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Research Article

Refrigerant progression - an investigation into eco-sustainability with evolution and viability of fourth generation refrigerants

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ABSTRACT

Global warming is one of the most pressing issues the world is facing today. The refrigeration sector, one of the major contributors to global warming, needs to follow a methodological approach to address this issue. This paper evaluates the overall warming impact along with the thermodynamic performance of the different generations of refrigerants in the cascade refrigeration system. The main aim of this comparative study is to present a comprehensive outlook on the environmental impact of refrigerants. A different perspective on refrigerant selection to reduce global warming is also discussed. R600a, R290, R12, R22, R134a, R152a, R245fa, R1234yf, and R1234ze are used in the high-temperature circuit, while R32 is used in the low-temperature circuit. Exergy and energy analyses are done for thermodynamic performance, and total equivalent warming impact (TEWI) assessment is carried out to show global warming produced. While the refrigerant couple R152a/R32 shows the best thermodynamic performance with maximum COP, minimum exergy destruction, and maximum second law efficiency, R1234yf/R32 displays the worst thermodynamic performance. R12/R32 shows maximum TEWI while R290/R32 shows minimum TEWI. The first-generation refrigerants are found to be most environmentally friendly followed by the third and fourth. Fourth-generation refrigerants have the highest indirect emissions, which make their TEWI comparable to R134a. It is concluded that thermodynamic performance plays a significant role in reducing TEWI as indirect emissions account for the major part of the TEWI, and therefore, the global warming potential cannot be the only basis for refrigerant selection. This study suggests that first-generation refrigerants and R152a can be better alternatives.

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INTRODUCTION

In the twenty-first session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP 21, 2015), it was agreed to limit the increase in global average temperature to well below 2°C above pre-industrial levels and pursue efforts to limit the temperature rise to 1.5 °C [1]. But it is observed that global emissions have grown at a faster rate since 2016 [2], and global atmospheric mole fractions of greenhouse gases reached record levels in 2018 [3]. The past five years are the five warmest on record, and the past decade, 2010–2019, is also the warmest on record [3]. Now we are on the brink of missing the opportunity to limit global warming to 1.5 °C and the world may warm by more than 3 °C by the end of this century unless we cut greenhouse gas emissions by 7.6% every year from now on until 2030 [4]. The estimated number of cooling appliances in 2019 was 3.6 billion and projected to increase to 9.5 billion by 2050 [5]. As per the International Institute of Refrigeration (IIR) 2014 estimates, the refrigeration sector accounted for 7.8% of global GHG emissions [6].

Since refrigeration systems are significant contributors to global warming, very stringent regulations are being made to reduce emissions from this sector. The recent one is the Kigali Amendment that was adopted on 15 October 2016 by the 28th Meeting of Parties to the Montreal Protocol, and it came into force on 1 January 2019 to achieve over 80% reduction in HFC consumption by 2047 [7]. This amendment made the Montreal Protocol an even more powerful weapon against global warming. But this amendment only focussed on reducing the direct part of total emission from the refrigeration sector whereas these affect the environment in two ways – Direct and indirect [8].

Presently, there is an effort to shift to low GWP (Global Warming Potential) refrigerants such as first-generation, low GWP third-generation, and fourth-generation refrigerants. But among these, the fourth-generation refrigerants are seen as the way out.

REFRIGERANT PROGRESSION – A WALKTHROUGH

Natural refrigerants, being the earliest refrigerants used in human history, are called first-generation refrigerants. The first-generation refrigerants included those which worked and were available. Water and air were some of the very first refrigerants considered. The first closed vapor compression refrigeration system, with ethyl ether, was proposed by Perkins in 1834. The natural refrigerants used most since the 19th century include R717 and R744, and the hydrocarbons include R600a and R290. But these had their issues to address. Carbon dioxide was also considered, but it required high-pressure machinery, and its condensation was difficult in many cases, owing to low critical temperature. Ammonia was flammable and toxic and reacts with copper. R600a and R290 had safety concerns in large usage. In short, most of these first-generation refrigerants were flammable, toxic, or both.

So, there was a need to find a refrigerant that is stable, non-toxic, non-flammable, and could be used in domestic refrigeration systems. Around 1930, CFC refrigerants (chlorofluorocarbon) were introduced. Thomas Midgeley found that the carbon compounds formed by halogens (iodine, bromine, chlorine, and fluorine) could be sufficiently stable. Although Methyl chloride (R40) was already being used since 1878, it was toxic, flammable, and unstable because the hydrogen bond to the carbon atom was not strong enough. So, R12 (CCl2F2) was selected as it does not include hydrogen and proved to be a good refrigerant candidate. Later many other CFCs and HCFCs (hydrochlorofluorocarbons), namely R11, R13, and R22, came into existence, and among those, HCFC such as R22 (CHClF2) dominated over others. R22 superseded R12 as the latter required a larger compressor for the same refrigerating effect compared to ammonia whereas R22 required swept volume similar to ammonia. The 1960s and 1970s saw large-scale production and application of these refrigerants, but these had one problem - they were eating out the ozone layer, leading to a phenomenon called Ozone Depletion, which was discovered in 1974. Then in 1985, the ozone hole over the Antarctic was reported [9], and the world was quick to react. The Montreal Protocol was signed in 1987 to phase out ozone-depleting substances. It was decided to phase out CFC by 2010 and HCFC by 2040 in all countries [10]. And thus, the era of CFC and HCFC was about to come to an end. These were termed second-generation refrigerants. The search began to find other refrigerants with properties on par with HCFCs and with no chlorine, as that was the culprit behind ozone depletion. It put the HFCs on the frontline, and R134a started replacing second-generation refrigerants. These refrigerants that had either very low or zero ODP were categorized as third-generation refrigerants. Other refrigerants being used include R32, R152a, R143a, and R404a. Another suitable candidate was R245fa, a derivative of propane. But the major disadvantage of HFCs, which caught the world's attention, is their high GWP, and hence these were targeted to be progressively phased out after the Kyoto Protocol was signed in 1997 [11]. European Directive 2006/40/EC banned the use of fluids with GWP more than 150 in mobile air conditioning [12-13]. In addition to EU regulations, some European countries also approved taxes on HFC (hydrofluorocarbon) acquisition [13]. Later, EU Regulation no. 517/2014 was signed to prohibit the use of R134a, R404a, and 410a (GWP of 1430, 3922, and 2088 respectively), the most widely used refrigerants in refrigeration and air conditioning system [14].

With all this, the focus has turned to low GWP refrigerants such as HFOs (hydro fluoro-olefins) that have very low GWP and zero ODP. Some examples are R1234yf and R1234ze. These are called fourth-generation refrigerants.

Cascade refrigeration systems (CRS) are widely used in supermarkets and industries such as chemical, food, pharmaceuticals, etc., in which the temperature ranges from -30˚C to -100˚C. It is because CRS can attain very low temperatures. It is also very economical and efficient as compared to single-stage VCRS [34, 35]. Exergy and energy analyses can be incorporated to find the impact of different refrigerants on the thermodynamic performance of the cascade refrigeration system.

