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SELECTION OF ENVIRONMENT-FRIENDLY REFRIGERANTS AND THE CURRENT ALTERNATIVES IN VAPOUR COMPRESSION REFRIGERATION SYSTEMS

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ABSTRACT
In this paper, the processes of selecting environment-friendly refrigerants that have zero Ozone Depletion Potential (ODP) and low Global Warming Potential (GWP) were analysed. Various compositional groups of halocarbon refrigerants and their environmental problems were discussed. This paper also focuses on the refrigerants found on the matrix triangles of methane and ethane derivatives for the selection of appropriate environment-friendly refrigerants. Trade-offs in flammability, toxicity, chemical stability and atmospheric lifetime, and consideration of compounds without chlorine content, scaled down the refrigerants to R23 and R32 from methane derivatives and R152a, R143a, R134a and R125 from ethane derivatives. These refrigerants are recommended for further investigations to ascertain their suitability in vapour compression refrigeration systems. Alternative refrigerants that are currently employed in the systems were discussed. This revealed their areas of shortcomings which researchers must focus in order to make them acceptable worldwide.

INTRODUCTION

Refrigeration and air-conditioning play important roles in modern life. They are not only providing comfortable and healthy living environments, but have also come to be regarded as necessities for surviving severe weather and preserving food. However, accelerated technical development and economic growth throughout the world during the last century have produced severed environmental problems, forcing us to acknowledge that though these technological advances may contribute to human comfort, they are also threatening the environment through ozone depletion and global warming (Hwang et al., 1998; Bolaji, 2005).

The linkage of the CFC refrigerants to the destruction of the ozone layer which has been recognised, is attributable to their exceptional stability because of which they can survive in the atmosphere for decades, ultimately diffusing to the rarefied heights where the stratospheric ozone layer resides. The inventors of these refrigerants could not have visualized the ravaging effects of the refrigerants on the ozone layer. They intentionally pursued refrigerants with the exceptional stability that was imposed as one of the necessary requirements of the ideal refrigerant they were called upon to invent (Cavallini, 1996).

The primary requirements of the ideal refrigerant before the discovery of CFC refrigerants were as follow: it should have normal boiling point in the range of -40°C to 0°C; it should be nontoxic; it should be nonflammable; and it should be stable. None of the refrigerants available at that time, including sulphur dioxide, carbon dioxide, ammonia, methyl chloride, and ethyl chloride; could meet any of the requirements. The CFC refrigerants fulfilled all the primary requirements and heralded an unprecedented revolution in the refrigeration and air-conditioning industry (Bhatti, 1999).

Today, the litany of the requirements imposed on an ideal refrigerant has increased. The additional primary requirements now include zero ozone depletion potential (ODP) and zero global warming potential (GWP). According to Calm et al. (1999), the environmental concerns relating to ozone depletion and global warming were not dreamt of when Midgley and associates invented the CFC refrigerants. Therefore, the engineers have to begin searches for the alternatives to CFC refrigerants, which will fulfill these new requirements in addition to the earlier primary requirements for the ideal refrigerants. This paper analyses the processes of selecting environment-friendly halocarbon refrigerants that have zero ODP, non-flammable, non-toxic and low GWP. It also examines and discusses the current available alternative refrigerants in vapour compression refrigeration system.

VAPOUR COMPRESSION REFRIGERATION SYSTEM AND THE ENVIRONMENT

Vapour compression refrigeration system is the most widely used refrigeration method for air-conditioning of large public buildings, private residences, hotels, hospitals, theatres, restaurants and automobiles. It also used in domestic and commercial refrigerators, large-scale ware houses for storage of food and meat, in refrigerated trucks and host of other commercial and industrial services. A vapour compression refrigeration system uses circulating liquid refrigerant as a medium which absorbs and removes heat from the space to be cooled and subsequently rejects that heat elsewhere.

