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### Alternative Refrigerants: A Review

S.K. Kalla\*, J.A. Usmani

\* Research Scholar, Department of Mechanical Engineering, Jamia Millia Islamia, New Delhi -110025  
(Delhi), India

[skkalla@yahoo.com](mailto:skkalla@yahoo.com)

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#### Abstract

During the last decade, substantial research activities have been undertaken regarding refrigeration cycles and systems with particular emphasis on the replacement of refrigerants like R134a by refrigerants like hydrocarbons which have negligible GWP (Global Warming Potential). Besides using eco-friendly refrigerants, thrust has been given upon devising methods to increase the efficiency of the refrigeration cycle/system, which will also contribute to reducing emission of GHG (Green House Gases). This paper provides a review of the efforts to replace the HFCs (hydrofluorocarbons) which are harmful to the environment.

**Keywords:** Refrigerant; Global warming; COP; VCR

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#### Introduction

The increasing energy consumption is more prominent in the industrial sector and is mostly related to the heavy inductive machinery like motors, refrigeration and air-conditioning units etc. These refrigeration and air-conditioning units contribute to the major share of the energy consumption because of heavier compressor used in such systems. Refrigeration and air conditioning (RAC) play a very important role in modern human life for cooling and heating requirements. It covers a wide range of applications starting from food preservation to improving the thermal and hence living standards of people. The utilization of these equipments in homes, buildings, vehicles and industries provides for thermal comfort in living/working environment and hence plays a very important role in increased industrial production of any country. The increasing demand of energy primarily for RAC and HP (Heat Pump) applications (around 26–30%), degrades environment, produces global warming and depletes ozone layer, etc. Therefore to overcome these aspects there is urgent need of efficient energy utilization methods.

The refrigeration industry is puzzled by the two of the most pressing environmental issues, namely, global warming and ozone depletion. It is logical that these two seemingly distinct, albeit, intricately related challenges be addressed together not only through new working fluids but also through innovative thermodynamic cycles. At the same time

the novelty must be combined with practical viability keeping in view the current state of system practices. The vapour compression refrigeration (VCR) with the positive displacement compressors (such as reciprocating, rotary, and scroll or screw compressors) continues to be the workhorse of cooling demands. Solid adsorption, liquid absorption, thermoelectric and thermo-acoustic cycles offer limited other options. Vapour absorption has been the most tested out among them. However, it lacks the benefit of scalability to low cooling capacities and is limited by the choice of working pairs. The most investigated combination is lithium bromide - water system, which cannot be used below about 5 °C, and is handicapped by operation at sub atmospheric pressures. Also, it cannot be used in a hybrid compression system with conventional compression of water vapour. Ammonia- water is the other most widely investigated pair, which has the problem of carryover of water vapour into the refrigeration circuit, need for high pressures and reservations on acceptability of ammonia in small scale refrigeration units. Thermoelectric systems are seldom scalable to large capacities and the thermo-acoustics is still in developmental stages.

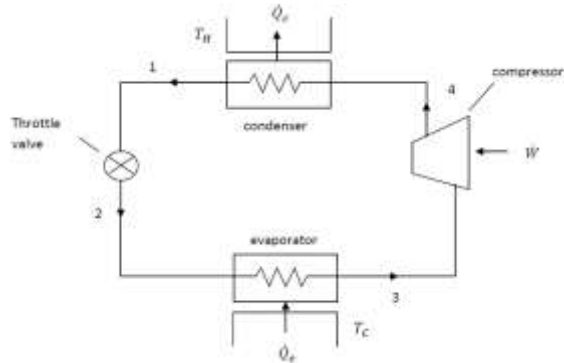
The researches which have been undertaken include exergy analysis of replacement of CFCs by zero ODP (ozone depleting potential) refrigerants in domestic refrigerators and other refrigeration

systems. In this paper a detailed review of the efforts to use alternative refrigerants has been carried out.

## Materials and methods

### Use of Alternative Refrigerants as Replacement of CFCs

In evaluating the thermodynamic performance of various alternative refrigerants, energy (first law) analysis can be used. But first law is concerned only with the conservation of energy. It does not provide information on how, where, and the amount of performance is degraded. As a complement to the present materials and energy balances, exergy calculations can provide increased and deeper insight into the process, as well as new unforeseen ideas for improvements. Fig. 1 shows the schematic diagram of a vapour compression refrigeration system which utilizes a refrigerant as a medium of heat transfer.



