Eco-Friendly Refrigerants as Substitutes for HFC134a - a Review

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Abstract

In developing country like India, most of the VCR systems based on halogenated refrigerant are used due to its excellent properties. How-ever, the halogenated refrigerants having adverse environmental impacts such as ODP and GWP. Hence conversion of such systems to eco-friendly ones will be a major thrust area for refrigeration sector in the time to come. As and when an existing system of R134a has to be recharged it is suggested to retrofit the system with new/natural and alternative refrigerants to full fill the objectives of the Montreal and Kyoto protocols. Presently, hydrocarbon mixtures and pure hydrocarbons are available in market to replace R134a, but the optimum ratio and mass fraction to be used for better and safe performance of the system is given by only few researchers. This paper reviews the various theoretical and experimental studies carried out around the world with eco-friendly HC and HCM refrigerants, which are going to be the promising alternatives. The problems with HCM refrigerants when they use as a retrofitted are also analyzed.

Keywords — *Environment friendly Refrigerant, R134a, HCM.*

I. INTRODUCTION

Refrigeration is defined as any process of heat removal from a particular space. More specifically, refrigeration is that branch of science which deals with the process of decreasing and maintaining the temperature of any space or material below the temperature of the atmosphere[1]. According to ASHRAE, it is defined as the science of providing and maintaining temperature below that of surroundings [2].

Since the first vapor compression refrigeration system made by Jacob Parkins in 1834, a large number of chemical substances have been tried and tested as working fluids or refrigerants. Starting from ethyl chloride, ammonia, carbon dioxide, sulphur dioxide, methyl chloride, propane, iso-butane and water, the industry developed gradually, but a great breakthrough occurred with the invention of the dichloroflouromethane substances in 1930 by Thomas Midgley and Albert Henne. By then, the family of chemicals that included chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) became the most dominant types of refrigerants due to their properties of non- corrosiveness, non-flammability, non-toxicity and non-irritability[3].

Air conditioning and refrigeration applications at domestic, industrial and commercial levels are becoming an essential part of present day living. Refrigeration and air conditioning system requirements are increasing day by day with the changing lifestyle. The accelerated technical development and economic growth of most countries during the last century have resulted in recognition of the fact that man-made products contributing to human comfort have side effects threatening our health and harming the environment; due to global warming and ozone depletion. In addition it was also found that these refrigerants were significant greenhouse gases. These concerns are the biggest reasons for recent technical innovations in the field of refrigeration and air conditioning [4]. Chlorofluorocarbons (CFCs) and Hydrochlorofluorocabons (HCFCs) have been used in refrigerators and air conditioners as a working refrigerant as well as blowing agents in foam. CFCs and HCFCs are now being regulated because of ozone depletion. Hydroflourocarbons (HFCs) can be short and mid-term replacements, but may not be permanent due to their high global warming potential (GWP) [5]. The need to find a long term solution calls for the use of natural refrigerants. The refrigerator and air-conditioning industries have started to address the future challenges. Within limited time the HCFCs including R-22 will also have to be substituted.

Montreal protocol (MP) on substances that deplete ozone layer was established to phase-out the production and consumption of ozone depleting substances. The Kyoto protocol (KP) in 1997 has decided to put HFCs together with other five gases such as CO_2, N_2O, CH_4, PFCs and SF_6 in one basket of controlled substances [6]. Alternative refrigerants to CFC-12, are HFC-152a, HFC-134a, MP66/39, HC-290/600a etc. HFC-134a is non-flammable and has zero ozone depletion potential but serious GWP. Hydrocarbon refrigerants are flammable. They have zero ozone depletion potential and a greenhouse warming potential approaching zero. Many researchers have reported performance evaluation of hydrocarbon mixtures by both experimental and simulation methods[1-5].

II. COMMONLY USED REFRIGERANTS

A. Air (molecular weight 28.97)

Air is one of the refrigerant which used from ancient time in refrigeration systems and approximated as a perfect gas. Its COP is of the order of 0.6 and thus not suitable for refrigeration system on commercial scale. It is generally used for aircraft air conditioning, where efficiency is not of much importance[10,12].

B. Ammonia (molecular weight 17, NH_3)

It is one of the oldest refrigerant which was commercially used in places where, toxicity is secondary. Its boiling point -33^oC at atmospheric pressure, COP is of the order of 4.0 and it gives higher refrigerating effect per unit mass of the refrigerant. It is inflammable. It is cheaper in cost and as low specific volume. Recent new applications of ammonia involve small direct-expansion systems for supermarket refrigeration, water chillers and heat pumps for air conditioning of residential buildings; all of them are closed indirect systems[2,12].

C. Carbon dioxide (CO_2 - molecular weight 44)

Excellency of CO_2 is its low boiling point which makes its suitable for low temperature refrigeration. Critical temperature is 31^oC, due to which it is unsuitable for use in countries like India, because of hot climate and its critical pressure is too high. The coordinates of the critical point also indicate that, when working with CO_2, the pressure levels are far higher than in conventional systems. This required the development of suitable components. Carbon-dioxide has been successfully used in a prototype automotive air conditioner (an application with high relative direct global warming impact when using HFC134a), and excellent prospects are also predicted in commercial refrigerating units with associated tap-water heating, and in high-temperature range heat pumps. It is not only non-flammable but also works as fire extinguisher. It is stable and immiscible with lubricant oil [1,12].

