International Journal of Emerging Technology and Advanced Engineering
Volume 3, Special Issue 3: ICERTSD 2013, Feb 2013, pages 400-409
An ISO 9001:2008 certified Int. Journal, ISSN 2250-2459, available online at www.ijetae.com

ENVIRONMENTAL IMPACTS OF HALOGENATED REFRIGERANTS AND THEIR ALTERNATIVES: RECENT DEVELOPMENTS

Sudipta Paul[1*], Achinta Sarkar[2], Bijan Kumar Mandal[3]

[1]*UG Final Year Student, Bengal Engineering and Science University, Shibpur, Howrah-711103 West Bengal, India*

[2]*PhD Scholar, Department of Mechanical Engineering, Bengal Engineering and Science University, Shibpur, Howrah- 711103, West Bengal, India*

[3]*Professor, Department of Mechanical Engineering, Bengal Engineering and Science University, Shibpur Howrah, West Bengal, INDIA*

[+]Corresponding author email:paul.sudipta03@gmail.com

ABSTRACT

A certain percentage of the vapor compression based refrigeration, air conditioning and heat pump systems continue to run on halogenated refrigerants due to its excellent thermodynamic and thermo-physical properties along with the low cost. However, the halogenated refrigerants have adverse environmental impacts such as ozone layer depletion potential and global warming. Hence, it is necessary to look for alternative refrigerants to full fill the objectives of the international protocols (Montreal and Kyoto) and to satisfy the growing worldwide demand. In this context, the use of "natural" refrigerants (air, CO_2 or ammonia) becomes a possible solution. We introduce in this study the merit of redeploying these natural refrigerants as an alternative solution to replace halogenated refrigerants. This paper reviews the various experimental and theoretical studies carried out around the globe with environment friendly alternatives such as hydrocarbons (HC), hydroflurocarbons (HFC) and their mixtures, which are going to be the promising long-term alternatives. In addition, the technical difficulties of mixed refrigerants and future challenges of the alternatives are also discussed.

Keywords: Vapor compression refrigeration, Halogenated refrigerants, Montreal and Kyoto protocol and ozone layer depletion.

1. INTRODUCTION

The primary global environmental impacts from air conditioning and refrigeration systems occur due to emissions of halogenated refrigerants and of gases associated with energy use. Those gases usually are released at the power plants, chillers, cold storages. In this context most of the developed countries reduced the production and consumption of halogenated refrigerants, which demands for suitable alternatives. The discovery of the ozone-depleting properties of CFCs and HCFCs refrigerants, and of their global warming potential, led to the Montreal Protocol (1987) and the London and Copenhagen amendments (1990, 1992), which scheduled the end of production of CFCs by the end of 1995 and of HCFCs by 2030. As Fig. 1[1] shows, the production of CFCs and HCFCs has fallen dramatically in the last few years. Hence HC and HFC based refrigerants with zero ODP and low GWP are considered to be long-term alternatives.

Although the ozone-depletion potential (ODP) of some HFCs is zero, their global warming potential (GWP)--related to the greenhouse effect-can be large. On the other hand, HC refrigerants have flammability issues, which restrict the usage in existing systems. However the flammability issue can be avoided by blending HC refrigerants with HFC refrigerants. It is possible to mix HC refrigerants with other alternatives such as HFC refrigerants. The solubility of HC/HFC mixtures with mineral oil has been found to be good. The GWP of HC/HFC mixtures is less than one third of HFC, when it is used alone.

An alternative to HFCs is the use of naturally occurring substances (refrigerants), namely, ammonia, hydrocarbons (HCs), carbon dioxide (CO_2), water, and air. These natural refrigerants have zero ODP, and the majority also has zero GWP. However, some of them can be flammable and/or toxic.

This paper gives a comprehensive review of the various experimental and theoretical studies carried out with environment friendly alternatives in refrigeration, air conditioning and heat pump applications. Also in the next sections, an analysis of the application conditions for natural refrigerants is made, as well as a review of the recent research and development on that subject.

2. ATMOSPHERIC HAZARDS

The halogenated refrigerants are a family of chemical compounds derived from the hydrocarbons (methane and ethane) by substituting chlorine and fluorine atoms in the place of hydrogen. The emission of chlorine and fluorine atoms present in halogenated refrigerants is responsible for the major environmental impacts with serious implication for the future development of the refrigeration based industries. The discovery of the ozone-depleting properties of CFCs and HCFCs refrigerants, and of their global warming potential led to different protocol and amendments.

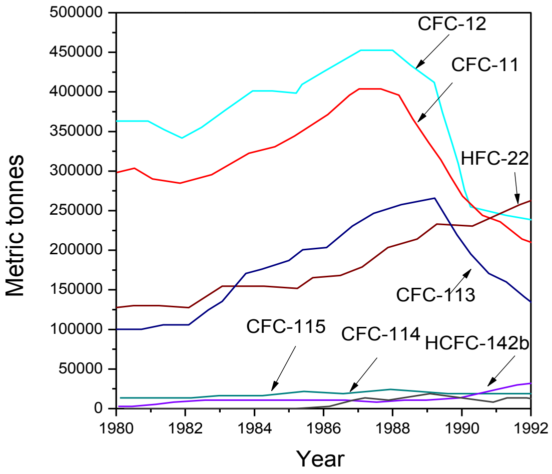

Fig.1. Production of halogenated refrigerants

2.1 Effects on Ozone Layer

The first crucial environmental impact that struck the refrigeration based industries is ODP due to artificial chemicals into the atmosphere. The chlorine based refrigerants are stable enough to reach 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). Molina and Rowland [2] gave the detail effect of chlorine on the ozone layer. About 90% of the ozone exists in the stratosphere between 10 and 50 km above the earth surface.

