

CHAPTER 37

CFC REFRIGERANTS AND STRATOSPHERIC OZONE: PAST, PRESENT AND FUTURE

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ABSTRACT

Scientists understanding of the interactions between ozone and the chlorofluorocarbon (CFC) refrigerants in the stratosphere have continued to increase since mid-1970s. This paper reviews the worldwide efforts to reduce the environmentally harmful effects of CFC refrigerants on the stratospheric ozone layer over the last 20 years. It examines the global environmental issues that catalysed recent changes in refrigeration industry. It discusses the effects of ozone depletion, the benefits of the CFC phase-out, the present and the future alternatives to CFC refrigerants.

1.0 INTRODUCTION

Chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants, which have been used as refrigerants in a vapour compression refrigeration system, were known to provide a principal cause to ozone depletion and global warming. The Montreal Protocol restricts the production and use of these refrigerants, leading to their ultimate phase out for most uses (Kim *et al.*, 2002).

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, 1998). Nearly all of the early refrigerants were flammable, toxic and some were highly reactive with metals and seals. 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 (1998), 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. Chlorofluorocarbon refrigerants were invented in 1928 by Thomas J. Midgley, Jr. and his associates, all employed in a small private research laboratory at Dayton, Ohio, supported by General Motors Corporation. The refrigerant generations are shown in Fig. 1.

The linkage of the CFC refrigerants to the destruction of the ozone layer which has been established recently 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 (Bhatti, 1999). The primary requirements of the ideal refrigerant in 1978, which have now increased because of this issue of ozone layer depletion are normal boiling point in the range of - 40 °C to 0 °C, nontoxic, noncorrosive, non-flammable and stability. None of the refrigerants available at that time, including sulphur dioxide, carbon dioxide, ammonia, methylchloride,

ethylchloride and isobutene, could fit the bill (Bhatti, 1999). Table 1 shows the characteristic of the common refrigerants known in 1928.

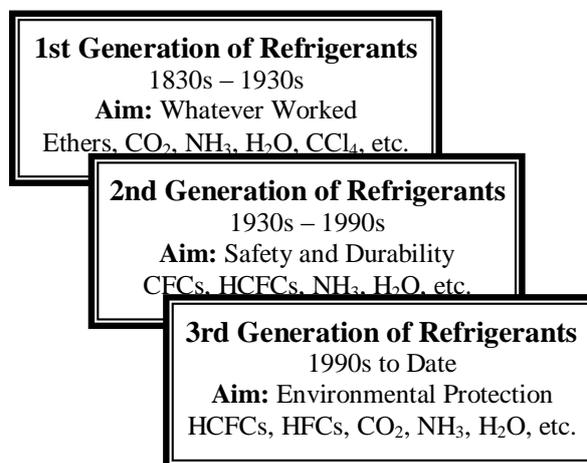


Fig. 1: The refrigerant generations (Source: Calm, 2002)

In the past, refrigerants have been selected on the basis of suitable qualifying properties, such as, low flammability and toxicity and good materials compatibility. Also considered are a qualitative assessment of transport and thermodynamic properties such as, the desirability of a low viscosity, high latent heat, and operation away from the critical point. The performance of refrigerants which satisfied these criteria were then calculated for various applications and compared with each other (McLinden, 1988).

The CFC refrigerants fulfilled all the primary requirements and heralded an unprecedented revolution in the refrigeration and air-conditioning industry. Today, the litany of the requirements imposed on an ideal refrigerant has increased. The additional primary requirements now include zero ozone depletion potential and zero global warming potential (McLinden, 1988).

According to Bhatti (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 fulfil these new requirements in addition to the earlier primary requirements for the ideal refrigerants.

Table 1. Characteristic of the common refrigerants known in 1928.

Refrigerants	Characteristics	Flammability	Toxicity
Air	Does not liquefy readily	Non-flammable	Nontoxic
Water	High freezing point	Non-flammable	Nontoxic
Carbon dioxide	Low critical point	Non-flammable	Nontoxic but asphyxiant
Ammonia	Satisfactory	Very slightly flammable	Toxic but gives ample warning
Sulphur dioxide	Satisfactory	Non-flammable	Toxic but gives ample warning
Methyl chloride	Satisfactory	Slightly flammable	Toxic and gives no warning
Methyl bromide	High freezing point	Slightly flammable	Toxic and gives no warning
Butane	Satisfactory	Highly flammable	Nontoxic

(Source: Bhatti, 1999).

