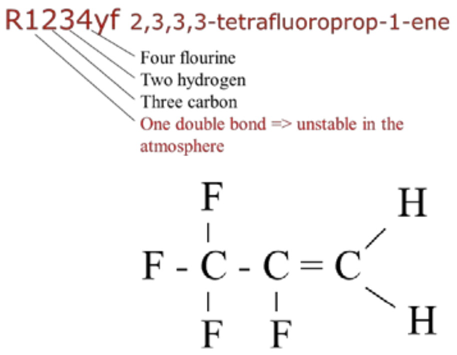
As a result of the Montreal Protocol, the refrigeration industry had to find new refrigerants not containing chlorine. During the 1980s and 1990s large research efforts were spent on the search for new refrigerants and assessing the candidate refrigerant's properties, possible toxicity and environmental impact. In 1995, the fully halogenated chlorinated refrigerants, like R11 and R12 were forbidden in many countries. The substitute fluid for R12, the most used CFC refrigerant, was R134a, a hydro fluoro carbon (HFC) with vapour pressure curve similar to that of R12. Already at this time, environmentalists and concerned scientists were raising their voices against the global introduction of new synthetic refrigerants, due to the risk of unknown environmental effects.

Soon after the transition to refrigerants without chlorine content, another global environmental issue became the key concern, global warming. Interestingly, the ousting of the CFCs and HCFCs also meant a drastic decrease in contribution to the global warming, as the HFCs have considerably lower GWP than the CFCs and HCFCs. Still, the GWP potentials of the most common HFCs are more than one thousand times higher than carbon dioxide. As an example, the GWP (compared to CO2) of R134a is around 1400. Even if the global warming impact due to the emissions of refrigerants has decreased considerably, there is still reason for concern. The use of refrigerants is expected to increase considerably in the near future due to several reasons: Increased living standards in the densely populated areas in hot climates will increase the demand for air conditioning and refrigeration, urbanization will lead to longer transport and thereby more demand for refrigerated transport and storage, increased energy prices and increased share of energy distribution in the form of electricity will lead to increased use of heat pumps for heating both in the built environment and in industry. For this reason, a gradual change towards low GWP fluids can be expected, based on legislation as well as on customer demand. An example of the influence of customer demand is the introduction of hydrocarbons in refrigerators and freezers on the European market. This change was initiated by Greenpeace, which took the initiative, together with a small German company, DKK Scharfenstein, to demonstrate the possibility of using hydrocarbons in refrigerators at a fair (Greenfreeze). Due to customer demand, the larger companies were encouraged to follow. Now most refrigerators and freezers sold in Europe use isobutane as refrigerant, and several hundred millions such installations have been sold in total [Palm, 2008]. The realization of the contribution to global warming of the release of refrigerants has lead also to legislatory measures. In some countries, the authorities have put high taxes on HFC-refrigerants. In Denmark, a total ban of HFC installations with charge higher than 10 kg was introduced. Most importantly, the European Parliament decided to ban any fluid with a GWP above 150 in the AC systems of new car models from 2011, and in all new cars from 2017 [EU, 2006]. This resulted in a frenetic work on developing air conditioning for new refrigerants. The powerful German car industry first jointly decided to use carbon dioxide as the new refrigerant, but a few years later, they announced that they would go for a new synthetic HFC refrigerant, R1234yf, instead. The large chemical companies, DuPont and Honeywell, being the ones mainly pushing this refrigerant, have thereby secured a large and important market for their products. Unfortunately, the companies have not been able to produce the quantities of refrigerant required by the market, and recently, the European Parliament announced that the requirement on using low GWP refrigerants has been postponed. Still, several car manufacturers are expected to start delivering cars with R1234yf as refrigerant during 2012.

2 RECENT DEVELOPMENTS

2.1 The "HFO refrigerants"

Recently, much attention has been focused around a "new" group of refrigerants called olefins, or hydro-fluoro-olefins, HFOs. Olefin is an old name for hydrocarbons with one or more double bonds, i.e. what is elsewhere since long called alkenes. The HFO-fluids thus are all HFCs. It is perhaps not correct to call these fluids new, as they have been considered before during the search for substitutes for CFCs. However, due to the double bond, they have been considered too unstable to be suitable as refrigerants. This property has now been turned into an advantage, as the double bond ensures a short



atmospheric lifetime and thereby a low GWP for these fluids

R1234yf is one of the two HFO refrigerants expected to be put on the market on a large scale within the next few years. This refrigerant is one of several belonging to a family of fluids which can be characterized as propene derivates. Propene is a hydrocarbon with three carbon and six hydrogen atoms, having one double bond in the carbon backbone. By substituting any or several of the six hydrogen atoms in the molecule for fluorine atoms, different compounds are formed. Based on the international numbering of refrigerants, these would be called R1270 (propene), R1261, R1252, R1243, R1234, R1225, R1216, each number in the chain indicating one more hydrogen atom exchanged for a fluorine atom. As there are different ways of combining the hydrogen and fluorine atoms to the carbon backbone, two or three additional letters are needed to identify any of the 31 compounds in the family. More on the terminology is found e.g. on the ASHRAE web page [ASHRAE, 2007]. With the substitution of hydrogen for fluorine, the flammability decreases.

Figure 3: Schematic of R1234yf

Unfortunately, the compounds with most fluorine, R1225 and R1216, are found to be poisonous. The R1234, on the other hand, are not toxic but slightly flammable.