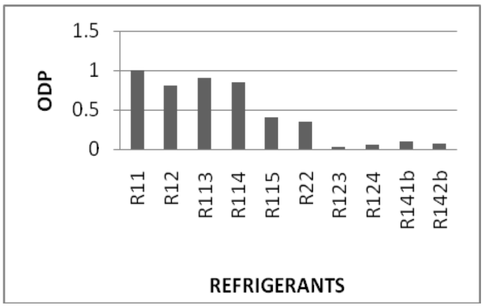

Fig.2. Ozone depletion potential of pure CFC and HCFC refrigerants

The first phase out schedule for the harmful refrigerants formulated by the Montreal protocol (1987) and was made stringent during the follow-up international meetings. The ODP values of pure CFC and HCFC refrigerants are shown pictorially in Fig. 2[3].

2.2 Effect on global worming

The second major environmental impact is GWP, which is due to the absorption of infrared emissions from the earth, causing an increase in global earth surface temperature. While solar radiation at 5800 K and 1360 W/m^2 arrives the earth, more than 30% is reflected back into space and most of the remaining radiation passes through the atmosphere and reaches the ground. By radiating energy with a spectral peak in the infrared wavelength range this solar radiation heats up the earth approximately as a black body. This infrared radiation cannot pass through the atmosphere because of absorption by GHG including the halogenated refrigerants. As a result, temperature of atmosphere increases, which is called as the global warming. During the formulation of Kyoto protocol, countries around the world have voluntarily committed to reduce the GHG emissions. HFC refrigerants have relatively large values of atmospheric lifetime and GWP compared to chlorine based refrigerants. The GWP values of pure and mixed refrigerants are illustrated in Figs. 3–5[3].

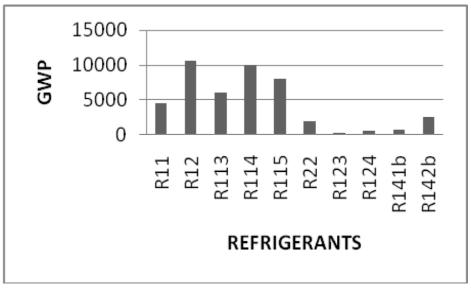

Fig.3. Global warming of pure CFC and HCFC refrigerants

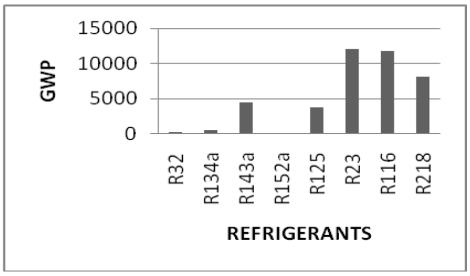

Fig.4. Global warming of pure HFC refrigerants

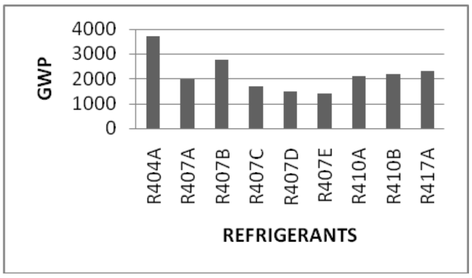

Fig.5. Global warming of HFC mixtures

3. RECENT STUDIES

A large number of experimental and theoretical studies are carried out pertaining to HC, HFC and their mixtures as alternatives to halogenated refrigerants by researchers from various parts of the globe. A brief summary of these investigations have been presented in the following sections for comparative assessments of different refrigerants from performance and environmental impact points of view.

3.1 Refrigeration Plants

An experiment carried out by Doring *et al.* [4] with R507 (binary mixture of composed of R125/R143a in equal proportion by weight) as an alternative for R502 in a low temperature freezer showed that the discharge temperature was approximately 8 K below and COP was 4–5% higher than that of R507. The refrigeration capacities of R507 are 5–6% higher than the capacities of R502. The comparison study by Goktun [5] of the performance of R502 and five HFC mixtures (R404a, R407A, R407B, R507 and quaternary HFC mixture composed of R32, R125, R143a and R134a) as alternatives in low temperature applications show that the R404A is the best alternative on the basis of environmental properties and safety with similar volumetric capacity and lower discharge temperature.

An experiment carried out by Xuan and Chen [6] with the ternary mixture of R161/R125/ R143a (10:45:45 percentage by weight) shows that physical properties of R161 mixture are similar to R502 and environmental properties of R161 mixture are lesser than R502 and R404A.

The COP of R161 mixture and R404A are equal at low evaporator temperatures and its discharge temperature is slightly higher than R404A. The COP of the mixture was greater than R404A at higher evaporator temperatures and its discharge temperature was found to be lower.

Also the experiment with binary mixture composed of R744 and R290 at 71:29 mole fractions as alternative to R13 in cascade refrigeration system showed that COP and capacity of the mixture are greater than R13. The discharge temperature of the mixture is found to be greater than that of R13.

