Chapter

Refrigerant Mixtures

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Abstract

Evolution of refrigerants has a history since the introduction of air conditioning systems by Sir Willis Carrier. The first generation air conditioning systems used natural refrigerants like air, water, carbon dioxide etc. But the need of low temperature requirements in residential and industrial air conditioning systems has forced the air conditioning field to use chloro flouro carbon type refrigerants, which was introduced by Dupon in the previous century. Physical and chemical properties of CFC type refrigerants were very good and satisfactory and so it was used in almost all refrigeration and air conditioning systems. The main disadvantage of CFC type refrigerants is harming the ozone layer and contributing much to the global warming. This chapter reviews the use of CFC type and introducing alternate type of refrigerants.

Keywords: Refrigerants, Chloro Flouro Carbon, Ozone, Global Warming, Emission, Environment, Alternate refrigerants

1. Introduction

Carbon dioxide (CO_2) is a naturally arising gas by the method of photosynthesis into organic matter. A derivative of fossil fuel ignition and biomass burning, it is also released from the changes in the use of lands and other industrial activities. Earth's radiative stability is continuously disturbed primarily by carbon di oxide. CO_2 is considered to be a reference gas for the measurement of other greenhouse gases and thus having a Global Warming Potential of 1. The rate of global warming increase is because of the climate change and escalation in the concentrations of atmospheric carbon dioxide.

This is because of the increase in the custom of using carbon based fuels especially in the present modern world. CO_2 is also a key cause of marine acidification as it softens in water to produce carbonic acid. The earth's radiative balance gets disturbed because of the continuous addition of greenhouse gases in the atmosphere. As a result, we observe an increase in the earth's surface temperature and extreme changes in climate, rise in sea levels, and harmful effects on world agriculture. Since the past two decades, global emissions of carbon dioxide have risen by 99%, or on an average 2.0% for a year, and it is expected to rise by another 45% by the end of 2030, or increase in the rate of 1.6% per year.

2. History and evolution of chloro flouro carbons (cfc)

The emergence of chloro flouro carbons which are popularly known as CFC has not happened in a day. Natural refrigerants like water, carbon di oxide were used in

Sl.No	Year	Refrigerant	Comment
1	1930	—	Announcement of the development of Fluorocarbon refrigerant
2	1931	R-12	Commercial refrigerant
3	1932	R-11	Commercial refrigerant
4	1933	R-114	Commercial refrigerant
5	1934	R-113	Commercial refrigerant
6	1936	R-22	Commercial refrigerant
7	1943	R-11 & R-12	Developed to use as an aerosol propellants
8	1945	R-13	Introduced as a commercial refrigerant
9	1949	R-500	Patented by carrier corporation
10	1952	—	Manufacture of fluorocarbon refrigerants
11	1955	R-14	Introduced as a commercial refrigerant
12	1957- 1963	—	Production of fluorocarbon refrigerants started by other industries
13	1961	R-502	Introduction of R-502 in a commercial manner
14	1975	R-12 & R-13	Thermodynamic properties were established

Table 1.
History and evolution of chloro flouro carbons.

refrigeration and air conditioning industry in the past which did not impose any destructive effects to the environment and ozone layer. Later on, chloro flouro carbons were introduced by the company Dupon in the year 1930, as a result of remarkable developments in the refrigeration industry. CFC's were released to the atmosphere carelessly during service and repairing of refrigeration and air conditioning equipment. Then it reaches the topmost layer of the atmosphere and destroys the ozone layer, which leads to many harmful effects to humans, animals and crop cultivation. Below **Table 1** shows the brief history and the evolution of chloro flouro carbons.

3. Need of moving towards natural refrigerants

In early 1970s, scientists come to know about the hazardous impacts contributed to the earth's atmosphere by Chlorofluorocarbons (CFCs). CFCs were widely used as foams, refrigerants and thinners for many industrial applications. UV-B radiation which is passing through the ozone depletion areas from the sun can spread straight to the Earth's surface and will cause distinctive harms in the human cells, plants and animals. And this is because of the ozone layer destruction by CFC's. An international treaty was decided at Montreal, Canada, to ensure further damage of ozone layer. The outcome of Montreal protocol was to begin the phasing-out the usage of CFCs and other Ozone Depleting Substances (ODS) like Hydro chloro fluorocarbons (HCFCs).

Hydro fluoro carbons (HFCs) are considered to be one of the major, fastest growing, and most potent, greenhouse gases. In the past two decades, discharges of hydro fluoro carbons (HFCs) have been increasing swiftly. HFC's are the substitutes for chlorofluorocarbons and hydro chloro fluoro carbons (HCFCs). But stratospheric ozone is not destroyed by HFC's, but they are considered to be one of the effective greenhouse gases with a significant global warming potential (GWP) [1]. Many commercial refrigeration systems, such as beverage coolers, vending machines, ice cream freezers, open deck coolers and freezers used in hypermarkets

Refrigerant	ODP (ozone depletion potential)	GWP (global warming potential)
CFC	High	Very High
HCFC	Very Low	Very High
HFC	Zero	High
HC	Zero	Insignificant
CO_2	Zero	Insignificant
Helium used in Coolers	Zero	Zero

Table 2.
ODP and GWP of popular refrigerants.

use Hydro chloro fluorocarbons (HCFCs) and Hydro fluoro carbons (HFCs) gases as refrigerants. HCFCs are one of the ozone depleting agents and they have to be phased out as per the Montreal Protocol.

