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Environmental assessment of natural and fourth-generation synthetic refrigerant blends for sustainable cooling in India

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Climate change is a critical global concern, driven in part by the continuous increase in greenhouse gas (GHG) emissions. The refrigeration and air conditioning industries significantly contribute to these emissions through the use of hydrofluorocarbons (HFCs), which are potent GHGs. This study evaluates the environmental impacts of natural and fourth-generation synthetic refrigerants to support the development of a sustainable cooling action plan for India. Focusing on low global warming potential (GWP) refrigerant blends, the study investigates the atmospheric oxidation pathways of HFOs—R1234yf, R1234ze(*Z*), R1234ze(*E*), and R1243yf—alongside propane, identifying a 90 : 10 propane–R1234yf blend as a promising alternative to R32 in residential split air conditioners up to 7 kW. Thermodynamic analysis reveals that this blend achieves a 15% improvement in both volumetric cooling capacity and coefficient of performance compared with R32 while significantly lowering GWP to the level of R1234yf. Environmental and economic assessments show that the blend emits approximately 5.1 tCO_2e annually, which is 22 times lesser than R32, and offers cost benefits due to its reduced capital and environmental expenditures. The total environmental impact metric for the simulated blend indicates that CO_2-equivalent emissions can be reduced up to 96% when R32 is replaced with the R1234yf + propane blend. Based on these findings, this study proposes key policy imperatives for accelerating the adoption of natural refrigerants in India, in alignment with the Kigali Amendment's HFC phasedown schedule.

Sustainability spotlight

The global demand for cooling is projected to be driven by developing countries like India, Brazil and China. The cooling demand in India is large, and air-conditioner and refrigerant sales are expected to grow six-fold by 2038. Owing to this cooling demand and the climate impacts of HFCs, the design of low-GWP alternatives is a major requisite in addressing climate impacts from the cooling sector. In order to decouple the energy demand and climate impact, several initiatives, including finding climate-friendly alternatives and shifting to natural refrigerants, have been proposed. The present study explores the possibility of achieving sustainable cooling in the residential sector in India with the use of natural and fourth-generation synthetic refrigerant blends. The use of the propane + R1234yf blend as an alternative for R32 is suggested to be better in terms of energy efficiency, environmental impact and economic feasibility. Following the technical, environmental and economic criteria, policy imperatives for sustainable cooling in the residential sector of India through the use of natural refrigerants are derived. This work thus provides a sector-driven approach to reduce GHG emissions from the cooling sector in India to considerable extent.

1. Introduction

Two of the biggest challenges the world is currently experiencing are global warming and climate change.[1] For ages, humans have been making drastic impacts on the environment. However, the effects of human activity have only started to spread globally since the start of the industrial revolution.[2] In its fourth assessment report, the Intergovernmental Panel on Climate Change (IPCC) reported the increase in global average air and ocean temperatures, widespread melting of snow and ice, and rising global sea level and stated that the climate system is "warming".[3] Thus, climate change, in more general terms, results from human-induced activities.[1] Rapid urbanization has led to a significant increase in the dependency on various sectors of energy. Among the various sectors that are energy-driven, the cooling sector plays a major role. The increasing demand for space cooling and product refrigeration is driven by factors such as climate change, economic expansion, population growth, and urbanization.[4] Rising global temperatures are expected to lead to a 25% increase in cooling degree days by 2050. This increase will be more concentrated in places with warm climates and rapidly growing income and

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population.[5] The cooling services industry accounts for more than 10% of worldwide GHG emissions.[6] The cooling sector is one of the major factors responsible for increasing global warming.

