Study of Future Refrigerant for Vapor Compression Refrigeration Systems

I. Vinoth kanna and K. Subramani

1 Introduction

In the early days, natural refrigerants were used, but there was little to no safety regulations so systems ended up using very dangerous refrigerants. Some were highly flammable, and some were even toxic. Soon scientists realized the markets need for better and safer refrigerants [1, 2].

Then, in the 1930s they developed CFCs, which were scientifically tested and were safer to use. They were nonflammable, nontoxic, and a non-corroding gas, which was cheap to produce, so they seemed ideal [3, 4]. However, in the 1970s they realized that the chlorine molecules within these were completely destroying our ozone layer and were banned.

In the late 1970s and early 1980s, experts developed HCFCs which had far less damaging effects on the ozone; however, HCFCs were still able to damage the ozone layer because they contained chlorine molecules [5].

To solve the issue of ozone destruction, scientists came up with HFCs, which did not contain chlorine; this meant they would not destroy the ozone layer [6, 7]. However, they later realized HFCs still damage the environment because they are greenhouse gases and so these are beginning to be phased out also.

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2 Ozone Layer Depletion

The ozone-depleting chemicals rise up into the stratosphere, and the chemicals are swept into the winds of the polar vortex, which is a ring of fast-moving air that circles the South Pole, and the chemicals have been building up here since CFC refrigerants first started being used [8].

This buildup in the South Pole has been destroying the ozone layer by burning a hole through it [9, 10]. The laws and regulations on the use of chemicals in refrigerants have been increasingly tightened over the years and as this continues, the plant will have time to repair this hole. Let us just briefly learn why and how this has been burning a hole in our ozone layer [11].

In our planet first, we have the troposphere, and then, we have the stratosphere [12, 13]. The ozone layer exists within the stratosphere. The ozone layer protects us from the suns UV rays that are very harmful and cause cancer.

Within the ozone layer, we have the ozone molecule, which has three oxygen atoms; these absorb the UV rays [14]. The CFC molecules rise up into the stratosphere, and the UV rays cause the chlorine atoms to break off [15, 16].

This separation of the chlorine atom causes a chemical reaction, resulting in the chlorine atom stealing an oxygen atom from the ozone molecule [7, 17]. This creates a chlorine monoxide molecule and a separate oxygen molecule. The ozone layer is unable to support these new molecules and so a gap is formed in the stratosphere [6, 12, 18]. The bigger the hole gets, the more UV rays will be able to reach us.

3 Global Warming Potential

The other problem with the refrigerants is their global warming potential (GWP) [3, 6, 10, 12, 14, 19–21]. If the infrared rays pass through our atmosphere, it will hit the earth surface and most are rebounded back into space with a few rebounding and staying within the atmosphere [14].

Scientists since discovered that many of the chemicals in the refrigerants prevented infrared rays from pass through them, so as they build up in the atmosphere they prevent the rays from leaving which causes heat treatment and this is leading to climate change. Although there are many contributors to this and many are man-made [8].

4 History of Refrigerants

Refrigerants have been introduced since the 1800s, a variety of changes made by the scientist in order to meet required GWP and ODP [22, 23]. Figure 1 shows the periodic changes of refrigerant in history.

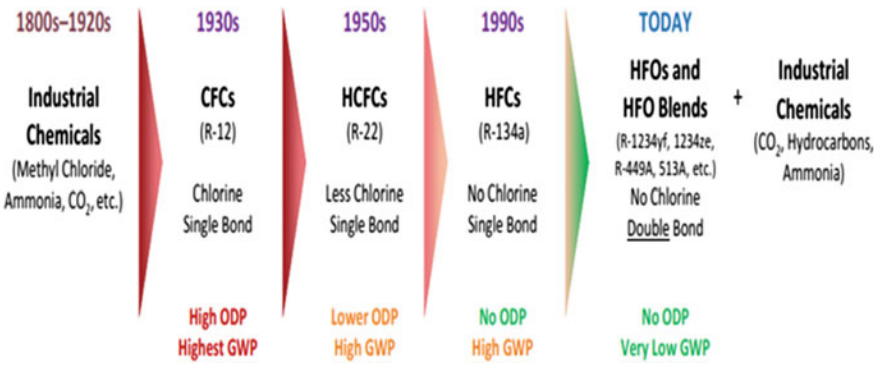


Fig. 1 History of refrigerants

Selection of refrigerants for the future will need to balance performance (capacity and efficiency), safety and sustainability, and total cost of system ownership [24].