D. Halocarbon refrigerants

The halocarbon compounds are obtained after replacing one or more hydrogen atoms of hydrocarbon substances i.e. ethane or methane by one or more halogens i.e. chlorine, fluorine and bromine. They are in general non flammable, non toxic and stable refrigerant but they are not environmental friendly. Some of the refrigerants coming under this category are following:

1. Refrigerant-12 (CCl_2F_2)

It was most widely used refrigerant in the domestic and large commercial establishments. It is discontinued now-a-days due to its contribution to ozone layer depletion [2].

2. Refrigerant-13($CClF_3$)

R13 have positive pressure even at low temperature i.e.193 K. R13 having higher specific volume and it is suitable for centrifugal compressors. Low temperature can be achieved by R13 in cascade refrigeration system [2,9].

3. Refrigerant-22($CHClF_3$)

R22 is more soluble in water than R12. It is very common refrigerant for the large refrigeration system and is preferred than that of R-12. Today it is used in packaged air conditioners and liquid chillers. But due to environmental reasons it will be obsolete from Indian refrigeration industries up to 2020 [1,2,8].

4. Methyl-Chloride(CH_3Cl_2

Its boiling point corresponding to 1 bar is about 249 K, melting and critical points are 176 K and 416 K respectively. Since it is a poisonous refrigerant so used carefully. It is very toxic and irritating refrigerant. It requires larger size drier than that of R-12 [8,12].

E. Hydro-fluorocarbon (HFC) refrigerants :

Refrigerant-134a (R134a): R134a is a member of the family of HFC refrigerants that were virtually unused prior to 1990. The HFC family is similar in composition to CFC's and HCFCs, they have become the primary focus of the refrigeration industry as a long-term substitute for traditional refrigerants. HFCs are not miscible with traditional mineral oils so alternative synthetic lubricants are recommended, synthetic polyester (POE), either alkyl benzene (AB) or polyalkylen glycol (PAG) being the recommended lubricants. R134a has been at the forefront of HFC development, it operates at similar pressures to R12 and is compatible with most materials and is considered to be a reliable retrofit for R12 chillers. It has also been used as a component in refrigerant mixtures[9].

1. Pure fluorinated hydrocarbons (R152a)

R152a was another potential replacement candidate for R12. It has very low global warming potential (GWP) values compared to other candidates. The flammability of R152a compared to non-flammability of R134a is a major drawback. Theoretically, it is expected that the energy consumption of R152a is about 3-4% lower than that of R134a. However, experimental results shows that the measured performance of a refrigerator charged with R152a and that of an equivalent system charged with R134a (with the same compressors energy efficiency ratio, EER) did have essentially the same performance. It was confirmed that the ester oils have good miscibility, insulating characteristics and reliability in durability tests. However, the flammability aspect together with the liability concerns of refrigerators manufactures as not led to an application of R152a[11].

2. Refrigerant R404A

It is a mixture of hydrofluorocarbon (HFC) substances. It consist of 52 wt. % R143a, 44 wt. % R125 and 4 wt. % R134a and form nearly azeotropic mixture. It is designed to replace R22 and R502 CFC refrigerants. Its boiling point at normal pressure is -46.5°C, its liquid density is 0.485g / cm^3. An additional alternative for those same systems could be the R404A blend, a very low–glide mixture with properties close to those of HCFC22 and therefore requiring minor redesigns. However, one possible drawback is its high GWP index value; TEWI value should be given higher priority. As with all mixtures containing HFC125, a loss of efficiency may be experienced at high condensation temperatures, due to the low critical temperature of this mixture component[12].

F. *Hydrocarbons*

Hydrocarbon consist carbon and hydrogen atoms and form colorless fluid which is in the gaseous state. The refrigerants of this category are more suitable for low temperature application. The use of hydrocarbons in new sector are confined to simple, hermetically sealed systems with a limited charge and operating at non sub-atmospheric pressure. In these applications, the charge of hydrocarbons is limited to approximately 50 g. In single-temperature and three-star refrigerators the energy consumption compares favorably with appliances using HFC13a. Hydrocarbon refrigerants are flammable and highly explosive when they exposed to air. They are non poisonous, but are anesthetics in varying degrees varying from ethane to propane. They also affect rubbers so, sealing is major problem with them. The same composition is also related with the molecular weight of individual fluids. In the commercial sector, some systems are being converted to indirect ones which enable use of hydrocarbons (or ammonia) in the remote machine-room under appropriate safety conditions. Another possibility currently under investigation involves use of indirect ammonia systems with normal brines directly supplied to the medium-temperature cabinets, while the low-temperature cabinets work with individual's propane systems whose condensers are cooled by the brine circuit. In certain countries such as USA, the attitude towards flammable refrigerants is exactly the opposite; in fact they are not pursued due to potential liability exposure[7,12,13,38].

1) ***Refrigerant-Iso-butane (R600a)* :**

R600a is an organic compound. It has been reported that R600a (HC600a) could be used as an additive to tackle the oil return problem in the evaporator. Hydrocarbons have taken over from R134a for domestic refrigerators in certain parts of the world. The most commonly used hydrocarbon is isobutene [CH $(CH_3)_3$]. Iso-butane (R600a) is a surprising choice because of the large volumetric flow required but the high critical temperature 135°C and low cycle pressures combines to produce a very quiet and efficient system. The safety records as been excellent[12,14,22].