Even though the phasing out of CFC's are a great success in developed countries, there is still a delay in phasing out of HCFC's in the developing countries. There is a need of awareness among the general public about the safe use of fluorinated refrigerants and their adverse effects to our planet earth. Necessary training for the refrigeration and air conditioning technicians in the developing countries as this will ensure the safe recovery of these harmful refrigerants. There is a repeated history prevailing now in the use of natural refrigerants in the air conditioning industry. Because of the climatic changes and associated global warming problems, nowadays natural refrigerants are preferred in place of CFC's. In the present technology in the refrigerant sector, two ozone-friendly refrigerant technologies are available instead of CFC's: 1. Fluorinated refrigerants (HFC's) which are harmful to climate and 2. Natural refrigerants which not harmful to environment. So it is obvious and mandatory to move towards the use of natural refrigerants which have advantages on climate ozone layer. The **Table 2** as shown below present the ODP and GWP of popular refrigerants.

4. Green house gas emission

Green house gas emission is because of six potential gases. Green house gas emission in Oman during 2000's was around 30 million metric tons [2]. Refrigerant leakage can be a small quantity, but it can be a considerable source of greenhouse

Symbol	Name	Common Sources
CO_2	Carbon Dioxide	Resultant gas from combustion, manufacture of cement products, Etc.
CH_4	Methane	Landfills, manufacture and refining of natural gas and petroleum, fermentation from the digestive system of livestock, cultivation of rice, resultant gas from combustion, etc.
N_2O	Nitrous Oxide	Gas output from combustion, fertilizers, manufacture of nylon, manure, etc.
HFC's	Hydro fluoro carbons	Refrigerants, smelting of aluminum, manufacturing of semiconductor devices, etc.
PFC's	Fluorocarbons	Aluminum production, semiconductor industry, etc.
SF_6	Sulfur Hexafluoride	Transmissions and distribution of electrical systems, circuit breakers, production of magnesium etc.

Table 3.
Sources and properties of greenhouse gases.

gas emission. The below **Table 3** show the common sources and their properties which are responsible for the greenhouse gas emission.

5. Global warming potential

Carbon di oxide is considered to be the knob of earth's thermostat and it is an amazing tracer gas. Even a small change in the Co_2 concentrations makes a big difference to the global surface temperature [3]. Greenhouse gases have the properties of active radiative or heat-trapping nature. Comparing the properties of greenhouse gases, are done by indexing them according to their Global Warming Potential. The ability of a GHG to trap heat in the atmosphere comparative to an equivalent quantity of carbon dioxide is called GWP. Carbon dioxide has the value one (1), though the most prevalent, is the least powerful GHG. So, the greenhouse gases are expressed in carbon dioxide equivalents. The unit of GWP potential is million metric tons (MMTCDE) of carbon dioxide and greenhouse gas emission from an electrical appliance can be calculated by using the formula,

$$\frac{\text{Hours} \times \text{No.of days} \times \text{Watts}}{1000}\ \text{KWh}$$

$$\text{KWh} \times \text{Emission factor} = \text{Kg of } Co_2$$

Earth's life is protected from sun's harmful UV rays by ozone layer which is formed as a thin layer in the stratosphere. Ozone layer depletion was identified by the scientists during 1980. As a result of this, depletion of earth is likely to receive more amount of UV radiation, so that there is a strengthened chance of overexposure to UV radiation and the subsequent wellbeing effects. The below **Figure 1** depicts the formation and destruction of ozone depletion process. The sun's yield of UV B does not change. It is obvious that, less ozone means, more exposure of UV B radiation from the sun. The amount of UV B measured at the surface of Antarctic poles is two times during the annual ozone hole.

5.1 Mechanism of ozone depletion by CFC's

Ozone layer is destroyed in the stratosphere 15 to 20 Km directly above the earth surface by CFC's. Ozone concentrations are measured in Dobson units. 1 Dobson unit denotes 1 ozone molecule for every 1 billion air molecules. The meaning of ozone hole is the loss of ozone in a particular area. Greatest ozone hole is recorded in Antarctica continuously. The characteristics of ozone are, it is an allotrope of oxygen, and it is deadly to human beings if it is inhaled [4]. Human beings existence in the earth is very important and this is ensured by the protective layer ozone, as it filters or captivates ultra violet radiations which are usually short in wave length (280 – 320 nm). Ultra violet radiations can cause serious problems to humans such as sun burns, skin cancer, and eye disorders.

Figure 1.
Ozone formation and depletion process.

One of the chief characteristics of Chloro flouro carbons is, they do not dissolve in water and highly inert to water solubility. That is the reason they are not destroyed or dissolved even during in rain and stay in the atmosphere for many years and move slowly towards the stratosphere. The chloro flouro carbon molecules split off into chlorine atoms from the CFC molecules when they come in to contact with the ultra violet rays. The primary split of the CFC molecules are shown in the below equation.

$$CCL_3F(g) \xrightarrow{\text{UV radiation}} CCl_2F\ (g) + Cl_{(g)}$$

Ozone layer is destroyed particularly by these single chlorine molecules.

$$Cl\ (g) + O_3(g) \rightarrow ClO + O_2(g)$$

Considerable amount of oxygen atoms are present in the stratosphere, because it produces oxygen atoms regularly by go through photo chemical breakdown. This will lead to the renewal of chlorine atoms in the stratosphere. So a lone CFC molecule can dismiss many ozone molecules.

$$ClO\ (g) + O \rightarrow O_2 + Cl\ (g)$$

5.2 Photochemistry of ozone and Chapman's cycle for ozone loss

Ozone was first discovered by a German chemist, Christian Friedrich in the year 1939. Ozone present in the stratosphere is formed by the chemical reactions between oxygen and sunlight. The production of stratospheric ozone is because of the chemical reaction balance.

