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Environmental Assessment and Characteristics of Next Generation Refrigerants

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Heat pump systems are often considered as one of the major contributors to environmental problems due to the usage of chlorofluoro, hydrochlorofluoro, and hydrofluoro carbon-based refrigerants. Earlier versions of refrigerants used to have high ODP as well as GWP. However, next generation refrigerants that are environmentally benign with excellent thermophysical properties are still under development stage. This study reviews the historical development of refrigerants, their environmental impacts and observes the viewpoint for present options in terms of Montreal Protocol, Kyoto Protocol, and EU F-gas regulation. The discussion extends to the actions of international agreements on the phase-out of hydrochlorofluorocarbons for developed and developing countries. This study also highlights the approach of large heat pump industries in Asia region regarding the use of various refrigerants. The direct CO_2 emission per year from air-conditioning and refrigeration sectors due to the system leakage is assessed. It also examines the major contributors of CO_2 emission in every year among the various sectors for providing per kilowatt cooling effect. Finally, the ideal cycle performance is compared to various refrigerants and stated the current best option.

Keywords: CO_2 emission, environmental assessment, heat pump system, refrigerant

1. Introduction

Climate change as a consequence of global warming and ozone layer depletion is one of the most momentous threats the world is facing today[1)]. The greenhouse gas concentration in the troposphere is increasing especially due to the manmade activities, like transportation, industrialization and power generation, etc. This gas absorbs the infrared radiation which results in increased atmospheric temperature known as climate change. The radiation energy is measured by global warming potential (GWP) which is defined as the infrared radiation amount that the gas can absorb, relative to carbon dioxide (GWP = 1), integrated over a time interval of 20, 100 and 500 years[2)]. Refrigerant used in the heat pump systems is responsible for the global warming and ozone layer depletion. Total equivalent warming impact (TEWI) is a tool for an appropriate measure of a refrigerant impact to global warming. Hwang et al.[3)] defined two types of global warming effects. Firstly, the direct global-warming potential which is owing to the leakage of refrigerants and other pollutants from the systems. Secondly, the indirect global-warming potential which is related to the carbon dioxide emission during combustion of fossil fuels (oil, natural gas, and coal) to generate electricity. The combined effect of direct refrigerant emission and energy consumption of a heat pump system are acknowledged as TEWI[2)].

About 11 km above the earth surface ozone layer exist in the atmosphere and acts as a safeguard for earth for thousands years[2,4)]. Ozone layer consists of ozone (O_3) molecules with a high concentration. All the harmful ultraviolet rays of the sun are efficiently absorbed by this layer. Any kind of demolition of this layer can cause significant destruction to the environment and the life on earth[2, 5].

Heat pump technologies play a significant role in our everyday life. It offers not only comfortable and healthy living and working atmospheres but also considered as inevitabilities for preserving food and medicine at extreme weather[2]. With the change of lifestyle and economic solvency, the demand and supply of such systems have gradually increased. However, conventional air-conditioning (A/C) and refrigeration systems consume a considerable amount of electricity and use refrigerants like chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), which possesses high global warming potential (GWP) as well as ozone layer depletion potential (ODP)[6]. Currently, Hydrofluorocarbons (HFCs) are considered as an alternative to the CFCs and HCFCs. This refrigerant has no ODP, but it has high GWP. Many studies[7-10] have been focused on hydrofluoroolefins (HFOs) as it has very low GWP. Notable researchers are also focusing natural refrigerants such as CO_2, water, and ethanol for thermally driven adsorption A/C and refrigeration systems[11-15]. These systems are considered as an alternative to the conventional systems in the near future.

In this study, the historical development of refrigerants and environmental impact of widely used refrigerants in A/C and refrigeration systems have been focused. The international agreements which are related to phase out of CFCs, HCFCs and HFCs refrigerants are discussed. The guidelines of the international treaties to phase-out HCFCs in developed and developing countries are mentioned. In addition, the study focuses on attitude and approach of the large manufacturing industry of heat pump systems in Asia region. Finally, the direct CO_2 emission from leakage of the various systems is calculated. The analysis has been done based on the leakage rate and initial charged amount of different refrigerants in various types and sizes of A/C and refrigeration systems.