2) ***Refrigerant-Propane (R290)***

R290 is the industrial designation for propane as a refrigerant. Hydrocarbons have been used extensively in the early years of refrigeration but a number of technical and safety issues caused them to be abandoned when CFC refrigerants became available. They are compatible with the materials and lubricating oils used in conventional refrigeration's systems. Hydrocarbons have excellent properties as refrigerants they naturally exist in the atmosphere and have neither ozone depletion potential nor significantly global warming potential. In 1991 a German manufacturer Foron announced a range of hydrocarbons based refrigerators and by 1996 almost the whole of the German market in refrigeration units are based on the new Green Freeze technology. The British company Calor Gas supply hydrocarbons under the trade name CARE. The most important issue regarding hydrocarbons as refrigerants is their flammability; some claims have been made regarding the explosion hazard of hydrocarbon refrigerants as horrendous even in systems with small cares such as domestic refrigerators. This has been countered however by the work of James and Missenden, who tested several refrigerators, cared with R290 for bomb in cabinet accident. In all the refrigerators tested the measured quantity of refrigerant was less than 40g and in the worst case accident the explosion and fire was unable to scorch the combustible liner of the fried. Procedures and standards such as BS4434 of 1995 have now been established with regard to refrigeration safety. In order to avoid an explosive build up of hydrocarbons in the event of a leak color recommended that the maximum mass of refrigerant in a domestic unit be restricted to 200g [3,12,14].

G. *Azeotropic refrigerants*

In some situations for a particular ratio, the mixtures behave like a single compound having a fixed boiling point corresponding to a given pressure. Azeotropic mixtures are either low boiling point or high boiling point mixtures. Such mixtures are called azeotropic mixture and the refrigerants are grouped under 500 series. The refrigerant R-500 is an azeotrope of 73.8%, R-12 and 26.2% R-152a by weight. The refrigerant R410A and R410B are near azeotropic mixtures. The power requirements of R-500 are approximately same as R-12 and R-22 but the compressor displacement is greater as compared to R-22 and some-what less than that of R-12 [2,15].

H. *Zeotropic refrigerants*

The special features of zeotropic mixtures present both draw backs and positive advantages when used in refrigeration technology in place of a single compound refrigerant. However, some major concerns in the use of zeotropic mixtures are just consequences of fractionation, which derives from the difference in composition between liquid and vapor-phase at thermodynamic equilibrium. Fractionation may cause a change in overall composition of the residual mixtures as consequences of leakage from a component of the refrigerating circuit where the refrigerant is present in both phases. It is evidently desirable that the equipment be topped up after a leakage with the as-formulated composition refrigerant, without suffering noticeable adverse changes in performance and without the composition sifting to the flammable region if as is the case with R407C, the non-flammable mixed refrigerant contains a flammable component. This occurs in most situations with the proposed mixtures, as experimenting and simulation results indicate. Only in extreme cases would servicing a system after a fluid loss require the removal of the residual refrigerant and its replacement with a new charge. When zeotropic mixture evaporates inside tubes, the more volatile component evaporates first and the remaining liquid becomes rich with less volatile component. HC additives with HFC134a behave like a zoetrope. Zeotropic mixtures shall be assigned an identifying number in the 400 series. This number designates which components are in the mixture but not the amount of each.

Zeotropes are differentiated with different amounts (percent by mass) of same components. Below mentioned are the numbers (are in chronological order) of the zeotropic refrigerants approved by ASHRAE[12,16].

Example:

R407A (R32/R125/R134a::20/40/40)
R407B (R32/R125/R134a :: 10/70/20)
R407C (R32/R125/R134a::23/25/52)
R407D (R32/R125/R134a :: 15/15/70)
R407E (R32/R125/R134a :: 25/15/60)

Table 1 - Properties of Refrigerants[4].

Refrigerant	Properties	Replaces	Molecular (wt.)	Critical Temp. (°C)	Boiling Point (°C)	ASHARAE Safety code
R404A	R125/R143a/R134a (44:52:4)	R502, R22	97.60	72.10	-46.50	A1
R407C	R32/R125/R134a (23:25:52)	R22	86.20	87.30	-43.56	A1
R410A	R32/R125 (50:50)	R22	72.58	72.50	-51.53	A1
R417A	R125/R134a/R600 (46.6:50:3.4)	R22	106.75	89.90	-38.00	A1
R161	Pure Fluid	R502	89.41	102.20	-46.08	A1
R132a	Pure Fluid	R12	102.03	101.10	-26.50	A1
R152a	Pure Fluid	R12, R134a	66.05	113.30	-24.00	A2
R600a	Pure Fluid	R12, R134a	58.12	134.70	-11.60	A3
R600	Pure Fluid	R12, R22	58.12	152	-0.5	A3
R290a	Pure Fluid	R12, R22	44.1	96.7	-42.1	A3
RC270	Pure Fluid	R12, R134a	42.08	125.2	-33.3	A3
R1270	Pure Fluid	R22	42.08	92.4	-47.7	A3
R717	Pure Fluid	-	17.03	132.3	-33.3	B1
R744	Pure Fluid	R12, R22	44.01	31.1	-78.4	A1
R507	R125/R143a (50:50)	R502	98.9	70.9	-47.1	A1
R123	Pure Fluid	R12, R11, R22	152.93	183.8	27.8	A1
R12	Pure Fluid	-	120.93	112	-29.79	A1
R22	Pure Fluid	-	86.47	96.2	-40.8	A1
R502	R22/R115 (48.8:51.2)	-	111.64	80.7	-45.4	A1

