

Natural Refrigerants and Its Application: A Comprehensive Review

Pradip Kailas Patil¹, Rishi Dewangan², Hemant Krishnarao Wagh³

¹Research Scholar, Amity University Rajasthan, Jaipur, India

²Assistant Professor, Amity University Rajasthan, Jaipur, India

³Associate Professor, R C Patel Institute of Technology, Shirpur, Maharashtra, India

pradip214@gmail.com

Received on: 17 March, 2024

Revised on: 20 April, 2024

Published on: 22 April, 2024

Abstract – Refrigeration and air conditioning are essential in both residential and industrial sectors. They have a significant influence on our day-to-day lives. They've also led to global environmental problems including global warming and ozone depletion. It is strongly suggested that the usage of dangerous synthetic refrigerants be phased out to decrease ozone depletion and counteract climate change effects. There is no net increase in greenhouse gas (GHG) emissions from the usage of natural refrigerants in the environment. The use of environmentally friendly refrigerants might be a viable solution to the problem of global warming. When choosing new refrigerants, however, a thorough analysis is required. The study identifies areas where the existing literature is lacking and recommends potential areas for further research.

Keywords- Natural refrigerant, Global warming, Ozone depletion, Nano refrigerants.

I. INTRODUCTION

Refrigeration is a long-established technology. The process of removing heat from a substance or enclosed space to keep it at a temperature lower than the surrounding air is called refrigeration. [1]. A substance or mixture that, in a heat cycle, reversibly changes phases from a liquid to a gas and back is known as a

refrigerant. Refrigerants are used as a heat transfer fluid in many different types of equipment, including water heaters, air conditioners, heat pumps, and refrigerators. Appropriate refrigerants are employed for applications requiring selective cooling and heating [2]. Before electricity was invented in the 1880s, refrigeration technology was employed by human civilization. Oliver Evans is credited with creating the idea of ether-based refrigeration in 1805. In 1834, Jacob Perkin invented the first refrigeration machine, based on this idea. Other researchers used various substances as mediating fluids in refrigeration systems: gasoline in the 1860s, NH₃ in 1873, CO₂ in 1886, and SO₂ in the 1890s. From 1830 to 1930, the most popular refrigerants were ether, NH₃, CCl₄, HCOOCH₃, HCs, CO₂, SO₂, H₂O, and CHCs. CCl₄, HCOOCH₃, HCs, CO₂, SO₂, H₂O, and CHCs. The majority of these refrigerants were hazardous, combustible, extremely reactive, and prone to mishaps. [3]. A natural refrigeration fluid is a type of refrigerant that is environmentally friendly and is a solution to ozone depletion and global warming and is the ultimate solution to these problems [4]. The refrigerants are divided into generations, which are explained further down. The behaviour of many generations of refrigerants is seen in Table 1[5].

Table 1- Different generation of refrigerant

Sr. No.	Generation of refrigerants	Behaviours of refrigerants
1	First generation 1830-1930s	Whatever worked Ethers, CO ₂ , NH ₃ , SO ₂ , HCOOCH ₃ , HC ₈ , H ₂ O, CCL ₄ , CHC ₈ .
2	Second generation 1931-1990s	Safety and durability CFCs, HCFCs, HFCs, NH ₃ , H ₂ O.
3	Third generation 1990-2010s	Ozone Protection (HCFCs), HFCs, NH ₃ , H ₂ O, HC ₈ , CO ₂ .
4	Fourth generation 2010.	Global warming Zero/low ODP, low GWP.

Refrigerants from the First Generation

In the early 1800s, when mechanical refrigeration first emerged, natural refrigerants were employed. Refrigerators made from the late 1800s to 1929 used first-generation refrigerants such as methyl chloride, ammonia, and sulfur dioxide. The typical refrigerants over the first 100 years were whatever was available and functional. Numerous first-generation refrigerants were highly reactive, and nearly all of them were either toxic, flammable, or both. The following sections go through the features of several of the first-generation refrigerants.

Water is a well-known refrigerant that has been used in refrigeration for more than a century. Globally, water (R-718) is readily accessible and recognized as a non-toxic, non-flammable substance.