2. Historical development of refrigerants

The refrigerant is the heat transfer fluid in refrigeration and air-conditioning systems. It absorbs heat from one area, such as space which needs to be cooled, and reject heat into outdoors, usually by evaporation and condensation, respectively[16]. Conventional vapor compression system is used to provide thermal comfort. Fig. 1[17] shows the schematic diagram of a typical vapor compression cycle comprises the following four essential elements: an evaporator, where the refrigerant evaporates by taking heat from the external environment. A mechanical compressor, which sucks the evaporated vapors to compress and expel it at a higher pressure and temperature. The compressor consumes a considerable amount of electrical energy. A condenser, in which the vapor refrigerant condenses by transferring a certain amount of heat to the outdoor environment. An expansion valve, through which the liquid refrigerant returns back to the evaporator, with a lower pressure to repeat the cycle.

According to the information available in open literature Oliver Evans[18] in 1805 suggested using evaporative two-phase fluid in a closed cycle to freeze water into ice. He proposed a system that can produce a cooling effect by evaporating ether. Jacob Perkins and Richard Trevithick are influenced by that idea and proposed an air-cycle system for refrigeration in 1828. Perkins[19] in 1830 invented a vapor the compression machine by using sulfuric (ethyl) ether as a refrigerant. The common refrigerants for the first generation (1830-1930s) were familiar solvents and other volatile fluids whatever worked as a refrigerant at that time. Almost all of those refrigerants were not environment-friendly because of flammability, toxicity, or both, and some were highly reactive to the heat exchanger material. Some common early refrigerants were ethers, CO_2, NH_3, SO_2, HCs, H_2O, CCl_4[20]. The second generation (1931-1990s) refrigerants were famed by a shift to fluoro-chemicals for safety and durability. Midgley and Henne[21,22] invented Freon in 1928 as a refrigerant. Well-known refrigerants in the second generation were CFCs and HCFCs (R11, R12, R22, R502) and NH_3. Commercial production of R12 started in 1931 followed by R11 in 1932[23,24]. Ammonia (NH_3) is one of the older types of refrigerant and remains until now, the most prevalent refrigerant in large, industrial systems particularly for beverage, storage, and food. CFCs are responsible for creating the hole in the ozone layer. The Vienna Convention and resulting Montreal Protocol designed to phase out the production of ozone-depleting substances (ODSs). Therefore, the primary focused of the third generation refrigerant (1990-2010s) was HCFCs and HFCs for the longer term, such as R123, R134a, R410A, R404A, many blends and also NH_3[20]. Actually, most of the third generation refrigerants had ODP and high GWP. Therefore, fourth generation (from 2010 to now) is mainly focused on zero ODP and low GWP refrigerants.

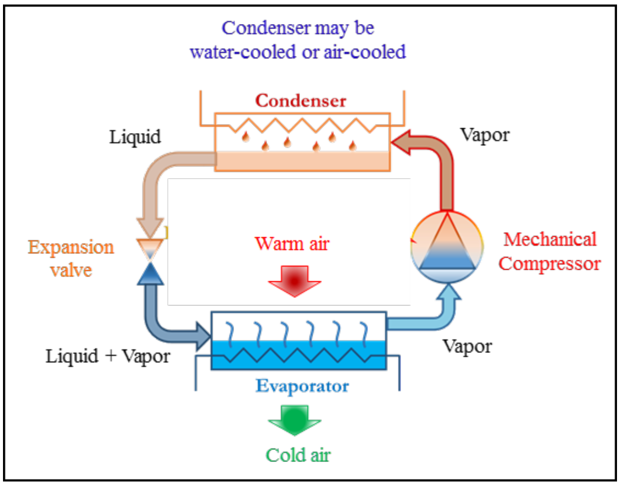

Fig. 1. Schematic diagram of a typical vapor compression refrigeration cycle[17].

3. International regulations

The international community took many steps (Vienna Convention, Montreal Protocol, London Agreement, Copenhagen Conference, Kyoto Protocol, EU F-gas regulation and Paris agreement 2015) to limit the production of CFCs and then to ultimate prohibition those owing to the innovation of the hole in the ozone layer caused by the chlorine contained in CFCs.