**Figure 1:**

#### *Vapour compression refrigeration cycle.*

The GWP (global warming potential) of some common refrigerants is shown in Table 1.

**Table 1. GWP of some refrigerants**

Refrigerant	GWP
R134a	1430
R290	<20
R600a	<20
R436A	<20

Padilla et al. experimentally verified that R413A could be an ozone friendly, exergy efficient and safe viable alternative to R12 for domestic and small commercial refrigeration systems with the main advantage that it can be replaced directly without the need to replace or modify any system component. In a study by Dalkilic and Wongwises, an ideal vapour-compression refrigeration system was used for the performance analysis of alternative new refrigerant mixtures as substitutes for CFC12, HFC134a, and

CFC22. Considering the comparison of performance coefficients (COP) and pressure ratios of the tested refrigerants and also the main environmental impacts of ozone layer depletion and global warming, refrigerant blends of HC290/HC600a (40/60 by wt.%) and HC290/HC1270 (20/80 by wt.%) were found to be the most suitable alternatives among refrigerants tested for R12 and R22 respectively. The refrigeration efficiency, the performance coefficient (COP) of the system, increases with increasing evaporating temperature for a constant condensing temperature in the analysis. Better performance coefficient values (COP) than those of the non superheating/subcooling case were obtained as a result of this optimization.

Arora and Kaushik presented a detailed exergy analysis of an actual vapour compression refrigeration (VCR) cycle. A computational model was developed for computing coefficient of performance (COP), exergy destruction, exergetic efficiency and efficiency defects for R502, R404A and R507A. The results indicated that R507A is a better substitute to R502 than R404A. The efficiency defect in condenser was highest, and lowest in liquid vapour heat exchanger for the refrigerants considered. They used EES (Engineering Equation Solver) software for this purpose. Hwang et al. compared R-290 and two HFC blends for walk-in refrigeration systems. To help provide a clear understanding of the relative performance potential of HFCs (R-404A and R-410A) as compared to R-290 for walk-in refrigeration systems representing direct expansion commercial refrigeration systems with small charge, an experimental evaluation of the three refrigerants was investigated. To compare the environmental impact of refrigerants over the entire life cycle of fluid and equipment, including power consumption, the life cycle climate performance (LCCP) of the three refrigerants were evaluated based on measured data. The estimated LCCPs at various emission rates indicate that the LCCP of R-290 is always lower than that of R-404A. The LCCP of R-410A is lower than that of R-290 as long as the annual emission is kept below 10%. It was concluded that R-410A has less or equivalent environmental impact as compared to R-290 when safety (toxicity and flammability), environmental impact (climate change), cost and performance (capacity and COP) are considered. Coil Designer and VapCyc software were used in this study. Copetti et al. in their theoretical study presented the results to characterize the hydrocarbons propane (R290) and isobutane (R600a) to be used in refrigeration systems in substitution for the R22. The performances of these refrigerants in refrigeration cycles are compared by

using a standard refrigeration cycle, with evaporation temperatures between  $-20^{\circ}\text{C}$  to  $10^{\circ}\text{C}$  and condenser temperature of  $40^{\circ}\text{C}$ . This study was carried out with the aid of the Cycle\_D simulation program. The refrigerants thermodynamic properties were obtained from REFPROP (NIST). The results showed that both R290 and R600a can be R22 substitutes in this range of application. The hydrocarbon R600a presented a better thermodynamics behavior than the R22 in the majority of the analyzed performance parameters, mainly for evaporation temperatures higher than  $-10^{\circ}\text{C}$ . The hydrocarbon R290, showed similar results to the R134a.