2.0 OZONE AND HUMANKIND

For more than million years, ozone molecules in the atmosphere have safeguarded life on this planet. Over the past half-century, humans have placed the ozone layer in jeopardy. We have unwillingly polluted the air with chemicals that threaten to eat away the life-protecting shield surrounding our world. When CFCs and other ozone-depleting chemicals are emitted, they mix with the atmosphere and eventually rise to the stratosphere, there; the chlorine and the bromine they contain catalyse the destruction ozone. The destruction of the ozone layer leads to higher levels of ultraviolet radiation (UV) reaching Earth's surface.

The term "Ozone" comes from the Greek word meaning "smell", a reference to ozone's distinctively pungent odour. Each molecule contains three oxygen atoms bonded together in the shape of a wide triangle. In the stratosphere, new ozone molecules are constantly created in chemical reaction fueled by power from the sun. The recipe for making ozone starts off with oxygen molecules (O₂). When struck by the sun's rays, the molecules split apart into single oxygen atom (O), which is exceedingly reactive. Within a fraction of a second, the atoms bond with nearby oxygen molecules to form triatomic molecules of ozone, O₃, (Kowalok, 1993).

As the sun's energy produces new ozone, these gas molecules are continuously destroyed by natural compounds containing nitrogen, hydrogen, and chlorine. Such chemicals were all present in the stratosphere (in small amounts) long before humans began polluting the air. Nitrogen comes from soils and the oceans, hydrogen comes mainly from atmospheric water vapour, and chloride comes from the oceans. The stratospheric concentration of ozone therefore represents a balance, established over the oceans, between creative and destructive forces. The total level of ozone in the stratosphere remains fairly constant, an arrangement resembling a tank with open drains. As long

as the amount of water pouring is equals the mount flowing out the drain holes, the water level in the tank stays the same. In the stratosphere, the concentration of ozone does very slightly, reflecting small shifts in the balance between creation and destruction (Anderson *et al*, 1989). For many years, the natural ozone system worked smoothly, but now human beings have upset the delicate balance by polluting the atmosphere with additional chlorine concentrations in the stratosphere.

3.0 STRATOSPHERIC OZONE DEPLETION

The first major environmental concern to strike the refrigeration based industries was depletion of the ozone layer as the result of the emission of anthropogenic (man-made) chemicals into the atmosphere. The ozone depleting effect is caused by the migration of very stable refrigerants of the CFC type to the upper atmosphere (stratosphere). It is generally accepted that in the stratosphere, the stable CFC refrigerants become involved in catalytic reactions which have the effect of breaking down ozone without first destroying the chlorine released from the CFCs. The most harmful CFCs have an active ozone destroying life in the stratosphere of over 100 years. Since ozone layer filters out harmful ultraviolet (UV) radiation which might otherwise reach the surface of the earth, its depletion could result in high concentration of UV radiation on the earth surface (Adegoke, 1994).

3.1 Worldwide Efforts to Reduce the Effect of CFC Refrigerants

As reported by Bhatti (1999), Rowland and Molina proposed that the emission of chlorinated man-made chemicals to the atmosphere could damage the stratospheric ozone layer. Subsequently, an extensive worldwide programme of stratospheric ozone monitoring has confirmed that there is a pattern of depletion which is most pronounced over the Antarctic during springtime. As a consequence, a series of intergovernmental agreements have been formulated, beginning in 1985 with the Vienna Convention on the Protection of the ozone layer and the Montreal Protocol on substances that deplete the Ozone Layer in 1987. These were followed by London, Copenhagen, Vienna, Montreal and Beijing Amendments of 1990, 1992, 1995, 1997 and 1999 respectively (UNEP, 2000). The measures to phase out the production and use of materials with high ozone depletion potentials (ODPs) emanated from the Montreal Protocol and its amendments. These materials include chemicals containing chlorine and bromine use as refrigerants, solvents, foam blowing agents, aerosol propellants, fire suppressants and for other purposes.