5 Industrial Gases as Refrigerants

Industrial gases were introduced in the year 1800, and it has been used up to the year 1920 [25].

- Not new, some of the earliest refrigerants.
- Used currently where they make sense (safety and efficiency concerns).
- Rebranding as "natural" products, but:
  - The so-called natural refrigerants are actually industrial gases produced in large chemical processing facilities [26, 27].
  - These facilities use energy to create or isolate, purify CO_2, hydrocarbons, and ammonia [26, 28].
  - They also use feedstocks and generate wastes similar to other chemical manufacturing processes [27, 29].

6 Hydrocarbon Manufacture

Hydrocarbons are produced in an oil refinery or natural gas processing plant [2, 9]. There are several process steps to produce high purity refrigerants such as propane and isobutane. Figure 2 shows the details of natural gas production steps.

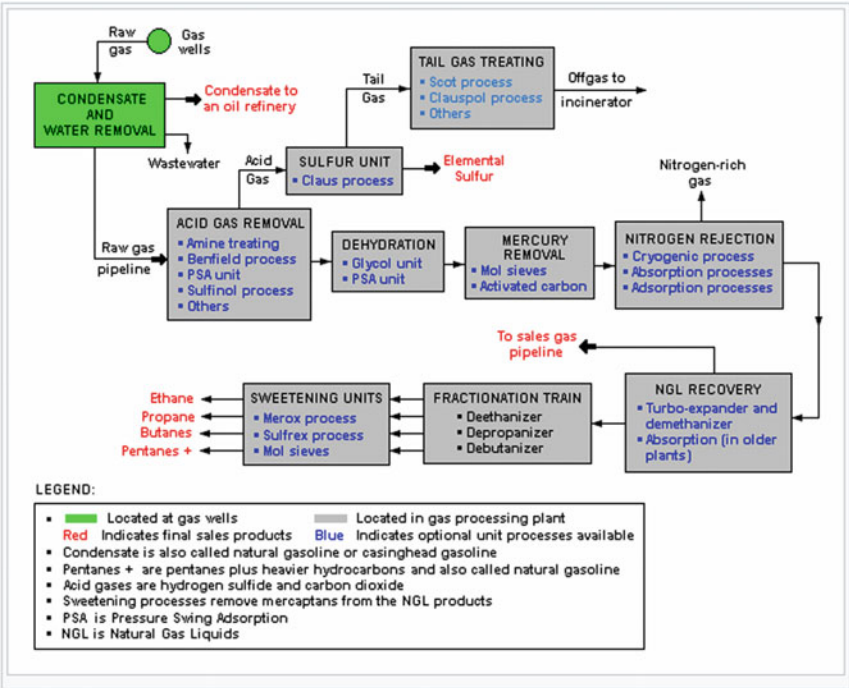


Fig. 2 Natural gas process steps

6.1 Example Processing Steps

- Condensate and water removal,
- Mercury removal,
- Nitrogen removal,
- Natural gas liquid recovery,
- Fractionation,
- and Sweetening purification units

7 Ammonia Manufacture

Ammonia is primarily produced by the reaction of nitrogen with hydrogen. However, there are several steps preceding this, starting with natural gas feedstock (Fig. 3):