Zhang and Niu used a new binary mixture of R744 and R290 as an alternative natural refrigerant to R13. Its environmental performance is friendly. It has an ODP of zero and GWP smaller than 20. Experimental studies for this mixture and R13 were performed on a cascade refrigeration system only with modification to capillary in low-temperature circuit. COP and refrigeration capacity of this binary mixture were higher than those of R13, at the same time, condensing pressure, evaporating pressure, compression ratio, and discharge temperature were also higher than that of R13 when the high-temperature circuit of cascade refrigeration system was kept invariable. The new binary mixture of R744 and R290 is considered as a promising alternative refrigerant to R13 when the evaporator temperature is higher than 201 K. Venkataramanmurthy and Senthil Kumar presented an experimental comparison of energy, exergy flow and second law efficiency of R22 and its substitute R436b vapour compression refrigeration cycles. It was found that the evaporating temperatures have strong effects on the exergy flow losses and on the second law efficiency and COP of the cycle but little effects on the other components of the exergy losses. The second law efficiency and the COP increased, and the total exergy loss decreased with decreasing temperature difference between the evaporator and refrigerated space and between the condenser and outside air. The reasons for low exergy efficiency were due to large exergy destructions in the compressor and the condenser.

Chen and Prasad presented a performance comparison analysis of vapour-compression refrigeration systems using refrigerant HFC 134a and CFC 12. The analysis was based on computer simulation of actual cycles rather than the ideal cycles. A comparison of these two systems from a thermodynamic point of view was presented using exergy loss as a performance evaluation criterion. These results indicated that the HFC 134a system was only slightly inferior to the CFC12 systems due

to a higher (about 3%) exergy loss with HFC 134a. COP of the system using HFC 134a was 3% lower than that using CFC 12. The increase in total exergy loss was primarily due to the expansion device and the compressor. With the increasing environmental concern on global warming, hydrofluoro-olefin (HFOs), possessing low GWP, has attracted great attention of many researchers recently. In their study, Zhang et al. developed non-azeotropic mixtures composed of HFOs (HFO-1234yf, HFO-1234ze (z), HFO-1234ze (e) and HFO-1234zf) to substitute for HFC-134a and CFC-114 in air-conditioning and high-temperature heat pump systems, respectively. The cycle performances were evaluated by an improved theoretical cycle evaluation methodology. The results showed that all the mixtures proposed in the study were favorable refrigerants with excellent thermodynamic cycle performances. M1A presented lower discharge temperature and pressure ratio and higher COP<sub>c</sub> (Coefficient of performance in cooling) than that of HFC-134a. The volumetric cooling capacity was similar to HFC-134a. It can be served as a good environmentally friendly alternative to replace HFC-134a. M3H delivered similar discharge temperature as CFC-114 did. And the COP<sub>h</sub> (Coefficient of performance in heating) was 3% higher. It exhibits excellent cycle performance in high-temperature heat pump and is a promising refrigerant to substitute for CFC-114. And the gliding temperature differences enable them to exhibit better coefficient of performance by matching the sink/source temperature in practice. Because the toxicity, flammability and other properties are not investigated in detail, extensive toxicity and flammability testing needs to be conducted before they are used in a particular application.

Wang et al. presented the refrigerant HFC-161 as an alternative refrigerant to HFC-410A in a small scale refrigeration system. Theoretical cycle performances of HFC-410A, HFC-32 and HFC-161 were calculated and analyzed under the rated working condition. The results showed that the COP of HFC-161 is 10.0% and 17.8% higher than that of HFC-32 and HFC-410A, respectively, and the discharge temperature of HFC-161 is the lowest among these refrigerants. Experimental results showed that the HFC-161 can achieve higher COP by 15–25% than HFC-410A and HFC-32, and the discharging temperature of HFC-161 is much lower than that of HFC-410A and HFC-32. The power consumption and cooling capacity of HFC-161 were the smallest among these refrigerants. These results showed that HFC-161 is a promising alternative refrigerant to HFC-410A for small-scale refrigeration systems, which supply a very valuable reference for the actual

system of HFC-161. Kulcar et al. described the replacing of refrigerant R22 in a cooling system for preparing chilled water, used for cooling reactors producing phenol-formaldehyde resins. After analyzing the existing state and the capabilities of the cooling system, the refrigerant R22 was replaced with refrigerant R407C. For both refrigerants a calculation of the cooling system has been made, the results of which were given in the form of diagrams depending on the evaporation temperature of the refrigerant. Profitability evaluation of replacing a refrigerant was carried out using the method of the net present value (NPV), the coefficient of profitability and the period of time in which the investment is going to return itself. Also the calculations of the savings of electrical energy needed for the running of the compressors and the price of chilled water were done, using the method of internal profitability level (IPL).