III. PRESENT INDIAN SCENARIO

Since the year of 2002, the use of CFC refrigerants in most of the systems were stopped. A particular refrigerant is adopted against CFC refrigerant because of many factors like suitability for the particular application, never the less availability and cost also play an important role. The halogenated refrigerants such as R12, R22, R134a and natural refrigerant like R717 are widely available at cheaper cost. The HC and HFC mixtures (such as R404a, R407C and R410A) are not presently produced indigenously and hence have to be imported at a higher cost. This is the reason that's going to affect the development in refrigeration and air conditioning sector in India and also the adopting the environmental friendly substitutes in the recent future [4,17].

A. Home refrigeration

Indian home refrigerator Industry is working since last 50 years. There are eight major home refrigerator producers in the Indian market, out of which four are producing hermetic compressor. Home refrigerator produced in India in the range of 65 liters to 580 liters capacity. Most of the presently manufactured Indian refrigerators use R134a as the refrigerant. The choice of substitute to R134a is narrowed down to R152a and hydrocarbon refrigerants. Refrigerators produced before 2000 were presently running on R12. The goals of the Montreal protocol to be fulfilled by replacing halocarbon refrigerants by hydrocarbon mixtures or R134a / hydrocarbon mixtures without any modification in the prevailing system [1,2,4].

Table 2 - Experimental Investigation carried out in India with domestic refrigerators [4].

Authors	Refrigerant	Alternatives	Conclusion
Devotta and Kulkarni (1996)	**R12**	**R290 / R600a**	Energy consumption for CFC-12 and the hydrocarbons mixture are comparable. The Pull-down test results revealed that the final freezer and food compartment temperature are very much higher when the refrigerator is retrofitted either with a hydrocarbon blend. The performance was approved by optimum capillary length and refrigerant charge. The ice making time for both the refrigerators are more or less the same.
Sekhar et al. (2004)	**R12**	**R134a/(R290/ R600a)(R134a/9 % HC mixture)**	The energy consumption was reduced by 4-11% with 3-8% higher COP. The discharge temperature was found to be lower than R12. Temperature glide in the evaporator is within 3^{o}C.
M. Mohanraj et al. (2007)	**R134a**	**R290/ R600a (45 /55)**	It has been reported that above mixture is an energy efficient and environment friendly alternative due to its reduced energy consumption by about 4% with 12K lower than that of R134a. The environment impacts of hydrocarbon refrigerant mixture are negligible compared to R134a.

B. Commercial and industrial refrigeration

The refrigerants R134a and R12 are used in most of the commercial freezers like bottle coolers, visit coolers, Chest freezers, display cabinets, water coolers and walk in coolers. Yearly production of commercial refrigerated cabins (such as chest freezers, display cabins, bottle coolers and visit coolers) water coolers and walk in coolers in India were projected to be about 40000, 27000 and 500 units, respectively. Nearly 80% of these units are produced by SME's (Ministry of environment and Forest 2005). The option of suitable substitute to R134a in commercial usage is R152a and hydrocarbon mixtures. The proposed demand of production of milk chilling and cold storages in India is going to be 14000. Apparently most of the milk chilling plants and cold storage are using ammonia and few of them on R502. Ammonia will be most popular in the industrial refrigeration's sector due to its acceptable environment properties (zero ODP and GWP). The substitute choice for R502 is R507 and hydrocarbon mixtures for low temperature industrial applications [2,4].

C. *Air conditioners, heat pumps and chillers*

In India it is estimated that 10 Lakhs room air conditioner is being produced with R22 as refrigerant every year, which includes window, split and packaged air conditioning units (Devotta et al. 2005b). The capacity of the window air conditioners ranges from 0.5 TR to 2TR.

In the Indian Market R407C and R410 is easily available this can be used as substitute to R22 in air conditioning applications. Yearly estimated 4000 central air conditioning chillers were installed; most of these chillers were using R22 and R11. Due to the lack of availability of this refrigerant only few of chillers were presently installed with R123. The long-term substitute to R11 and R22 or the chillers applications is R123 [4,10].

D. *Automobile air conditioners* :

Annually about 50000 units of automobile air conditioner are produced by three manufacturers in India. Mostly these units systems are based on R134a. The selection of substitute to R134a is R152a and hydrocarbon mixtures. Before year 2000, the car air-conditioning units which installed were running on R12 only. The selection of substitute to R12 and R134a is the mixture composed of R134a with hydrocarbon mixture or hydrocarbon mixtures and R152a.

In Indian Market the halogenated refrigerants like R22, R134a, R123, R404A, R407C, R410A and R507 will go to capture the next decade due to its high efficiency, safety and their current strong position. The technologies identified for producing new products in this sector are listed in below table 1.2 and 1.3 [4,9].