An experiment by Park and Jung [7] with two pure HC refrigerants (R1270 and R290) and three binary mixtures composed of R1270, R290 and R152a as alternatives to R502 in low temperature refrigeration applications states that all refrigerants tested had 9.6–18.7% higher capacity with 17.1–27.3% higher COP than that of R502. The compressor discharge temperature of R1270 was similar to that of R502, while those of all the other refrigerants were 23.7– 27.9 ºC lower than that of R502. The charge requirement was reduced up to 60% as compared to R502. Miscibility of all these refrigerants with mineral oil was reported to be good. The above alternatives offer better system performance and reliability than R502 and can be used as long-term substitutes for R502 due to their excellent environmental properties.

3.2 Domestic Refrigeration

Out of the total global warming and other environmental hazards a certain percentage is responsible for refrigerant leakage and energy consumption from domestic refrigerators. The different type of hydrocarbons and their mixtures that can be used as an alternative in domestic purposes are discussed in the following section.

3.2.1 Hydrocarbon refrigerants as alternatives

To find out the substitutes for CFC12 and CFC22 many investigation have been carried out. The experimental study carried out on the application of hydrocarbon mixtures to replace HFC134a in car air conditioners. The measured data are obtained from an automotive air-conditioning test facility using HFC134a as the refrigerant. The experimental study of Wongwises and Chimres, [8] on the application of a mixture of propane (R-290), butane (R-600), and isobutene (R-600) in domestic refrigerator to replace HFC134a showed that a 60%/40% propane/butane mixture was the most appropriate alternative refrigerant. The refrigerating effect of various mixtures compared to R-12, R-134a, R-22 are shown in the fig.6-9 [8]

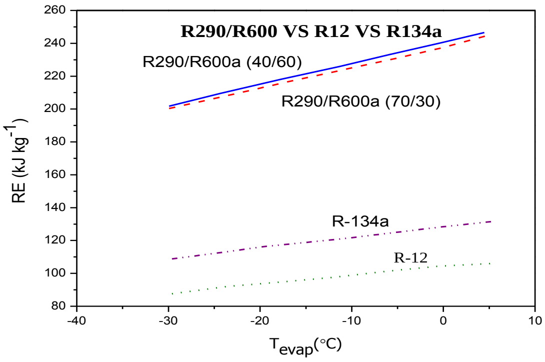

Fig.6 Refrigerating effect R-290 vs R-12 vs R-134a

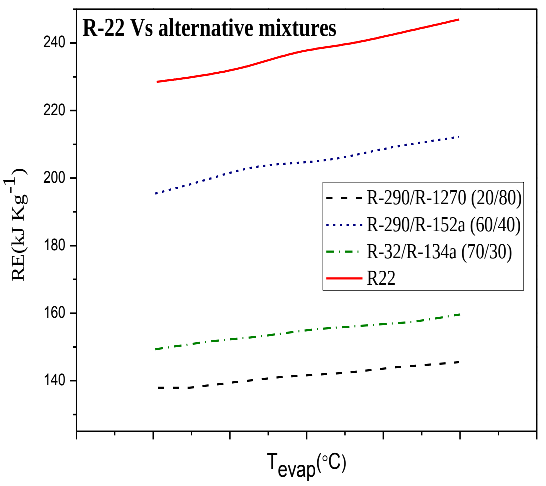

Fig.7 Refrigerating effect R-22 vs alternative mixtures

The variation of pressure ratio (P_{cond}/P_{evap}) w.r.t. the evaporator temperature is shown in the figure below.

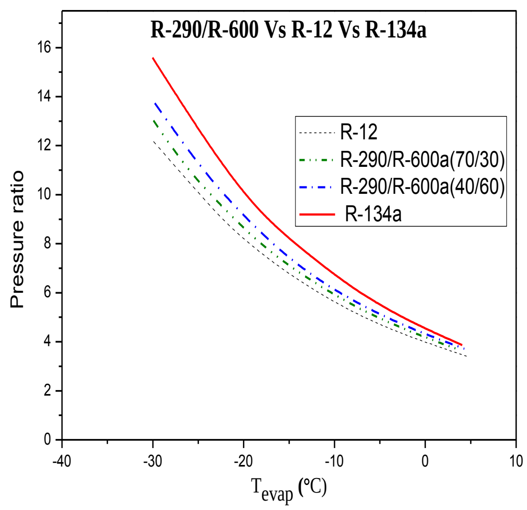

Fig.8 Pressure ratio R-290/R600a vs R-12 vs R-134a

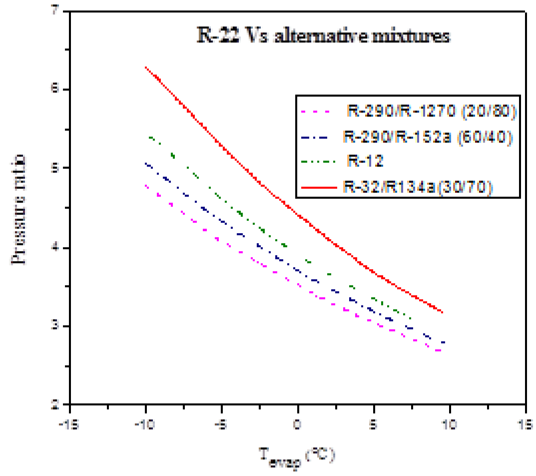

Fig.9 Pressure ratio R-22 vs alternatives

In Table 1 [8] significant parameters of refrigeration cycle performance under different conditions are calculated taking R12 and R22 respectively as the reference for the same condensing (50^0C) and evaporation temperature (-10^0C). The specific volume of the suction vapour decreases which increase in the mass flow rate as the evaporation temperature (T_{evap}) increases. The effects of changed concentrations on the performance parameters can be seen from these figures and also from Table 1. The volumetric refrigeration effect (VRC), in other words, the volumetric capacity, is defined as the cooling capacity per unit of vapour volume at the exit of the evaporator. A high cooling capacity can be obtained from a high volumetric capacity refrigerant for a given swept volume in the compressor, it is expressed as,

VRC = ρ. RE, where ρ is the density of working fluid.