Rocca and Panno presented the results of an experimental analysis comparing the performance of a vapour compression refrigerating unit operating with R22, and its performance in comparison to a new HFC fluid, substituting the former according to Regulation No 2037/2000. In particular, the plant working efficiency was first tested with R22 and then with three new HFC fluids: R417A, R422A and R422D. The investigation verified that despite the case of substitution and the advantage of being able to continue to use mineral oil as a lubricant in the compressor, the performance with the new tested fluids did not result as efficient as when using R22. Palm presented a comparison of the properties and performance of hydrocarbons as refrigerants in small-size heat pump and refrigeration systems (<20 kW cooling). A listing of several commercially available systems was also presented. The designs, safety precautions and performances of some of these systems were described. As a general conclusion, it was shown that using hydrocarbons will result in COPs equal to, or higher than, those of similar HFC systems. It was also shown that components suitable for hydrocarbon systems were available on the market, even though the number of large size hermetic compressors was limited. A major concern, which should not be taken lightly, is the safety issue. Reduced charge through indirect systems and compact heat exchangers, outdoor placing of the unit, hydrocarbon sensors and alarms and forced ventilation are all steps which may be applied to reduce the risks under normal operation.

Spatz and Motta reported that due to the ongoing global phase-out of R-22, which was still the most widely used refrigerant around the world, there was a need to replace this refrigerant in many different

applications. They focussed on a thorough evaluation of the R-22 replacement options for medium temperature refrigeration applications. It included a thermodynamic analysis, comparison of heat transfer and pressure drop characteristics, system performance comparisons using a validated detailed system model, safety issues, and determination of the environmental impact of refrigerant selection. Three potential alternatives to the R-22 were studied: two HFCs (404A and R-410A) and one HC (R-290). An HFC refrigerant, R-410A, was shown to be an efficient and environmentally acceptable option to replace R-22 in medium temperature applications.

### Results and discussion

An ideal vapour-compression refrigeration system is used in various studies for the performance analysis of alternative new refrigerant mixtures as substitutes for CFC12, HFC134a, and CFC22. After considering the comparison of performance coefficients (COP) and pressure ratios of the tested refrigerants and also the main environmental impacts of ozone layer depletion and global warming, refrigerant blends of HC290/HC600a (40/60 by wt.%) and HC290/HC1270 (20/80 by wt.%) are found to be the most suitable alternatives among refrigerants tested for R12 and R22 respectively. In the analysis, the refrigeration efficiency, the performance coefficient (COP) of the system, increases with increasing evaporating temperature for a constant condensing temperature. Performance coefficient values (COP) are better than those of the non-superheating/subcooling case.

### Conclusion

The present study investigates some methods to reduce emission of GHG (Green House Gases). The following conclusion is drawn: Refrigerant blends of HC290/HC600a (40/60 by wt. %) instead of CFC12 and HC290/HC1270 (20/80 by wt. %) instead of CFC22 are found to be replacement refrigerants among other alternatives. This study can be useful as it includes a review of the strategy for alleviating global warming.

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##### S.K.Kalla

**Suneel K. Kalla** received the B.E. degree in Mechanical engineering from National Institute of Technology (NIT), Srinagar, India, and M.Tech. degree in Energy and environmental management from Indian Institute of Technology (IIT), Delhi, India. Currently he is working towards PhD degree at Jamia Millia Islamia University, New Delhi, India. He has 4 publications in the area of refrigeration. He has a strong interest in environmental engineering and energy efficiency of refrigeration systems.

Email: [skkalla@yahoo.com](mailto:skkalla@yahoo.com)



##### J.A.Usmani

**Jamshed A. Usmani** has a strong research interest in energy and environmental management. He is currently with department of mechanical engineering, Jamia Millia Islamia University, India. He has received PhD in energy studies from, Indian Institute of Technology (IIT), Delhi, India. He has published five papers in international journals and two papers in national journal. Dr. Usmani visited Basrah, Iraq on teaching assignment in F.I.T. Basrah, Iraq, Ministry of Higher Education and Scientific Research, Iraq and served as Assignment Lecturer for about 4 years.

Email: [jausmani@yahoo.com](mailto:jausmani@yahoo.com)