Exergy analysis is one of the best tools to find out the losses in the system while finding the same through energy analysis is not possible [39]. Exergy destruction, which is due to irreversibility, can be estimated through exergy analysis [40]. The main aim of exergy analysis is to determine the maximum useful work and degradation of energy. T.S. Lee et al. did energy and exergy analysis to determine the optimal condensing temperature of the cascade condenser and to maximize COP and minimize exergy destruction of the cascade refrigeration system by using CO2 and NH3 [37]. Yataganbaba et al. investigated the impact of evaporating and condensing temperature on two-evaporator vapor compression refrigeration systems by selecting refrigerants R1234yf, R1234ze, and R134a doing calculation with the help of EES. They also found that exergy analysis is the best way for thermodynamic analyses. They showed that although R134a has a bit better thermodynamic performance, R1234ze is the best alternative to R134a due to its environmentally friendly properties [15]. Karber et al. showed that R1234yf can be a better replacement to R134a in the domestic refrigerator [16]. Other low GWP refrigerants from the third generation such as R152a have also been identified for use, and studies show that they can replace R134a. Bolaji et al. performed experimental work on a domestic refrigerator and examined the effect of evaporator temperature on COP, exergy flow destruction, exergy efficiency on four components by using R152a, R134a, and R12 and found that R152a constantly performs better than R134a and R12 [17]. Bolaji et al. did an experimental study with refrigerants R152a and R32, having zero ODP and low GWP and are environment-friendly refrigerants, to replace R134a in a domestic refrigerator. The author found that COP increases by 4.7% and consumed less energy by using R152a. They also concluded that the performance of R152a is better than R32 and R134a throughout the conditions and that R152a can be used as a replacement for R134a in the domestic refrigerator [18]. Cabello et al. did an experimental study for comparison of R152a/R744 and R134a/R744 in cascade refrigeration system (a pair suitable for commercial and industrial applications) to substitute high GWP R134a with low GWP R152a to reduce the greenhouse effect and they found that there is no great achievement in saving and worsening energy, but feasible to replace R134a with R152a [19].

But one cannot deny that natural refrigerants are the only class of refrigerants that have been alive since the refrigeration word was first coined. Now also many studies are going on to return to these refrigerants as they are environment friendly. There are few refrigerants from this class that has been extensively used (such as ammonia). Though there are few safety concerns associated with these refrigerants, these can be used in sealed spaces with low refrigerant charges. R600a and R290 are globally perceived as having safety concerns, but these are perfectly safe with systems that use small refrigerant charge amounts (typically less than 120 g, 1⁄4 lb for R600, and 150g for R290) [20-21]. Joybari et al. found that using 60g of R600a shows similar results as R134a. At the optimum condition, the amount of charge required for R600a was 50 g, 66% lower than the R134a. The low charge requirement not only has economic advantages but also significantly reduces the risk of flammability of the hydrocarbon refrigerants [22]. Rasti et al. experimented on a domestic refrigerator by using refrigerant R436A, R600a, HC type compressor, R600a, and HFC type compressor. They found that refrigerator working with R436A and R600a shows lower TEWI (Total Equivalent Warming Impact) and R600a shows lower exergy destruction by using HC type refrigerator and HFC refrigerator [23].

Sanchez et al. experimented with five low GWP refrigerants: R290 and R600a (HC); R134a and R152a (HFCs); R1234ze and R1234yf (HFOs) and found that R290 increases COP, cooling capacity, and power consumption; R600a and R1234ze reduces the cooling capacity and COP [24].

The above literature studies reveal that the researchers did many experimental and theoretical investigations to find suitable refrigerants for the cascade refrigeration system. However, to the best of the author's knowledge, no case studies on generation-wise comparison of refrigerants in a cascade refrigeration system are there, comparing the performance indexes and TEWI to paint a comprehensive outlook on the environmental impact. However, the rapid increase in global warming has triggered the need to analyze the overall footprints of refrigerants on the environment rather than just comparing the thermodynamic performance or GWP.

This paper presents the comparison of the majorly used refrigerants from different generations and few new potential refrigerants (Table.2) in the cascade refrigeration system. Refrigerants are compared on their thermodynamic performance and environmental impact. COP, exergy destruction, and second law efficiency are the parameters analyzed for thermodynamic performance analysis and TEWI for environmental impact analysis. Further, it extrapolates the relation between performance and global warming caused by refrigerants to showcase the overall effect on the environment. This case study also attempts to find the viability of the low GWP fourth-generation refrigerants.

GLOBAL WARMING – QUANTIFICATION

Global warming associated with the refrigeration systems can be calculated by different methodologies – GWP, TEWI, and LCCP. Although GWP alone provides a measure of the direct warming potential of refrigerants, it does not consider the system performance. TEWI considers both direct and indirect emissions from refrigeration systems. LCCP is a holistic approach, and in addition to TEWI, it accounts for warming impact during manufacturing, delivery, operation, and recycling.

Makhnatcha et al. show that TEWI is simpler than LCCP and the additional contribution of LCCP compared to the TEWI is negligible [25]. Many studies have used TEWI to find the environmental impact of refrigeration systems [23, 26-29].

2.1 Total Equivalent Warming Impact

This approach considers the two significant ways in which refrigeration systems can add to global warming.

Direct emissions

Direct emissions are due to leakage of refrigerants in the environment during operation, maintenance, and end of life. These account for the deteriorating effect of the GWP of the refrigerants on the environment. Leakage rate depends on two factors - pressure and refrigerant. The leakage rate is estimated to be around 10-15% per year [30-31].

Indirect emissions

Indirect emissions are due to the emissions generated at the power plant to supply electricity to refrigeration systems (assuming electricity is generated from fossil fuels). According to current estimates, RACHP equipment represents between 25% and 30% of the global consumption of electricity [32].

Total equivalent warming impact (TEWI)

TEWI is the indicator of the total warming impact of refrigeration systems. It is the summation of direct and indirect emissions from refrigeration systems. While performance parameters (affecting work consumption) govern indirect emissions, the GWP of refrigerants and the leakage govern direct emissions. So both factor combined derives the warming impact of a refrigerant. It can be calculated by the following equation [33]:

$$TEWI = m * GWP * n + P * \beta * n \tag{1}$$

In the above equation, the first part represents the direct emissions and the second part indicates the indirect emissions related to refrigeration systems.

THEORETICAL SYSTEM MODEL

Cascade Refrigeration System

Figure.1 shows Pressure enthalpy (P-h) diagram and Fig.2 shows block diagram of cascade refrigeration system. The cascade refrigeration system (CRS) consists of two circuits, High Temperature Circuit (HTC) and Low Temperature Circuit (LTC), and both circuits are connected by the cascade heat exchanger that acts as a condenser for LTC and evaporator for HTC. In this study, HTC works on refrigerant R134a, R152a, R245fa, R1234yf, R1234ze, R22, R12, R600a, R290 and LTC uses refrigerant R32. R32

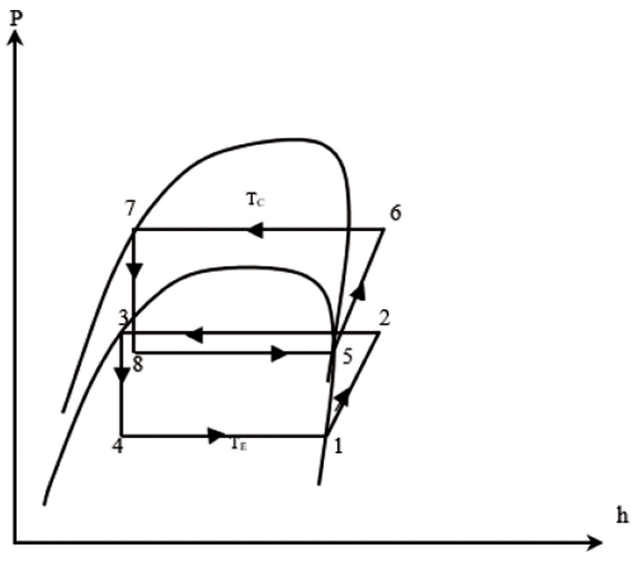

Figure 1. P-h diagram of cascade refrigeration system (CRS).