Table 3 - Air Conditioners, Heat Pumps and Chiller Units[4].

Authors	Refri.	Substitutes	Equipments	Conclusion
Devotta et al. (2005a)	R22	R290	Windows Air conditioners	Cooling capacity of R290 was lower by 6.6 - 9.7%. Energy consumption was lower by 12.4-13.5%. COP was higher by 2.8 - 7.9%. R290 has low condenser capacity than R22 in the range between 12.3 - 18.7%. Pressure drop in both evaporator and condenser were found to be lower than R22.
Devotta et al. (2005b)	R22	R407C	Windows Air conditioners	Lower COP by 8.2 -13.6%. Refrigerating capacity was less by 2.1 - 7.9%. The power consumption was high by 6 - 7%. Discharge pressure of R407C was higher by 11-13%. Evaporator capacity was also lower by 3.3 - 6%.
Jabaraj et al. (2005)	R22	R407C / 20% HC	Windows Air conditioners	Lower Energy consumption by 5 -10.5%. Higher R. E. by 9.5 - 12.5% and higher COP by 8 - 11%. Pull down time was lower than that of R22 by about 32.51%. Higher Discharge pressure by 3.7 - 11.46%.
Kumar and Rajagopal (2007)	R12 (70:30)	R123 / R290	Chillers	Discharge temperature was less than R12 by about 5 to 22^{o}C. Actual COP of the mixture was higher. Operating pressure is slightly higher than that of R12.

IV. ENVIRONMENTAL IMPACT

When considering the environment impact of various substances their lifetime is of major consideration as long-lived substances can have an impact that is significantly larger than the concentration in the atmosphere would suggest. The stability of refrigeration which is so important in refrigeration role prevents them broken down in the low level atmosphere and it is not until they reach an altitude of 20 km where they can be attacked by strong UV sunlight that this occurs. This is unfortunately in the region of the ozone layer that can then be attacked by the active chlorine atoms released from the refrigerant molecules. The destruction of the ozone starts when chlorine reacts with O_3 to provide CIO and O_2. The CIO then reacts with free oxygen atoms to form CI and O_2. The process can destroy up to 1000 ozone molecules for each, chlorine and before it reacts with methane to form ozone begins HCI or with NO_2 to form chlorine nitrate ($CIONO_2$). The ozone depletion potential is defined as an index that indicates the ability of refrigerants and other chemicals to destroy stratospheric ozone molecules based on a value of 1000 for R11. The accepted measures for the assessing the global warming impact of a refrigeration system is the total equivalent warming impact (TEWI) expressed in terms of kg of CO_2. Extended over the lifetime of a refrigeration unit this is an indication of the total impact including the contribution made by the CO_2, produced in producing the electricity to power the refrigerating unit. The exact value that are assigned to the TEWI are a function of many variables including the efficiency and type of electricity generation plant, the efficiency of the refrigeration unit itself and the rate of leakage. This can be illustrated by considering typical supermarket refrigeration systems of capacity 150kW. When charged with R12 / R31a / R401a, a direct cooling will be provided but in the event of the system being charged with propane (R290) indirect cooling will be provided for safety reasons that will increase the energy consumption by 8%. The refrigeration charge was taken to be 450kg and the annual leakage 10%. The annual energy consumption of the base line refrigeration unit charged with R12 is 250,000 kWh, where as the corresponding figure for the other refrigerants R134a are 257,557 kWh; R290 are 277137 kWh and for R401a are 249636 kWh. [4,17,37].

A. Ozone depletion potential (ODP)

The first major environmental impact that surprised the refrigeration based industries is ODP due to man-made chemicals into the atmosphere. Molina and Rowland (1974) produces in details that chlorine based refrigerants are stable enough to create problem in the stratosphere, where the chlorine atoms act as a catalyst to destroy the stratospheric ozone layer (which protects the earth surface from direct UV rays). About 90% of the ozone exists in the stratosphere between 10 and 50 kilometers above the earth surface. The first phase out the schedule for the harmful refrigerants formulated by the Montreal Protocol (1987) and was made stringent during the follow-up international meetings [4,9,17,19].

B. Global warming potential (GWP)

The global warming potential of a chemical results from the combination of its atmospheric lifetime and radiation forcing, together with the time frame for evaluation. The radiation forcing is the change in net-irradiation at the tropo-pause due to the change in atmospheric concentration of a trace gas resulting from a pulse release of that gas. The radiation efficiency is the radiation forcing for a unit change in atmospheric concentration. The increase in pressure within atmosphere, green house gases and other halogenated refrigerants absorbs the infrared radiations and do not allow these radiations to pass through the atmosphere & by that the temperature of atmosphere increases [19,20,22].

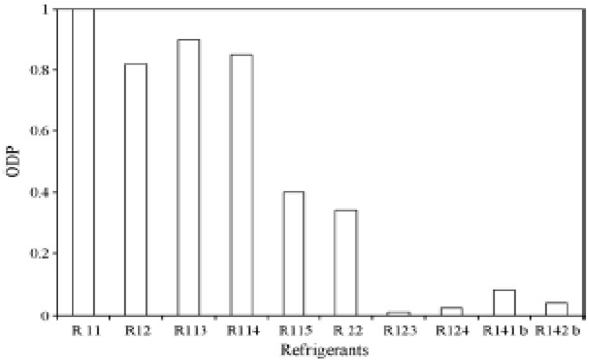

Fig: 1 - ODP of pure CFC and HCFC refrigerants[4].