One ozone molecule is broken into one oxygen molecule and the remaining oxygen molecule is absorbed by the ultra violet radiation [5]. The photochemistry of ozone depends on the interaction of sun's radiation with the in atmospheric gases, particularly with oxygen.

A clear understanding of ozone layer was first assumed by Chapman in the year 1930. According to Chapman, when oxygen is hit by high energy photon, it is fragmented into two oxygen atoms. The below equation depicts Chapman's reaction.

$$O_2 + \frac{hc}{\lambda} = O + O$$

Where h = plank's constant.
C = Speed of light (wavelengths shorter than 242 nano meters)

$$\lambda = \text{wavelength of photon}$$

Ozone production by solar ultra violet radiation produce more amounts of ozone than the actual amount of ozone present in the atmosphere. The production of ozone is balanced by ozone loss.

$$O3 + O \rightarrow O2 + O2$$

5.3 Effects of ozone layer weakening

5.4 Effects on human health

UVB causes nonmelanoma skin cancer and plays a major role in malignant melanoma development and it is evident by many Laboratory and epidemiological studies. Also, UVB causes eye cataracts. In general, sunlight contains some UVB, even with normal ozone levels. And it is advisable that there should be always a limit to the exposure to sun.

5.5 Effects on plants and marine creatures

Even a small amount of UV B radiation present in the sunlight will cause an impact in the physiological and evolving processes of plants. Damages to early developmental stages of fish, shrimp, crab, amphibians and other animals are caused by UV B rays. Some of the most severe effects of UV B radiation exposure to plants and animals are decrease in their reproduction capacity and reduced larval development. Even a small increase in UV (B) exposure could result in significant reduction in the size of the population of animals that eat these minor creatures.

5.6 Hydrocarbons as refrigerants

CFC -12 is having high ODP and very high GWP. Promising substitutes for CFC-12 are hydro carbons which do not have any halogen compounds. The satisfactory characteristics of hydrocarbons are environmentally safe, energy efficient, technologically reliable refrigerants. Hydrocarbons arise naturally formed from solidified plant matter, and throughout the world initiate as oil and natural gas. Flammability is the characteristic feature of HC type refrigerants and it is the concerning point to be considered as a refrigerant in air conditioning and refrigeration systems, even though it exhibits very low GWP values [6].

Lower paraffin's such as propane, butane, and isobutene were successfully used as refrigerant before the arrival of CFCs. The thermodynamic properties of the hydrocarbons are much better than any of the other alternatives to CFC's. Hydrocarbons are available at low price all over the world and are compatible with commonly used lubricants and materials of construction used in refrigeration systems. Hydrocarbons are very economical and they are readily available in most parts of the world.

6. Phase change materials as refrigerants

Using phase change materials in air conditioning systems can be an effective method for improving the process of cooling as well as minimizing the size of the system. The nature of phase change materials is they will absorb, store and release large amount of heat. Generally, the temperature of PCM increases with the increase in the ambient temperature. Researchers conducted various studies in using phase change materials for the use in air conditioning systems. Co_2 emission and power consumption of the systems using phase change materials are better in comparison with the conventional systems [7]. Around 7% of electrical power consumption reduction was observed in the air conditioner designed by Nataohorn Chaiyat and Tanongkiat Kiatsiriroat with PCM bed in comparison with the normal air conditioner [8]. During the transition period, the PCM melts and so absorbs heat. A reverse process happens when the PCM temperature is decreased [7]. Thermodynamic properties of CFC and Hydrocarbons are mentioned in the below **Table 4**.

6.1 Applications of PCM

1. **PCM used in wall systems:** PCM's have been successfully used in the middle layer of the wall systems and it is evident from many studies. PCM embedded in the wall systems can reduce the indoor air temperature up to 4.2°C [9].

Refrigerant	Critical temp (°C)	Boiling temp (°C)	Density (kg/m^3)	Heat of vaporization (kj/kg)
Propylene	91.4	−47.8	1.955	440.16
Propane	96.8	−42.1	2.019	425.92
I-Butylene	146.6	−6.3	2.550	391.58
Isobutylene	144.7	−7.0	2.500	397.02
Isobutene	135.0	−11.7	2.668	366.03
n-Butane	152.0	−0.5	2.703	387.81
R-12	112.0	−29.7	6.240	166.0

Table 4.
Thermodynamic properties of CFC and hydro carbons.

2. **Better energy performance in air conditioners:** Energy reduction in air conditioners can be achieved by using paraffin wax as a phase change material. A previous study reveals that the PCM temperature and the temperature of the air leaving the PCM bed were satisfactory around 2.73% and 4.61%, respectively. The cost of electricity saving of the improved system was about 9.10% when compared with the standard system [10].