The current official position is that CFC production and use have already been phased out in the industrialized countries. All production is to cease by the year 2006. However, CFC production remains well above target levels – to the extent that 2010 would now appear to be a more realistic phase out data than 2006 (McMullan, 2002). This excess production is being driven by the continued sale of CFC-based systems in developing countries, and the export of used equipment from industrialized to developing countries (UNEP, 2000).

For HCFCs, the official phase-out dates are 2030 for the industrialised countries and 2040 for the developing

countries. In Montreal, the EU pushed for an earlier HCFC phase out date 2015, but this was defeated following opposition by the United States, Canada, and some developing countries (UNEP, 2000). The EU proposal was based on the increasing availability of non-depleting substitutes for HCFCs and on recent evidence that many HCFCs are acutely toxic following regular exposure. Meanwhile, different countries are adopting their own phase-out strategies. For example, Germany has banned the use of HCFC-22 in new plants after the year 2000 (McMullan, 2002).

3.2 The Effects of Ozone Depletion

Ozone plays a critical role in screening harmful ultraviolet radiation. Because of the strong absorption of solar ultraviolet by Ozone in the stratosphere, it is virtually impossible for ultraviolet rays between 200 and 300 nm to penetrate to the earth's surface at 290 nm, the radiation is 350 million times weaker than at the top of the atmosphere (Giannini, 1986). UV radiation is typically broken down into three parts (Fig. 2). UVA (320 to 400 nm), UVB (280 to 320 nm), and UVC (200 to 280 nm). UVC is quickly absorbed by small amounts of ozone, so that none gets to the earth's surface. UVB is partially absorbed and about half of the UVA is absorbed by ozone or scattered.

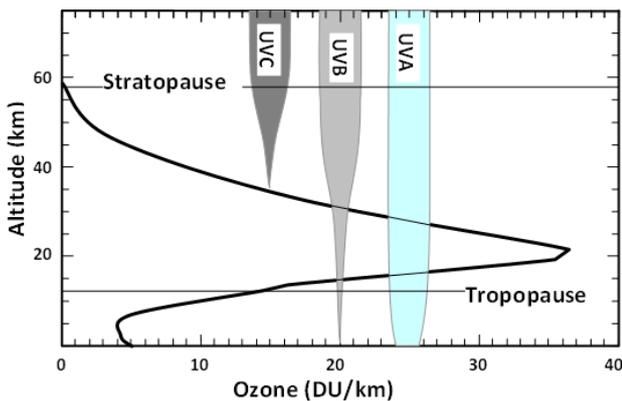


Figure 9. The Screening of UV by Ozone. (Source: Newman, 1998)

3.2.1 Effects of Ozone Depletion on Human Health

Laboratory and epidemiological studies demonstrate that UVB causes nonmelanoma skin cancer and plays a major role in malignant melanoma development. In addition, UVB has been linked to cataracts and immune system suppression. All sunlight contains some UVB, even with normal ozone levels. It is always important to limit exposure to the sun. However, ozone depletion will increase the amount of UVB and the risk of health effects (Green and Battistutta, 1990).

3.2.2 Effects of Ozone Depletion on Plants

Physiological and developmental processes of plants are affected by UVB radiation, even by the amount of UVB in present – day sunlight. Despite mechanisms to reduce these effects and a limited ability to adapt to increase levels of UVB, plant growth can be directly affected by UVB radiation. Indirect changes caused by UVB (such as changes in plant form, how nutrients are distributed within

the plant, timing of developmental phases and secondary metabolism) may be equally, or sometimes more, important than damaging effects of UVB. These changes can have important implications for plant competitive balance, herbivores, plant diseases, and biogeochemical cycles (Sinclair *et al.*, 1990).

Other effects of ozone depletion are on marine ecosystems such as phytoplankton from the foundation of aquatic food webs and materials such as synthetic polymers, naturally occurring biopolymers, as well as some other materials of commercial interest are adversely affected by solar UV radiation. Any increase in solar UVB levels will therefore accelerate their breakdown, limiting the length of time for which they are useful outdoors.