In contrast to CFCs, R-718 exhibits a greater refrigeration effect, yet it requires ten times the volumetric flow for equivalent refrigeration capacity, thereby raising the operational costs of axial or centrifugal compressors. [6, 7]. Water is cheap and has great thermodynamic and chemical characteristics. Apart from these advantages, there are technological challenges because to the huge specific volume at low temperatures. Two of the problems include high compressor output temperatures and a high pressure ratio throughout the compressor.

Ammonia, an antiquated coolant used in absorption and vapour compression refrigeration systems (VCRs), is referred to by the acronym R717. Reduced molecular weight, a wide working temperature range because of its high critical point, considerable latent heat of vapourization, and easy leak detection are some of the advantages of R717. Conversely, R717 has a number of

shortcomings. It is combustible, irritating, and extremely toxic. Ammonia is difficult to keep dry because of its high attraction to water [8,9].

Copper and most copper alloys are corroded by it when it includes water. At high discharge temperatures, ammonia has a tendency to break down, producing hydrogen and nitrogen. As these gases enter the condenser, their pressures are added to the condensing pressure, increasing the total pressure head and the use of power [10].

Sulphur dioxide was a common refrigerant in the 1920s and 1930s, but it was eventually supplanted by methyl chloride and then by more desired fluorocarbon refrigerants. It's extremely poisonous, yet it's not explosive or flammable. In its pure form, it is non-corrosive, but when it combines with moisture, sulfurous and sulfuric acids are produced that are incredibly corrosive [11].

Methyl chloride was first used in 1878. The gas methyl chloride is characterized by its colorlessness, high flammability, and mildly pleasant odor. Methyl chloride is a methane-series halocarbon with many of the qualities desirable in a refrigerant, which explains its widespread usage in both residential and commercial applications in the past. When methyl chloride poured out of freezers in the 1920s, there were several fatalities. As a result, next-generation refrigerants have been discovered [12]. Table 2 lists a few first-generation refrigerants and their attributes.

Table 2- Refrigerant properties

Substance	R Number	M (kg/kmol)	NBP (°C)	GWP	ODP
Carbon dioxide	R-744	44.01	-55.6	1	0
Ammonia	R-717	17.03	-33.3	0	0
Sulphur dioxide	R-764	64.06	-10.0	0	0
Ethyl ether	R-610	74.12	35	0	0
Dimethyl ether	R-170	46.07	-25	0	0
Methyl chloride	R-40	50.49	-24.2	16	0.02

Refrigerants from the Second Generation

The second generation refrigerants differ by using chlorofluoro compounds for durability and safety. CFC refrigerants gave rise to the 2nd generation of refrigerants. CFC is a high-mass, non-toxic, and inflammable gas. This refrigerant is easy to compress into a liquid and evaporates quickly, carrying away a lot

of heat. Here are some of the generation's refrigerants, along with their thermodynamic characteristics and uses [13].

R-11 is a non-explosive and non-flammable. There are a number of applications for it such as small building air conditioning, factories, department shops, theatres, and so on. The solvent and secondary refrigerant is R-11 refrigerant. Low operating pressures and a strong propensity to destroy the ozone layer are two issues that have limited the usage of this refrigerant [14].

R-12 is a flexible refrigerant that may be utilized in various refrigeration and air conditioning systems. Domestic refrigerators liquid chillers and freezers, dehumidifiers, water coolers, transport refrigeration, water fountains, and ice makers all employ refrigerant R12 [14,15].

R12 is an extremely stable CFC that does not degrade under intense working circumstances. Regrettably, the CFC has a serious risk of contributing to ozone depletion. R- R-401a, 134a, and R-401b are some of the substitute refrigerants that are replacing R12 in the phase-out process [15].

Refrigerants from the Third Generation

They were largely refrigerants with limited ozone depletion potential. Table 3 lists the properties of various third-generation refrigerants. Hydrofluoroolefins (HFO), a novel family of fluorocarbon refrigerants with the potential for lower GWP, has been created. Their primary benefit, besides their low GWP, is that they may be used with existing refrigeration system designs. It is still a fluorinated gas even if this is advantageous to the sector and its customers [16].