3. **Use of phase change materials in refrigerators:** A refrigerator was designed and developed by Azzouz et al. and it was observed that, the compressor running time was decreased about 25% when compared with the conventional systems.

4. **Latent heat thermal storage:** Phase change materials are used widely for the latent heat storage systems in heat pumps, solar energy systems etc.

5. **Medical Industry:** In medical field, the energy storage characteristics of PCM is used for transporting blood, and hot & cold therapies [11]

6. **PCM used for energy efficient housing:** PCM's are widely used for energy efficient housing applications. Thermo-chromic PCM's are used as window coatings for better visual performance. Solid to liquid PCM's are used for the latent thermal energy storage and constant temperature applications [12].

7. Application of hydrocarbons as a refrigerant in commercial refrigeration systems

Worldwide attempts are being made to eliminate the use of Chloro-fluorocarbons (CFCs) because chlorine released from CFCs migrates to the stratosphere and destroys the stratospheric ozone layer. An international treaty known as Montreal Protocol was formed to regulate the production and trade of ozone-depleting substances. Sultanate of Oman is one among the signatories of the Montreal Protocol. During July 2003 a workshop was organized by Ministry of Regional Municipalities, Environment & Water Resources in collaboration with the UNIDO and UNEP at Muscat to train the trainers to phase out the CFCs in Sultanate of Oman. The author was also one of the participants of the workshop. After the workshop it is felt to review the available literature of the various refrigerants, especially hydrocarbons, as alternative to CFCs and hence this article. This article is primarily intended to provide a brief summary about completed /going on works during the last toe decades to use hydrocarbon as refrigerants in commercial refrigeration systems.

Among the commonly used CFCs, **dichlorodifluoromethane** (CFC-12) is one of the most widely used refrigerants in various applications such as Domestic Refrigerators, Bottle, Coolers, Deep Freezers, Water Coolers, and Mobile Air Conditioners etc. The excellent characteristics of CFC – 12 have lead to the development of highly efficient and reliable compressors and other refrigeration system components. Studies have shown that these refrigeration appliances give satisfactory performances for approximately 15 to 20 years. This high degree of reliability has caused the consumers to expect long services from these appliances in general. This necessitates extensive evaluation of alternative refrigerants before adopting them for commercial use. **The ideal substitute for CFC-12 should be non-toxic, non-flammable, chemically stable, compatible with refrigeration system materials and lubricants and have transport and thermodynamic properties similar to or better than CFC-12.** In addition, the ideal substitute should have zero Ozone Depleting Potential (**ODP**) and low Global Warming Potential (**GWP).** However, there is no such single substance, which possesses all these properties.

Though, the CFCs were characterized in 1890, but the development of fluorocarbon refrigerants was announced in 1930. Since then CFCs never looked back. Some of the historical highlights in the progress of refrigeration and the development of refrigerants are outlined in **Table 5**.

The prevalent refrigerants and refrigerant mixtures from halogenated hydrocarbon family in use are R-11, R-12, R-13, R-14, R-22, R-113, R-114, R-500 and R-502. In developed countries various steps have been already taken to control the use of ozone depleting refrigerants**.** In developing countries conversion from CFCs to alternatives is still a major issue.

S.#	Year	Refrigerant	Comment.
1	1930		The development of Fluorocarbon refrigerant was announced.
2	1931	R-12	Introduced as a commercial refrigerant.
3	1932	R-11	Introduced as a commercial refrigerant.
4	1933	R-114	Introduced as a commercial refrigerant.
5	1934	R-113	Introduced as a commercial refrigerant.
6	1936	R-22	Introduced as a commercial refrigerant.
7	1943	Mixture of R-11 & R-12	Developed to use as an aerosol propellants
8	1945	R-13	Introduced as a commercial refrigerant.
9	1949	R-500	Patented by carrier corporation
10	1952	—	Manufacture of fluorocarbon refrigerants started by Allied Chemical Corporation.
11	1955	R-14	Introduced as a commercial refrigerant.
12	1957,1958, 1963		Manufacture of fluorocarbon refrigerants started by other companies.
13	1961	R-502	Commercial Introduction of R-502
14	1975	Mixture of R-12 & R-13	Establishment of thermodynamic properties over the whole range of composition.

Table 5.
Historical development of refrigerants.

As per the recent guidelines from the Environment Protection Agency USA, phasing down of HFCs and manufacturing of alternate refrigerants to CFCs and HFCs is the most significant environment policy to be practiced globally [13].

Montreal Protocol asks for abandoning the use and production of ODS in phased manner. It currently has the following control schedules for chemicals used as refrigerants:

- a phase out by 1.1.1996 of CFCs in the developed countries.
- a grace period until 2010 for a CFC phase out in the countries operating under paragraph 1 of Article 5 (the developing countries), with a freeze in 1999 and gradual reduction steps thereafter.
- a HCFC control schedule for the developed countries which requires gradual phase out of HCFCs over the period 1996 – 2020 (a freeze in 1996, a virtual phase out by 2020, a complete phase out by the year 2030), based upon a cap of 2.8% of the 1989 CFC consumption and the 1989 HCFC consumption (in ODP- tones);
- a HCFC control schedule for the developing countries, which lags that of the developed countries by 10 years.

The Montreal Protocol does not address non-ozone depleting chemicals According to Mc Linden over thirty years of research and development will be required to arrive at and maintain the family of refrigerants which are being used today.