3.2.3 Benefits of the CFC Phase-Out

The chlorofluorocarbon phase out is an important turning point in the recovery of the ozone layer and this will produce benefits for the environment, businesses, and individuals. The phase out of CFCs is expected to have direct health benefits, including reduced incidence of skin cancer and cataracts, decreased risks to human immune systems and increased protection of plant and animal life from excessive UV exposure. Also CFC phaseout provided an impetus to develop and invest in a new energy efficient air-conditioning and refrigeration equipment.

4.0 Global Warming

The second major environmental concern is climate change or global warming. This did not become a major area of attention until after the responses to ozone depletion had been initiated. Concerns on this issue are now beginning to complicate our handling of ozone depletion.

Global warming arises because of the greenhouse effect. According to Ko *et al.* (1994), the frequency distribution of the radiation coming from the sun closely approximates that from a black body at a temperature of about 5800 K, the spectrum wavelengths range from less than 1 nm to hundreds of metres: the peak in the spectrum is in the visible region at about 500 nm. When solar radiation (1360 Wm^{-2}) arrives at the earth, about 30% is reflected back into space and most of the remainder passes through the atmosphere to the ground. This heats up the earth, which then behaves approximately as a black body, radiating energy with a spectral peak in the infrared. This infrared radiation cannot pass through the atmosphere because of absorption by water vapour, and other infrared absorbers. As a consequence, heat energy is trapped and the temperature at the surface of the earth is higher than it would be without the insulating blanket of the atmosphere.

Global warming is a good thing in itself and allows life to exist in all its variety (Segelstad, 1998). The concern is that man's activities are increasing the concentration of greenhouse gases in the atmosphere, so causing the amount of absorbed infrared radiation to increase, and leading to increased atmospheric temperatures and consequent long-term climate changes.

The amount of radiant energy that the refrigerants absorb is measured by an index called global warming potential (GWP). GWP is the amount of infrared radiation that the gas can absorb, relative to carbon dioxide (with an

assigned GWP of 1), integrated over a period of 100 years. A more appropriate measure of a refrigerant contribution to global warming is based on a concept called total equivalent warming impact, or TEWI. Hwang *et al.* (1998) described two types of global warming effects. The first is the direct global-warming potential that is due to the emission of refrigerants and other pollutants. The second type is an indirect global-warming potential, which results from the emission of carbon dioxide due to the consumption of energy obtained from the combustion of fossil fuels (Oil, natural gas, and coal). The combined effect of the two global – warming potentials is known as the total equivalent warming impact (TEWI).

4.1 Problem of CFC Refrigerants and Ozone Depletion

One of the unique characteristics of the chlorofluorocarbon refrigerants is their exceptional stability. An impressive evidence of this was obtained in 1973 by the British scientists, who happened to measure the atmospheric concentration of one member of the chlorofluorocarbon family of refrigerants, R11, and they noted that this concentration was very close to the concentration one would expect taking into account all known amounts of R11 released into the atmosphere since its introduction in 1933. This was the first signal that the chlorofluorocarbon refrigerants are exceedingly stable and can survive in the atmosphere for decades (Hummel *et al.*, 1991).

4.1.1 The Problem of CFC and Ozone in the Early 1970s

No one dreamed human activity would threaten the ozone layer until the early to mid-1970s, when scientists implicated a widely used class of chemicals known as CFCs, which were most commonly known as the aerosol propellant in spray cans. CFCs contain chlorine, fluorine, and carbon atoms arranged in an extremely stable structure (Gamlen *et al.*, 1986).

Through decades of use, CFCs proved themselves to be ideal compounds for many purposes. They are nontoxic, non-corrosive, non-flammable, and unreactive with most other substances because of their special properties, they make excellent coolants for refrigerators and air conditioners. CFCs also trap heat well; so manufacturers put them into foam products to serve as heat insulation materials. Most scientists had not worried about how CFCs would affect the atmosphere. But two chemists, Rowland and Molina, began considering these wonder compounds, and they uncovered something disturbing. CFCs were extremely stable in lower atmosphere where they would break apart when bombarded by the sun's high-energy radiation. CFCs therefore carried millions of tons of extra chlorine atoms into the stratosphere, adding much more than the amount of chlorine supplied naturally by the oceans in the form of methyl chloride (Rowland, 1999).