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and other ozone-depleting substances (ODSs), which are used in refrigerants, are powerful greenhouse gases. The Montreal Protocol's mandatory phase-out of these compounds, as well as the associated emission reductions and lower atmospheric concentrations, has made a substantial contribution to climate protection. This accomplishment, in addition to the core purpose of protecting the ozone layer, is significant. According to estimates, the yearly net emissions averted by the Montreal Protocol was around 10 Gt CO_2-eq. in 2010, which is more than five times the Kyoto Protocol's annual reduction target for the period 2008–2012.[7] Due to the ozone depleting potential (ODP) of the CFCs and HCFCs, they are banned in the Montreal Protocol and replaced with hydrofluorocarbons (HFCs).[8] HFCs have been utilized as a refrigerant in refrigeration, air conditioning, and heat pumps (RACHP) for over 30 years, as an alternative to ODS. However, most HFCs are greenhouse gases with high or extremely high global warming potential (GWP) (up to 14 800).[9] Thus, the increasing use of HFCs in refrigeration and air conditioning (RAC) appliances will lead to global warming. To mitigate the production and emission of HFCs, the Kigali Amendment to the Montreal Protocol came into action in 2016, which targets an 85% reduction in the emission of HFCs by 2047.[7]

Owing to climate change and also extreme events, it is anticipated that developing nations like China, India, Brazil, and Indonesia will propel the rise in worldwide cooling demand.[10] Electrification, rising household income, and the resulting rise in appliance ownership are the main factors driving this trend. Other significant reasons include urbanization and the predominance of emerging countries situated in warm regions that are becoming hotter and more humid due to climate change.[11] India currently has the largest unmet cooling demand in the world, but its low adoption rate of air conditioning (8% of the current Indian households have room ACs) and refrigeration equipment is not expected to persist.[12] Projections suggest that air conditioner sales will grow six-fold by 2038, with a similar growth in refrigeration.[10,12] Due to the increasing demand for cooling and its effect on the climate, and to promote sustainable cooling, various policies and strategies have been implemented in India. The India Cooling Action Plan (ICAP) is a notable policy aspect that is framed to reduce energy consumption and greenhouse gas emissions related to cooling. India is predicted to experience an eleven-fold increase in cooling energy demand by 2037–2038, putting it in third place in the world today for energy consumption.[13] The increasing need for cooling would put pressure on India's energy resources and hasten global warming. Through the promotion of energy-efficient cooling techniques and technologies, the ICAP aims to reduce greenhouse gas emissions and energy usage related to cooling[14] and to improve access to sustainable cooling for all. The ICAP promotes cost- and energy-efficient cooling practices and technology with the goal of enhancing access to sustainable cooling.[14]

Aside from the ICAP, there are many other technological interventions, as well as policy mechanisms, to promote an energy-efficient and environmentally friendly cooling sector. The technological advancements in the area of sustainable cooling include developing low-GWP refrigerants with synthetic refrigerant blends. Hydrofluoroethers (HFEs) and hydrofluoroolefins (HFOs), produced as blends with HFCs, are designed as alternatives to HFCs. However, the HFCs again possess high GWP, making their use less beneficial. On the other hand, HFOs have GWPs within the upper limit of 150. HFOs, while offering a more environmentally friendly alternative to traditional refrigerants, face several technical and economic challenges.[15] One of the biggest challenges with HFOs is their compatibility with existing equipment. Integrating them with existing equipment can be costly and time-consuming due to compatibility issues. Their flammability also necessitates stricter safety measures and impacts system designs.[16] Their lower boiling points increase leakage risks, raising maintenance costs and environmental concerns. Additionally, HFOs are more expensive than traditional options, with limited availability in some regions, and pose recycling challenges due to the specialized requirements.[17] In light of these challenges, the shift towards using natural refrigerants, such as NH_3, CO_2, and hydrocarbons, is becoming increasingly attractive. These refrigerants have a much lower GWP than HFOs, and they are also widely available and cost-effective.