Table 1 Performance of different refrigerants with T_{cod}= 50°C and T_{evap}= -10°C in a VCR cycle

Refrigerant (By wt. %)	**Pr. ratio (P_{cond} /P_{evap})**	**RE (kJ kg^{-1})**	**VRC (kJ m^{-3})**	**COP**
R-12	5.562	98.6	1273.912	3.233
R-22	5.476	138.0	1273.912	3.180
R-134a	6.570	121.1	1215.844	3.097
40%R600+60 %R290	6.492	240.2	836.376	2.826
40%R600+60 %R290	5.807	225.9	1066.248	2.907
50%R600+50 %R290	6.668	242.4	742.229	2.886
50%R600a+5 0%R290	5.936	225.2	969.936	2.921
70%R134a+3 0%R32	6.328	149.5	969.936	2.955
80%R1270+2 0%R290	4.789	228.40	1215.844	2.997
20%R152a+8 0%R290	5.025	197.4	1066.248	2.820

ISSN 2250-2459, *Volume 3, Special Issue 3: ICERTSD 2013, Feb 2013, pages 400-409*

An investigation with HC mixtures composed of R290 and R600 at different mass ratio in a 240 l capacity domestic refrigerator by replacing the R134a is carried out. Wongwises and Chimres [9] reported that R290/R600 mixture (in the ratio of 60:40, by mass fraction) is the most appropriate alternative to R134a due to its excellent thermodynamic and environmental properties. The refrigerator working with above HC mixture requires less energy consumption per day compared to R134a due to its high latent heat. A performance study carried out by Fatouh and El Kafafy [10] with a 280 l R134a based domestic refrigerator with liquefied petroleum gas (LPG) composed of R290, R600a and R600 (60:20:20 by mass fraction) as an alternative. The pressure ratio and power consumption of LPG mixture with a combination of 5 m capillary tube length and charge of 60 g was reduced by 7.6%, 5.5% and 4.3% respectively with a 7.6% higher COP. On-time ratio and energy consumption of LPG refrigerator is lower by nearly 14.3% and 10.8% respectively, compared to that of R134a.

Hammed and Alsaad [11] studied the performance of 320 l R12 based domestic refrigerator using R290:R600:R600a (50:38.3:11.7 by weight) as an alternative. It has been reported that the COP of refrigerator using this mixture is 3.7 with an evaporator temperature of 16ºC and condensing temperature of 27ºC (compared to R12, which has a COP of 3.6). The thermodynamic analysis of R290/R600a as an alternative in 299 and 465 l R12 domestic refrigerators indicated that the R290/R600a in composition range 0.2–0.6 mass fraction of HC290 yields an increase in COP up to 2.3% as compared to R12. Power consumption and pull-down test indicate that the energy efficiency was improved by 3–4% with slightly higher capacity than that of R12. The study of the performance of the R12 retrofitted system carried out by Akash and Said [12] 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 results in that 80 g of LPG mixture showed best performance and higher cooling capacities compared to that of R12.

3.2.2. Hydrocarbon/Hydroflurocarbon mixtures

The experimental study [14] with (R600/R290/R134a) at various quantities in R12 domestic refrigerator shows that it is possible to use HC/HFC mixture as an alternative to R12 in a domestic refrigerator without changing the mineral oil (lubricant). The hydrocarbon mixture (R290/ R600/R134a) in the mass ratio of 25:25:30 and the charge amount of 80 g had performance characteristics very close to that of R12. The discharge temperature of the mixture was found to be lower than that of R12 for a wide range of evaporator capacity. The volumetric efficiency of the compressor is slightly higher and mass flow rate of the mixture was found to be 40% lower. These are the major advantages for R12 retrofitting with above mixture.

4. PROBLEMS OF REFRIGERANT MIXTURES

The technical difficulties of the alternative refrigerant mixtures are listed below:

(a) The major problem of the refrigerant mixtures is the occurrence of pinch points in the condensers and evaporators during phase change due to non-linear variation in refrigerant properties, which reduces condenser and evaporator effectiveness. [15].

(b) Non-isothermal behavior of the refrigerant mixtures creates ambiguity in selecting the components of the refrigeration system from the manufacturer's catalogue.

(c) Perfect glide matching can be achieved only in certain heat exchanger geometries such as shell and tube, concentric tubes, counter flow and flat plate heat exchangers.

(d) Conventional method of heat exchanger design is not fully valid for the case of mixed refrigerants [16].

(e) Non-linearity of the mixtures influences to decreasing the temperature difference at inlet and outlet may lead to increase in heat exchanger area to achieve the desired capacity.

(f) Composition shift due to leakage of refrigerant of the mixed refrigerants leads to change in pressure, temperature, capacity and efficiency [17].

(g) Mixed refrigerants require liquid receiver and suction line accumulator due to composition variation in phase change [18].

5. NATURAL REFRIGERANTS

Considering the problems faced by the refrigeration industry using different halogenated refrigerants, scientists are now urging in favour of using natural refrigerants. Some of the commonly used natural refrigerants are discussed below.