Among those regulations, the Montreal Protocol is a revolutionary international agreement which is signed to save the stratospheric ozone layer. It was agreed in 1987 and substantially revised several times in between 1989 to 2016, and it has been the most successful international agreement to date[25)]. The Montreal Protocol has led to a significant movement in phasing out main ozone-depleting substances, including CFCs, HCFCs, halons, and a number of other chemicals which contains chlorine and bromine. As a result of this agreement, the ozone layer is slowly recovering, and it is expected to return to its 1980 levels within this century. However, due to phasing out of ozone-depleting substances, HFCs started to use as substitutes in numerous applications. HFC-410A and HFC-134a are two widely used refrigerant in residential A/C and automobile A/C, respectively. HFCs can significantly influence climate for their high value of GWP. Some HFC refrigerants have low GWP of less than 20; others are potent greenhouse gases with GWP of thousands to tens-of-thousands. It can be clear from Table 1 that HFCs could significantly influence climate in the future if they continue to release in the atmoshphere[24)].

The Kyoto Protocol is an international agreement which is connected to the 1992 United Nations Framework Convention on Climate Change (UNFCCC) that commits State Parties to reduce greenhouse gas emissions by setting internationally binding emission reduction targets. Kyoto Protocol recognized developed counties are more responsible for emitting a high level of greenhouse gas and places a more substantial burden on developed countries under the principle of common but differentiated responsibilities. The Kyoto Protocol was adopted in Kyoto, Japan, on 11 December 1997 and entered into force on 16 February 2005. Currently, there are 192 parties to this Protocol. The Kyoto Protocol is implementing the objective of the UNFCCC to combat global warming by reducing greenhouse gas concentrations in the atmosphere to an average of 5 percent in the first commitment period (2008-2012) and 18 percent in the second commitment period (2013-2020) to its 1990 level. (Art. 2)[26)].

To control the emission of fluorinated greenhouse gases in the atmosphere, the European Union (EU) has adopted two legislative acts: MAC (Mobile air-conditioner) Directive and F-gas Regulation to check the limit of the total amount of F-gases sold in the EU market from 2015 to onwards. The MAC Directive prohibits the use of F-gases which has GWP higher than 150 in new types of cars and vans introduced from 2011, and in all new cars and vans produced from 2017. The F-gas Regulation first adopted in 2006, then it was replaced by the Regulation EU No 517/2014 which is effective from January 1, 2015. The target is to phase down the F-gas in steps to one-fifth of its 2014 sales levels in 2030[27)].

The COP21 (21st Conference of the Parties) under the UNFCCC held in Paris, France (30 November to 13 December 2015). The primary objective of COP21 was to negotiate a legally binding climate agreement among 195 countries to retain global temperature warming since 1800 well below 2.0°C (preferably 1.5°C) by 2100[28)].

4. Environmental effects of commonly used refrigerants

The environmental impact and safety classification of widely used refrigerants are shown in Table 1. Both CFCs and HCFCs have ODP and GWP. However, HFCs have only GWP. After the Montreal Protocol signed in 1987, the CFCs and HCFCs are gradually banned due to their harmful effect on the ozone layer. Most of the existing refrigerant in commercialized A/C systems are HFCs. Although HFCs does not have an impact on the ozone layer, they have GWP[29)]. Research has been intensified to find alternative refrigerants to conventional HFCs after adopting the above mentioned international protocols.

5. HCFC-22 (R22) phase-out timetable

The performance of R22 in A/Cs and refrigerators is excellent compared to all other refrigerants. After the Montreal Protocol 1987, the R22 is to be phased out due to its ozone-depleting properties. According to the protocol, the R22 will be phased out by 2020 and 2030 from the developed countries and developing countries, respectively. It is important to mention that by 2020 total ban of R22 in developed countries whilst 35% reduction in consumption and supply of R22 in developing countries. Table 2 and Table 3 show the phase-out timetable of R22 from developed and developing countries, respectively[34)].

Currently, different industries across the world are working hard to find an alternative to R22. Some of them are blends, which is a mixture of two or more pure refrigerants, and are considering as an alternative to R22, which are R404, R410A, R134a, etc. Preliminary study shows that these gases are not useful as an alternative to R22. Sometimes the new refrigerants require structural modification of the existing A/C systems due to the volumetric pressure of the refrigerants and operation condition of the system.