Global action plans and the action plans to reduce the use and step by step phasing out of HFC type refrigernats was agreed by all the countries under the 2015, Paris amendment. In the year 2016, in Kigali, Ruwanda, around 197 countries had accepted for an amendment for the phasing down of HFC type refrigerant which was recommended by the Montreal Protocol. Phasing down of HFC type refrigerants has to be completely executed within the next 30 years [13].

8. HFC 134A: Present day refrigerant

HFC-134a (Tetra fluro ethane) presently is the leading candidate to replace CFC-12. The main culprit chlorine atom is absent in the molecule of HFC-134a, hence this substance provides excellent chemical and thermal stability, significantly better than CFC-12.It has got zero Ozone Depleting Potential (ODP) and Global Warming Potential (GWP) of 0.115. All toxicological studies on HFC-134a have been completed including one-year inhalation study with favorable results. Wilson et al. conducted a detail study and reported the thermodynamic properties of HFC-134a. The thermodynamic properties of HFC-134a are very much similar to CFC-12. Normal boiling point (NBP) of HFC-134 a is – 26.8 deg. C which is very near to normal boiling point of CFC-12 (−29 .8 deg. C). McLinden considered the use of HFC-134a to be the most realistic refrigerant to CFC-12. Thermal conductivity and viscosity were measured over a temperature range temperatures and reported by Shank land et al. Lot of research works were carried out on different aspects of using HFC134a as a real substitute to CFC12. The use of oil in HFC 134 a systems requires a very stringent quality control. Some researchers reported that HFC-134a has been proved as a fully reliable refrigerant in retrofitting CFC-12 systems including centrifugal chillers, semi-hermetic reciprocating and screw compressors and HFC-134a is not the most suitable option for the hermetic systems.

Boot in his paper “Overview of Alternatives to CFCs for Domestic Refrigerators and Freezers” concluded that alternatives beyond HFC-134a must be considered owing to the inefficiency of HFC-134a when used in a refrigerator. Vineyard et al. performed tests with HFC-134a in a standard household refrigerator and concluded that HFC-134a consumes more energy than that of CFC-12. From the thermodynamic data, it can be estimated that HFC-134a has a lower capacity and operates at lower suction and higher discharge pressure than CFC-12 for the same evaporating and condensing temperatures. Based on this information, a larger compressor would be necessary to achieve capacities equivalent to those obtained with CFC-12.

9. Hydrocarbons as refrigerants

Hydrocarbon refrigerants, which do not contain any halogen atom, are promising substitute for CFC-12. Hydrocarbons are environmentally safe, efficient, and technologically reliable refrigerants and insulation foam-blowing agents. Hydrocarbons are naturally occurring substances formed from fossilized plant matter, and found throughout the world as oil and natural gas. Lower paraffin's such as propane, butane, and isobutene were successfully used as refrigerant before the advent of chlorofluorocarbons**.** The thermodynamic properties of the hydrocarbons are much better than any of the other alternatives known. (Refer the **Table 4**). Hydrocarbons are available at low price all over the world and are compatible with commonly used lubricants and materials of construction used in refrigeration systems. Hydrocarbons are relatively cheap to produce and they are readily available in most parts of the world.

The need to find substitutes for CFCs during the 1990s has led refrigeration industry back to using hydrocarbons which have no impact on the ozone layer and insignificant contribution to global warming. Since 1992, hydrocarbon refrigeration has become the technology of choice in many domestic markets in Western Europe. In Germany, 100 per cent of the industry has already converted to hydrocarbon technology. All of the major European companies, such as Bosch/Siemens, Electrolux, Liebherr, Miele, Quelle, Vest frost, Whirlpool, Bauknecht, Foron, and AEG are selling hydrocarbon refrigerators. They are available in many sizes, and a wide variety of models, including some with no-frost freezer compartments. There are over 100 different hydrocarbon refrigerator models on the European market.

The main drawback of these refrigerants is their high inflammability, which has prohibited their use. But modern innovations have greatly improved the safety of hydrocarbon technologies. Besides due to very low charge of hydrocarbons (the amount of propane or butane in a domestic hydrocarbon refrigerator is only 40 to 60 g equivalent to two to six cigarette lighters, depending on the size of the refrigerator) in small capacity refrigeration system inflammability does not present a problem The present level of technological development and safety measures available have made it possible to use hydrocarbons as working fluids in domestic refrigerators. Most consumers in Southern countries are already familiar with hydrocarbons in the form of LPG (liquid petroleum gas a propane and butane mix), as it is widely used for cooking in the home. According to Pearson of Star Refrigeration over 50 million refrigerators using hydrocarbon as a refrigerator have been produced and not a single accident due to flammability was reported. The main motivation to adopt hydrocarbons in spite of their high inflammability is their being **eco-friendly**. The hydrocarbons do not destroy ozone layer and their GWPs are hundred times lower than that of CFCs and ten times lower than other CFC substitutes. Among hydrocarbon pure fluids, propane and isobutene are finding much attention as a substitute to CFC-12 in recent years [14].