5.1 Air

It has been used in the past, but nowadays it is mainly used in aircraft air-conditioning. The operating cycle used with air as working fluid is the reverse Joule-Brayton cycle, in which only sensible heat is exchanged. As it is an open cycle, there are no problems regarding leakages and charges. Its COP strongly depends on heat exchanger, compressor and expander efficiencies. The lower values obtained with former reciprocating equipment led to the use of rotary compressors and expanders, with a much better isentropic efficiency. In this cycle, the decrease in COP due to the decrease in the lowest cycle temperature is much smaller than in vapour compression cycles. This way, the cycle is more attractive at lower temperatures. The development of an air-cycle refrigerator has been reported, [19], where a temperature of -45°C is expected. A development program concerning the use of screw compressors and expanders in an air cycle was also reported [20].

Int. J Emerging Technology and Advanced Engineering
ISSN 2250-2459, *Volume 3, Special Issue 3: ICERTSD 2013, Feb 2013, pages 400-409*

5.2 Ammonia

Ammonia is a widely used in medium and large refrigeration systems. As it is toxic and flammable it requires special safety precautions, and in many applications it requires an indirect system. In spite of its toxicity, its strong odour acts as an alarm and mixable with water, which allows water cleaning systems to be effective. It is also known that its lower explosion limit is equal to 15% by volume and its ignition temperature is 630°C. Thus, it is moderately flammable. It requires a strong ignition source, being less flammable than hydrocarbon refrigerants. Ammonia is rather inexpensive when compared with synthetic refrigerants. However, combined with water, ammonia can be corrosive to copper and copper alloys, which makes this refrigerant an expensive alternative to existing systems operating with CFCs or HCFCs, since most of the piping is made of copper.

The efficiency of vapour compression cycles operating with ammonia is very good. The cycle COP (coefficient of performance), compared to CFCs, HFCs and other alternative refrigerants, and is favorable, as can be seen in Fig. 10 [1]. The poor miscibility between ammonia and compressor oil (lubricant) has advantages and disadvantages. As advantages, one can mention its easier separation and the reduced risk of fire. The main disadvantage is the need of a separate mechanism to return the oil to the compressor. Due to the toxic and flammable characteristics as mentioned earlier, the use of ammonia as a refrigerant has been restricted in many countries, especially in commercial and residential applications. Nowadays, the main applications of ammonia are water chillers in air-conditioning and process cooling systems, medium/large-capacity heat pumps and commercial refrigeration in supermarkets designed to use an HCFC (R-22) or ammonia, with a small cost of conversion. The most promising applications of ammonia are at temperatures up to 80°C.Recent and future research should be focused on low charge in large-capacity systems and also on small units, for which little knowledge and components exist, as well as on applications above 80°C.

5.3 Hydrocarbons

The most common hydrocarbons that fulfill the requirements of the cooling technology are propane (R-290) propylene (R-1270) and blends with propane and butane (R-600) or isobutene (R-600a). These refrigerants are highly flammable, the lower and higher explosion limits ranging between 1.5/2.1% and 8.5/l 1.4% by volume, and the ignition temperature ranging from 365 to 491°C. Hydrocarbons have been used as refrigerants for many years in the petrochemical industry, where handling of flammable fluids is customary.

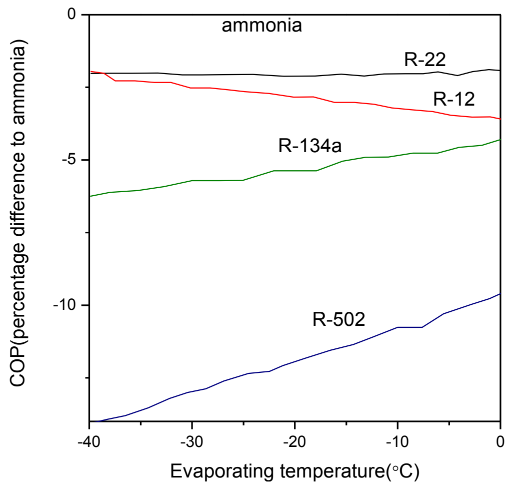

Fig.10. Relative COP of an isentropic vapour compression cycle for different refrigerants [5].

Due to their flammability, hydrocarbons are mainly regarded as an alternative in systems with low working fluid charge. In fact, research projects are being carried out in order to study the behavior and components of low charge vapour compression systems of relatively large capacities. These projects indicate that propane systems have a heating capacity, when used as a heat pump, which is about 8% lower than R-22, while the COP is 5-7% higher which is shown in Fig. 11[1]. It was also shown that the refrigeration charge of a propane system is reduced by about 50%, when compared with R-22, for the same geometry. This is due to its smaller molar mass. When R-22 is to be substituted by propane, the costs of the necessary changes (expansion valve, lubricant) are negligible when compared with the costs of the substitution by HFCs. Hydrocarbons have been used in low charge systems in residential and commercial applications (water and space heating) and low-capacity air-conditioners for automotive/transport and space cooling. Also in fig.12 [8] how the COP of an R-22 system with different hydrocarbon mixtures varying with the working fluid evaporation temperature is shown.