Figure 1 shows schematic diagram of a standard vapour compression refrigeration system. The refrigeration system is made up of four major components: condenser, evaporator, compressor and expansion device. In the evaporator, the liquid refrigerant vaporizes by absorbing latent heat from the material being cooled, and the resulting low pressure vapour refrigerant then passes from the evaporator to the compressor. Compressor is the heart of refrigeration system. It pumps and circulates refrigerant through the system, and supplies the necessary force to keep the system operating. It raises the refrigerant pressure and hence the temperature, to enable heat rejection at a higher temperature in the condenser.

Condenser is a device used for removing heat from the refrigeration system to a medium which has lower temperature than the refrigerant in the condenser. The high pressure liquid refrigerant from the condenser passes into the evaporator through an expansion device or a restrictor that reduces the pressure of the refrigerant to low pressure existing in the evaporator. It regulates or controls the flow of liquid refrigerant to the evaporator.

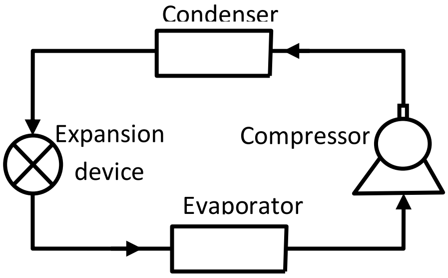


Figure 1: Standard vapour compression refrigeration system

Chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants used in vapour compression refrigeration systems have become a subject of great concern for the last few decades. The problem is not with refrigerants inside the systems, but with their release to the environment (Radermacher and Kim, 1996). Those that were used in the systems nearly a century ago such as carbon dioxide, sulphur dioxide, ammonia and methyl chloride were more or less environment-friendly, but the quest of scientists and engineers for refrigerants with better safety, thermo-physical and chemical properties led to the development of CFC refrigerants (Lorentzen, 1995). This gave a big boost to the refrigeration industry in terms of reduced cost, increased efficiency and higher reliability.

However, one of the serious environmental hazards caused by these refrigerants is the stratospheric ozone depletion. The stratospheric ozone layer plays a beneficial role by absorbing most of the biologically damaging ultraviolet sunlight called UV-B coming towards the earth. Recent investigations have shown that these human made chemicals (CFCs and HCFCs) are responsible for the observed depletion of the ozone layer. These ozone depleting compounds contain reactive gaseous atoms of chlorine, which react very rapidly with ozone via their oxide formation and thus decrease the concentration of stratospheric ozone (UNEP, 2000; and Calm, 2002). Hence, there is need for alternative refrigerants, which will fit to the requirements of vapour compression refrigeration systems.

COMPOSITIONAL GROUPS OF HALOCARBON REFRIGERANTS

Halogenated hydrocarbons (halocarbons) came into common use as refrigerants in the 1930's. The compositional groups are: chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Among them, most common groups are CFCs and HCFCs, however, there is currently a world-wide trend to seek "ozone safe" alternative refrigerants to conventional CFCs and HCFCs due to the environmental hazard of ozone depletion. Alternatives are certain hydrofluorocarbons (HFCs), which are ozone friendly refrigerants.

Chlorofluorocarbons (CFCs)

CFC refrigerants such as R11, R12, R113, R114 and R115 have been used extensively in the refrigeration and air-conditioning systems. CFCs were in popular use up to the mid-eighties. Production of CFCs was phased out by the Montreal Protocol in developed countries in 1st of January, 1996. Production in developing countries will be phased out in 2010. They are used in vapour compression processes with all types of compressors. The common CFCs are stable, safe, non-flammable and efficient, but they have also damaged the Earth's ecology.

Hydrochlorofluorocarbons (HCFCs)

HCFCs have been around almost as long as CFCs. R22 is the most widely used HCFCs in the world. These refrigerants have shorter atmospheric lifetimes and hence their ozone depletion potentials are lower than those of CFCs. Nevertheless, like CFCs, these refrigerants are being phased out as required by Montreal Protocol. Production has been capped and soon will be ratcheted down in developed countries. Developing countries also have a phase-out schedule but on an extended timeline.