Among the natural refrigerants, propane (R290) is gaining popularity due to its favourable environmental features, which include no ozone depletion potential (ODP) and a very low GWP of just 3. The high performance of propane is due to its excellent thermodynamic properties, good compatibility with system components, and low refrigerant charges, allowing smaller heat exchangers and piping.[18] R290 can be used in a variety of systems, including commercial refrigeration, large air conditioning and chiller systems, chill cabinets and vending machines, cold storage and food processing, small air conditioning units, heat pumps and water heaters, and transportation and industrial refrigeration. R290's characteristics differ somewhat from fluorocarbon refrigerants, with the main difference being that it is classified as a flammable refrigerant.[19,20] Experimental research was done on a commercial refrigeration unit that used R290 instead of R22. It was concluded that when R290 was utilised in place of R22, the capacity reduced by 13–20% but the coefficient of performance (COP) increased by 1–3%.[21] A refrigeration plant using R290 as a refrigerant provides promising opportunities to enhance energy efficiency in food industry cooling systems while reducing environmental impact.[22] Blends of propane with other natural refrigerants are also more environmentally friendly and exhibit good energy efficiency. An earlier study showed that R290 and its mixtures with isobutane (R290/R600a) are viable alternatives to R134a for high-capacity chest freezers.[23] Both theoretical analysis and practical testing reveal that R290 beats R134a in terms of refrigerant capacity and energy efficiency. Specifically, R290 has much better mass and volumetric refrigerating capacity than R134a, and the R290/R600a mixture improves volumetric refrigerating capacity and COP. In experiments, R290 lowered power consumption by 26.7% when compared to R134a, while the best R290/R600a blend (93.75/6.25 wt%) reduced power consumption by an additional 27.5%.[23]

The use of CO_2-propane mixtures considerably improves the performance and energy efficiency of automotive air conditioning systems. Theoretical and experimental data show that blending CO_2 with propane enhances the COP, with the best performance attained at a 60% CO_2 mass fraction, resulting in a 29.4% improvement over pure CO_2 systems.[24] Overall, propane achieves good efficiency and low cost but is highly flammable and poses a safety risk; therefore, it is not the best option for using in certain applications where safety is a concern. CO_2 has a good GWP of 1; however, it has low energy efficiency and requires high system costs due to its high operating pressure.

Among the HFOs, R1234yf, R1225yez, R1234ze, R1234zee and R1243zf have very low GWP for both 20- and 100-year time horizons (TH).[25] As reported in our recent study,[26] even if the GWP is less, the atmospheric oxidation potential (AOP) of the refrigerant gases upon oxidation with atmospheric oxidants plays a critical role in determining the environmental impact of the refrigerants in compliance with the Kigali Amendment. In assessing the environmental sustainability of refrigerants, AOP serves as a critical parameter for understanding how rapidly a compound reacts and degrades in the atmosphere. A higher AOP indicates a shorter atmospheric lifetime, which generally reduces the compound's direct contribution to global warming. However, AOP alone does not directly represent the radiative forcing or overall GWP of a refrigerant. While a refrigerant with high AOP may decompose quickly, the resulting degradation products can vary widely in their environmental impacts. Some may form short-lived species with negligible radiative effects, while others can lead to persistent byproducts, such as trifluoroacetic acid (TFA). Therefore, the assessment of AOP should be viewed as complementary to GWP, reflecting the reactivity and atmospheric fate of refrigerants, rather than their climate forcing strength. In this study, AOP is incorporated alongside GWP and Total Equivalent Warming Impact (TEWI) to provide a holistic understanding of both the lifetime-related degradation behaviour and warming potential of refrigerants and their blends.

With the above background, in the present study, the environmental impact of natural and fourth-generation synthetic refrigerant blends such as R1234yf, R1225yez, R1234ze, R1234zee and R1243zf, which lead to low-GWP refrigerants, is explored through simulation studies. Upon obtaining the environmentally friendly refrigerant, the blending between propane and the respective HFO and that between CO_2 and HFO is studied. The main motivation for the development of the propane/HFO and CO_2/HFO blends in the present study is based on minimizing environmental and economic impacts within the specific constraints of the Indian market. Although there are several blends available, the selection of these blends is driven by the need to address the gap in the existing market for cost-effective, low-GWP solutions that maintain satisfactory cooling performance. Through the analysis and the perspectives developed in the study, policy recommendations for achieving sustainable cooling in the Indian scenario are delivered.