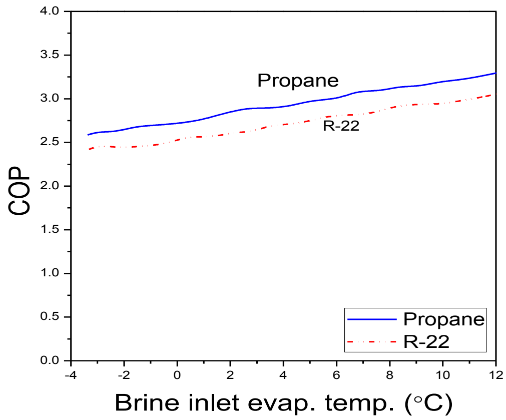

Fig.11. COP of a heat pump with R-22 and R-290, for different brine inlet evaporator

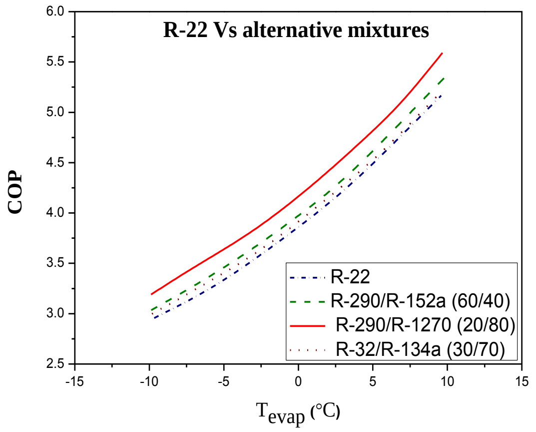

Fig.12. Variation of COP with evaporation temperature for HC mixtures

Due to their flammability, hydrocarbons are mainly regarded as an alternative in systems with low working fluid charge. In fact, research projects are being carried out in order to study the behavior and components of low charge vapour compression systems of relatively large capacities. These projects indicate that propane systems have a heating capacity, when used as a heat pump, which is about 8% lower than R-22, while the COP is 5-7% higher which is shown in Fig. 11[1]. It was also shown that the refrigeration charge of a propane system is reduced by about 50%, when compared with R-22, for the same geometry. This is due to its smaller molar mass. When R-22 is to be substituted by propane, the costs of the necessary changes (expansion valve, lubricant) are negligible when compared with the costs of the substitution by HFCs. Hydrocarbons have been used in low charge systems in residential and commercial applications (water and space heating) and low-capacity air-conditioners for automotive/transport and space cooling. Also in fig.12 [8] how the COP of an R-22 system with different hydrocarbon mixtures varying with the working fluid evaporation temperature is shown.

5.4 Water

The use of water in heat pump vapour compression cycles, for high-temperature applications (typically above 100ºC), has been recently studied. However, for lower evaporating temperatures there are not many reported studies. This is due to the very low density of water vapour, which sharply decreases the refrigeration capacity for temperatures below 100°C. In fact, the refrigeration effect of water (in kJ/kg) is roughly 20 times higher than that of R-12, but the necessary water vapour compressor should have to handle almost 200 times more volumetric flow, for a given refrigeration capacity. Therefore, the compressor is the key factor for these systems. Only axial or centrifugal compressors should be adequate for handling such high volumetric flows, with cost effectiveness.

Water vapour compression installations for water chilling (with a reduction of 30-50% in the energy consumption, compared to ammonia and HCFCs) and production of low-pressure steam (average process temperature of 65°C) are also going on. Studies are being carried out on the use of water in low-temperature cycles (below 100ºC), for heat pump air-conditioning systems. The absorption and absorption-recompression cycles previously mentioned in the ammonia section can operate using water as the main refrigerant. One way of reducing size, weight and cost of a traditional absorption system consists of using centrifugal fields in the heat exchangers, in order to enhance the heat and mass transfer coefficients. An experimental rotating disk prototype, operating with water and a mixture of metal hydroxides, is being developed [21] using the absorption-recompression cycle, a higher efficiency can be achieved. In recent years, several cooling systems using adsorption cycles have reappeared, using water as the refrigerant. Some work has been developed using metal-supported zeolites. Open evaporative cooling systems have been installed for comfort cooling in Sweden.

5.5 Carbon Dioxide

Unlike the other natural refrigerants previously mentioned, CO_2, is a non-flammable working fluid, odorless, with zero ODP and zero effective GWP, not toxic in practice. As it is heavier than air, it can cause suffocation in the same way as halocarbons. However, the density of CO_2, is approximately half that of different halocarbon refrigerants. The interest in carbon dioxide increased, due to the development of new motorcar air-conditioning systems. Furthermore, its liquid density is lower and, as a consequence, the system charge and size will also be lower, which increases the cost difference between CO_2, and halocarbons. Another advantage of CO_2, is its compatibility with normal lubricants and construction materials. Due to the thermodynamic properties of CO_2 the vapour compression cycle and the components of the system should differ from the ones with low-pressure refrigerants as in case of a trans-critical cycle. In fact, for moderate ambient air temperature, the pressure at which the fluid rejects heat must be supercritical, with variable fluid temperature. As pressure and temperature are independent properties in the supercritical region, the system must have a high side-pressure adjustment, since the COP is pressure dependent. The COP has a maximum value for a given high side pressure. The high pressure (> 100 bar), combined with the low molar mass of CO_2, and reduces the volumetric flow and the dimensions of the system components (compressor, valves, piping). In motorcar and transport air-conditioning an efficient system was recently developed [22] enabling efficient operation and simple high side-pressure control; the measured COP of the system was similar to one with R-12,also in heat-pump water heaters it is expected that the system COP would be 20% higher than the R-134a .

