

The Use of Natural Refrigerants in Refrigeration and Air Conditioning Systems: A Review

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Abstract. The refrigeration and air-conditioning sector is now undergoing a crucial phase where all the existing conventional refrigerants are being permitted to be neither produced nor consumed. For a better future, there is an immediate demand to look for clean refrigerants which are eco-friendly. The world is now looking for the refrigerants which do not contribute to the ozone layer depletion and global warming. The use of natural refrigerants like CO₂, NH₃ and hydrocarbons such as R290, R600, R600a and blends of hydrocarbons are possible solution to this problem and are being used efficiently in many systems. In this paper the importance of reconsidering the use of natural refrigerants to replace the synthetic refrigerants has been discussed. A review on the different systems where natural refrigerants are being used and modifications to such systems that could ensure better efficiency has been presented.

Keywords: Ammonia; Carbon dioxide; COP; Hydrocarbons; Natural refrigerants

1. Introduction

The natural refrigerants like water, methyl chloride, sulphur dioxide, carbon dioxide and ammonia were used in the beginning of the invention of mechanical refrigeration. But unfortunately, most of them proved to be toxic and flammable. Thus, chlorofluorocarbon (CFC) refrigerants came into picture and served as excellent and efficient refrigerants for years till the 1970s. In 1973 Prof. James Lovelock discovered Freon to possess high ozone layer depletion potential (ODP) [1]. The Montreal protocol stopped the production and consumption of such ozone layer depleting CFC refrigerants. Then, the hydro fluorocarbon (HFC) refrigerants were used as alternatives to CFCs. But, HFCs have high global warming potential (GWP). More than 190 countries gathered in Kigali, in 2016 and adopted an amendment to the 1989 Montreal Protocol to eliminate HFC gases. Now, the search for new alternative refrigerants which can replace the conventional CFC and HFC refrigerants, without compensating the performance of the systems has become a challenge. The natural refrigerants like CO₂, NH₃ and hydrocarbons have zero ODP and GWP and are considered to be the long term replacements to CFCs and HFCs. The natural refrigerants failed back in those days, due to the problems of toxicity and flammability. The present day technology can easily handle such problems. Thus, the use of natural refrigerants could be the best possible solution to stop the environmental destruction caused by the conventional CFC and HFC refrigerants [2].

2. Properties of ideal refrigerants

Theoretically any fluid presents a potential for refrigeration, but practically the fluids should show some basic properties to be used as effective refrigerants. Some of such criteria are as follows [3]:



- The refrigerants should have low boiling point and low freezing point.
- The refrigerants should be selected mainly for its high latent heat of vaporization.
- They must be harmless: non-toxic, non-flammable, non-explosive and non-corrosive.
- The pressures of the refrigerants, should allow their use in a refrigeration system with a reasonable size of the pipes and compressor.
- They must have high miscibility with lubricating oil.
- They should give high COP in the working temperature range.
- Finally, the most important criteria in the present day world is that the refrigerant should have zero ozone layer depletion potential and very low global warming potential.

The properties like ODP, GWP and flammability for different refrigerants have been shown in table 1.

Table 1: Properties of different refrigerants [4]

Refrigerant group	Refrigerant example	ODP	GWP	Atmospheric lifetime (years)	Flammability
CFCs	R11, R12, R115	0.6-1	4750-14,400	45-1700	Non-flammable
HCFCs	R22, R141b, R124	0.02-0.11	400-1800	1-20	Non-flammable
HFCs	R407C, R32, R134a	0	140-11,700	1-300	Non-flammable
HFOs	R1234yf, R1234ze, R1234yz	0	<0-12	-	Flammable
Natural Refrigerants	R744, R717, HC(R290, R600, R600a)	0	0	Few days	Flammable

In this paper, the properties and performances of natural refrigerants have been discussed with focus on hydrocarbons and their mixtures as refrigerants in particular. The use of hydrocarbons and their mixtures in various systems like domestic refrigeration and air-conditioning, automobile air-conditioning, heat pumps and chillers has been presented.

3. Natural refrigerants

The natural refrigerants such as carbon dioxide, ammonia and hydrocarbons (R290, R600, and R600a) are among those refrigerants that are considered as long time replacements for CFCs. The natural refrigerants show zero ODP and very low GWP. Among the natural refrigerants, ammonia, carbon dioxide and hydrocarbons have a broader range of application. Thus, it is very important to know both the advantages and disadvantages of using these refrigerants.