Table 1. Features of widely used refrigerants according to IPCC 5th assessment report 2014[31,32,33,34].

Compositional group	Refrigerant number	Chemical formula	Ozone depletion potential (ODP)	Global warming potential (GWP)	Safety group
CFCs	R11	CCl_3F	1	4660	A1
	R12	CCl_2F_2	1	10200	A1
	R113	CCl_2FCClF_2	0.8	5820	A1
	R114	$CClF_2CClF_2$	1	8590	A1
	R115	$CClF_2CF_3$	0.6	7670	A1
HCFCs	R22	$CHClF_2$	0.055	1760	A1
	R123	$CHCl_2CF_3$	0.02	79	B1
	R124	$CHClFCF_3$	0.022	527	A1
	R142b	CH_3CClF_2	0.065	1980	A2
HFCs	R23	CHF_3	0	12400	A1
	R32	CH_2F_2	0	677	A2L
	R125	CHF_2CF_3	0	3170	A1
	R134a	CF_3CH_2F	0	1300	A1
	R143a	CH_3CF_3	0	4800	A2
	R152a	CH_3CHF_2	0	138	A2
	R410A	R32 (50%) R125 (50%)	0	1900	A1

Table 2. R22 phase-out timetable for developed countries[35].

Year	Action
1987	Imposed the Montreal Protocol
1996	Start halt on 1989 level consumption plus additional payment
2004	35% supply reduction of R22
2010	75% supply reduction of R22
2015	90% supply reduction of R22
2020	Total Ban of R22 (for servicing existing systems up to 0.5% of base level consumption can be used till 2030)

Table 3. R22 phase-out timetable for developing countries[35].

Year	Action
1987	Imposed the Montreal Protocol
2013	Start halt at a base level of average 2009 and 2010
2015	10% supply reduction of R22
2020	35% supply reduction of R22
2025	67.5% supply reduction of R22
2030	Total Ban of R22 (for servicing existing systems up to 2.5% of base level consumption can be used till 2040)

6. Approach of heat pump industries

The world's first time Daikin Industries, Ltd. employed R32 for residential A/C. It is a Japanese multinational A/C production industries which have branches in Japan, China, Australia, India, Philippines, Southeast Asia, Europe, North America, and South America[36]. Currently, R410A is the most commonly used refrigerant in developed countries. Daikin[37] reported that if all R410A are shifted to R32, the impact to global warming from HFCs in 2030 would be minimized by the CO_2 equivalent of about 800 million tons (19%) compare with the continuous use of R410A. They also mentioned that if emerging countries converts from R410A and R404A to R32, the global warming impact will decrease by approximately 46%. R32 has low GWP value (675) and zero ODP. It possesses also following characteristics which make it an attractive alternative: R32 decreases charging volume by 30% compared to R410A; it shows higher efficiency (10% compared to R410A), and R32 provides improved performance at severe outside temperature. Fig. 2 represents the characteristics of possible next generation refrigerant[37,38].

After the successful introduction of R32 in Japan, Panasonic is ready to drive the refrigerant change in Asia and Europe. This company had already released R32 systems in the Nordic market in September 2015. Moreover, Panasonic is now introducing new R32 systems to the rest of Europe. This company is ongoing to manufacture the new systems that include R32[39]. Samsung (A/C) and refrigerator in India are still using R22 which has ODP and R410A for the slipt type A/C whereas Isobutane (R600a) is for refrigerators[40].

In the case of Hitachi in India, refrigerant for A/C unit is R410A whereas refrigerant for a refrigerator is R600a[41]. The largest A/C manufacturing company in India is Voltas limited are manufacturing heating, ventilation and A/C, refrigeration systems widely. However, most of the refrigerants in A/C unit are R22 and few are R410A[42].