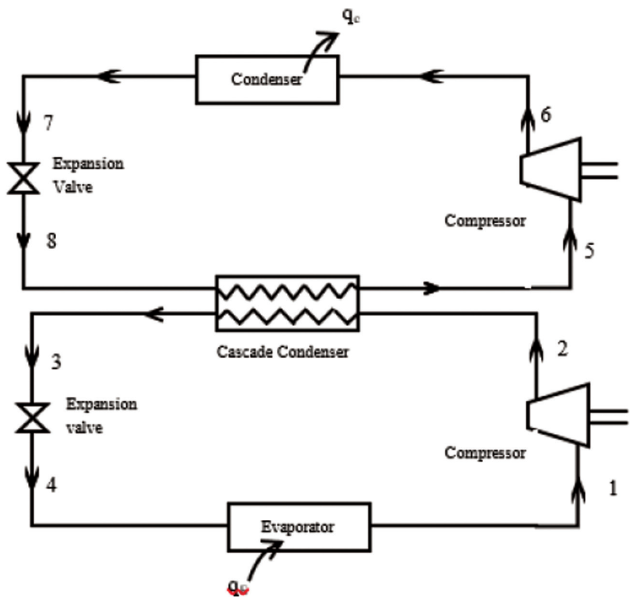

Figure 2. Schematic diagram CRS.

refrigerant works in low temperature cycle because of its low boiling point (Table-2). Other examples of refrigerants with low boiling point that can be used in place of R32 in LTC include R23, R41 and R404a [42].

Mathematical Modelling

Engineering Equation Solver (EES) is used to obtain the results for the theoretical mathematical model that is developed as per the law of thermodynamics. Below assumptions are made for calculation:

1. All the components are assumed steady flow process.
2. Pressure energy and kinetic energy are negligible.
3. The compression and expansion processes are adiabatic
4. Heat loss and pressure drop are negligible in connecting pipes and heat exchangers.

Basic parameters assumed have been shown in Table.1.

Governing Equations for Simulation

Energy and exergy balance equation has been used in CRS for thermodynamic performance and also to calculate the various parameter.

Mass balance:

$$\sum \dot{m}_i = \sum \dot{m}_o \quad (2)$$

$\dot{m}$ is mass flow rate

Energy balance equation:

$$\dot{Q} + \sum \dot{m}_i h_i = \dot{W} + \sum \dot{m}_o h_o \quad (3)$$

$\dot{Q}$ is heat transfer rate, $\dot{W}$ is work transfer rate and h is specific enthalpy

Exergy balance equation:

$$\sum \dot{E}_{x_i} = \sum \dot{E}_{x_o} + \dot{E}_{x_D} \quad (4)$$

Table.1. Basic Parameters and Assumptions [41,38, 33,43]

Heat Input in LTC evaporator, $Q_{e,I}$	70 kw [41, 38]
$T_{cas,c}$	268K
Ambient Temperature, T_a	303K
$T_{cas,E}$	258K
T_7	313K
Mechanical Efficiency, η_m	0.85
LTC Evaporator temp. variation	199K to 207K
HTC Condenser temp. variation	305K to 313K
Leakage rate (per year)	15% of IC
GWP for Electricity production (kg eq CO2/kWhr)	0.571 [33,36]
Initial refrigerant charging amount (kg)	2 kg per kW cooling load [33]

$\dot{E}_{x_i}$ is inlet exergy rate, $\dot{E}_{x_o}$ is outlet exergy rate and $\dot{E}_{x_D}$ is exergy destruction rate

Exergy balance for control volume

$$\dot{E}_{x_D} = \sum \left[\left(1 - \frac{Ta}{T}\right) \dot{Q} \right]_o - \dot{W} + \sum \left(\dot{m}e\right)_i - \sum (\dot{m}e)_o \quad (5)$$

Specific equations for each component:

For high temperature circuit

1. Compressor

Mass balance:

$$\dot{m}_6 = \dot{m}_5 \quad (6)$$

Energy balance:

$$\dot{W}_{HT} = \frac{\dot{m}_5 \left(h_{6s} - h_5\right)}{\eta_{m,HT}} \quad (7)$$

$\dot{W}_{HT}$ work rate and $\eta_{m,HT}$ mechanical efficiency for compressor of high temperature circuit

Exergy balance:

$$\left(\dot{E}_{x_D}\right)_{HT,comp} = \dot{W}_{HT} - \dot{m}_5 \left[\left(h_6 - h_5\right) - T_a \left(S_6 - S_5\right) \right] \quad (8)$$

$\left(\dot{E}_{x_D}\right)_{HT,comp}$ is compressor exergy destruction rate of high temperature circuit

2. Expansion valve

Mass balance:

$$\dot{m}_8 = \dot{m}_7 \quad (9)$$

Energy balance:

$$h_8 = h_7 \quad (10)$$

Exergy balance:

$$\left(\dot{E}_{x_D}\right)_{HT,exp} = \dot{m}_8 T_a \left(S_7 - S_8\right) \quad (11)$$

$\dot{Q}_{HT,exp}$ is expansion valve exergy destruction rate of high temperature circuit

3. Condenser

Mass balance:

$$\dot{m}_7 = \dot{m}_6 \quad (12)$$

Energy balance:

$$\dot{Q}_{HT,cond} = \dot{m}_7 \left(h_6 - h_7\right) \quad (13)$$

$\dot{Q}_{HT,cond}$ is condenser heat transfer rate of high temperature circuit

Exergy balance:

$$\left(\dot{E}_{x_D}\right)_{HT,cond} = \dot{m}_7\left[\left(h_6 - h_7\right) - T_a\left(S_6 - S_7\right)\right] \tag{14}$$

$\left(\dot{E}_{x_D}\right)_{HT,cond}$ is condenser exergy destruction rate of high temperature circuit

4. Cascade condenser

Mass balance:

$$\dot{m}_5 = \dot{m}_8,\ \dot{m}_3 = \dot{m}_2 \tag{15}$$

Energy balance:

$$\dot{Q}_{LT,cond} = \dot{m}_5\left(h_5 - h_8\right) = \dot{m}_3\left(h_3 - h_2\right) \tag{16}$$

$\dot{Q}_{LT,cond}$ is condenser heat transfer rate for low temperature circuit

Exergy balance:

$$\begin{aligned}\left(\dot{E}_{x_D}\right)_{LT,cond} &= \dot{m}_5\left[\left(h_8 - h_5\right) - T_a\left(S_8 - S_5\right)\right] \\ &\quad - \dot{m}_3\left[\left(h_3 - h_2\right) - T_a\left(S_3 - S_2\right)\right]\end{aligned} \tag{17}$$

$\dot{Q}_{LT,cond}$ is condenser exergy destruction rate for low temperature circuit

For low temperature circuit

5. Compressor

Mass balance:

$$\dot{m}_1 = \dot{m}_2 \tag{18}$$

Energy balance:

$$\dot{W}_{LT} = \frac{\dot{m}_1\left(h_{2s} - h_1\right)}{\eta_{m,LT}} \tag{19}$$

$\dot{W}_{LT}$ work transfer rate and $\eta_{m,HT}$ mechanical efficiency of compressor for low temperature circuit.