3.1. Water

Water is the best known refrigerant and its ease of availability makes it very popular. The other important aspects of water are low cost and safety. However, water can be used only for high temperature applications, due to the very low density of water vapour, which sharply decreases the refrigeration capacity for temperatures below 100°C. The refrigeration effect of water is roughly 20 times higher than that of R-12, but a compressor of very large capacity should be employed in case of water. The cost also increases with the size of the compressor [5].

3.2. Carbon Dioxide

Carbon dioxide (designated as R744) is a non-flammable, non-toxic, odourless, inexpensive working fluid with zero ODP and zero effective GWP. It can be obtained as a waste product from different processes. 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 CO₂ and halocarbons. Pearson [6] reviewed the development of the old carbon dioxide systems, considering the technical, commercial and social reasons for their slow development and subsequent decline. Carbon dioxide is heavier than

air and thus causes suffocation. Also, the high pressures associated with CO₂ prevent it from being used in existing regular systems. Thus, it is usually used in systems with modifications. Polzot *et al.* [7] evaluated the energy performance of a R744 refrigeration system, which provides refrigeration and other heating facilities like providing domestic hot water for a supermarket. Sharma *et al.* [8] found that the implementation of CO₂ transcritical booster systems or cascade/secondary loop systems in supermarkets using optimized operating conditions lead to reduced direct greenhouse gas emissions while achieving comparable energy consumption.

3.3. Ammonia

Ammonia (R717) has excellent thermodynamic properties as compared to halo carbons. The important advantages of ammonia are its tolerance to normal mineral oils, low sensitivity to small amounts of water in the system, simple leak detection, unlimited availability and low price. However, it is unsuitable to domestic, automotive and small commercial refrigeration and heat pump systems, due to pungent smell and flammability. On the contrary, the pungent smell of ammonia also helps in easy leak detection at a concentration as low as 5 ppm in air while thousand times higher concentration is required for any accident to take place. The performance of a hybrid refrigeration system with combined sorption and conventional vapour compression refrigeration machine driven by dual source (heat and/or electricity) was studied by Lychnos and Telto [9]. Ammonia was used as refrigerant in the entire system. The overall hybrid system coefficient of performance ranged between 0.24 and 0.76.

3.4. Hydrocarbons

The most common hydrocarbons (HC) are propane (R-290), propylene (R-1270) and blends with propane, butane (R-600) and isobutane (R-600a). The use of hydrocarbons as refrigerants is not just good for the environment, but also it can reduce the energy consumption. HC and their mixtures were found to be the good substitutes for replacing R12 and R134a in domestic and commercial refrigeration systems. Kim *et al.* [10] observed the performance of a hydrocarbon refrigerant, R600a, as an alternative for R-12 household auto-defrost refrigerator/freezer. The test results showed that the energy efficiencies and the cooling speeds with R-600a were improved by 1-11% and 3-10%, respectively, compared to R-12. Ahamed *et al.* [11] compared thermodynamic performance of a domestic refrigerator using pure butane and isobutane as refrigerants. The COP of the system as obtained by Ahamed *et al.* [11] using R134a, R600 and R600a has been shown in figure 1. They found that the exergy and energy efficiencies of isobutane were 50% and 75% higher than that of R-134a.

Mohanraj *et al.* [12] theoretically assessed the possibility of using R152a and hydrocarbon refrigerants such as R290, R1270, R600a and R600 as alternatives to R134a in domestic refrigerators. They observed that the coefficient of performance (COP) of R290 and R1270 were lower than that of R134a only by about 2.3% and 1.9% respectively. Vaghela [13] investigated different alternative refrigerants as a drop in substitute of R134a for automobile air conditioning system. The thermodynamic properties of different alternative refrigerants i.e. R290 and R600a were found to be better than R134a. Choudharia and Sapali [14] carried out comparative performance analysis of R290 with R22 on a standard vapour compression cycle. It was also observed that the refrigerant mass flow rate required for the system with R290 as refrigerant is lower by 50% compared to that with R22 as shown in figure 2. Park and Jung [15] tested the performance of two hydrocarbon refrigerants R290 and R1270 as substitutes to R22. They noted that these hydrocarbons provide good performance with reasonable energy savings without any environmental problems and thus can be used as long-term alternatives for residential air-conditioning and heat pumping applications.

3.5. Hydrocarbon Mixtures

The mixtures of pure refrigerants were also found to give good results in refrigeration systems. Dalkilic and Wongwises [16] studied a traditional vapour-compression refrigeration system using refrigerant mixtures based on R134a, R152a, R32, R290, R1270, R600, and R600a in various proportions and their results were compared with that of R12, R22, and R134a as possible alternative replacements. The HC refrigerant blends of HC290/HC600a (40/60 by weight) instead of CFC12 and HC290/HC1270 (20/80 by weight) instead of CFC22 were recognised to be suitable replacements.