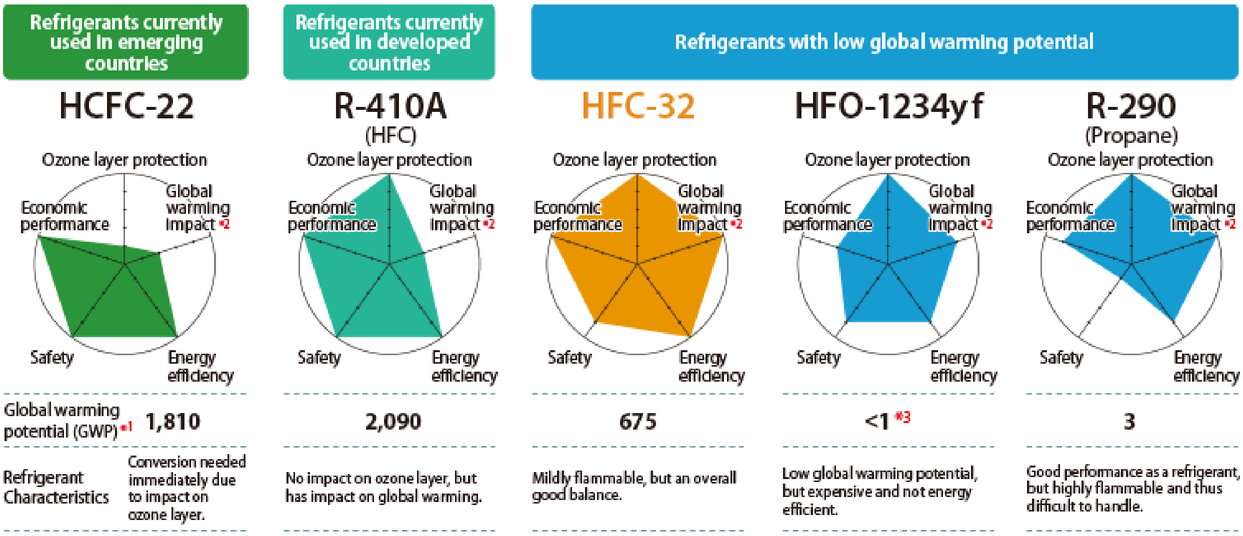

Fig. 2. According to Daikin, characteristics of possible next generation refrigerant for residential and commercial air conditioners[38]. Here GWP values were reported according to IPCC 4th assessment report 2007 (AR4).

In the case of Fujitsu general, different types of refrigerants are used in different countries or region. Based on the available data, it can be mentioned that in Japan, Fujitsu general uses R32 refrigerant for A/C. However, in Bangladesh and India, this company uses R410A as a refrigerant for room and commercial A/C system. Furthermore, R410A is also used in Thailand, however, this company is now adopting R32 as a new refrigerant[43].

7. Assessment of global warming potential

Gschrey et al.[44] mentioned that the impact of fluorinated gases (F-gases) to global warming would rise from roughly 1.3% (2004) to 7.9% (2050) of expected total CO_2 emissions[45,46]. Still, most of the refrigerants used in refrigeration and A/C systems are F-gases (Bauer et al.[47]). Leakage of refrigerant gases from these systems influences the environment in two ways (Koronaki et al.[48]). Firstly, there is a direct effect due to the GWP of the leaked gas, and secondly, there is an indirect effect owing to the energy consumption by the system (Grace et al.[49]). In this study, the direct impact due to high GWP of refrigerants has been considered. The leakage rate of refrigerant is different for different systems. According, UK Greenhouse Gas (GHG) inventory for 2007, Table 4 represents the leakage rates for the different types of refrigeration and A/C system[48].

For investigating the direct GHG emission four cases such as room A/C, domestic refrigeration, commercial refrigeration, and industrial refrigeration are considered. Furthermore, HCFC (R22), HFCs (R410A, R134a, and R32), HFO (R1234yf, R1234ze) and natural (R600a) refrigerants have been used for the assessment of direct global warming impact. Refrigerant charge into system depends on system type and capacity. Poggi et al.[50] mentioned the specific charge amount per kW capacity based on the size of the heat pump systems. Fig. 3 shows the specific charge (kilogram per kilowatt) amount in complete systems for different applications using different refrigerants[51]. It can be observed that initial charging amount of refrigerant in different kinds and sizes is different.

Table 4. Direct GHG emissions rate by refrigeration and air-conditioning sectors[48].