2. Methodology

2.1 Policy framework

The study provides a comprehensive overview of nationwide cooling demand in India, encompassing air conditioning, ventilation, and refrigeration. The analysis extends to all five cooling sectors within the country: (i) space cooling in buildings, (ii) mobile air conditioners, (iii) refrigeration, (iv) cold chain, and (v) industrial process cooling. The primary focus is on preparing a demand analysis for cooling across sectors. This includes a breakdown of sector-wise annual carbon emissions and annual energy consumption projections until 2087 under both Business as Usual (BAU) and improved scenarios. The BAU scenario represents the reference pathway for India's cooling sector, assuming a continuation of present-day trends in technology, refrigerant usage, and energy efficiency, without the implementation of additional policy measures or interventions. The BAU projections are derived using baseline data for 2017 and extended to 2087, considering population growth, urbanization, and climate-driven increases in cooling degree days. Conversely, the improved scenario incorporates the effects of policy interventions such as the Energy Conservation Building Code (ECBC), enhanced appliance efficiency standards, and greater adoption of natural and low-GWP refrigerants, as envisioned under the ICAP (ICAP, 2019). These two scenarios provide comparative insights into the potential environmental and energy benefits of sustainable cooling strategies. The study also aims to identify which sectors contribute the most to carbon emissions and energy consumption, thereby exacerbating global warming. As the demand for cooling increases, this study addresses the urgent need for a policy intervention in the form of a comprehensive cooling action plan for India.

The Government of India has recognized the need to reduce GHG emissions from the cooling sector and has introduced various policies to achieve this goal. To reduce cooling demand, improving energy efficiency and promoting natural refrigerants with low emissions are major goals of the government. The key policy aspects for the cooling sector in India are illustrated in Fig. 1. The present study, through a systematic modeling approach with supported data, will help guide policy interventions for the Indian cooling sector.

2.2 Atmospheric oxidation potential (AOP) of HFOs and natural refrigerants

The atmospheric oxidation of five HFOs, R1234yf, R1225yez, R1234ze, R1234zee and R1243zf, is studied through their reaction with OH radicals, which is the atmospheric bleaching agent. The HFOs possess H and F atoms that can be abstracted by OH radicals, leading to new products through atmospheric transformations. Upon oxidation, the HFCs/HFOs are degraded completely through several radical propagation and chain-