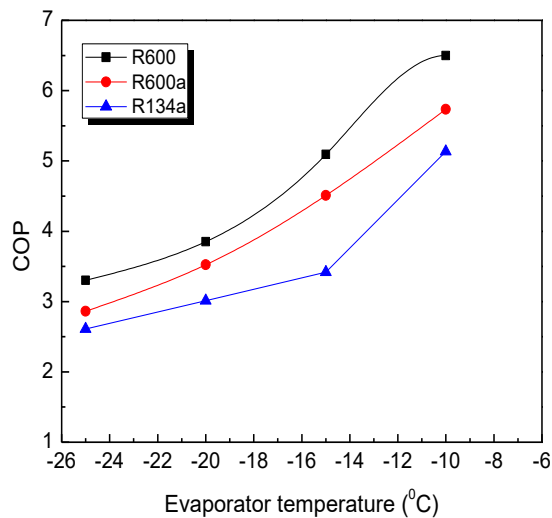


Figure 1. Variation of coefficient of performance (COP) with evaporator temperature.

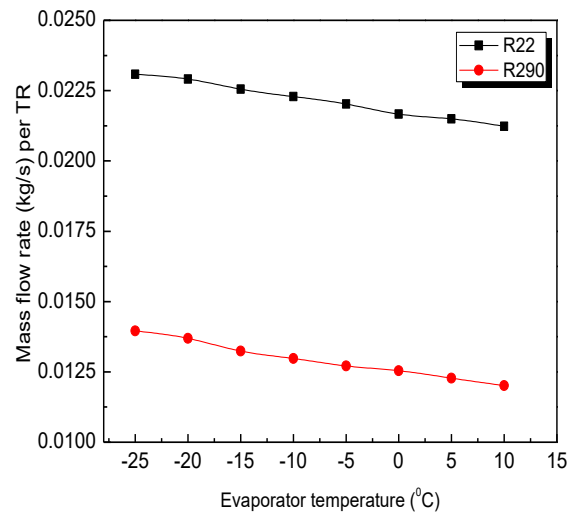


Figure 2. Variation of mass flow rate of the refrigerant with evaporator temperature

Yu and Teng [17] used hydrocarbon refrigerant mixtures in a R134a refrigerator to evaluate the performance and feasibility using these alternative refrigerants by conducting the no-load pull-down test and 24-hour on-load cycling test. The mixtures of R290/R600a in the proportions 65/35, 50/50 and 0/100 were named as HC1, HC2 and HC3 respectively. The comparisons of these refrigerant mixtures with R134a in terms of COP have been shown in figure 3 with HC1 showing highest values. Shaik and Babu [18] studied the thermodynamic performance of a 0.8 TR window air conditioner with ten binary refrigerant mixtures consisting of propylene (R1270) and propane (R290) based on actual vapour compression refrigeration cycle. They considered R1270-R290 in the ratios 25-74, 35-65, 45-55, 55-45, 65-35, 75-25, 85-15 and named them M1, M2, M3, M4, M5, M6, M7, M8, M9 and M10 respectively. The COP of these refrigerants has been compared to that of R22 as shown in figure 4. They found that all mixtures showed comparable COP to that of R22 with mixtures M7 and M8 showing almost equal performance.

Ahamed *et al.* [19] presented a review on the exergy analysis on vapour compression refrigeration systems. They observed that hydrocarbons are refrigerants having low ODP and GWP. They concluded that mixtures of hydrocarbons with R134a showed better performance. Park *et al.* [20] investigated the performances of two pure hydrocarbons and seven mixtures composed of propylene, propane, HFC152a, and dimethyl ether to substitute R22 in residential air-conditioners and heat pumps. They noted that the coefficient of performance of these mixtures was up to 5.7% higher than that of R22 at the evaporation and condensation temperatures of 7°C and 45°C respectively. Jwo *et al.* [21] investigated the performance of home refrigerators using mixture of hydrocarbon refrigerants, R-290 and R-600a with each 50% component ratio, instead of the refrigerant R-134a. They found that the total consumed energy was reduced by 4.4% and mass flow rate of the refrigerant was reduced by 40%. Mohanraj *et al.* [22] reported that HC mixtures and R152a could be substitutes for R12 and R134a in domestic refrigeration sector while R290, R1270, R290/R152a, R744 and HC/HFC mixtures to be the best long-term alternatives for R22 in air conditioning and heat pump applications. Also, R123 was found to be an attractive alternative to R11, R12 and R22 in chillers applications, whereas R152a and HC mixtures were found to be a best option for automobile air conditioners. In another work, Ahamed *et al.* [23] observed that pure R-290 is a high flammable refrigerant. They noted that mixing of R-290 with R-22 reduced the global warming potential of R22, and also reduced the flammability. This mixture was also found to enhance heat transfer compared to that of R-22. Palm [24] presented a comparison of the properties and performances of hydrocarbons as refrigerants in small-size heat pump and refrigeration systems. Also, they concluded that the risks caused by the flammability of the hydrocarbons can be reduced by designing the systems for minimum charge of refrigerant, careful leak detection during production, hermetic design with minimum number of