6. RECENT DEVELOPMENTS

The automotive industry now is pursuing three primary candidates to replace R-134a in mobile air conditioners, namely carbon dioxide and R-1234fy in direct expansion systems and R-152a in indirect (‘‘secondary loop’’) systems employing an intermediate heat transfer fluid (HTF). Despite carbon dioxide’s appeal as a ‘‘natural refrigerant’’ and favorable findings in some reported bench and vehicle tests. With this system concerns exists with the system complexity and weight, especially in small vehicles and hot climates, and resulting impacts on overall emissions including penalties from increased fuel consumption.

As a single-compound refrigerant, R-1234yf offers similar thermo physical properties to R-134a, thus minimizing equipment changes, and has met criteria for stability and compatibility. It also offers an exceptionally low direct GWP of 4 on a 100-yr integration basis. Chronic (long-term, repeat exposure) and reproductive toxicity testing of R-1234yf is incomplete, but the results for acute (short-term, single exposure) and sub chronic (intermediate term, repeat exposure) are favorable. Its production will require stringent process control, and possibly also cleanup procedures, to prevent inclusion of toxic contaminants. The cost of R-1234yf is likely to be significantly higher than for R-134a, especially initially. Still, at least two major chemical manufacturers [23] working jointly and redirected their focus to R-1234yf in direct expansion systems and the major automobile manufacturers now are evaluating it. Most manufacturers also terminated R-152a pursuit as a global alternative in direct-expansion systems predicated on its limited flammability, despite difficulty in ignition when released into engine compartments, concluding that it ‘‘is not suitable for use in vehicles not designed for flammable refrigerants’’. Evaluation continues in indirect systems with identified advantages especially in small vehicles and in warm climates.

Many studies are evaluating carbon dioxide and other ‘‘natural refrigerants’’ in stationary applications. Carbon dioxide use in the low stage of cascaded systems for industrial refrigeration is now common, though it primarily displaces ammonia use in this application. Carbon dioxide use in heat pump water heater is increasing, especially in Japan where service-water heating accounts for approximately 30% of residential energy use. Carbon dioxide use also is increasing, especially in Europe, for commercial refrigeration both as a refrigerant and in indirect (‘‘secondary loop’’) systems. The latter application both facilitates significant reduction in refrigerant charge amount and opens further prospects for use of ammonia, ammonia blends (such as one commercialized with R-E170, dimethyl ether), hydrocarbons, R-152a, and other flammable refrigerants for both retail display cases and preparation and storage areas in supermarkets.

Hydrocarbon refrigerants, notably R-600a (isobutane) and isobutane blends have displaced R-12 and later R-134a and now dominate in domestic refrigerators in Europe, but not in North America and especially not in the United States. Although widely perceived as a safety concern, that is not the case for refrigerators that have very small refrigerant charge amounts (typically less than 120 g, 1⁄4 lb).

One of the oldest refrigerants, ammonia remains the refrigerant of choice in industrial systems and especially so for food and beverage processing, which often require large internal volumes and flexibility in system modification, as well as storage. Ammonia interest renewed in Europe and especially so in northern Europe. Concerns with its flammability, and to a lesser extent also skin corrosivity, limit broader acceptance in other locations, particularly in warmer climates commonly using larger chillers in proximity to densely occupied spaces. Water continues as the primary refrigerant in large absorption chillers and chiller heaters, primarily those using lithium bromide as the absorbent. Despite occasional citation of water use in smaller absorption systems, its primary role there is with ammonia as the refrigerant and water as the absorbent. Studies are underway to further develop chillers using water and especially so to cool deep mines, for which there is heightened sensitivity to pumping burdens and to subsurface refrigerant leaks whether flammable or nonflammable. The need for operation in deep vacuum and use of multistage compressors typically axial designs in large capacities employing turbo-compressors, limits attraction to water for mechanical-vapor-compression chillers, though research continues with some attention to innovative compressor designs.

8. CONCLUSION

The phase out of CFCs and HCFCs has led to research into alternative refrigerants. The governing selection criteria for the new generation will add low GWP (initially 150 or less, determined for 100- yr integration) to old requirements for suitability, safety, and materials compatibility. Although the majority of natural refrigerants have been well known for a long time, their use was almost abandoned with the appearance of synthetic refrigerants. Their low cost, together with minimum environmental impact, turn them into very interesting alternatives. Although several solutions are already commercially available, much research work is still to be done regarding the systems and cycles with which natural refrigerants operate. Based on the results regarding the performance, it can be understood that HC mixtures and R152a are found to be better substitutes for R12 and R134a in domestic refrigeration sector. R290, R1270, R290/R152a, R744 and HC/HFC mixtures are found to be the best long-term alternatives for R22 in air conditioning and heat pump applications.

R123 was found to be an attractive alternative to R11, R12 and R22 in chiller applications. R152a and HC mixtures are found to be a best option for automobile air conditioners. The use of low environmental impact refrigerants like the natural refrigerants (R290, R1270 and R744) and HC/HFC refrigerants in air conditioning and heat pump applications play a vital role in the developing countries India for reducing the environmental impact of halogenated refrigerants. Many refrigerants currently viewed as new alternatives, including many HFCs, soon could become old rejects. Given the scarcity of viable options, future refrigerant selections warrant collective consideration of all environmental issues together, with integrated assessments, rather than piecemeal treatments that risk elimination of good overall options for minor or even indiscernible impacts for individual issues.