Hydrofluorocarbons (HFCs)

HFCs are relatively new refrigerants whose prominence arose with the phase out of CFCs and HCFCs. HFCs have no ozone depletion potential (ODP = 0). Table 1 shows environmental effects of some common halocarbon refrigerants. HFCs are used in vapour compression processes with all types of compressors. The common HFCs are efficient and their safety is classified as A1 (lower toxicity and no flame propagation)

Table 1: Environmental effects of some common halocarbon refrigerants

Compositional group	Refrigerants	Ozone depletion potential (ODP)	Global warming potential (GWP) (100 years' horizon)
CFCs	R11	1	3800
	R12	1	8100
	R113	0.8	4800
	R114	1	9000
	R115	0.6	9000
HCFCs	R22	0.055	1500
	R123	0.02	90
	R124	0.022	470
	R141b	0.11	630
	R142b	0.065	2000
HFCs	R23	0	11700
	R32	0	650
	R125	0	2800
	R134a	0	1300
	R143a	0	3800
	R152a	0	140

(Sources: Hwang et al., 1998; Calm and Domanski, 2004; Bitzer, 2007)

SELECTION OF ENVIRONMENT-FRIENDLY REFRIGERANTS

The first century of refrigerant was dominated by innovative efforts with familiar fluids in almost prototypical machines. The aim then was to use “whatever worked” and the goals were to provide refrigeration and later, durability (Calm and Didion, 1998a). Nearly all of the early refrigerants were flammable, toxic and some were highly reactive.

The second generation of refrigerants stemmed from a 1928 search for safer refrigerants, to enable broader use in domestic refrigerators. According to Calm and Didion (1998a), Midgley Jr., and his associates Henne and McNary, scoured property table for candidates deemed to be stable, neither toxic nor flammable, and having a desired boiling point. The refrigerant generations are as summarized in Figure 2

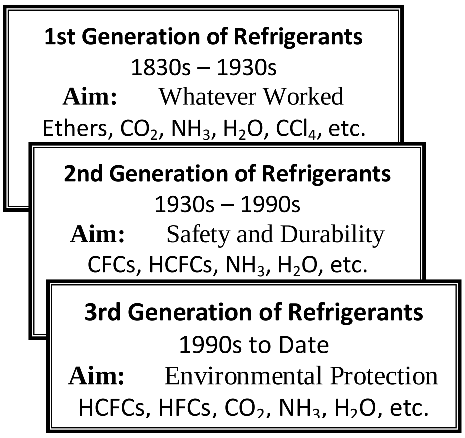


Figure 2: The refrigerant generations

Many researchers (Calm, 2002; Adegoke, 2002; Bolaji, 2008) have suggested that possible environment-friendly refrigerants with zero ODP and low GWP could be selected from the full array of derivatives of methane and ethane.

Full array of Methane and Ethane Derivatives

Figure 3 shows the full array of methane derivatives. As shown in the figure, there are 15 possible compounds comprising various numbers of H, F and Cl atoms that can be derived from methane (CH_4). The carbontetrachloride CCl_4 is placed at the top vertex of the triangle with the low left vertex occupied by methane molecule CH_4 and the lower right vertex occupied by carbon tetrafuoride CF_4. For each row below CC14, one Cl atom is replaced by an H or F atom. According to this arrangement, the compounds by the right from CCl_4 to CF_4 are fully halogenated compounds.

A systematic gradation of the properties of the compounds can be explained with the aid of Fig. 3. There is a regular pattern of decrease in the normal boiling point as we proceed from CCl_4 toward CH_4. The compounds that contain relatively higher proportion of H are flammable and those that contain lower proportion of H are less flammable.

Figure 4 shows the full array of ethane derivatives. As shown in this figure, there are 28 possible compounds comprising various numbers of H, F and Cl atoms that can be derived from ethane (C_2H_6). This arrangement of the compounds is similar to the arrangement shown in Fig. 3. One significant respect in which the compounds in Fig. 4 differ from those in Fig. 3 is that with two C atoms in C_2H_6; it is possible to have different arrangements of the attached atoms of H, Cl and F with the same chemical formula of the compounds. When these arrangements are taken into account, they yield 55 possible halocarbon compounds.