connections, use of spark-proof electric components and ventilation of confined spaces. Siang and Sharifian [25] worked on the idea of extending the capillary tube of a portable air-conditioner in order to decrease the amount of refrigerant charge in the system. The results showed a significant reduction of 63.9% in the amount of propane in the capillary tube and liquid line, and a reasonable decrease 8.3% in the maximum speed of refrigerant for the air conditioner.

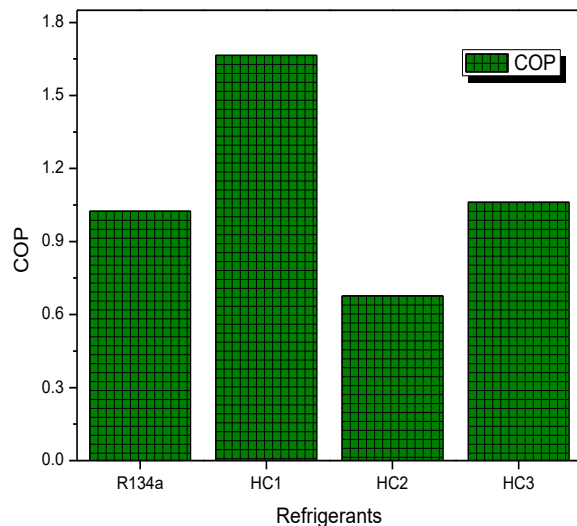


Figure 3. Comparison of COP for HC mixtures of R290 and R600a with R134a.

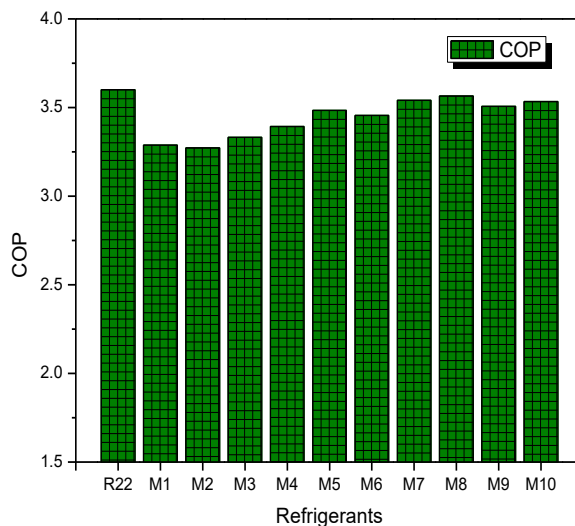


Figure 4. Comparison of COP for HC mixtures of R1270 and R290 with R22.

4. Conclusions

The following conclusions can be drawn on the use of natural refrigerants from this review work:

- The natural refrigerants should be studied and experimented to the maximum because the future regulations on synthetic refrigerants could be severe.
- The hydrocarbons and their mixtures serve as good refrigerants for different refrigeration and air-conditioning systems.
- The pure hydrocarbons R290 in place of R22 and R600a instead of R12 and R134a are found suitable for air-conditioning and refrigeration systems respectively.
- Also, R290/R600a mixture and R290/R1270 mixture may be good substitutes for R12 and R22 respectively.
- The drawbacks of hydrocarbons like flammability and toxicity can be overcome by using minimum charge and careful leak detection systems respectively.
- The flammability can also be reduced when hydrocarbons are used in mixtures.