Type of equipment	Annual leak rate
Domestic refrigeration	0.30%
Stand-alone commercial applications	2.00%
Medium & large commercial applications	11.00%
Industrial refrigeration	8.00%
Residential/commercial air-conditioner	8.50%

The direct global warming impact per kW capacity has been calculated using equation (1)[51]. Leakage occurs mostly near the compressor side. It is happing when the pressure of gas increased; it is much higher than atmospheric pressure compressed by the compressor. In this study, condenser temperature has been considered 40°C to calculate the pressure of leakage gas, as it is an isobaric process. Therefore, leakage rate differs from one refrigerant to another, as their operating pressure are different.

$$\begin{aligned}&\text{Direct global warming impact}\\&= \text{Refrigerant charge (kg/kW)}\\&\times \text{Leakage rate of initial charge (per year)}\\&\times \text{GWP of refrigerant}\end{aligned} \quad (1)$$

Fig. 4 represents direct emission amount of CO_2 per kW/year for the residential A/C system. It can be seen that R22 shows high emission rate with contains ODP value. HFC group (R410A, R134a, and R32) does not contain any ODP, however high GWP emission rate has been observed. It is highlighted that R32 shows quite low CO_2 emission compared to other HFCs, which is recently promising worldwide. HFOs and natural refrigerant emit almost zero emission.

However, due to low system performance and flammability, these refrigerants need further study to use in every sector. A similar trend has been observed for domestic, commercial and industrial refrigeration systems. Fig. 5 shows the comparison of direct emission amount of CO_2 per kW/year for the various system. It is observed that industrial and commercial refrigeration systems are a significant contributors to direct emission of GHG because of the high leakage rate and high amount of initial charging of refrigerant.