Trade-offs in Flammability, Toxicity and Atmospheric Lifetime

In order to select possible alternatives to the offensive refrigerants from the full array of methane and ethane derivatives, it is necessary to evaluate some refrigerants based on the criteria of inflammability, toxicity and chemical stability concerning atmospheric lifetime. Fig. 5 illustrates the trade-offs in flammability, toxicity, and atmospheric lifetime with changes in molecular chlorine, fluorine and hydrogen content.

As illustrated in Fig. 5, increasing the hydrogen content make the substance flammable since H is highly flammable. The fully halogenated compounds are totally nonflammable since all the hydrogen atoms have been replaced with halogen atoms. There is also a pattern for toxicity. According to Calm (2002), the Cl-containing compounds in the top left side of the triangle are more toxic than the F-containing compounds toward the lower right corner of the triangle.

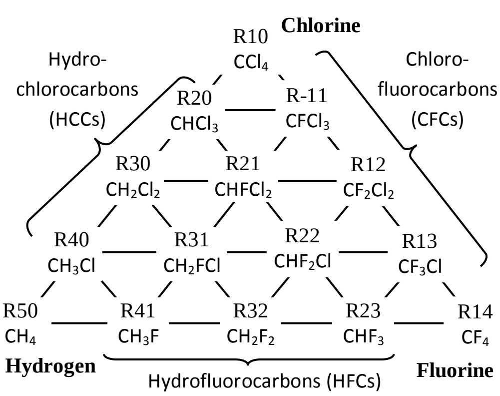


Figure 3: Derivatives of Methane (CH_4)

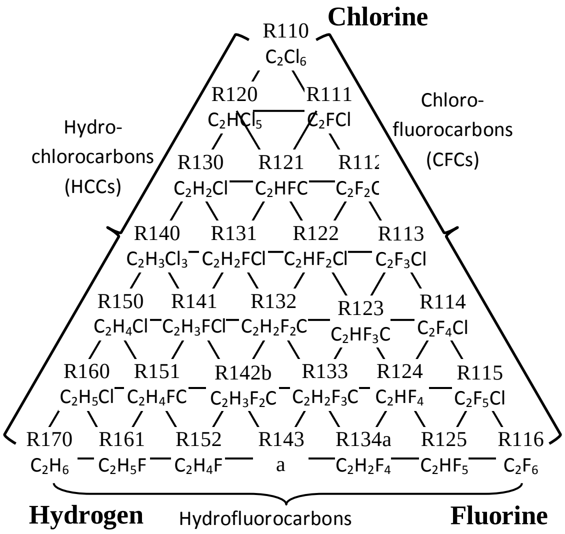


Figure 4: Derivative of Ethane (C_2H_6)

Increasing the fluorine or chlorine content increases atmospheric stability, this lengthens atmospheric lifetime. As illustrated in Fig. 6, increasing the chlorine content in refrigerant molecules generally increases the ODP. Compounds that contain no chlorine have ODPs that are nearly zero (Bhatti, 1999). Likewise, increasing the fluorine content generally raises the GWP. Substituting hydrogen tends to shorten the atmospheric lifetime. Compounds with very short lives will have low ODPs, since most emissions will decompose before reaching the stratosphere. They also will have low GWP values, since their atmospheric persistence will be comparatively short in duration (Calm, 2002).

The alternative refrigerants that are nontoxic, low-flammable and environment-friendly can be selected from the compounds occupying the remaining unshaded portion in Figure 5. Comparing Figure 3 and Figure 4 with Figure 5, to select compounds without chlorine content, reduces the unshaded portion to the bottom row where we have R23 and R32 refrigerants in Figure 3, and R152a, R143a, R134a and R125 refrigerants in Figure 4.