9.1 Propane (HC-290)

Propane has been tested in the small capacity refrigeration systems. Propane can be considered as an alternative for HCFC-22.The high latent heat requires low refrigerant charge in the system. The performance of propane is comparable to CFC-12 and HCFC-22 and considered to be better than HFC-134a. Granryd et al. designed a heat pump prototype with propane as refrigerant as an alternative to HCFC-22. Use of HFC 134 (a) will be decomposed as acids and poisonous substances, which is worse than the use of CFC. So use of natural refrigerants like hydro carbons was suggested by Lorentzen [6].

9.2 Cyclopropane (HC-270)

Cyclopropane is also a promising refrigerant for domestic refrigerators. Kim et al. carried out simulation and experimental studies using HC-270 as a refrigerant in a single evaporator refrigerator and found encouraging results with respect to energy consumption. It was reported that cyclopropane results in lower energy consumption by 6 to 7% and 17% increase in volumetric capacity as compared to CFC-12 single evaporator refrigerator.

9.3 Isobutane

Isobutane exhibits a higher normal boiling point (−11.85 deg. C) compared to CFC-12 (−29.8 deg. C) and requires about 80% larger displacement volume in the compressor than CFC-12 to obtain an equivalent cooling capacity. Ray Riffe et al. investigated the use of isobutane as a refrigerant in refrigerator/ freezer with the use of dual cycle (D.R, 1995). His conclusions were

- For same refrigeration capacity, the amount of charge required by isobutene is 50% less than that of CFC-12.

- In order to achieve the same cooling capacity as that of CFC-12, compressor is to be replaced with a larger displacement compressor.

- Suction pressure (gauge) is slightly negative.

- Noise level of Isobutane refrigerator is much lower in comparison to CFC-12, and Isobutane results are quite encouraging.

From the above discussion it is quite apparent that there are **limited numbers of pure fluids that can function as substitute for CFCs.** mixing of refrigerants allow adjustments or tuning of the most desirable properties to provide suitable alternatives. Of course, other properties are also altered and thus the craft of developing a mixture is to obtain a final fluid with all desirable properties in the operating range. Mixtures provide a flexibility of modulating the capacity by varying the composition of the constituents. Refrigerant mixtures are solutions, i.e. they have constituents, which are equally dispersed and cannot be mechanically separated. There are three categories of mixtures.

9.4 Azeotropes

Azeotropes are also known as constant boiling point mixtures. This class of refrigerant mixture **behaves as if it were a single component during its phase change** (In the phase change the proportion of each constituent in the new phase is the same as in the original phase). Azeotropic mixtures usually behave like a fluid. This property is of great use when the refrigerant mixture leaks and it has to be recharged. However, the recharging of Non Azeotropes is much more complex [15]. The advantage of using Azeotropes as refrigerants is that, during leak in one of the components, it does not change the composition of the remaining refrigerant. Since the composition of an azetropic mixture is produced is a role of temperature, no true azeotropic mixtures be present in refrigeration. But the composition change of the azeotropic mixtures is very small. Azeotropic mixtures have been very commonly used in refrigeration, such as cold storage. Refrigerant R 502 is a mixture of R 22 and R 152 (a). R 410 (a), is a mixture of R 32 and R 125 is an important non-ODS azeotropic mixture used in place of R 22.

9.5 Near azeotropes

Azeotropes rigorously exist at only one composition for given temperature and pressure. However for all practical purposes, minor deviations are acceptable for many refrigerant systems. For this broader range the term 'Near Azeotropic Mixture' (**NEARM**) is used. The advantage of utilizing this category is that many more possible alternatives become available.

9.6 Non-azeotropes

Non – Azeotropes are also called as zeotropes. A zeotropic blend is also a combination of two or more components. The components of this refrigerant have diverse boiling points. These components will evaporate and condense at unlike temperatures. In order to fully understand zeotropic blends we must also understand fractionation and glide [16].

Non-Azeotropes, which change their composition continuously during phase, change. These mixtures do not possess a sharp boiling point but boil over a range of temperature. This feature is intimately tied to the improvement of system's efficiency if appropriate hardware changes are made to the system heat exchangers. The change of temperature with phase change is called Temperature Glide.

When heat transfer fluids exchange heat with Non Azeotropic Refrigerant Mixtures (NARMs) in a constant current flow mode, the thermodynamic irreversibility can be reduced by matching the temperature glide (NARM side) against the temperature drop (Heat Transfer Fluid side) resulting in an increase in the coefficient of performance.

As already stated, because of limitation of single fluids as alternative to CFC-12 and also the flexibility in modulating the capacity by varying the composition of the constituents, mixtures are emerging as a viable solution to CFC-12 alternatives.

10. Mixtures of propane and isobutane

Propane and Isobutane will combine pretty happily as both are non-polar. Butane molecules will be broken and are replaced by the molecules of butane and Propane molecules. Propane-isobutene mixture has the benefit of modulating the capacity to permit their use with compressor designed for use with CFC-12. The binary mixture ratio can conceivably be designed using boiling point as a guideline such that the disparate requirements of the freezer and the fresh food compartment in domestic refrigerators can be balanced. The normal boiling point temperature for HC-290/ HC-600a mixture (each 50% by mass) ranges from −32 deg. C to −24 deg. C which is very close to normal boiling point of CFC-12 [17].

The mixture in comparison to CFC-12 possesses very high latent heat of vaporization and low value of density (1/3 of CFC-12), which makes the mixture attractive because of its low charge requirement and circulation rates. The charge levels are approximately 40% that of CFC-12. One of the important advantages of

R-600a/ R-290 blends is that it is compatible with mineral oils and commonly used materials for manufacturing of refrigeration systems and requires minimal changes in the refrigeration systems. The mixtures do not contain any halogen atom and hence the possibility of forming acids in the presence of moisture is eliminated [6].