Exergy balance:

$$\left(\dot{E}_{x_D}\right)_{LT,comp} = \dot{W}_{LT} + \dot{m}_1\left[\left(h_2 - h_1\right) - T_a\left(S_2 - S_1\right)\right] \tag{20}$$

$\left(\dot{E}_{x_D}\right)_{LT,comp}$ is compressor exergy destruction rate for low temperature circuit

6. Expansion valve

Mass balance:

$$\dot{m}_4 = \dot{m}_5 \tag{21}$$

Energy balance:

$$h_4 = h_3 \tag{22}$$

Exergy balance:

$$\left(\dot{E}_{x_D}\right)_{LT,exp} = \dot{m}_3 T_a\left(S_3 - S_4\right) \tag{23}$$

$\left(\dot{E}_{x_D}\right)_{LT,exp}$ is expansion valve exergy destruction rate for low temperature circuit

7. Evaporator

Mass balance:

$$\dot{m}_1 = \dot{m}_4 \tag{24}$$

Energy balance:

$$\dot{Q}_{LT,evap} = \dot{m}_1\left(h_1 - h_4\right) \tag{25}$$

$\dot{Q}_{LT,evap}$ is evaporator heat transfer rate for low temperature circuit.

Exergy balance:

$$\left(\dot{E}_{x_D}\right)_{LT,evap} = \left(1 - \frac{T_a}{T_E}\right)\dot{Q}_{LT,evap} + \dot{m}_1\begin{bmatrix}\left(h_1 - h_4\right) \\ -T_a\left(S_4 - S_1\right)\end{bmatrix} \tag{26}$$

$\left(\dot{E}_{x_D}\right)_{LT,evap}$ is evaporator exergy destruction rate for low temperature circuit

The COP for high temperature circuit

$$COP_{HT} = \frac{\dot{Q}_{HT,evap}}{\dot{W}_{HT}} \tag{27}$$

and COP for low temperature circuit

$$COP_{LT} = \frac{\dot{Q}_{LT,evap}}{\dot{W}_{LT}} \tag{28}$$

The total COP for cascade system is

$$COP_{total} = \frac{\dot{Q}_{LT,evap}}{\dot{W}_{HT} + \dot{W}_{LT}} \tag{29}$$

and carnot COP of cascade system

$$COP_{carnot} = \frac{T_E}{T_C - T_E} \tag{30}$$

Second Law Efficiency is calculated by

$$\eta_{II} = \frac{COP_{total}}{COP_{carnot}} \tag{31}$$

Total Exergy destruction rate of cascade system is calculated by

$$\left(\dot{E}_{x_D}\right)_{Total} = \left(\dot{E}_{x_D}\right)_{HT,comp} + \left(\dot{E}_{x_D}\right)_{HT,evap} + \left(\dot{E}_{x_D}\right)_{HT,cond} + \left(\dot{E}_{x_D}\right)_{LT,cond} + \left(\dot{E}_{x_D}\right)_{LT,comp} + \left(\dot{E}_{x_D}\right)_{LT,\exp} + \left(\dot{E}_{x_D}\right)_{LT,evap} \quad (32)$$

Refrigerant Selection

The most widely used refrigerants are selected from all the generations along with some promising candidates to draw a comparison. The physical properties of the selected refrigerants are shown in table.2.

Model Validation

The present work is validated with works of Messineo and Panno [38] in order to prove the correctness of the model. Table 3 shows the comparison of present model with reference model (Messineo and Panno). The values of input parameters for the comparison are T_e (LTC evaporating temperature) = -35°C, T_c (HTC condensing temperature) = 35°C, isentropic efficiencies = 0.7, ΔT (temperature difference in cascade heat exchanger) = 5°C, degree of superheating and subcooling in both HTC and LTC is zero. The authors did not clearly reveal the software they used but it is estimated that it could be Engineering Equation Solver (EES). The results of the present study match with the reference model with deviation in a range of 0.43 to -1.06. The validation shows that the EES model developed is reliable.

RESULTS AND DISCUSSION

This paper presents a three-part analysis. The first part analyzes the thermodynamic performance with the variations in evaporating (LTC) and condensing (HTC) temperature in a cascade refrigeration system. It calculates the COP, second law efficiency, and exergy destruction. The second part analyzes the total warming impact by calculating TEWI with variation in the above parameters. It also draws the relation between TEWI and performance indexes. The third part provides a comparison for different generation of refrigerants to showcase how the impact of refrigeration systems on the environment has changed with the refrigerant progression from the early days of refrigeration to the present day.

Table 2. Physical properties of refrigerants

Refrigerant	Generation	Molecular wt.(kg/kmol)	NBP (°C)	T_c (°C)	P_c (MPa)	ODP	GWP
R600a	First	58.12	-11.7	134.7	3.64	0	4
R290		44.1	-42.2	96.7	4.25	0	3
R22	Second	86.47	-41.4	96.2	4.99	.055	1760
R12		120.90	-29.8	112	4.14	1.0	10900
R134a	Third	102.03	-26.1	101.1	4.06	0	1430
R152a		66.05	-24.0	113.3	4.52	0	133
R245fa		134	14.9	154.1	3.65	0	1030
R32		52.02	-51.7	78.2	5.8	0	550
R1234ze	Fourth	114.04	9.745	109.37	3.64	0	7
R1234yf		114.04	-29.45	94.7	3.38	0	4

Table 3. Validation results for COP of the present model and the reference model of Messineo and Panno [38] using the same data

Refrigerant pair	Reference model	Present model	Deviation
R717/R744	1.71	1.709	-0.06%
R290/R744	1.63	1.637	0.43%
R600/R744	1.7	1.699	-0.06%
R410A/R744	1.61	1.593	-1.06%
R134a/R744	1.65	1.654	0.24%
R404A/R744	1.53	1.535	0.33%

Thermodynamic Performance Analysis

Thermodynamic performance analysis is done by calculating COP, second law efficiency, and exergy destruction with variation in both LTC evaporating and HTC condensing temperature for refrigerants belonging to different generations. Fig.3-5 shows the effect of the rise in LTC evaporator temperature on the actual COP, second law efficiency, and total exergy destruction. From fig.3, it is clear that actual COP increases with the increase in the LTC evaporator temperature as when evaporator temperature increases, the work input to compressor decreases, and refrigerating effect increases leading to an increase in COP. Second law efficiency also follows the same trend as depicted in fig.4, the reason being the reduction in the temperature difference (cooling medium and ambient). Due to the increase in COP and second law efficiency, the heat losses reduce, and hence the exergy destruction reduces with the increase in evaporator temperature as evident from fig.5. It is observed that the highest COP and second law efficiency and lowest exergy destruction is shown by R152a/R32, followed by R245fa/R32, R12/R32, R22/R32, R600a/R32, R134a/R32, R1234ze/R32, R290/R32 and lastly R1234yf/R32, at all points with variation in LTC evaporating temperature.

But in the case of variation in HTC condensing temperature, the trend for COP, exergy destruction, and second

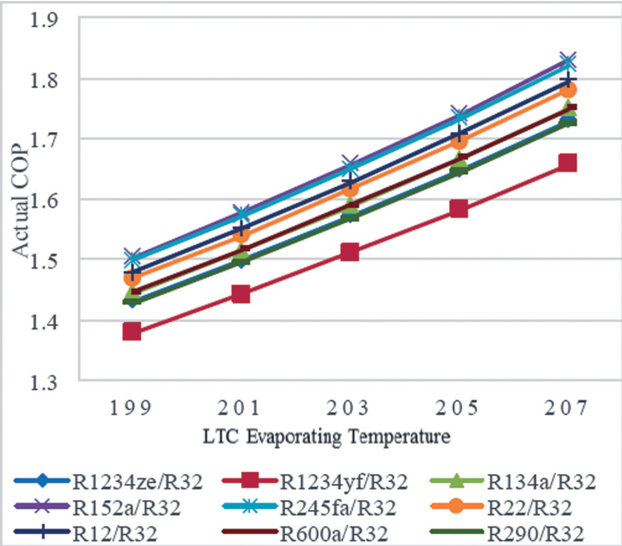

Figure 3. Variation of COP with LTC evaporating temperature.