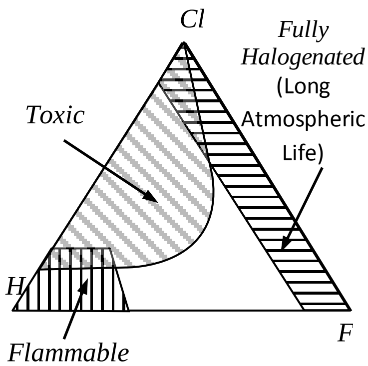
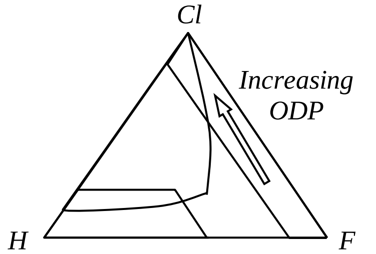
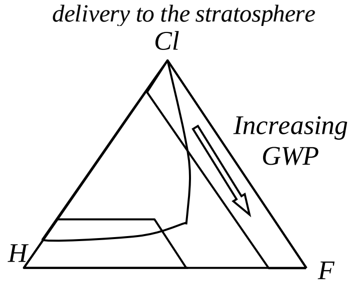


Figure 5: Trade-off in flammability, toxicity, and atmospheric lifetime with changes in molecular chlorine, fluorine and hydrogen contents.

(Source: McLinden and Didion, 1987)



(a) Ozone depletion depends on chlorine (or bromine) content and delivery to the stratosphere



(b) Direct global warming depends on infrared absorbency and longevity

Figure 6: Chlorination and fluorination impacts on ozone depletion and global warming potentials.
(Source: Calm and Didion, 1998b)

THE CURRENT ALTERNATIVE REFRIGERANTS IN VAPOUR COMPRESSION REFRIGERATION SYSTEMS

Although, the production and use of the fully halogenated CFC refrigerants will be phased out under the auspices of the Montreal Protocol, the partially halogenated HCFC refrigerants such as R22 and R123 may remain in use for years to come as they are not as stable as the fully halogenated refrigerants, therefore, they cause little damage to the ozone layer (Table 1). Studies have shown that environmental benefits of R123 outweigh its ozone impact, therefore, the production is allowed for another three decades (Bhatti, 1999). Many possible alternative refrigerants are currently under investigations to address areas of their shortcomings. The possibilities include hydro-carbons (HCs), refrigerant mixtures, carbon dioxide (CO_2) and hydrofluorocarbons (HFCs)

Hydrocarbons as Alternative Refrigerants

Hydrocarbons (HCs) are the class of naturally-occurring substances that include propane, pentane and butane. HCs are excellent refrigerants in many ways - energy efficiency, critical point, solubility, transport and heat transfer properties. They are environmentally sound alternative for CFCs and HFCs. Hydrocarbons and their mixtures have zero ozone depletion potential and global warming potential (Table 2), they have no significant refrigeration related problems. The major concern is with their flammability. The fire and explosion data of hydrocarbon

Table 2: Environmental effects of some hydrocarbon refrigerants

Data	Refrigerants		
	Propane (R290)	n-butane (R600)	Iso-butane (R600a)
Natural	Yes	Yes	Yes
ODP	0.0	0.0	0.0
GWP, 100 years	0.0	0.0	0.0
Density at 25°C (kg/m^3)	492.7	532.5	550.7
Flammability limits (Vol. %)	2.1 – 11.4	1.7 – 10.3	1.9 – 10.0
Molecular mass (kg/kmol)	44.1	58.1	58.1

(Source: Perry and Green, 1997; Fatouh and Kafafy, 2006)

substances are given in Table 2, and as far as place of installation and operation conditions in households are concerned, non-flammable refrigerants are preferred. This makes hydrocarbon not to be a good alternative (Sattar et al., 2007).

Refrigerant Mixtures as Alternative Refrigerants

According to Gopalnarayanan (1998), refrigerant mixtures have received renewed interest from designers in the process of searching for new alternatives, since by mixing two or more refrigerants a new working fluid with the desired characteristics can be created. For example, by adjusting the composition of a blend containing high-pressure and low-pressure refrigerants, the vapour pressure of the final fluid can be tailored to match that of the CFC or HCFC being replaced. By blending refrigerants, it is possible to create new blends that are nonflammable but still contain moderately flammable refrigerants.