Rowland and Molina hypothesized that the chlorine build up from CFCs would spell severe trouble for the ozone layer. According to their predictions, each chlorine atom could destroy 100,000 ozone molecules, meaning that decades of CFC use could cause substantial declines in the concentration of tropospheric ozone. Any drop in ozone level would allow more ultraviolet light to reach the Earth's surface. This effect holds severe consequences for life on the planet. Exposure to ultraviolet light enhances an individual's risk for skin cancer and cataracts so an

increase in this radiation could lead to more cases of such diseases. Ultraviolet light also harms food crops and other plants as well as many species of animals (Moan and Dahlback, 1992).

Therefore, political leaders faced a tough decision on the subject of CFCs. For example, in the United States, these extremely reliable chemicals formed the centre of a multibillion-dollar industry. Though the Rowland/Molina hypothesis warned that CFCs might endanger the health of the planets inhabitants, but officials feared that a ban on such chemicals would disrupt many segments of society. Then the question was whether it worthwhile to face economic hardships solely because of a scientific hypothesis and its predicted effects. Decision makers also knew that the ozone layer belonged to the entire world, meaning that all countries would have to address the problem.

4.1.2 The Problem of CFC and Ozone in 1974 – 1984

The first attempts to assess the problem of effect of CFC on ozone layer produced dire forecasts, suggesting that CFCs could destroy perhaps half the ozone shield by the middle of the next century. Yet experts did not know how much to believe these early estimates, because they were based on a very simplistic understanding of chemical reactions in the stratosphere. Over the next few years, researchers took many different routes to discover the extent of the ozone depletion. Experiments in the laboratory allowed chemists to gauge how quickly chlorine destroyed ozone molecules. Other scientists launched balloons that carried instruments up into the stratosphere, where they measured the concentrations of key chemicals that controlled ozone levels. All this information fed into new computer models that predicted how chemicals would affect the ozone layer (Kerr, 1988).

By 1976, many experts had grown convinced that CFCs did indeed present a serious threat. In the United State (the world's largest producer and user of CFCs), the public called for the government to place limitations on these chemicals. Civic leaders launched boycotts against items that used CFCs, and some companies even eliminated the compounds their products. The U.S. and some other governments responded in 1979 by banning the sale of aerosol can containing CFCs. Because spray cans represented the largest use of these chemicals, the ban led to an abrupt levelling off of CFC production (Schoeberl and Hartmann, 1991).

The U.S. ban on CFC propellants in spray cans caused a temporary pause in the growing demand for the offending compounds. But atmospheric researchers knew that danger still threatened the protective ozone layer. Meanwhile, companies continue to produce these chemicals for use in air-conditioners, in insulation, and in the cleaning of electronic parts. Most countries aside from the United States continued to use CFCs in spray cans. Therefore, worldwide use of the chemicals continued, and levels of CFC production began to rise again. The increase in CFC use rekindled worldwide attention to the threat of ozone destruction, spurring countries in 1985 to sign an international agreement (Vienna convention). The convention called on negotiators to draw up a plan for worldwide action on this issue (Schoeberl and Hartmann, 1991).

4.1.3 The Problem of CFC and Ozone in 1985 - 1990

In May 1985, shocking news spread throughout the scientific community. British researchers reported finding dramatic declines in ozone values over Antarctic, each spring “holes” in the ozone layer. The certainty of the depletion of the global ozone shield and the jarring unexpectedness of the ozone-hole’s appearance motivated countries to act. In September 1987, diplomats from around the world met in Montreal and forged a treaty unprecedented in the history of international negotiations. Environmental ministers from 24 nations, representing most of the industrialized world, agreed to set sharp limits on the use of CFCs and Halons (Rowlands, 1999).

