Refrigerants Used in HVAC Systems

The Evolution of Refrigerants in Air Conditioning Systems: A Chemical Perspective



George R. Carey, Jr.
VP, Fluid Industrial Associates
gcarey@fiainc.com
@Ask_GCarey

he chemical makeup of refrigerants used in air conditioning systems has undergone significant changes over the past century. These changes have been driven by a convergence of factors including environmental concerns, regulatory frameworks, technological advancements and economic considerations. Understanding the evolution of refrigerants requires an exploration of these factors and their impact on the chemical properties of the substances used.

Environmental Concerns

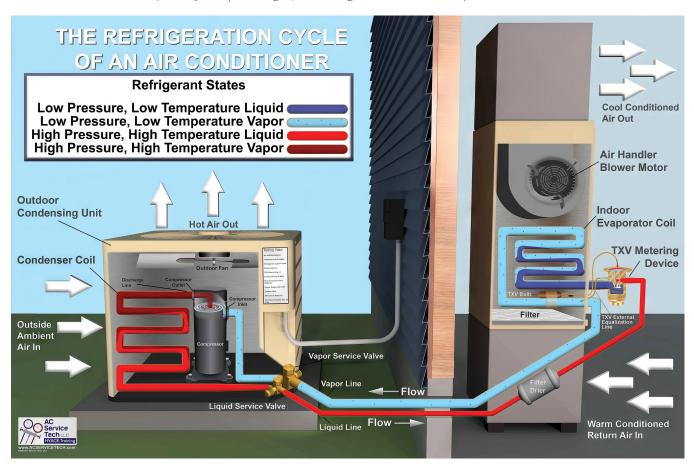
One of the primary catalysts for change in refrigerant chemistry has been the environmental impact of these substances. Early refrigerants, such as ammonia ($\mathrm{NH_3}$) and sulfur dioxide ($\mathrm{SO_2}$), while effective, posed significant health and safety risks due to their toxicity and flammability. The introduction of chlorofluorocarbons (CFCs) in the mid-20th Century marked a significant advancement. CFCs, such as dichlorodifluoromethane (R-12), were non-toxic and non-flammable, making them ideal for widespread use.

However, the stability of CFCs, once seen as an advantage, turned out to be a significant environmental liability. When released into the atmosphere, CFCs eventually reach the stratosphere, where they break down under ultraviolet light, releasing chlorine atoms.

These chlorine atoms then catalyze the destruction of ozone molecules, leading to the thinning of the ozone layer. This realization in the 1970s and 1980s led to international action spearheaded by the United Nations' Montreal Protocol on Substances That Deplete the Ozone Layer (Montreal Protocol of 1987). This became the international treaty to protect the earth's ozone layer by phasing out the production of ozone depleting substances (ODS).

Regulatory Structure

The Montreal Protocol and its subsequent amendments have been pivotal in shaping the landscape of refrigerant chemicals. With the phase-out of CFCs, the industry

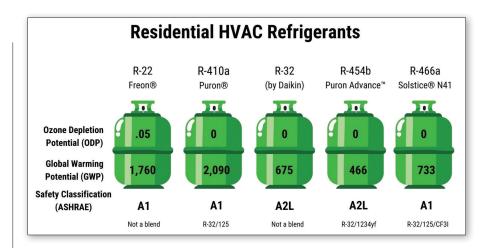


turned to hydrochlorofluorocarbons (HCFCs) as transitional solutions. Like R-22, HCFCs were less damaging to the ozone layer but still posed environmental risks and were subject to a phase-out schedule under the Protocol.

The search for more environmentally-friendly alternatives led to the development and adoption of hydrofluorocarbons (HFCs). HFCs, such as R-134a and R-410A, do not contain chlorine and thus do not deplete the ozone layer. However, they are potent greenhouse gases with high global warming potentials (GWPs).

As global awareness of climate change has grown, regulatory pressures have increased to phase down HFCs as well. The Kigali Amendment to the Montreal Protocol, adopted in 2016, sets forth a global phasedown of HFCs, pushing the industry towards even more sustainable alternatives. The U.S. obligations to the original Montreal Protocol were codified by Congress through the Clean Air Act (CAA) in 1990. Most recently, Congress codified the Kigali Amendment in the American Innovation & Manufacturing (AIM) Act in 2020. This act banned the use of HFC refrigerants because of their GWP. In October 2023, the U.S. Environmental Protection Agency (EPA) issued a final rule under the AIM Act that set dates to restrict the use of HFCs in refrigeration for hat pumps and air conditioning units. For residential and light commercial air conditioning and heat pumps, the final rule set a compliance date of January 1, 2025, and a limit of 700 for the GWP of refrigerants used in AC systems.

GWP uses carbon dioxide ($\rm CO_2$) as the reference standard, meaning $\rm CO_2$ has a GWP of 1. One of the post-Kigali replacement refrigerants is R32, which has a GWP of 675. The other common replacement is R454b, with a GWP of 467. Both R32 and R454b have no ozone depletion potential (ODP) and fall below the EPA's rule limit of 700. Additionally, both of these refrigerants have been in use in Europe for quite some time and are making their way to the U.S. market.



Technological Advancements

Technological innovations have been crucial in the development of new refrigerants. The need to balance environmental safety with performance and efficiency has driven extensive research and development.

Hydrofluoroolefins (HFOs) have emerged as a promising class of refrigerants. Composed of hydrogen, fluorine and carbon, HFOs have very low global warming potential compared to HFCs, zero ozone depletion potential and are designed to break down more quickly in the atmosphere—reducing their long-term environmental impact.

The quest for efficient and sustainable refrigerants has also led to a renewed interest in natural refrigerants. Substances such as carbon dioxide (CO₂ or R-744), ammonia (NH₃ or R-717) and hydrocarbons (such as propane, R-290) are being revisited and optimized for modern applications. These natural refrigerants typically have very low GWPs and are not ozone-depleting, making them attractive options from an environmental standpoint.

However, their use requires careful consideration of safety and system design due to their varying properties, such as flammability and operating pressures.

Economic Considerations

Economic factors also play a significant role in the evolution of refrigerants. The transition to new refrigerants often involves substantial costs related to the redesign and retrofitting of existing air conditioning systems. Manufacturers, therefore, need to balance the costs of compli-

ance with regulatory requirements and the development of new technologies with the market demands for affordable and efficient cooling solutions.

The industry's response to regulatory changes is also influenced by the availability and cost of raw materials used in the production of refrigerants. For instance, the production of HFOs requires specific feedstocks and chemical processes that can impact their market price and adoption rate. Moreover, economic incentives and penalties established by governments and international bodies can accelerate or slow down the transition to Greener refrigerants.

The Future of Refrigerants

The chemical makeup of refrigerants in air conditioning systems has evolved significantly, driven by the interplay of environmental imperatives, regulatory frameworks, technological advancements and economic considerations. From the hazardous early refrigerants to the environmentally damaging CFCs and HCFCs, and now to HFCs and emerging alternatives such as HFOs and natural refrigerants, the industry continues to innovate in pursuit of sustainable cooling solutions. The future of refrigerants lies in achieving a delicate balance between environmental responsibility, safety, efficiency and economic viability, ensuring that the cooling needs of society are met without compromising the health of the planet.

If you have any questions or comments, e-mail me at *gcarey@ fiainc.com*, call me at (800) 423-7187 or follow me on Twitter at *@Ask_Gcarey*. **ICM**