Refrigerant mixtures fall into two major groups, zeotropes and azeotropes. In zeotropic mixtures, as the name implies the liquid-vapour phase change does not occur at a constant temperature (at a fixed pressure) as in the case of pure fluids, but over a range of temperatures. Azeotropic mixtures, on the other hand boil at a single temperature, much as a pure fluid does. The temperature alternation during phase change is commonly called "temperature glide'. The higher temperature glide in zeotropes results in a phenomenon called fractionation, whereby higher and lower boiling components tend to separate. This could result in a change in the mixture's composition, which is undesirable, since it could alter the system's performance.

Carbon Dioxide (CO_2) as Alternative Refrigerants

Carbon dioxide had been used as a refrigerant in the 1930s and 1940s in vapour compression refrigeration systems. It was abandoned as a refrigerant because of lost capacity at higher ambient temperatures and the used of CFCs and HCFCs were preferred (Lorentzen, 1995). Also, its operating pressure is very high. One way to overcome this high pressure disadvantage may be a choice of cascade refrigeration system, where carbon dioxide refrigeration system is pre-cooled by other refrigeration system (Kim and Kim, 2002). It should be remembered, however, that two or more compressors are required in a cascade system depending on the number of refrigerants used, this will had to the system complexibility and cost.

Hydrofluorocarbons (HFCs) as Alternative Refrigerants

The hydrofluorocarbon refrigerants such as R134a, which may remain in use for even longer periods of time, are not as stable as the fully halogenated compounds such as R12. They have no ozone depletion problem associated with them, but their global warming potentials are relatively high. The HFC refrigerants have greatly ameliorated the problem of finding suitable replacements for CFCs refrigerants (Bolaji, 2010). They are not controlled by the Montreal Protocol since their ODPs are zero. But HFC emissions are regulated under the Kyoto Protocol; this treaty has not entered into force and may not do so unless amended to address measures by developing countries (Calm, 2002).

CONCLUSION

Vapour compression refrigeration system is the most widely used refrigerating method throughout the world. The CFC and HCFC refrigerants used in the systems have become a subject of great concern for the last few decades. The problem is not with refrigerants inside the system, but with their release to the environment. Earth is the only planet in the solar system with an atmosphere that supports life; therefore, preserving the ozone is one of the many essential steps necessary for the protection of life on the planet for future generations. CFCs and HCFCs were found harmful to the earth's protective ozone layer. Therefore, the Montreal Protocol and other international agreements prohibited production of CFC refrigerants after 1995 in developed countries. The producing and using of CFC refrigerants will be prohibited completely all over the world in the year 2010. In consequence, lots of researches have been done to find the suitable alternatives for CFCs.

This paper discusses various compositional groups of halocarbon refrigerants and their environmental problems. It also analyses processes of selecting environment-friendly refrigerants that have zero ozone depletion potential and low global warming potential. It focuses on the matrix triangles of methane and ethane derivatives. Refrigerants found on the full array of the derivatives were considered and trade-offs in flammability, toxicity, and chemical stability and atmospheric lifetime were carried out with changes in molecular chlorine, fluorine and hydrogen content.

The trade-offs and consideration of compounds without chlorine content scaled down the refrigerants to those in the bottom rows of matrix triangles of methane and ethane derivatives. The emerging refrigerants that are non-toxic, low-flammability and environment-friendly are R23 and R32 from methane derivatives, and R152a, R143a, R134a and R125 from ethane derivatives. In order to ascertain the suitability of these refrigerants in vapour compression refrigeration systems, further theoretical and experimental analyses are recommended to investigate their performances in the systems. Currently, hydrofluorocarbons (HFCs), hydrocarbons (HCs), and refrigerant mixtures are employed as alternatives in vapour compression refrigeration systems. Merits and demerits of these refrigerants were discussed to show areas of their shortcomings that researchers must focus in order to make them acceptable worldwide.

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