References

- [1] Calm J M 2008 The next generation of refrigerants—Historical review, considerations, and outlook. *International Journal of Refrigeration*, 31(7), 1123-1133.
- [2] Lorentzen G 1995 The use of natural refrigerants: a complete solution to the CFC/HCFC predicament. *International Journal of Refrigeration*, 18(3), 190-197.
- [3] Benhadid-Dib S and Benzaoui A 2012 Refrigerants and their environmental impact Substitution of hydro chlorofluorocarbon HCFC and HFC hydro fluorocarbon. Search for an adequate refrigerant. *Energy Procedia*, 18, 807-816.
- [4] Harby K 2017. Hydrocarbons and their mixtures as alternatives to environmental unfriendly halogenated refrigerants: An updated overview. *Renewable and Sustainable Energy Reviews*, 73, 1247-1264.
- [5] Riffat S B, Afonso C F, Oliveira A C and Reay D A 1997 Natural refrigerants for refrigeration and air-conditioning systems. *Applied Thermal Engineering*, 17(1), 33-42.

- [6] Pearson A 2005 Carbon dioxide—new uses for an old refrigerant. *international Journal of Refrigeration*, 28(8), 1140-1148.
- [7] Polzot A, D'Agaro P and Cortella G 2017 Energy Analysis of a Transcritical CO₂ Supermarket Refrigeration System with Heat Recovery. *Energy Procedia*, 111, 648-657.
- [8] Sharma V, Fricke B, and Bansal P 2014 Comparative analysis of various CO₂ configurations in supermarket refrigeration systems. *International journal of Refrigeration*, 46, 86-99.
- [9] Lychnos G and Tamainot-Telto Z 2014 Performance of hybrid refrigeration system using ammonia. *Applied Thermal Engineering*, 62(2), 560-565. *Applied thermal engineering*, 66(1), 507-518.
- [10] Kim M H, Lim B H and Chu E S 1998 The performance analysis of a hydrocarbon refrigerant R-600a in a household refrigerator/freezer. *Journal of Mechanical Science and Technology*, 12(4), 753-760.
- [11] Ahamed J U, Saidur R, Masjuki H H and Sattar M A 2012 An analysis of energy, exergy, and sustainable development of a vapor compression refrigeration system using hydrocarbon. *International journal of Green Energy*, 9(7), 702-717.
- [12] Mohanraj M, Jayaraj S and Muraleedharan C 2008 Comparative assessment of environment-friendly alternatives to R134a in domestic refrigerators. *Energy Efficiency*, 1(3), 189-198.
- [13] Vaghela J K 2017 Comparative Evaluation of an Automobile Air-Conditioning System Using R134a and Its Alternative Refrigerants. *Energy Procedia*, 109, 153-160.
- [14] Choudhari C S and Sapali S N 2017 Performance Investigation of Natural Refrigerant R290 as a Substitute to R22 in Refrigeration Systems. *Energy Procedia*, 109, 346-352.
- [15] Park K J and Jung D 2008 Performance of R290 and R1270 for R22 applications with evaporator and condenser temperature variation. *Journal of Mechanical Science and Technology*, 22(3), 532-537
- [16] 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(9), 1340-1349.
- [17] Yu C C and Teng T P 2014 Retrofit assessment of refrigerator using hydrocarbon refrigerants. *Applied thermal engineering*, 66(1), 507-518.
- [18] Shaik S V and Babu T A 2017 Thermodynamic Performance Analysis of Eco friendly Refrigerant Mixtures to Replace R22 Used in Air Conditioning Applications. *Energy Procedia*, 109, 56-63.
- [19] Ahamed J U, Saidur R and Masjuki H H 2011 A review on exergy analysis of vapor compression refrigeration system. *Renewable and Sustainable Energy Reviews*, 15(3), 1593-1600.
- [20] Park K J, Seo T and Jung D 2007 Performance of alternative refrigerants for residential air-conditioning applications. *Applied Energy*, 84(10), 985-991.
- [21] Jwo C S, Ting C C and Wang W R 2009 Efficiency analysis of home refrigerators by replacing hydrocarbon refrigerants. *Measurement*, 42(5), 697-701.
- [22] Mohanraj M, Jayaraj S and Muraleedharan C 2009 Environment friendly alternatives to halogenated refrigerants—A review. *International Journal of Greenhouse Gas Control*, 3(1), 108-119.
- [23] Ahamed J U, Saidur R and Masjuki H H 2014 Investigation of environmental and heat transfer analysis of air conditioner using hydrocarbon mixture compared to R-22. *Arabian Journal for Science and Engineering*, 39(5), 4141-4150.
- [24] Palm B 2008 Hydrocarbons as refrigerants in small heat pump and refrigeration systems—a review. *International Journal of Refrigeration*, 31(4), 552-563.
- [25] Siang J T and Sharifian A 2017 Extending the Capillary Tube of a Propane Air-conditioner to Reduce the Refrigerant Charge. *Energy Procedia*, 110, 229-234.