This is also a factor for better stability of these mixtures. **Table 4** shows the thermodynamic properties of few hydrocarbons and CFC-12. It follows from **Table 4** that pure hydrocarbons cannot be exact alternative to CFC-12. Meyer conducted experimental investigation with the use of hydrocarbon refrigerants for domestic refrigerators. It was found that an unchanged CFC-12 single temperature refrigerator had lower energy consumption with a refrigerant mixture of 50% propane and 50% isobutene compared to CFC-12. Based on these encouraging results FORON decided to develop single temperature refrigerators using hydrocarbon mixtures as refrigerants. This was the beginning of use of hydrocarbon mixtures as refrigerants in domestic refrigerators. Domanski et al. carried out a study of hydrocarbon refrigerants for residential heat pump systems and concluded that these mixtures were promising substitute. He examined the various benefits and discussed the Rankine Cycle System and component design issues and limitations when using a wide range of single component refrigerants, hydrocarbons, with the help of the READER code for residential size heating and cooling systems (Domanki, 1994).

Liu et al. (1994) conducted an experimental test with propane-isobutane as a drop in substitute in a domestic refrigerator/freezer unit. They kept all hardware components of the refrigerator/freezer as that of CFC-12 except the capillary tube, which was, lengthen to control the flow rate. They concluded that highest savings of 6.5% were achieved with a blend of 70% HC-290 and 30% HC-600 with a charge of 70 g.Kruse performed a theoretical evaluation of hydrocarbons and its mixtures as refrigerants in refrigerators, unitary air conditioners and heat pumps. He concluded that in general, **hydrocarbons have an inherent possibility of lower energy consumptions.** He also mentioned that refrigerators with hydrocarbons mixtures as refrigerant shows further possibility of energy improvement if they are designed by using Lorenz-Meutzner cycle. The major drawback of these mixtures, like other hydrocarbons, is the high inflammability. But the charge is only 1/3 to ½ that of CFC 12. Owing to the fact, inflammability does not pose a problem. However, proper safety precautions should be taken at different stages of manufacturing, charging and operating (Cichong Liu, 2016).

When the Montreal Protocol has phased out CFCs in the developed countries and has a regulatory regime for the phase out of HCFCs, the problem still is a major problem in developing countries. Awareness is to be created among the common people to save the planet earth. Developing countries should phase out ozone depleting chemicals in a very careful manner.

Global market will continue to develop & introduce new refrigerant chemicals. Statutory requirement is necessary to control the UN –organized sector who are dealing in HVAC industry.

11. Economic impact of the alternative refrigerants against cfc refrigerants

Every human being or a machine has a value. Mechanical machines are designed, fabricated and manufactured with different materials, and so cost is incurred for the manufacture of all the machineries. Almost all the residential air conditioners are vapor compression systems, which uses compressors. Compressor is the main component in any air conditioning system, and so it is the costliest component in an air conditioning system. Other components and the type of refrigerants used in the air conditioning systems will also contribute significantly to the total cost of the air conditioning system. The cost of one ton window air conditioner as an example is shown in the below **Figure 2**.

11.1 Cost analysis

Cost incurred in the design and fabrication of constructal designed window air conditioner is shown in the below **Figure 3**. Here, the compressor was replaced with a pump and so the major part of the cost is reduced. Also the refrigerant materials, phase change material and water were industrial waste from the refineries and natural resource respectively.

CFC type refrigerants were used in window air conditioners, and now it is is completely phased out and replaced with HFC type HC (Hydro carbon) type refrigerants. It is difficult to fill in these refrigerants in the same system which used CFC type refrigerants. The system needs lot of design changes and the air conditioning service technicians carelessly releases the harmful CFC gases into the

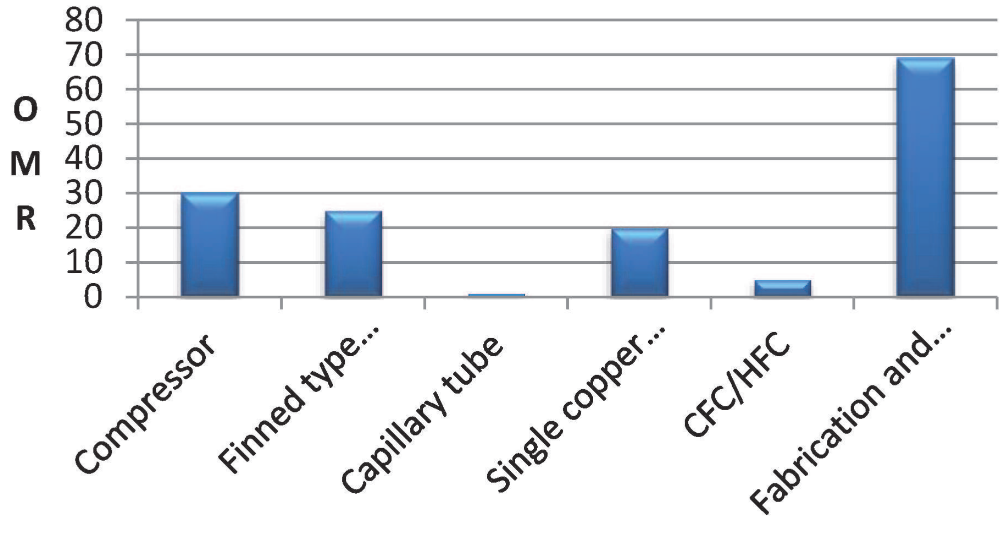

Figure 2.
Cost of one ton of window air conditioner.