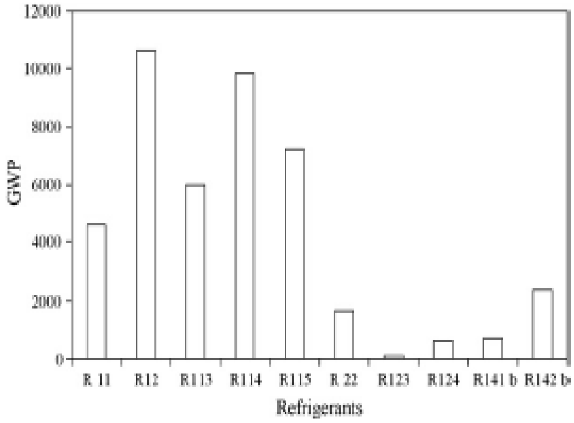

Fig: 2- GWP of pure CFC and HCFC refrigerants[4].

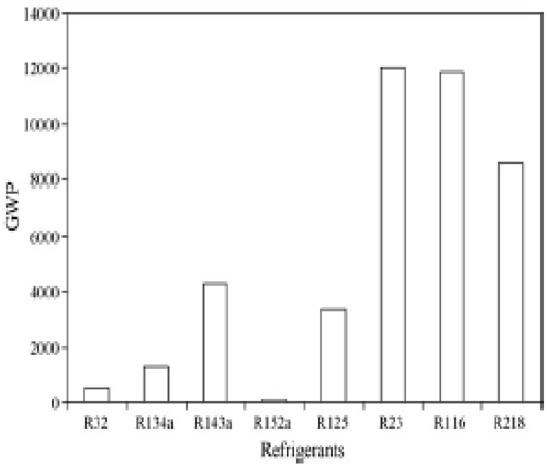

Fig: 3 - GWP of pure HFC refrigerants[4].

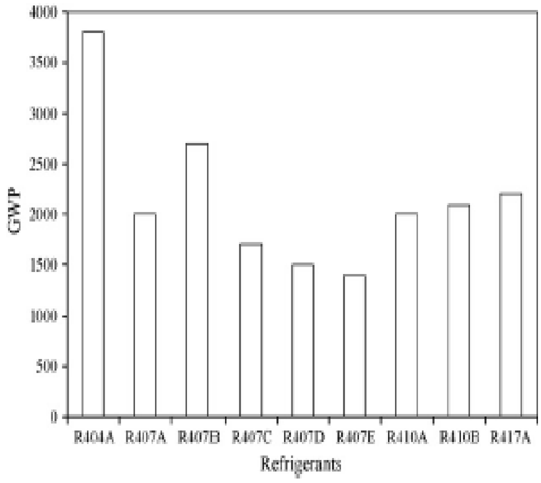

Fig: 4 - GWP of HFC mixtures[4].

V. PROTOCOLS

A. Montreal protocol

The Montreal protocol is an International treaty, on the ozone layer depleting substances (a protocol to the Vienna convention for the protection of ozone layer) Treaty designed to protect the ozone layer by facing out the production of numerous substances that are responsible for the ozone layer depletion. The treaty was opened on 16th Sep, 1987 for signature and entered into force on 1st Jan 1989 followed by a first meeting in Helsinki, May 1989 [4,9,18].

B. Kyoto protocol

The Kyoto protocol to the United Nations framework convention on climate change (UNFCCC) is an international treaty that sets binding obligations on industrialized countries to reduce emissions of green house gases. The UNFCCC is an environmental treaty, with the goal of preventing dangerous anthropogenic (i.e. human induced) interferences of the climate system. According to UNFCC website, the protocol recognized that developed countries, principally responsible for the current high level GHG emissions, in the atmosphere as a results of more than 150 years of industrial activity and places a heavier burden of developed nations under the principle of common but differentiated responsibilities. There are 192 parties to the convention: 191 states and the European Union. The protocol was adopted by parties to the UNFCCC in 1997 and entered into force in 2005 [4,9,11,18].

VI. LITERATURE SURVEY

1. In experimental study M. A. Alsaad, et al. have determined the performance of a domestic refrigerator with a propane/butane mixture called liquefied petroleum gas (LPG), comprising 24.4% propane, 56.4% butane and 17.2% iso-butane used as a possible replacement to the traditional refrigerant CFC-12. The refrigerator used in their study was of medium size with a gross capacity of 320 liter and was designed to work on CFC-12. It was found that the refrigerator worked efficiently when LPG was used as refrigerant instead of CFC-12. The evaporator temperature reached -15°C with COP value of 3.4 against 3.45, obtained from R12, at a condenser temperature of 27 °C and an ambient temperature of 20 °C. The results of their work indicated the successful use of this propane/butane mixture as an alternative refrigerant to R12 in domestic refrigerators[23].

2. Y. S. Lee et al. tested R600a in domestic refrigeration system. It was reported that COP lie between 0.8-3.5 in freezing application, refrigerant was 150g[24].

3. Tashtoush et al. tested with (R600/R290/R134a) at various quantities in R12 domestic refrigerator. It was reported that it was possible to use HC/HFC mixture as an alternative to R12 in a domestic refrigerator without changing the mineral oil (lubricant)[25].