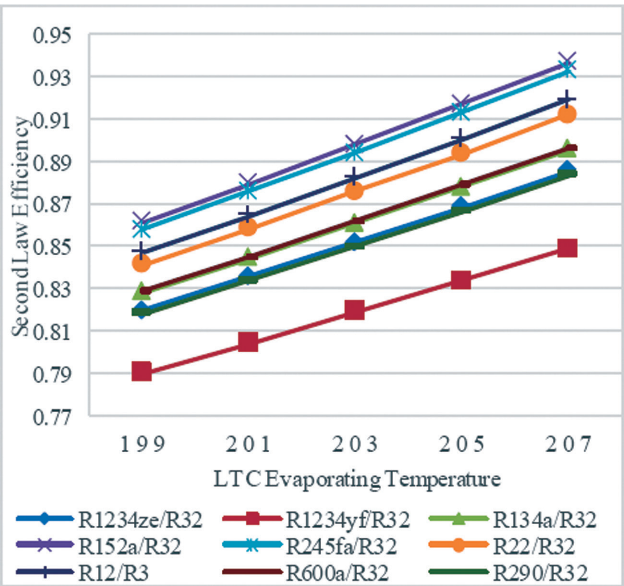

Figure 4. Variation of second law efficiency with LTC evaporating temperature.

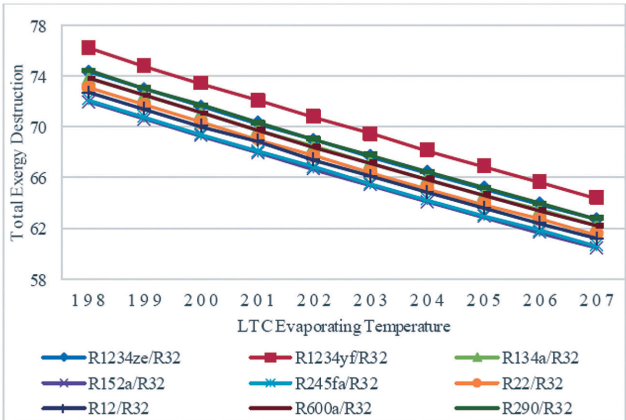

Figure 5. Variation of total exergy destruction with LTC evaporating temperature.

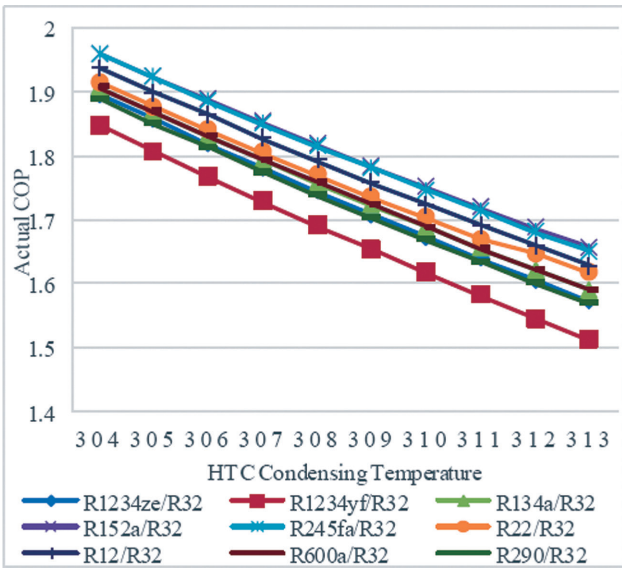

Figure 6. Variation of actual COP with HTC condensing temperature.

law efficiency are reversed, which is evident from fig.6, 7 & 8. In this case, also, R152a shows maximum COP, second law efficiency, and minimum exergy destruction at all temperatures.

Environment Impact Assessment

Environment impact assessment is necessary for conserving the ecological balance and can be achieved with TEWI analysis. Fig.9 shows the direct emissions for different refrigerants in HTC and R32 in LTC at different evaporator temperatures. Value for direct emission is maximum for R22/R32 couple and minimum for R290/R32. Direct emissions for R1234yf, R1234ze, R290, and R600a are comparable but are lesser compared to that for R12/R32, R22/R32, R134a/R32, and R245fa/R32 since their GWP values are extremely lesser compared to the latter (Table.2). We can see a decreasing trend for direct emission (fig.9) with increasing evaporator temperature for all refrigerants in HTC while that for R32, used in LTC, is constant. Direct emissions depend on GWP, leakage rate, and charge, which in turn is dependent on the cooling load. Since LTC cooling load and leakage rate are assumed to be constants throughout the study, the direct emissions for R32 are constant at

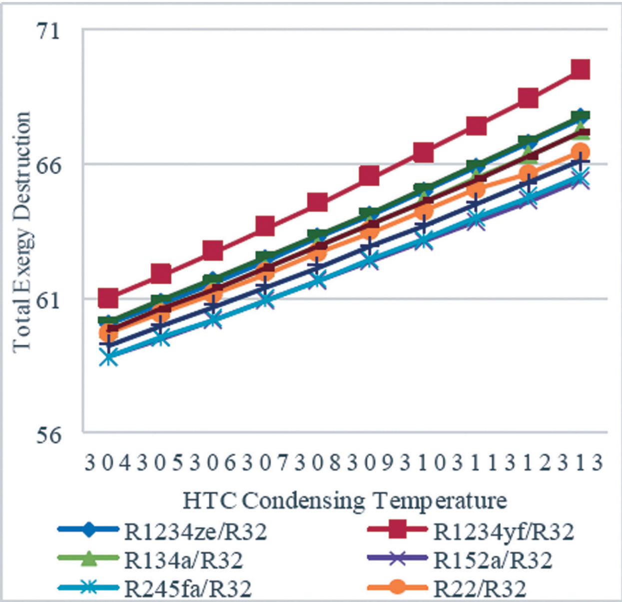

Figure 7. Variation of actual total exergy destruction with HTC condensing temperature.

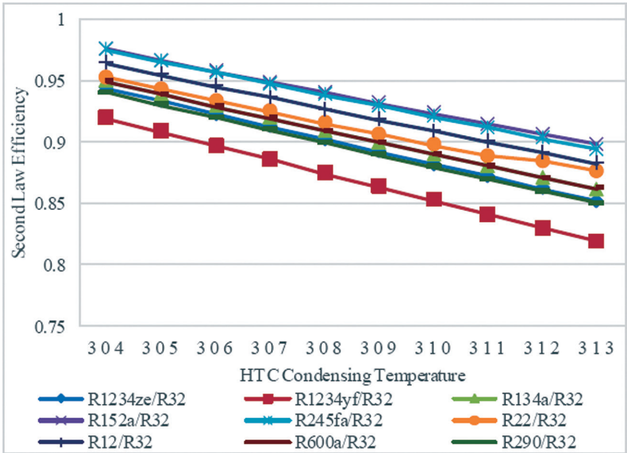

Figure 8. Variation of actual second law efficiency with HTC condensing temperature.