One important advantage of R1234yf is that the vapour pressure curve is very similar to that of R134a, the fluid now being used in mobile air conditioning. This means that only minor changes are necessary when re-designing systems now using R134a to R1234yf. The pressure levels, the swept volume of the compressors, the power of the compressor motors, the tube dimensions will all be the same or very similar. The transport properties, i.e. thermal conductivity and viscosity, are also similar, indicating that the necessary sizes of heat exchangers will also be the same. Practical tests confirm the theoretical predictions, and capacity and COP have been shown to be within a few per cent when retrofitting R134a systems with R1234yf.

As noted above, R1234yf is not poisonous, but slightly flammable, being placed in the group A2L according to ASHRAE. Its GWP is only 4, as compared to around 1400 for R134a, and the ODP is zero as it contains no chlorine. One concern, raised by authorities in Germany, is the possibility of formation of hydrofluoric acid on combustion or in contact with hot surfaces [UBA,2011]. Such formation, however, is possible also on combustion of other HFC refrigerants [Greenpeace 2009], [Honeywell, 2008]. A disadvantage of this refrigerant is the high cost, stated by different sources to be

6 to 16 times higher than that of R134a. The relatively complex structure, with several isomers and closely related compounds can be assumed to contribute to the high cost.

The second refrigerant in the same family, which will soon be available in commercial quantities [Milnes 2011] is R1234ze(E) (CF3-CH=CHF, trans). This fluid has slightly higher normal boiling point as well as higher critical temperature and pressure than R1234yf. This indicates the possibility of achieving higher COPs with this refrigerant than with R1234yf, but the pressure levels will be lower and the required compressor sizes for any given capacity will be larger. The enthalpy-temperature diagrams of R1234yf(E), R1234yf and several other refrigerants are shown in Figure 4.

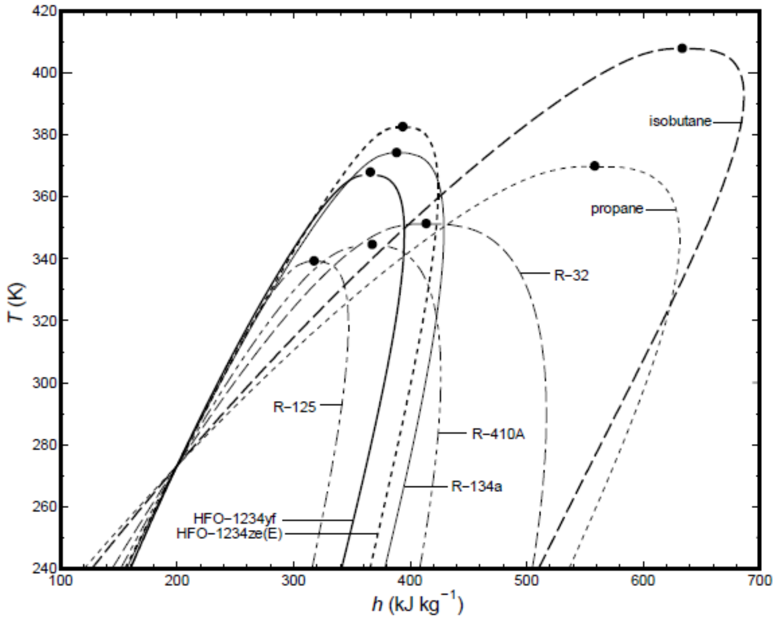


Figure 4: h-T diagrams for some new and old refrigerants [from Higashi, 2010]

Two other refrigerants which may be used more widely in the future should be mentioned here. The first is R152a. This HFC-refrigerant has previously been disregarded, as it is flammable. However, its thermodynamic and transport properties are favourable and the pressure levels are only slightly lower than for R134a. R152a was used in combination with R12, forming an azeotropic blend called R500. It has been considered as a replacement of R134a in mobile air conditioning (MAC) due to its low GWP (=140), and the maximum GWP-level of 150 for MAC according to EU legislation has been set to allow this refrigerant to be used.

The last new refrigerant which will be mentioned here is R32 (CH_2F_2). This refrigerant is also flammable and has for this reason not been used pure. However, it is used in combination with R125 forming the near azeotropic blend R410A, which is non-flammable and widely used in small air conditioning units. Its vapour pressure is considerably higher than of R134a, requiring special considerations in system design. Compared to the other synthetic compounds considered, it is a simple molecule which could be manufactured at a relatively low cost. Compared to the pure hydrocarbons, the heat of combustion is low.

Besides the pure fluids mentioned above, it is possible to design two- or three-component blends to get desired properties for special applications. Many such blends have been suggested and registered with the ASHRAE. Preferably, the blends should be azeotropes or near azeotropes, meaning that the vapour pressures of the constituents of the blend should be the same, ensuring a constant composition of the liquid and vapour phases during evaporation and condensation. Such fluids are easier to handle in practical applications, as there are small risks of composition shifts between different parts of the system and as such fluids often show better heat transfer performance than zeotropic mixtures.

3 CONCLUSIONS

The historic review given above has shown the limitations in the search for new refrigerants. The search done by Midgley and Henne has been repeated by several other researchers over the years, and the general conclusion is that we should not expect to find entirely new compounds suitable as refrigerants in the future.

The latest development in terms of refrigerants is the introduction of R1234yf as substitute for R134a in mobile air conditioning. This fluid has a very low GWP, but its use is hampered by the high cost. A closely related refrigerant on its way to the market is R1234ze(E). Other possible synthetic alternatives are R152a and R32, both of which have higher flammability than R1234.

The lesson learned from the effects of the CFCs and HCFCs on the ozone layer and their contribution to the global warming, is that synthetic substances may have unexpected effects in the natural environment. This is an argument for using substances which are naturally occurring in the environment as refrigerants. It is probable that the use of ammonia, carbon dioxide and hydrocarbons will increase in the future, and that we will see both natural and synthetic refrigerants being used in parallel.

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