4. Akash et al. studied the performance of the R12 retrofitted system with LPG (30% R290, 55% R600 and 15% R600a by weight) as an alternative at various charge amounts (50 g, 80 g and 100 g) for R12 in 240 L domestic refrigerator. The results reported that 80 g of LPG mixture showed best performance and higher cooling capacities compared to that of R12[26].

5. S.Joseph Sekhar et al. have conducted experimental analysis on a 165 liter, CFC-12 based household refrigerator retrofitted with eco-friendly refrigerant mixture of HFC134a/HC290/HC600a without changing the mineral oil. The performance as well as energy consumption were compared with the conventional one and it was concluded that mixture M09 (containing 9% HC blend by weight in the HFC134a) was the most promising alternative to conventional R12 system on the following bases:-
Energy consumption is reduced by 4.8 to 6.4%.
The system had been running successfully for more than 12 months, thus it was evident that the new mixture was compatible with mineral oil. The improvement in theoretical COP and actual COP were 3 to 12% and 3 to 8%, respectively[27].

6. Somchai Wongwises et al. have conducted study on a refrigerator designed to work with HFC-134a with a gross capacity of 239 liter. The mixture of three hydrocarbons: - It consisted of mixture of the three hydrocarbons (propane/isobutene/butane) in the ratio of 75/25/5, 100/0/0 and 50/40/10. The mixture of two hydrocarbons: - It consisted of propane/ butane

and propane/iso-butane in the ratio of 60/40. The mixture of two hydrocarbons (either propane/butane ‘or’ propane/iso-butane) in the ratio of 40/30 and rest HFC-134a.
In this way three groups of hydrocarbon mixtures were experimented and the best alternative of HFC-134a in each group was selected. Overall the conclusion drawn showed that the propane/butane (60/40 by wt. %) was the most appropriate alternative refrigerant to HFC-134a[28].

7. He et al. studied theoretically and experimentally with HFC mixture composed of Rl52a and R125 at different weight percentage (80:20, 85:15 and 90:10) as R12 alternative in a domestic refrigerator. The results of using R290, R600 and R600a hydrocarbons in a domestic refrigerator showed that R290 could not be used as an alternative refrigerant due to its high operating pressure in comparison with R134a. Although R600 and R600a represent many desirable characteristics such as operating pressure, mass flow rate and discharge temperature, although the compressor should be changed [29].

8. M. Fatouh et al. have tested liquefied petroleum gas (LPG) (60% propane and 40% commercial butane) for being used as a drop-in substitute for R134a in a single evaporator domestic refrigerator with a total volume of 10 ft3 (0.283 m3). Higher actual COP, lower on-time ratio and lower energy consumption of LPG refrigerator by nearly 7.6%, 14.3% and 10.8%, respectively, compared to those of R134a refrigerator were achieved. In conclusion, the proposed LPG seems to be an appropriate long-term candidate to replace R134a in the existing refrigerator[30].

9. K. Mani et al. analyzed experimentally the performance study on a vapour compression refrigeration system with the new refrigerant mixture R290/R600a as drop-in replacement was with CFC-12 and HFC134a. Experimental results showed that the refrigerant capacity of R290/R600a (68/32 by wt. %) mixture was higher in the range 19.9% to 50.1% at the lower evaporating temperature and 21.2 - 28.5% at the higher evaporating temperature than R12. The refrigerant R134a showed slightly lower refrigerating capacity than R12. Energy consumption of R290/R600a mixture was higher in the range 6.8% - 17.4% than R12 and 8.9% – 20% than R134a. The COP of R290/R600a mixture increases from 3.9% to 25.1% at lower evaporating temperatures and 11.8% to 17.6% at higher evaporating temperatures than R12.The R290/R600a (68/32 by wt. %) mixture can be considered as a drop-in replacement refrigerant for CFC-12 and HFC134a[31].

10. An experimental investigation has been made by M. Mohanraj et al. with hydrocarbon refrigerant mixture (composed of R290 and R600a in the ratio of 45.2/54.8 by weight) as an alternative to R134a in a 200 liter single evaporator domestic refrigerator. The results showed that the hydrocarbon mixture has lower values of energy consumption; pull down time and ON time ratio by about 11.1%, 11.6% and 13.2%, respectively, with 3.25 – 3.6% higher coefficient of performance (COP). The compressor discharge temperature of hydrocarbon mixture was found to be 8.5 °C to 13.4 °C lower than that of R134a. Quantity of charge was reduced up to 50% by replacing R134a by HCM, i.e., from 120g to 60g. Also the miscibility of HCM with POE was found to be good. The overall performance proved that the above hydrocarbon refrigerant mixture could be the best long term alternative to phase out R134a[32].

11. A.S. Dalkilic et al. conducted theoretical performance study on a traditional vapour-compression refrigeration system with refrigerant mixtures based on HFC134a, HFC152a, HFC32, HC290, HC1270, HC600, and HC600a for various ratios and their results were compared with CFC-12, HCFC-22 and HFC134a as a possible alternative replacements. Theoretical results showed that all of the alternative refrigerants investigated in the analysis had a slightly lower coefficient of performance (COP) than CFC-12, HCFC-22, and HFC134a for the condensation temperature of 50 °C and evaporating temperatures ranging between −30 °C and 10 °C. Refrigerant blends of HC290/HC600a (40/ 60 by wt. %) instead of CFC-12 and HC290/HC1270 (20/80 by wt. %) instead R22 were found to be replacement refrigerants among other alternatives in this paper as a result of the analysis[33].