REFERENCES

1. Riffat, S. B., Afonso, C. F., Oliveirat, A. C. and Reay, D. A., 1997, Natural refrigerants for refrigeration and air-conditioning systems. Applied Thermal Engineering, 17(1), 33-42.
2. Molina, M.J. and Rowland, F.S., 1974, Stratospheric sink for chlorofluoromethane: chlorine atom catalyzed destruction of ozone, Nature, 249, 810–812.
3. Calm, J.M. and Hourahan, G.C., 2001, Refrigerant data summery. Engineering Systems, 18, 74–88.
4. Doring, R., Buchwald, H. and Hellmann, J., 1997, Results of experimental and theoretical studies of the azeotropic refrigerant R507, International Journal of Refrigeration, 20, 278–284.
5. Goktun, S., 1998, An overview of ozone safe alternatives for R502, Energy, 23, 379–381.
6. Xuan, Y. and Chen, G., 2005, Experimental study on HFC161 mixture as an alternative refrigerant to R502, International Journal of Refrigeration, 28, 436–441.
7. Park, K.J. and Jung, D.S., 2007, Thermodynamic performance of R502 alternative refrigerant mixtures for low temperature and transport applications, Energy Conversion and Management, 48 (12), 3084–3089.
8. Dalkilic, A.S. and Wongwises, S., 2010, A performance comparison of vapour-compression refrigeration system using various alternative refrigerants. International Communications in Heat and Mass Transfer, 37, 1340-1349.
9. Wongwises, S. and Chimres, N., 2005, Experimental study of hydrocarbon mixtures to replace HFC134a in domestic refrigerators, Energy conservation and Management, 46, 85–100.
10. Fatouh, M. and El Kafafy, M., 2006, Experimental evaluation of a domestic refrigerator working with LPG, Applied Thermal Engineering, 26, 1593–1603.
11. Hammed, M.A. and Alsaad, M.A., 1999, The use of hydrocarbon mixtures as refrigerants in domestic refrigerators, Applied Thermal Engineering, 19, 1181–1189.
12. Akash, B.A. and Said, S.A., 2003, Assessment of LPG as a possible alternative to R-12 in domestic refrigerator, Energy Conversion Management, 44, 381–388.
13. He, M.G., Li, T.C., Liu, Z.G. and Zhang, Y., 2005, Testing of the mixing refrigerant HFC152a/HFC125 in domestic refrigerator, Applied Thermal Engineering, 25, 1169–1181.
14. Tashtoush, B., Tahat, M. and Shudeifat, M.A., 2002. Experimental study of new refrigerant mixtures to replace R12 in domestic refrigerators, Applied Thermal Engineering, 22, 495–506.
15. Venkatarathnam, G.S. and Sirinivasamoorthy, S., 1999, Effect of mixture composition on the formation of pintch points in condensers and evaporators for zeotropic mixtures, International Journal of Refrigeration, 22, 205-215.
16. Rajapaksha, L., 2007, Influence of special attributes of zeotropic refrigerant mixtures on design and operation of vapour compression refrigeration and heat pump systems, Energy conversion and Management, 48, 539–545.
17. Johansson, A. and Lundqrist, P., 2001, A method to estimate the circulated composition in refrigeration and heat pump systems using zeotropic refrigerant mixtures. International Journal of Refrigeration, 24, 798–808.
18. Rajapaksha, L. and Suen, K.O., 2004, Influence of liquid receiver on the performance of reversible heat pumps using refrigerant mixtures. International Journal of Refrigeration, 27, 53–62.
19. Saito T., Research and development of systems with natural working fluids in Japan. IEA Annex 22 Workshop on Compression Systems with Natural Working Fluids, Trondheim, Norway (1995).
20. Granryd E., Research and development of systems with natural working fluids in Sweden. IEA Annex 22 Workshop on Compression Systems with Natural Working Fluids, Trondheim, Norway (1995).
21. Chapman J. F., Welsby P. and Whitman D. J., 1992, Gas cooling-a worldwide overview, Proc. Building on Success, The Institution of Gas Engineers.
22. Thevenot R., 1979, A History of Refrigeration throughout the World, International Institute of Refrigeration, Paris.
23. DuPont Fluorochemicals and Honeywell, 2007. DuPont, Honeywell Announce Refrigerants Global Joint Development Agreement. Press Release. Wilmington, DE, and Morris Township, NJ, USA (29.03.07).

ISSN 2250-2459, *Volume 3, Special Issue 3: ICERTSD 2013, Feb 2013, pages 400-409*

AUTHOR BIOGRAPHY

Sudipta Paul persuing, BE (4th year) at Department of Mechanical Engineering at Bengal Engineering and Science University, Shibpur, India. He completed his schooling from Gobardanga Khantura High School in the year 2008.He has research interest in green energy, heat transfer, micro fluidics. He is now working on the project of developing the equation state for the pure and refrigerants using virial coefficients.

Achinta Sarkar got B.Tech degree from Kalyani Government Engineering College, India in 2009 and M.E. degree from Bengal Engineering and Science University, Shibpur, India in 2011. Presently he is a PhD scholar in Bengal Engineering and Science University, Shibpur, India.

Bijan Kumar Mandal got his B.Tech (Hons.) and M. Tech. degrees in Mechanical Engineering from the IIT, Kharagpur and Ph.D. from Jadavpur University. Currently, he is a Professor in the Department of Mechanical Engineering at Bengal Engineering and Science University, Shibpur. His areas of interest include alternative fuels and combustion.