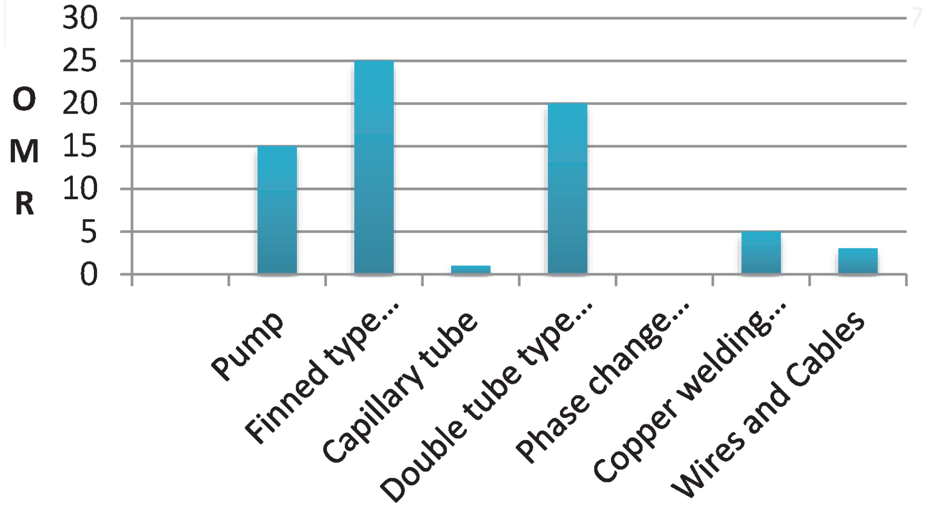

Figure 3.
Cost of Constructal designed window air conditioner.

Sl. No	Refrigerant name	Cost in INR	Cost in OMR	Cost USD
1	R134 (a)	Rs 390/Kg	R.O 2.02/Kg	USD 5.96/Kg
2	R 22	Rs 380/Kg	R.O 1.97/Kg	USD 5.13/Kg
3	R 404	Rs 400/Kg	R.O 2.08/Kg	USD 5.39/Kg
4	R 410 (a)	Rs 350/Kg	R.O 1.82/Kg	USD 4.72/Kg
5	R 32	Rs 395/Kg	R.O 2.05/Kg	USD 5.33/Kg
6	R 600 (a)	Rs 1000/Kg	R.O 5.19/Kg	USD 13.49/Kg
7	R414 (b) Hydrocarbon Blend	Rs 1250/Kg	R.O 6.49/Kg	USD 16.86/Kg
8	Phase Change Material	Rs 30/Lt	R.O 0.16/Kg	USD 0.40/Kg

Table 6.
Cost of refrigerant materials.

atmosphere. So, it is a good opportunity to retrofit the old window air conditioners with non CFC refrigerants. The total cost incurred for the fabrication of constructal designed window air conditioner was found to be around R. O 70/−, which was very much lesser than the normal vapor compression type window air conditioner. Cost can be further reduced by using the thrown away air conditioners and using the condenser and evaporator coils.

11.2 Cost of alternate refrigerants

Cost of refrigerants as per the current selling prices in the refrigeration and air conditioning markets in Oman and India are presented below. Phase change materials can be extracted from the industrial waste from the petroleum refineries. Hence, there is a huge potential to recycle the industrial waste and thereby contributing indirectly to safe environment (**Table 6**).

12. Summary

Refrigerants are the key substances used in all the conventional refrigeration and air conditioning systems. Refrigerants rub though out the system and removes heat by changing its phases during the course of operation. Use of refrigerants evolved from the day of first refrigeration and air conditioning equipment. Air, carbon dioxide, ammonia, sulfur dioxide were used as refrigerants during the early day air conditioning systems. But because of the need in very low temperature applications and human comfort conditions, different artificial refrigerants were came into use. Significant artificial refrigerants are chloro flouro carbons (CFC), Hydro flouro carbons (HFC). Though the temperature produced by these refrigerants are very good for wide applications in residences and industries. But they contribute indirectly to the ozone layer damage and global warming.

To ensure the safety of environment, use of CFCs are banned and to be phased out completely as per the guidelines by Montreal Protocol. Even though, phasing out of CFCs and HFCs are not happening in developing countries, and so the threat to the environment continues. This chapter, introduces the use of phase change materials) PCM) as a potential refrigerant in air conditioning systems. Since phase change materials are thrown as waste byproducts from the petroleum refineries, use of PCMs in air conditioning systems will be additional contribution for the safety of environment.

Nomenclature

cfc = chloro flouro carbon.
hc = hydro carbon
ac = air conditioner
k_{eff} = effective thermal conductivity
q_{pc} = heat flux
r_c = radius of centroid
α = void fraction
μ = viscosity of fluid
ρ = density of fluid
mmtcde = million metric tons of carbon dioxide equals
gwp = global warming potential

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