The Montreal Protocol established a new way of viewing environmental problems. In the past, the world had addressed such issues only after damage grew noticeable. For example, nations agreed to limit above ground nuclear tests once it became evident that these explosions poisoned the air and water with radioactivity. The Montreal agreement, however, tackled the ozone issue early, demonstrating a heightened sense of environmental responsibility (Rowland, 1999).

The fast-paced research of the late 1980s revealed that the original Montreal Protocol would not go far enough toward protecting the fragile ozone layer. Even with the 50 % cuts mandated by the treaty, levels of chlorine and bromine would still rise in the stratosphere, meaning that ozone loss would only worsen with time. Therefore, in June 1990, diplomats met in London and voted to significantly strengthen the Montreal Protocol. The treaty calls for a complete phase out of CFCs by the year 2000, a phase-out of Halons (except for essential uses) by 2000, and a rapid phase out of other ozone-destroying chlorine compounds carbontetrachloride by 2000 and methyl chloroform by 2005 (UNEP, 2000).

5.0 THE PRESENT AND FUTURE REFRIGERANT OPTIONS

5.1 The Present Refrigerant Options

Although the production and use of the fully halogenated chlorofluorocarbon refrigerants such as R11, R12, R13, R113, R114 and R115 will be phase out under the auspices of the Montreal Protocol, the partially halogenated chlorofluorocarbon 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 (Bhatti, 1999). Also, the fluorocarbon refrigerants such as R134a, which may remain in use for even longer periods of time. They have no ozone depletion problem associated with them, although they suffer from the drawback of a finite global warming potential (Calm, 2000).

Rigorous analyses of R22 and R123 by Calm *et al.* (2000), reveals that the ODPs of these refrigerants are very low, 0.034 and 0.012 respectively, therefore, their impact on ozone depletion are negligible. Further studies by Calm (2002), indicate that environmental benefits of R123 outweigh its ozone impact and justify reconsideration of its phase-out. The production of these refrigerants is allowed for another three decades (Four in developing countries) even without reconsideration. The refrigerant quantities

needed to service both existing and new R123 systems should be available for at least several additional decades. HFCs are not controlled by the Montreal Protocol since their ODPs are nearly 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).

5.2 The Future Alternative to CFC Refrigerants

The refrigeration industry is now well aware of the nature of the impacts of the ozone-related decision. Since the Montreal protocol was adopted, there has been considerable work aimed at identifying suitable replacements and overcoming application problems. These problems include efficiency and capacity changes, loss of temperature range, lubricating difficulties and lubricant compatibility (McMullan, 2002).

The range of possible alternative fluids is extensive and a list of some candidate fluids is given in Table 2. The possibilities include refrigerant mixtures, hydrofluorocarbons (HFCs), natural refrigerants such as CO₂, hydrocarbons (HCs) and perfluorocarbons (PFCs), The PFCs are unlikely to play a major role as CFC alternative, because they have high global warming potentials and extremely long life-times in the atmosphere (McMullan, 2002).

Table 2. List of Alternatives to CFCs and HCFC Refrigerants and their Environmental Effects.

Refrigerant	NBP (°C)	ODP (R11 = 1)	GWP (CO ₂ = 1)
<i>Example Alternative for CFC-11</i>			
CFC-11 (R11)	23.8	1.0	3800
HCFC-123 (R123)	27.9	0.02	90
HCFC-141b (R141b)	32.2	0.11	630
<i>Example Alternative for CFC-114</i>			
CFC-114 (R114)	3.78	0.8	9300
HCFC-124 (R124)	- 13.2	0.022	480
HFC-134 (R134)	4.67	0	1300
<i>Example Alternative for CFC-12</i>			
CFC-12 (R12)	- 29.79	1	8100
HFC-134a (R134a)	- 26.1	0	1300
R401A	- 33.0	0.037	1100
R409A	- 34.3	0.048	1400
<i>Example Alternative for HCFC-22</i>			
HCFC-22	- 40.75	0.055	1700
R407C	- 44.0	0	1600
R410A	- 52.7	0	1900
<i>Example Alternative for R502</i>			
R502	- 45.6	?	5500
R404a	- 46.5	0	3700
R507	- 46.7	0	3800
<i>Other Options – Natural Refrigerants</i>			
Air		0	0
Water		0	?
Ammonia		0	0
Carbon dioxide		0	1

NBP = Normal boiling point; ODP = Ozone depletion potential; and GWP = Global warming potential.