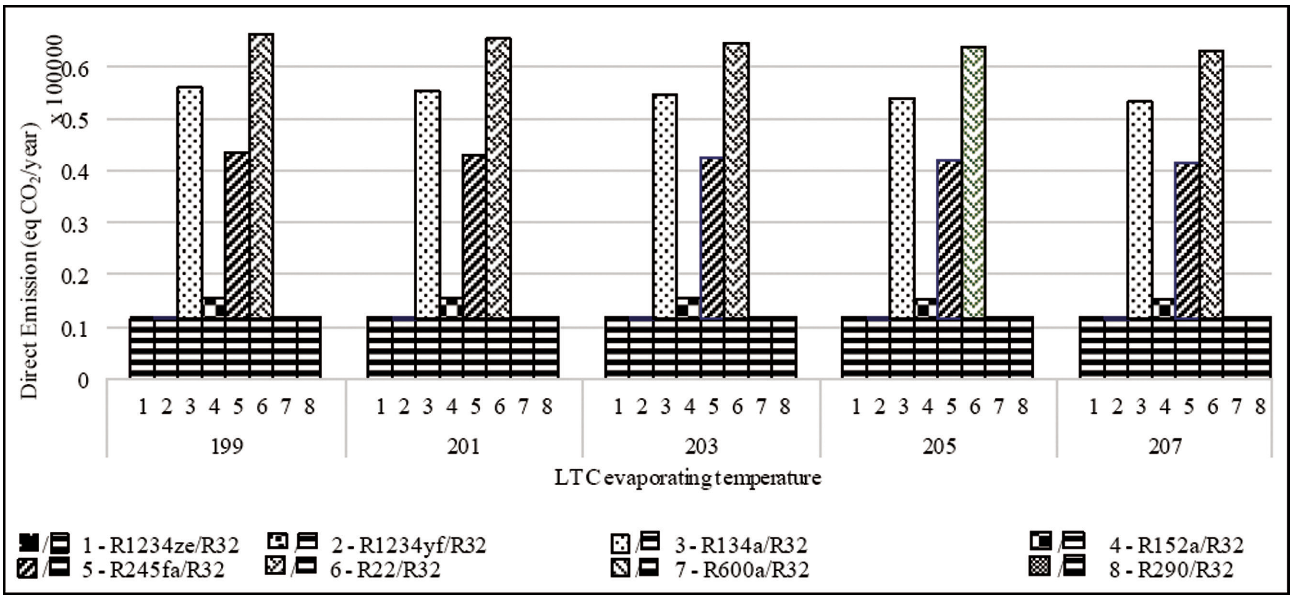

Figure 9. Variation of direct emissions with LTC evaporating temperature.

all temperatures. The decreasing trend for HTC is because the charge is a function of cooling load (Table.1), and it decreases as the HTC cooling load decreases with the increase in LTC evaporator temperature.

Fig.10 shows the variation in indirect emission with evaporator temperature. Indirect emissions are dependent on the thermodynamic performance as these emissions are the function of the energy consumed. R1234yf/R32, which has the worst thermodynamic performance, shows the maximum value of indirect emission owing to the highest work consumption, while R290/R32 shows the minimum value followed by R152a/R32. It is noticed that R152a/R32 does not have a minimum value of indirect emission even if R152a shows the best thermodynamic performance (and hence lowest specific work consumption) because its mass flow rate is a bit higher compared to R290. Indirect emission also shows a decreasing trend with an increase in evaporator temperature as thermodynamic performance increases.

The total direct emission of R12/R32 is higher than that for R22/R32 and R290/R32 by more than 524% and 2839% respectively, at all temperature points. Total indirect emission for R12/R32 is higher than that for R22/R32 and R290 by more than 134% and 200% respectively, at

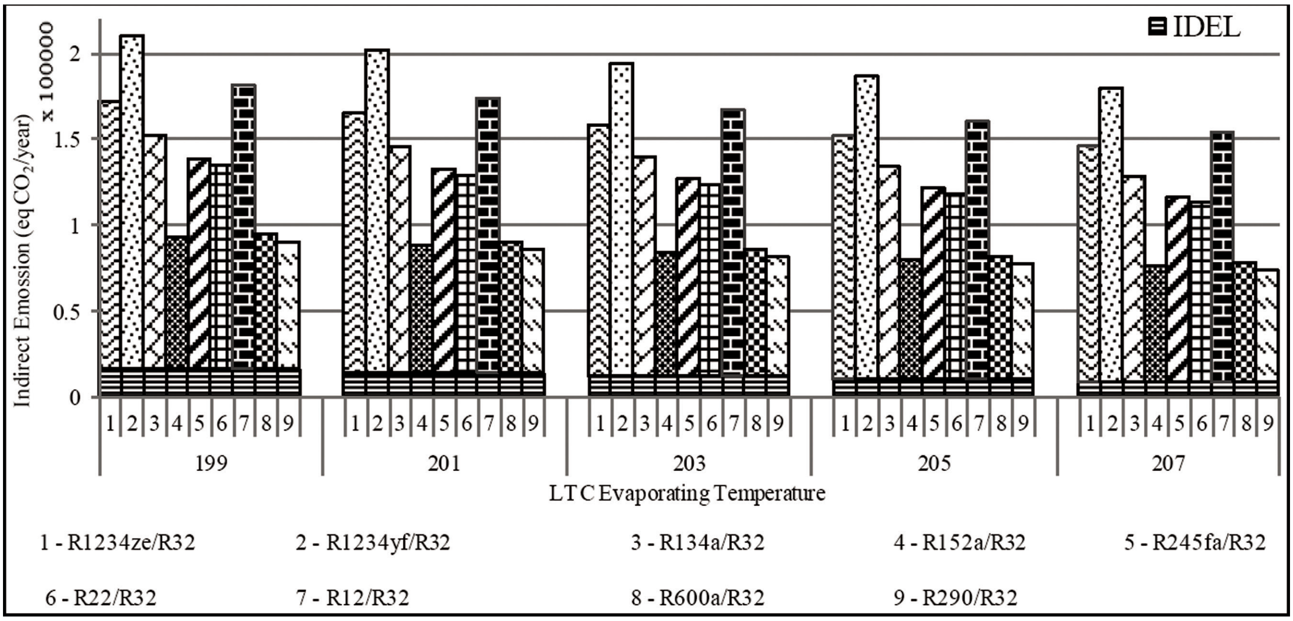

Figure 10. Variation of Indirect emissions with LTC evaporating temperature.

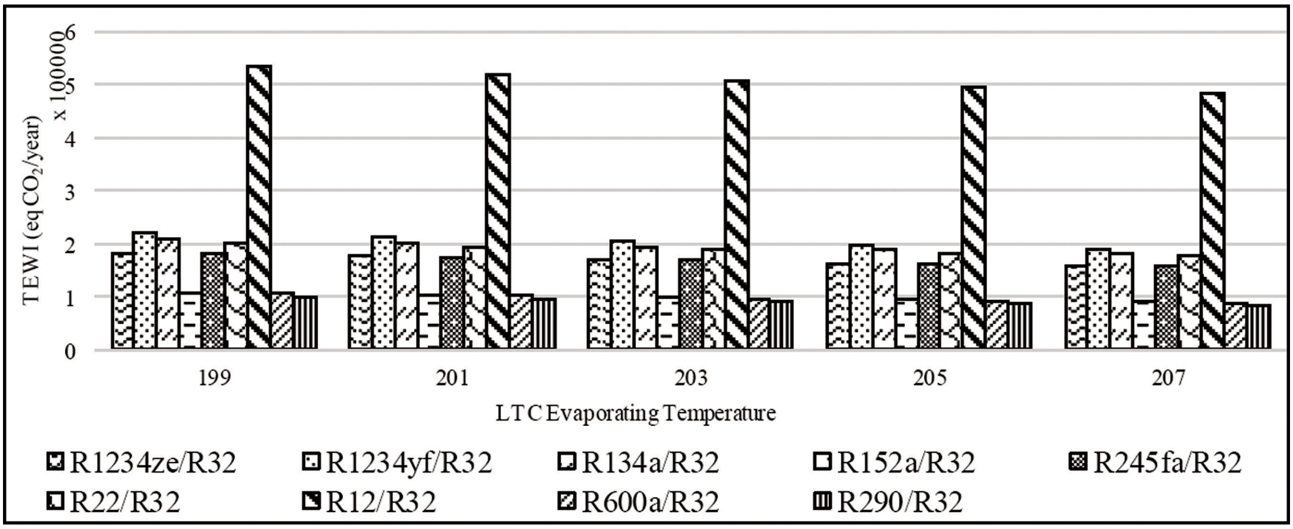

Figure 11. Variation of TEWI with LTC evaporator temperature.