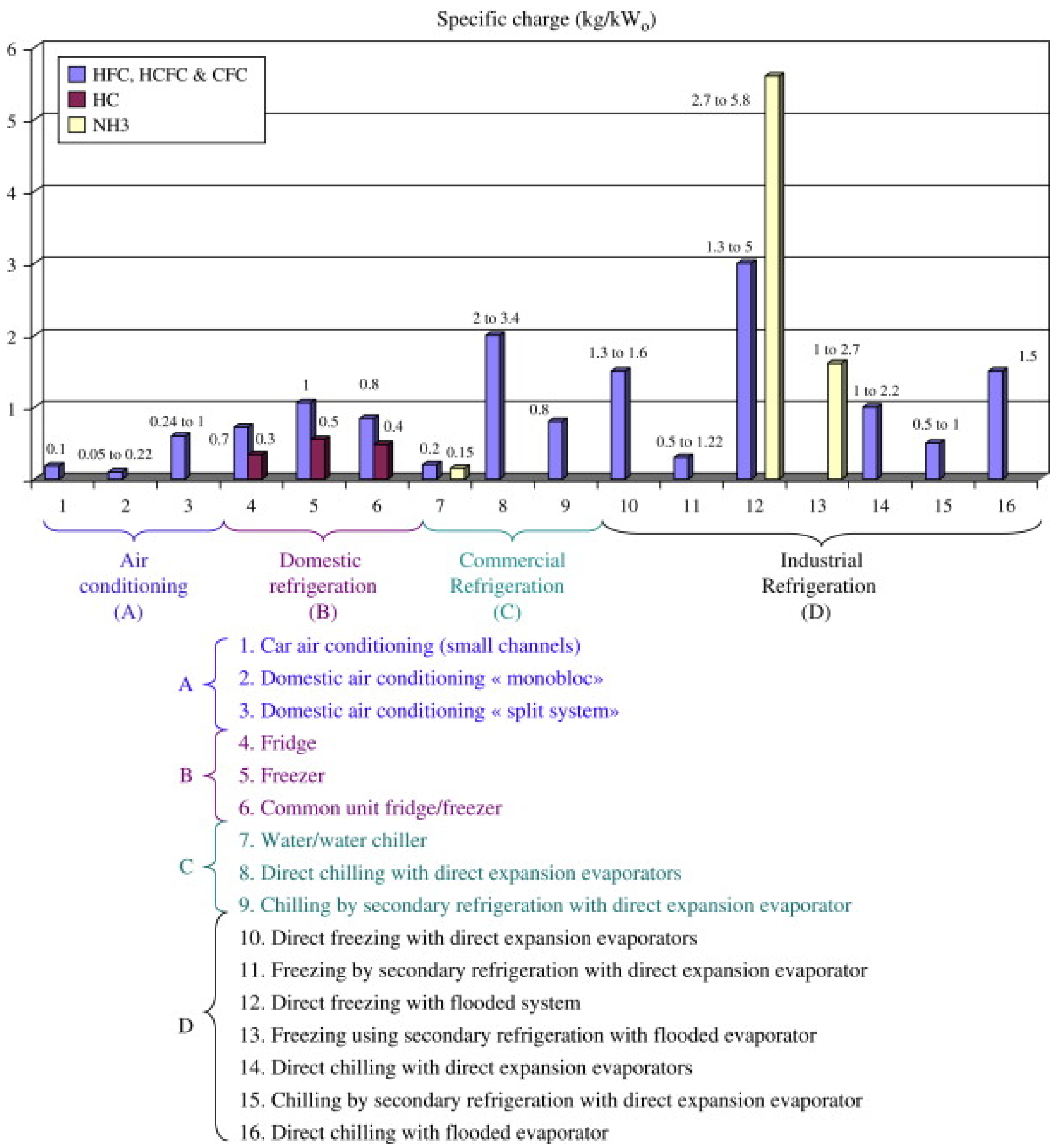

Fig. 3. Specific charge amount in complete systems for different applications using different refrigerants[50].

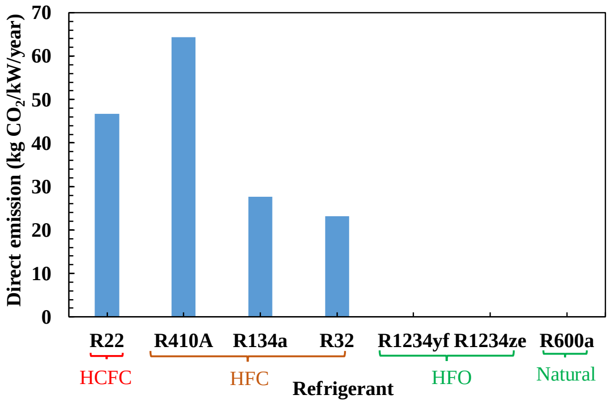

Fig. 4. Direct emission amount of CO_2 per kW/year from the residential air-conditioner.

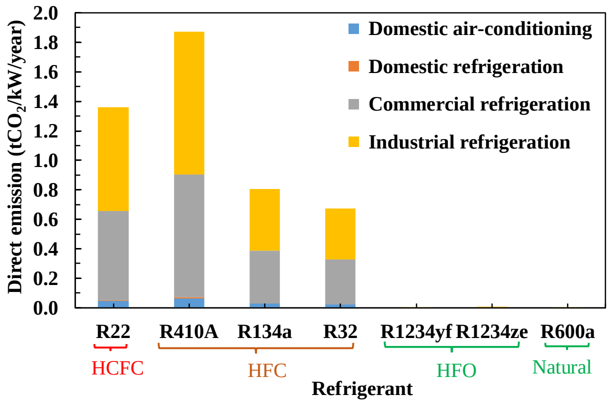

Fig. 5. Comparison of direct emission amount of CO_2 per kW/year from the various system.

8. Performance analysis

The Coefficient of performance (COP) based on a similar operational condition is calculated for well-known refrigerants employing thermos-physical properties from REFPROP V9.1 database. The COP of an ideal vapor-compression cycle is expressed as the ratio of enthalpy difference in the evaporator and compressor side. Same operating conditions are considered for all refrigerants for calculating COP. Condensation, evaporation, the degree of subcooling, and degree of superheat temperature are chosen at 35°C, 10°C, 5°C, and 3°C, respectively. Adiabatic compression efficiency is assumed 0.85. Fig. 6 represents the P-h (pressure-enthalpy) diagram of selected refrigerants. The ideal cycle is also drawn on the same figure for the studied refrigerants following the same operating conditions. Fig. 7 shows the comparison of ideal cycle performance of selected refrigerants. It can be seen that COP variation is not significant for the studied refrigerants. It is important to mention again that R12 and R22 both have high GWP and ODP whereas R410A has only GWP (2090). To fit with different regulations, mentioned earlier, new refrigerants should have low GWP but need similar or better performance for commercial aspect. In this context, R32 and R123yf both are suitable as an alternative. Though R32 is mildly flammable (A2L), its volumetric capacity is significantly higher than R410A which can reduce the system pipe size and increase the efficiency. R123yf shows higher COP, but the volumetric capacity of this refrigerant is significantly lower than R410A. Therefore, from the viewpoint of GWP, ODP, safety, and performance, R32 is found the best option and it can be used as a retrofit to the conventional refrigerant.