(Source: McMullan, 2002)

5.2.1 Hydrocarbon 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, well-behaved, compatible with mineral oils, good critical point, solubility, transport, and heat transfer properties. They are environmentally sound alternative for CFCs and HFCs. They give at least as good performance as the CFCs they are replacing. Hydrocarbons as a refrigerant have been known and used since the beginning of eighteenth century. The development of the inert CFCs in the 1930s put the HC technology in the background and CFCs have been applied since then in numerous refrigeration equipment. HCs have no significant refrigeration related problems. The major concern is with their flammability. However, interest in the use of pure (propane and butane) or mixed hydrocarbons as refrigerants in domestic and commercial refrigerators has increased in the last decade because they have neither ozone depletion effect nor global warming effect. They have been used from 1993 onwards as refrigerants for refrigerators and freezers in Europe.

5.2.2 Refrigerant Mixtures as Alternative

According to Gopalnarayanan (1998), refrigerant mixtures have receive 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. In other cases, blends are created to improve such system characteristic as compressor discharge temperature, or to improve lubricant circulation by adding a more lubricant-miscible refrigerant to the blend.

5.2.3 Carbon Dioxide Refrigerant as an Alternative

Carbon dioxide had been used as a refrigerant in the 1930s and 1940s in ships' refrigerator and other stationary systems. However, when ships passed through tropical regions refrigerant capacity dropped rapidly. Carbon dioxide was abandon as a refrigerant because of lost capacity at higher ambient temperatures and due to the introduction of CFC and HCFC refrigerants. Lorentzen (1994) summarized possible transcritical cycles with carbon dioxide covering car air-conditioners, large heat pumps, domestic and commercial refrigeration systems. He also described several cycles to pursue better performance while keeping the gas cooling pressure in the order of 10 MPa.

5.2.3 Replacement Fluids for R22 Refrigerant

R22, a hydrochlorofluorocarbon (HCFC), is the refrigerant used in virtually all air-conditioners and heat pumps because of its inherent efficiency and high refrigeration capacity. Provisions of the Clean Air Act (CAA) in the United State call for R22 to be phased out of "new equipment" by 2010 and allow production of smaller amounts of the refrigerant until 2020 for servicing installed

equipment. No single-component fluid has been identified as a replacement that would meet all performance, environmental, and safety requirements. The most likely replacements for R22 are binary or ternary HFC mixtures. In addition to being ozone safe, nonflammable, nontoxic and efficient, they have performance levels close to or superior to that of R22. One of these HFC mixtures, designated R407C, has shown equivalent capacity to R22 but efficiencies that averaged about 5% lower than R22 in soft-optimized equipment. (Kim *et al.*, 2002).

5.2.4 Replacement Fluids for R12 Refrigerant

CFC-12 (R12) is used solely in the majority of existing conventional household refrigerator/freezers, but commercial production of R12 in the U.S. was terminated at the end of 1995 in compliance with the clean Air Act amendments of 1990 and the Montreal protocol. A single-fluid chlorine-free replacement for R12 has been found in R134a. This refrigerant is the leading replacement for domestic applications and is being installed in newer refrigerator/freezer models.

6.0 CONCLUSION

Over the past half-century, humans have placed the ozone layer in jeopardy; the air has been polluted with chemicals that threaten to eat away the life-protecting shield surrounding our world. This paper discusses the ozone depletion and global warming which are the major environmental issues. It also discusses the process of ozone formation, depletion and effects. The emission of CFC refrigerants into the atmosphere depletes the ozone layer and allows the harmful ultraviolet (UV) radiation to reach the earth surface. This in turn lead to a greater incidence of skin cancer, cataracts, malignant melanoma, impaired immune systems and affects physiological and developmental processes of plants. The paper reviews the worldwide efforts to reduce the environmentally harmful effect of CFC refrigerants over the last 20 years. The present refrigerant options and the future alternatives to CFC refrigerants were examined.

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