all temperature points. (R12 is not depicted in fig.9 as its direct emissions are extremely high because of its very high GWP, and hence it is not feasible to show variation for other refrigerants, with R12 present in the graph.)

With both factors combined (direct and indirect emissions), TEWI variation is shown in fig 11 and 12. It is worth noting that TEWI has an inverse relationship with LTC evaporator temperature, while it has a direct relation with HTC condenser temperature. This variation is because indirect emission has an inverse relation with thermodynamic performance. With the enhancement in the efficiency and the thermodynamic performance of the system, work input decreases, and hence indirect emissions decrease. Direct emission, though does not contribute much to TEWI in most cases, decreases with an increase in LTC evaporating temperature, as explained above. Therefore, overall TEWI decreases with an increase in LTC evaporator temperature. It is also observed that R12/R32 couple shows maximum TEWI followed by R1234yf/R32, R134a/R32, R22/R32, R1234ze/R32, R245fa/R32, R152a/R32, R600a/R32, and R290/R32.

TEWI Analysis for Different Generation of Refrigerants

Refrigerants are categorized into different generations as per their features. This section compares these different generations of refrigerants based on TEWI to show how

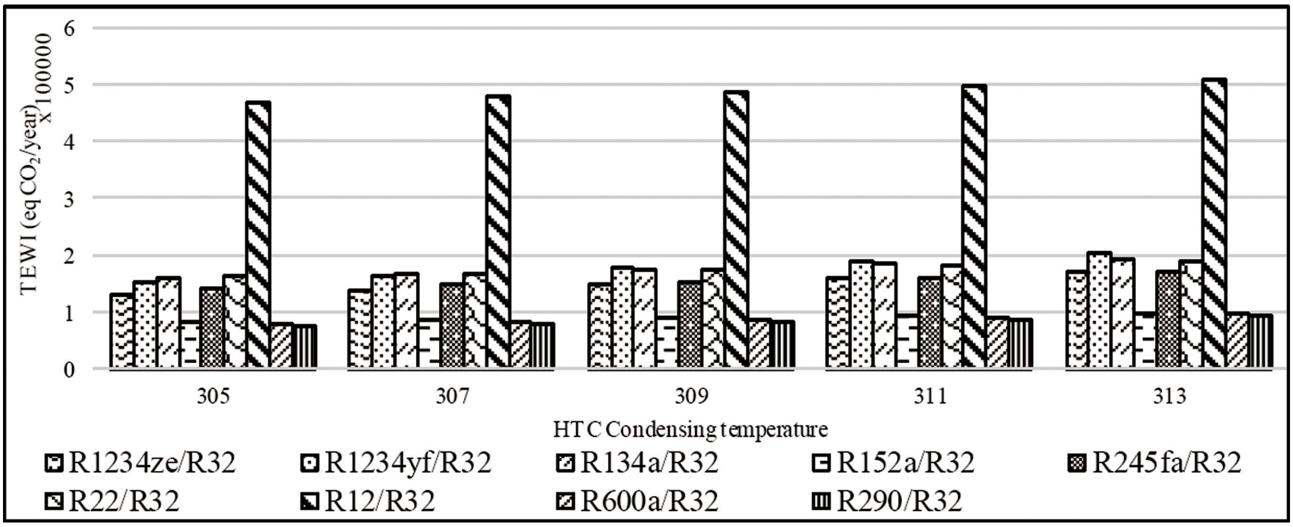

Figure 12. Variation of TEWI with HTC condensing temperature.

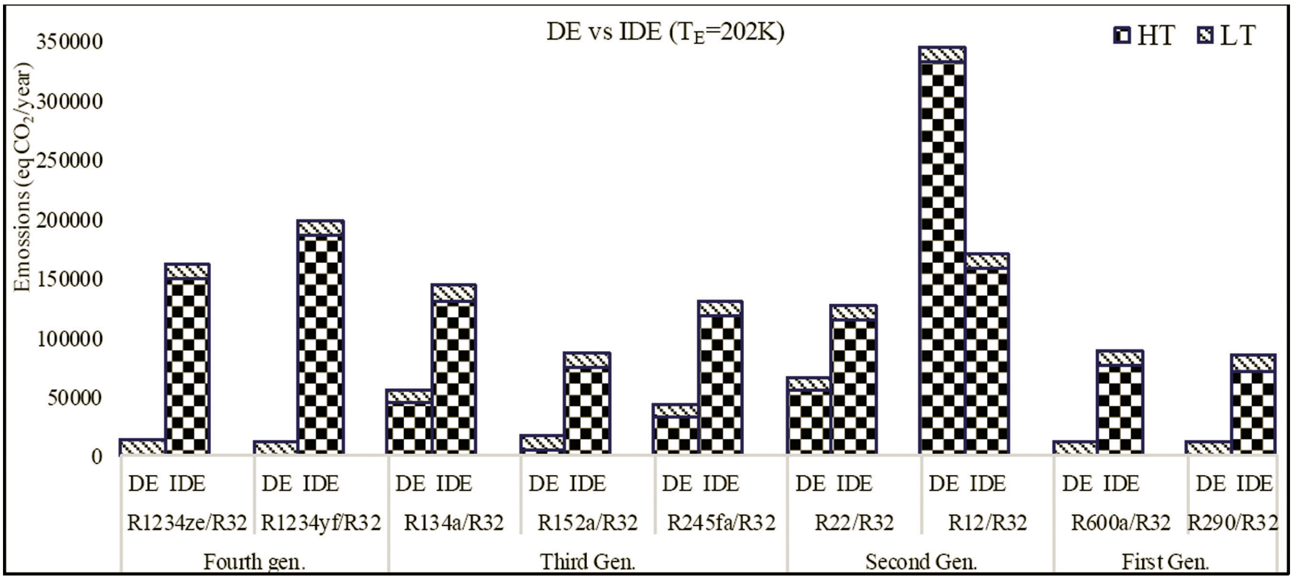

Figure 13. Total direct and indirect emissions of different pairs of refrigerants from different generation.