Table 3 - Properties of Third Generation Refrigerants

R Number	M (kg/kmol)	NBP (oC)	GWP
R-32	-52.02	-51.65	580
R-134A	102.03	-26.07	1300
R-404A	97.6	-46.6	3800
R-407C	86.2	-43.8	1600
R-410A	72.59	-51.6	1900
R-507	98.86	-47.1	4000

Natural refrigerants

In the chemical and biological processes of nature, natural refrigerants exist naturally without human intervention. Natural refrigerants (R-610) include water

(R-718), ammonia (R-717), sulfur dioxide (R-764), carbon dioxide (R-744), air (R728), and ethyl ethers. Up to the invention of high-performance synthetic refrigerants in the 1930s, natural refrigerants were the mainstay of the HVACR industry. A rapid increase in synthetic refrigerants and fossil fuels led to ozone depletion and global warming, causing scientific communities and manufacturing companies to switch from halogenated hydrocarbons to natural refrigerants and fossil fuels to renewable energy [8, 9].

The great flammability of hydrocarbon refrigerants is their most distinguishing feature. In reality, hydrocarbons make good refrigerants if steps are taken to offset and how their flammability affects them. Mineral oils can be mixed with them and they have a high critical temperature [17].

It is appropriate to use propylene (R1270) and propane (R290) in common refrigeration applications since their average boiling points are below -40°C , which makes them suitable for common refrigeration purposes [18]. In addition to having significantly higher boiling points than butane (R600), butane (R600) and isobutane (R600a) also have much higher critical temperatures, which improves their operational efficiency. The most effective usage of hydrocarbons has been in home refrigerators with R600a [18,19].

It is possible to use propane or propane mixes safely if proper precautions are taken and window air conditioners are installed in sealed systems. With the right precautions taken, propane may also be used for automobile air conditioning with a manageable degree of risk [20]. Although R1270 is much more expensive than propane, it functions similarly, hence it is unlikely to be widely used. Hydrocarbons will surely appear as a refrigerant for low-charge window air conditioners, notwithstanding their apparent unappealingness for large-scale air conditioning applications [21].

One non-toxic and non-flammable gas found in the environment is carbon dioxide. Although it requires high pressures to operate, carbon dioxide has been used as a refrigerant since 1862. It has no odor and is non-flammable, non-toxic, non-corrosive and non-explosive. When it comes to marine refrigeration, carbon dioxide is still a non-toxic substitute for methyl chloride and ammonia. On the other hand, the far less effective carbon dioxide was phased out in the 1950s when halocarbons were introduced in the 1930s. One of the

reasons carbon dioxide is not a very efficient refrigerant is because of its low critical temperature [22].

Table 4 - Properties of Third Generation Refrigerants

Compositional group	Refrigerant No	Refrigerant Name	Ozone depletion Potential (O.D.P.)	Global warming potential (GWP) 20; 100; Yrs.
Natural Refrigerants	R170	Ethane	0.0	3; 3
	R290	Propane	0.0	3; 3
	R600	Butane	0.0	3; 3
	R600a	Isobutene	0.0	3; 3
	R717	Ammonia	0.0	0; 0
	R744	Carbon Dioxide	0.0	1; 1
	R1270	Propylene	0.0	3; 3

CONCLUSION

Considering the conclusions drawn from this study on next-generation refrigerants, it is possible to conclude as follows: Based on these studies, some points can be addressed in the following manner:

- Low GWP and zero ODP should be the foundation for the development of next-generation refrigerants.
- The refrigerant R-12 is now substituted with R-409A. As for the refrigerant R-22, it can be replaced by non-ODP substitutes such as R-407F and R-422D.
- It is important to recognize the current revival of natural refrigerants, which is driven by advanced technology