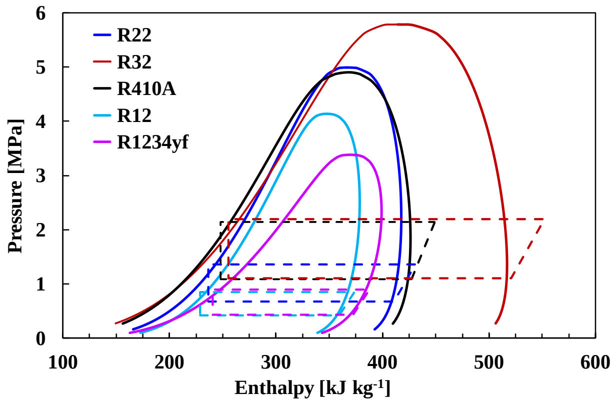

Fig. 6. Pressure versus enthalpy diagram with ideal cycle following same operating condition.

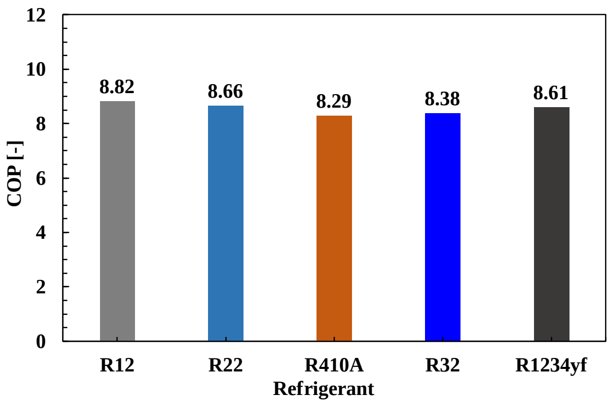

Fig. 7. Comparison of ideal cycle performance.

9. Conclusions

Regarding the use of zero ODP and low GWP based refrigerants, momentous advancements have been made over the last 20 years. The highest ozone-depleting substances (CFCs) are effectively phased out by the Montreal Protocol. This protocol is also creating substantial progress on HCFCs. Refrigeration and A/C industries are still using HCFCs and HFCs in different countries. The Kyoto Protocol promotes to use low GWP refrigerants. Consequently, manufacturing industries have been developing new and more eco-friendly refrigerants and shifted towards the low GWP refrigerants. Growing customer demands and regulations are always insisting the industry to lessen the further CO_2 emission from A/C and refrigeration systems. There is a direct and indirect effect of CO_2 emission from these systems. The direct impact is due to high GWP of leaked gas whilst indirect effect is due to the consumption of huge electricity by the systems. Both parameters depend on several factors such as GWP value of refrigerant, system type, and size. The assessment of direct emission of CO_2 per year shows low-GWP refrigerants emits a low amount of CO_2, as it was expected. Furthermore, the domestic A/C system releases low CO_2 per year to provide 1 kW cooling effect. On the other hand, commercial and industrial refrigeration system release a high amount of CO_2 compared to others. This is due to large size, high leakage rate and high initial charging amount of refrigerant. It can be reported that currently, R32 is the best option in the viewpoint of cycle performance, GWP and ODP issue. Many industries in developed countries are now using R32 or going to start to use R32. Owing to widely use of HFCs as replacement of CFCs and HCFCs, the emissions of HFCs are increasing. So, it is important to stress on leak detection as well as effective recovery and demolition of used refrigerants. The market is now seeing the emergence of HFOs and natural refrigerants to minimize the direct global warming effect from these systems. However, still needs more study on HFOs. To reduce to an indirect effect, it is urgent necessity to move to waste heat driven A/C and refrigeration systems from the conventional systems. However, the movement towards the new refrigerants and new systems from current types are a big challenge, as it depends on several factors such as refrigerant properties, system design, and economic viability.

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