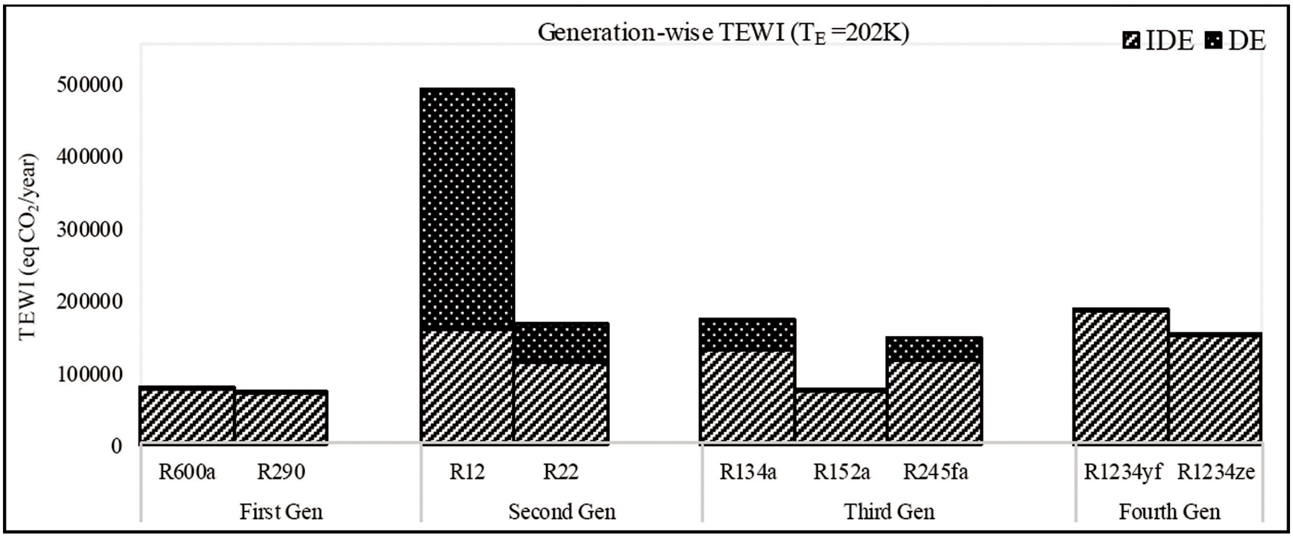

Figure 14. Generation wise TEWI (for refrigerants in HTC of CRS).

different generations of refrigerants have affected the environment and which factor is prominent.

Fig.13 dissects the overall warming impact of different refrigerants from different generations into direct and indirect emissions (at LTC Evaporator temp., TE = 202K). It is visible that the direct emission of the fourth-generation and first-generation refrigerant is negligible. The refrigerant R152a is a third-generation refrigerant that has very low direct emissions. R32, used in LTC, shows low direct and indirect emissions. The maximum value for direct emission is shown by R12/R32. It is worth noting that, for all generations, indirect emissions are higher than direct emissions except R12 from the second generation. The fourth-generation refrigerants have very low direct emissions but have very high indirect emissions. Their indirect emissions are even higher than that of third-generation refrigerants. This can be attributed to the bad thermodynamic performance of the fourth-generation refrigerants and their high mass flow rate.

Generation-wise overall warming impact can be seen in fig.14 (at TE = 202K). All refrigerants shown are employed in HTC. The second generation of refrigerants has very high TEWI, while the first-generation refrigerants and R152a from the third generation have the lowest TEWI. Although fourth-generation refrigerants do not affect much via direct emission, they have comparable TEWI values to the third-generation refrigerants because of their high indirect emissions. Few low GWP third-generation refrigerants, such as R245fa and R152a, do better than the fourth-generation refrigerants.

CONCLUSION

This study shows how the progression of refrigerants has affected the environment. It compares all the generations of refrigerants based on the warming impact and thermodynamic performances. The mathematical model developed helps to analyze the thermodynamic performance of refrigerants. COP, second law efficiency, and exergy destruction are calculated and compared for refrigerants, with variation in LTC evaporator and HTC condenser temperature. TEWI assessment is applied to evaluate the effect of these refrigerants on ecological sustainability by calculating the total amount of CO_2 released in the environment. Also, a comparison is drawn to see how the performance of refrigerants affects their warming potential. The findings are:

- R152, a low GWP third-generation refrigerant, shows the highest thermodynamic performance (maximum COP and second law efficiency, and minimum exergy destruction). It is followed by R245fa/R32, R12/R32, R22/R32, R600a/R32, R134a/R32, R1234ze/R32, R290/R32, and lastly R1234yf/R32.
- R1234yf, a fourth-generation refrigerant, shows maximum exergy destruction, and minimum COP and second law efficiency.
- Given the constant leakage rate and LTC cooling load, direct emissions for HTC decrease with an increase in evaporator temperature.
- R1234yf, R1234ze, R290, and R600a have very low direct emissions. Among these, R290 has the lowest value. R152a also has low direct emissions. However, it is considerably higher than that of first and second-generation refrigerants.
- Direct emission of R12/R32 is the highest. It is higher than that of R290/R32 by more than 2839%.
- R290/R32 displays the lowest indirect emission followed by R152a/R32, R600/R32, R22/R32, R245fa/R32, R134a/R32, R1234ze/R32, R12/R32. R1234yf/R32 shows the highest indirect emission.

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- Both direct and indirect emissions decrease with the increase in LTC evaporator temperature.
- Indirect emissions are higher than direct emissions. So, high TEWI shows poor thermodynamic performance, and hence we need to focus more on improving the system efficiency.
- TEWI displays an inverse relation with evaporator temperature, but a direct relation with condenser temperature, and this shows the effect of temperature selection on the environment.
- R290 shows the lowest TEWI, whereas R12 shows the highest.
- First-generation refrigerants are the most ecological refrigerants while the second-generation refrigerants are the worst as they have high ODP and TEWI.
- Few low GWP refrigerants from third-generation, such as R152a and R245fa have low TEWI, while R134a has high TEWI.
- It is crucial to reduce the total global warming produced by refrigeration systems. This might not be achievable by using fourth-generation refrigerants because, despite their very low direct emissions, their very high indirect emissions make them equally bad as R134a and R22 as far as global warming is concerned.

Furthermore, the below suggestions are based on the findings of this study:

- Refrigerant should not be chosen based on GWP alone, as this can be detrimental, although it is vitally important to reduce the GWP. The focus should also be on increasing the system efficiency.
- Fourth-generation refrigerants such as R1234yf and R1234ze cannot be a better alternative to R134a.
- R152a and first-generation refrigerants have lower TEWI compared to others and therefore, can be a viable option.
- Fourth-generation refrigerants can be a good alternative if indirect emissions are reduced either by shifting more to renewable sources of energy with the advancement in technology or by increasing the efficiency of the system. It is also worth mentioning that reducing indirect emissions not only reduces global warming but also saves energy.

NOMENCLATURE

$\dot{m}$	Mass flow rate (kg/s)
h	Enthalpy (kJ/kg)
S	Entropy (kJ/kg-K)
m	Leakage rate per annum (kg)
n	Number of years
P	Energy consumption (kWh per annum)

Greek Symbols

β	CO_2 emission for per kWh electricity generation (kg eq CO_2/kWh)
η	Efficiency (improve)
η_{II}	Second Law Efficiency

Subscripts

i	input
o	output
a	Atmospheric condition
LT	Low temperature
HT	High temperature
$evap$	Evaporator
$comp$	Compressor
exp	Expansion valve
$cond$	Condenser
cas	Cascade

Abbreviation

IC	Initial Charge
ODP	Ozone Depletion Potential
LCCP	Life-cycle Climate Performance
GWP	Global Warming Performance
IDE	Indirect emission
DE	Direct emission
RACHP	Refrigeration, Air conditioning and Heat Pump
LTC	Low temperature circuit
HTC	High temperature circuit
TEWI	Total Equivalent Warming Impact, eq CO_2/year
COP	Coefficient of Performance

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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