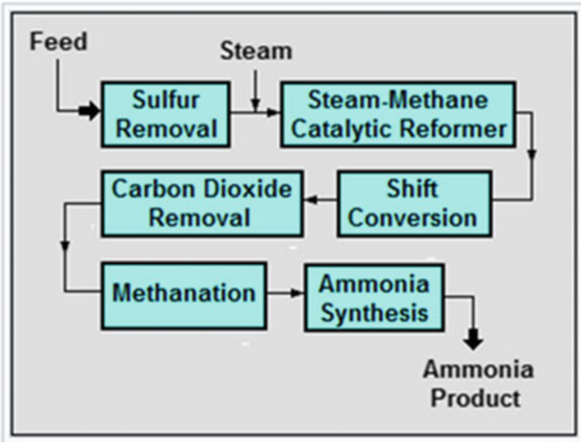


Fig. 3 Block flow diagram of the ammonia synthesis process

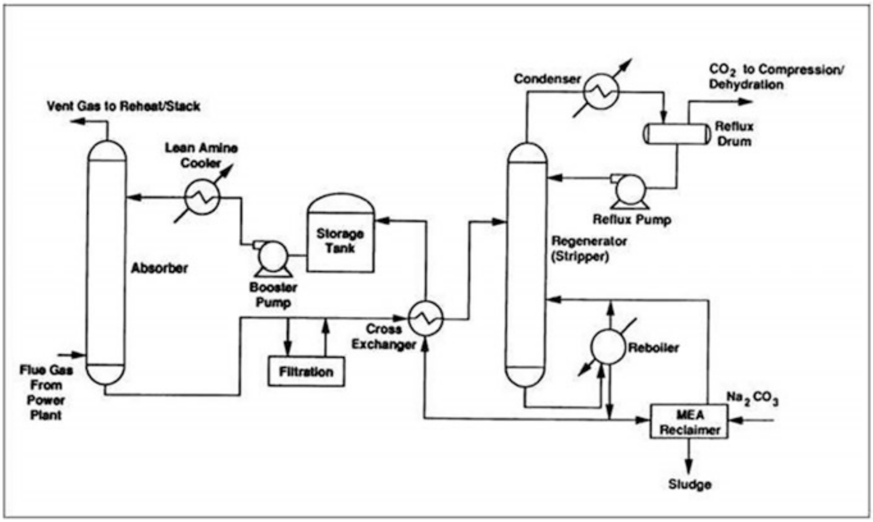


Fig. 4 Schematic diagram of the amine separation process

- Sulfur removal from natural gas feedstock:

$$H_2 + RSH \rightarrow RH + H_2S\ (\text{gas})$$

- Hydrogen sulfide absorption through beds of zinc oxide:

$$H_2S + ZnO \rightarrow ZnS + H_2O$$

- Catalytic steam reforming to form hydrogen plus carbon monoxide:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

- Catalytic shift conversion to carbon dioxide and more hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

- Carbon dioxide is then removed by absorption.
- Catalytic methanation to remove small amounts of CO and CO_2

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

- Hydrogen is then catalytically reacted with nitrogen to form anhydrous liquid ammonia and purified

$$3H_2 + N_2 \rightarrow 2NH_3$$

8 CO_2 Manufacture

CO_2 is primarily produced (Fig. 5) by:

- Combustion of fossil fuel (e.g., coal, oil, and gas)
- Separation of the CO_2 from the combustion product stream (e.g., flue gas—Fig. 4)
- Several purification steps

9 Future Refrigerant

9.1 Evaluation of Working Fluids in Refrigeration Systems

In general, we have a plenty of refrigerants in the universe, but we cannot use all as refrigerants in refrigerator, it should satisfy the following phenomenon [7, 13, 21].

Measurable data and objective chemical, physical, thermodynamic and environmental properties [4, 17].

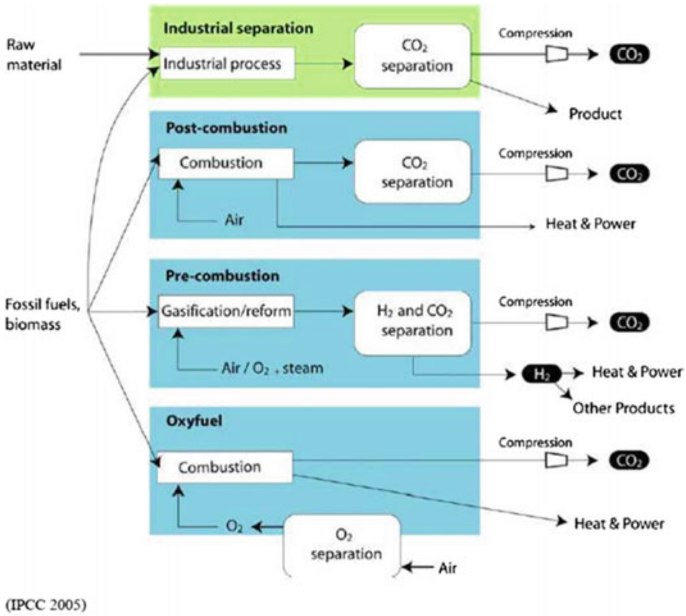


Fig. 5 CO_2 production options

Standard and reproducible engineering principles, measurements and testing [20, 23, 26].

For example:

- Boiling point,
- Vapor pressure,
- Heat capacity,
- Ozone depletion potential,
- Atmospheric lifetime,
- Global warming potential,
- Toxicity (acute, chronic, etc.),
- Flammability (LFL, UFL, and burning velocity) [3, 30],
- Heat of combustion [6, 18, 28],
- and Energy efficiency [7, 10, 16]

Table 1 Designing a low GWP molecule

Molecule	Structure	Atmospheric lifetime	GWP	Status
PFC-116	CF3–CF3 No hydrogen	10,000 years	11,100	No long used
HFC-134a	CH2F–CF3 2-H atoms	13 years	1300	Current refrigerator runs by using "HFC-134a" as a refrigerant
HFO-1234yf	CH2=CF–CF3 "Olefin"	10 days	<1	Future refrigerant to replace HFC-134a.