12. An investigation carried out to replace R134a by M. Rasti et al. with a mixture of propane and iso butane with a ratio of 56:44(R436A) by weight in a domestic refrigerator. The results of using R436A was reduction in mass of refrigerant by 50% and raised the energy efficiency index of the refrigerator from label "E" to label "D" according to Iranian National Standard No. 4853-2[34].

13. Chao-Chieh Yu et al. experimentally studied that hydrocarbon (HC) refrigerants in a small R134a refrigerator to evaluate the refrigeration performance and feasibility of using these alternative refrigerants by conducting the no-load pull-down test and 24-hour on-load cycling test. The results showed that the freezer temperatures considerably decreased when the HC refrigerants were used and that all of the HC refrigerants could be used in the R134a refrigerators after changing the capillary tube lengths. All of the HCs refrigerants calculated lower electricity consumption, lower on-time ratios, and higher energy factors (EFs) than R134a did. The EFs of HC1, HC2 and HC3 were 9.1%, 12.2% and 42.3% higher than that of R134a respectively. Using a higher proportion

of R600a in HC refrigerants can enhanced the EFs of refrigerants[35].

14. Mao-Gang He et al. studied and found the performance of natural refrigerant propane (R290) and its mixtures substituting for 1,1,1,2-Tetrafluoroetane (R134a) used in a large capacity chest freezer (BD-625). To examine the application possibilities of R290 and its mixtures to the large capacity freezer, their thermodynamic and refrigerant performances from both experimental test and theoretical analysis have been done. The theoretical analysis shows that R290 is higher by 87.7% and 54.2% than R134a in mastic and volumetric refrigerating capacity respectively, propane / Iso-butane (R290/R600a, 90/10 wt%) is higher by 48.3% and 2.4% than R134a in volumetric refrigerating capacity and Coefficient of Performance (COP) respectively. So R290 and its mixtures (R290/R600a) can meet the requirements of large capacity refrigeration's and energy conservation as the alternatives of R134a. The experimental test shows that the power consumption of the experimental freezer charged with R290 is lower by 26.7% than that of R134a; when it is used in the freezer, the optimal ratio of R290/R600a is 93.75/6.25 wt% and the corresponding power consumption is lower by 27.5% than that of R134a[36].

Table 4 - Future options of refrigerants in India[4].

Equipments	**Application**	**Future Options**
Refrigerator	Household (home)	HC mixtures, R152a
Walk in Coolers	Commercial	HC mixtures, R134a/R152a
Chest Freezers	Commercial	HC mixtures, R152a
Air Conditioners	Residential and Commercial Automobiles	R290, R407C, R410A, R407C/ HC mixtures, R152a
Chillers	Industrial	R123
Cold Storage	Industrial	Ammonia

VII. TECHNICAL PROBLEMS OF MIXED REFRIGERANTS

1. The major difficulty of the refrigerant mixtures is the occurrence of pinch points in the evaporator and condenser during phase change process due to non linear variation in refrigerant properties, which minimizes condenser and evaporators performances (Venkatarathnam and Sirinivasamoorthy,1999).
2. Non-isothermal behavior of the refrigerant mixtures creates ambiguity in selecting the components of the refrigeration system from the manufacturer's catalogue.
3. Perfect glide matching can be achieved only in certain heat exchangers geometries such as sell and tube, concentric tubes, counter flow and flat plate heat exchangers.
4. Conventional methods of heat exchanges designs are not fully valid for the case of mixed refrigerants. (Rajapaksha 2007)
5. Non-linearity of the mixtures influences to decreasing the temperature difference at inlet and outlet may lead to increase in heat exchangers area to achieve the desired capacity.
6. Composition shift due to leakage of refrigerant of the mixed refrigerants leads to change in pressure, temperature, capacity and efficiency (Johnsson and Lundqrist 2001).

7. Mixed refrigerants require liquid receivers and suction line accumulator due to composition variation in phase change (Rajapaksha and Suen, 2004).

VII. CONCLUSION

Hydrocarbons and its mixtures refrigerants are most promising alternatives as they are environment friendly. Many researchers have reported that the hydrocarbon mixed refrigerants are found to be an energy efficient and environmental friendly alternative option in domestic refrigerators. Hydrocarbon based refrigerator require safety precaution when they are used for domestic purposes, so further study is required to find out inflammable limits of HCM R600a/R290 (60/40 by wt. %). The GWP value of HFC and HC mixed refrigerant (at different mass ratio) is also one of the important parameter because if it's value of is with-in the permissible limit, then the HFC and HC mixed refrigerant are most promising alternative refrigerant to be retrofitted in the present VCR systems, because of its having HFC part in it which is non flammable. Very limited pure alternatives are available.

Therefore, the new refrigerant mixtures and refrigeration system should be developed.

Finally, different pure hydrocarbons fluids can be mixed in different mass ratio for future requirements of refrigeration and air conditioning industry.

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