REFERENCES

- [1] Emani, M.S., Roy, R. and Mandal, B.K., 2017. Development of refrigerants: a brief review. *Indian J. Sci. Res*, 14(2), pp.175-181.
- [2] 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), pp.33-42.
- [3] Halimic, E., Ross, D., Agnew, B., Anderson, A. and Potts, I., 2003. A comparison of the operating performance of alternative refrigerants. *Applied thermal engineering*, 23(12), pp.1441-1451.
- [4] Patil, P.K., Gupta, A.K. and Mathur, P., 2022, May. Enhancing refrigeration system efficiency by the use of nanorefrigerants/nanolubricants: A comprehensive review. In *AIP Conference Proceedings (Vol. 2393, No. 1)*. AIP Publishing.
- [5] Calm, J.M. and Hourahan, G.C., 2001. Refrigerant Data Summary. *Engineered systems*, 18(11), pp.74-77.
- [6] Calm, J.M., 2008. The next generation of refrigerants—Historical review, considerations, and outlook. *international Journal of Refrigeration*, 31(7), pp.1123-1133.
- [7] Li, Q., Piechna, J. and Müller, N., 2011. Thermodynamic potential of using a counter rotating novel axial impeller to compress water vapor as refrigerant. *International Journal of Refrigeration*, 34(5), pp.1286-1295.
- [8] Wang, J., Zhao, P., Niu, X. and Dai, Y., 2012. Parametric analysis of a new combined cooling, heating and power system with transcritical CO₂ driven by solar energy. *Applied energy*, 94, pp.58-64.
- [9] Mota-Babiloni, A., Navarro-Esbrí, J., Molés, F., Cervera, Á.B., Peris, B. and Verdú, G., 2016. A review of refrigerant R1234ze (E) recent investigations. *Applied Thermal Engineering*, 95, pp.211-222.
- [10] Bolaji, B.O., 2011. Performance investigation of ozone-friendly R404A and R507 refrigerants as alternatives to R22 in a window air-conditioner. *Energy and Buildings*, 43(11), pp.3139-3143.
- [11] Boumaza, M., 2010. Performances assessment of natural refrigerants as substitutes to CFC and HCFC in hot climate. *International Journal of Thermal and Environmental Engineering*, 1(2), pp.125-130.
- [12] Lorentzen, G. and Pettersen, J., 1993. A new, efficient and environmentally benign system for car air-conditioning. *International journal of refrigeration*, 16(1), pp.4-12.
- [13] Patil, P.K., Dewangan, R. and Wagh, H.K., 2024. Performance Of A Vapour Compression Refrigeration System Using Different Concentrations Of Go Nanolubricants And A Safe Charge Of R600a Refrigerant. *Migration Letters*, 21(S3), pp.1337-1345.
- [14] Eng, D.M. and AIRAH, F., 2002. *Air Conditioning and Refrigeration Industry Refrigerant Selection Guide-2003*. Australian Institute of Refrigeration, Air-Conditioning and Heating Incorporated.
- [15] Keblinski, P., Eastman, J.A. and Cahill, D.G., 2005. Nanofluids for thermal transport. *Materials today*, 8(6), pp.36-44.
- [16] Bhattad, A., Sarkar, J. and Ghosh, P., 2018. Improving the performance of refrigeration systems by using nanofluids: A comprehensive review. *Renewable and Sustainable Energy Reviews*, 82, pp.3656-3669.
- [17] Yang, L., Ji, W., Mao, M. and Huang, J.N., 2020. An updated review on the properties, fabrication and application of hybrid-nanofluids along with their environmental effects. *Journal of Cleaner Production*, 257, p.120408.
- [18] Alawi, O.A., Sidik, N.A.C. and Mohammed, H.A., 2014. A comprehensive review of fundamentals, preparation and applications of nanorefrigerants. *International Communications in Heat and Mass Transfer*, 54, pp.81-95.
- [19] Nair, V., Taylor, P.R. and Parekh, A.D., 2016. *Nanorefrigerants: A comprehensive review on its past,*

present and future. International journal of refrigeration, 67, pp.290-307.

- [20] Peng, H., Ding, G., Jiang, W., Hu, H. and Gao, Y., 2009. Heat transfer characteristics of refrigerant-based nanofluid flow boiling inside a horizontal smooth tube. *International journal of refrigeration*, 32(6), pp.1259-1270.
- [21] Sendil Kumar, D. and Elansezhian, R., 2014. ZnO nanorefrigerant in R152a refrigeration system for energy conservation and green environment. *Frontiers of Mechanical Engineering*, 9, pp.75-80.
- [22] Rasheed, A.K., Khalid, M., Rashmi, W., Gupta, T.C.S.M. and Chan, A., 2016. Graphene based nanofluids and nanolubricants–Review of recent developments. *Renewable and Sustainable Energy Reviews*, 63, pp.346-362.