9.2 Exact Meaning of Global Warming Potential (GWP)

GWP = Atmospheric Lifetime × Infrared Absorbance [5, 6, 23, 24]

Atmospheric Life → rates of destruction reactions (hydroxyl radical) (Table 1)

$$\mathrm{HFC} = \frac{[\mathrm{OH}-]}{k}$$

9.3 Designing a Low GWP Molecule

HFC (Fig. 6a) has only single bond whereas double bond in HFOs (Fig. 6b) quicker breakdown in the atmosphere, yet stable in systems [18] (Table 2).

9.4 Comparison of HFC Versus HFO

- Same operating conditions as 134a (similar P/T curve) (Graph 1 and Table 3).
- Capacity and efficiency is similar to HFC-134a.

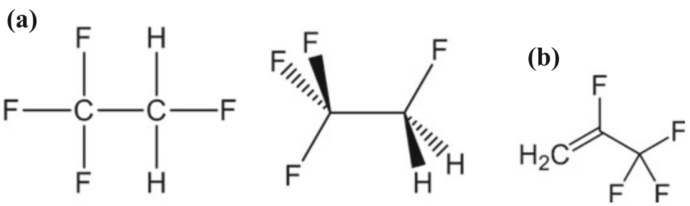
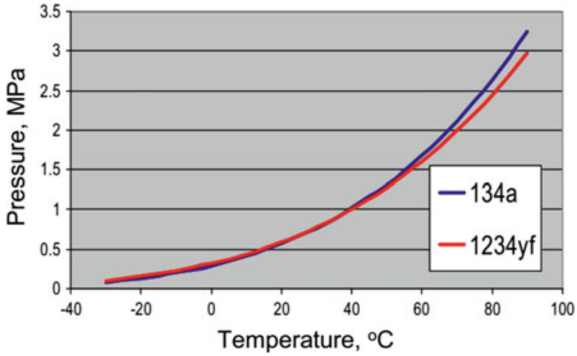


Fig. 6 **a** HFC, **b** HFO

Table 2 HFC versus HFO

	HFC-R 134a	HFO-R 1234yf
Formula	CH2FCF3	CF3CF=CH2
Molecular weight	102	114
ODP	0	0
GWP100 (ARS)	1300	<1
T, Critical point	102 °C	95 °C
Boiling point	−26 °C	−29 °C



Graph 1 *P*/*T* curve for R 134a and R 1234yf

Table 3 Refrigerant flammability classification

Highly flammable	3	Propane, Isobutane
Moderately flammable	2	R-152a
Mildly flammable	2L	R-1234yf, R-452B
Nonflammable	1	R-134a, R-410A

9.5 Refrigerant Flammability Classifications

To meet 2L flammability, burning velocity must be ≤ 10 cm/s [4, 7, 16, 28].

9.6 *Primary Flammability Parameters*

Parameter	Risk Trend
Lower LFL	↑
Larger (UFL – LFL)	↑
Lower MIE	↑
Higher UFL	↑
Higher HOC	↑

- **Lower/Upper Flammability Limits (LFL/UFL)**
  Minimum/maximum concentrations of a substance in air that exhibit flame propagation (usually shown as volume percentage in air) [3, 4, 30].
- **Minimum Ignition Energy (MIE)**
  Minimum energy required to ignite a flammable gas/air mixture. Sources with energy levels below this value will not result in an ignition [17, 18, 28].
- **Burning Velocity (BV)**
  Burning velocity is the velocity of a laminar flame under given values of composition, temperature, and pressure of a refrigerant [1, 13, 27].
- **Heat of Combustion (HOC)**
  While combustion, the amount of heat released per unit mass (or mole) of a substance is called Heat of Combustion [15, 19, 22].

9.7 *Flammable Property Comparison*

See Table 4.

10 Optimizing for the Future

Following balanced properties are needed to introduce a new refrigerant in the global market [3] (Fig. 7)

- Zero ODP
- Low GWP

Table 4 Flammable property comparison

	R-290 (Propane)	R-152a	R-717 (Ammonia)	R-1234yf
Safety rating	A3	A2	B2L	A2L
LFL (vol. %)	2.2	3.9	15.0	6.2
UFL (vol. %)	10.0	16.9	28.0	12.3
UFL – LFL (vol. %)	7.8	13.0	13.0	6.1
MIE (mJ)	0.25	0.38	100–300	>5000
BV (cm/s)	46	23	7.2	1.5
HOC (kJ/g)	46.3	16.5	18.6	10.7

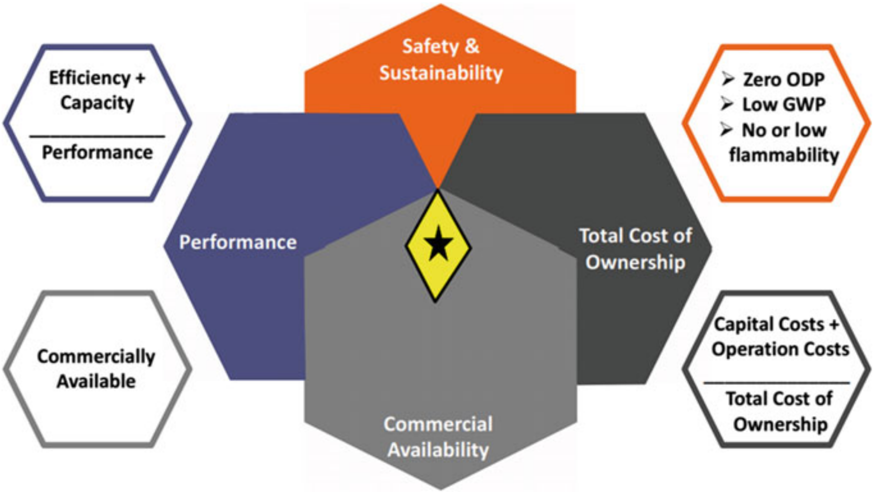
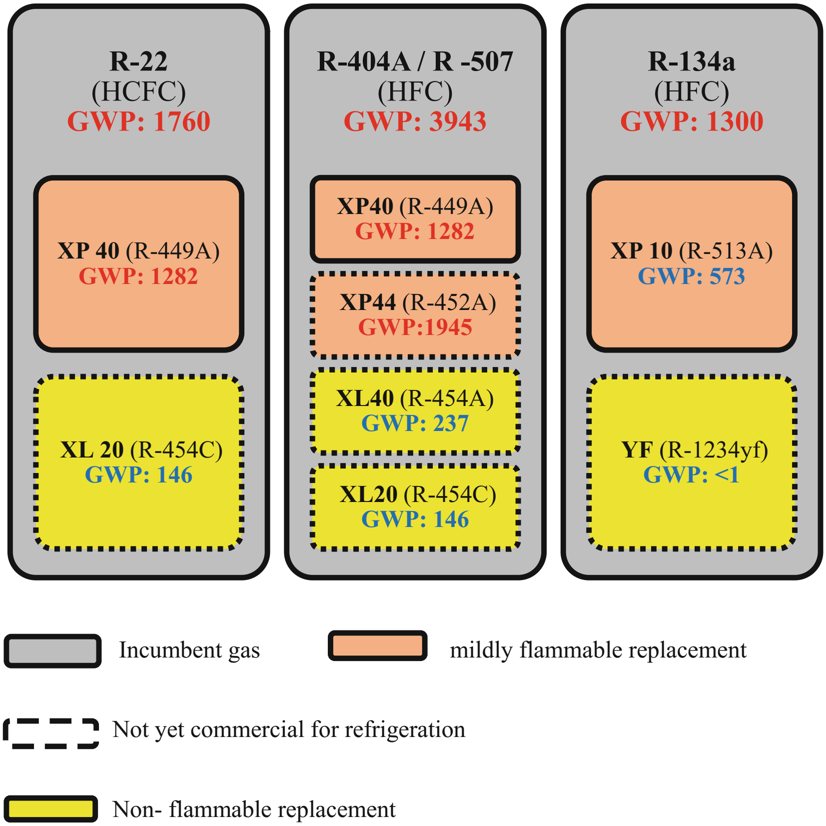


Fig. 7 Optimal balance properties [2, 6, 7, 30]

- No or low flammability
- Total cost of ownership
- Commercially available
- Performance
- Safety and sustainability

11 Low GWP HFO Products for Refrigeration



12 Conclusion

Refrigerants are greenhouse gases that contribute to global warming and many environmental metrics. Hence, a substitution is very much needed. Our motivation is to find substitute for refrigerant thereby reducing environmental problem like ozone depletion, GWP. In addition, hereby we conclude that R1234yf as a refrigerant for future refrigerator to meet our needs.

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