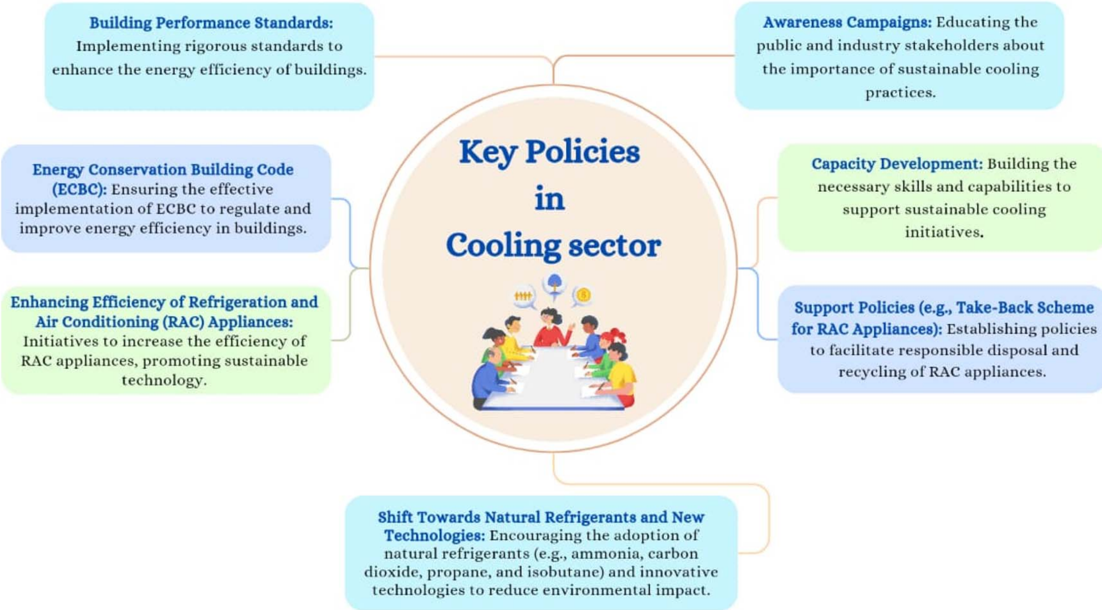


Fig. 1 Key policy aspects in the cooling sector.

termination steps. Certain HFCs/HFOs degrade into stable byproducts that remain potent GHGs. Therefore, determining the AOP by modelling OH-initiated degradation pathways is essential to evaluate both atmospheric lifetime and byproduct formation. Aside from the OH radical initiation, HFOs are prone to undergo oxidation by O_3, which leads to the generation of chloroform (CHF_3), which has been reported to be a significant factor in the global warming contribution of certain HFOs.[27] In the present study, the reaction pathways of HFOs with OH radicals were modelled using Density Functional Theory (DFT). The DFT-M06-2X functional with the 6-311++G(d,p) basis set was used to study the reactions. First, the geometries of the stationary points, such as maxima and minima, along the potential energy surface (PES) of the reaction were optimized at the M06-2X/6-311++G(d,p) level of theory. Harmonic vibrational frequency calculations were performed on the optimized geometries at the same level of theory to confirm the nature of the stationary points. All minima were confirmed with all positive frequencies, and each transition state had one imaginary frequency, confirming its maxima in one reaction coordinate. The connectivity between the transition state (which determines the energy barrier of the system) and the desired reactant and the product was verified through Intrinsic Reaction Coordinate (IRC) calculations. For energy barriers less than 7 kcal mol^{-1}, the AOP was assumed to be zero. These electronic structure calculations were performed using the Gaussian16 program package.[28] The same procedure was followed to understand the atmospheric oxidation pathways of propane upon reaction with OH radicals.

After obtaining the PES for the degradation of the above-mentioned HFOs with OH radicals, the HFO with the lowest AOP was chosen to blend with propane and CO_2. Further studies on the screening of blends and environmental impact studies will be performed with the HFOs exhibiting the lowest AOP.

2.3 Screening of refrigerant blends

The screening of refrigerant blends with the technical and operating conditions can be modeled using computational tools.[29,30] The results provide an initial input of which combinations of blends can be technically and environmentally compatible, before performing experiments. The blends of natural refrigerants with HFO were modeled using the Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) semi-empirical model from NIST.[31] The refrigerant blends were modeled based on their thermodynamic properties and technical and environmental compatibility. Evaluation of the introductory replacement mixes was based on volume cooling capacity (VCC), discharge line temperature (DLT) and condenser pressure (P_{cond}), which should be the same as those of the replaced refrigerant to ensure high system compatibility and minimal retrofitting. Details of the methodology used to calculate the technical parameters are given in the SI.

2.4 Environmental and economic analysis of the simulated blends

The total equivalent warming impact (TEWI) metric, which is a measure of the direct and indirect GHG emissions, is calculated using the following equation, which is adopted from the earlier studies:[32]

$$\mathrm{TEWI} = \{\mathrm{GWP} \times ((L \times m \times n) + (m \times (1 - \alpha)))\}_{\mathrm{Direct}} + \{E_a \times \beta \times n\}_{\mathrm{Indirect}} + \mathrm{AOP} \tag{1}$$

Here, the first term represents direct emissions, where L is the annual leakage rate, m is the refrigerant charge load, n is the operating life of the system, and α is the recovery or recycling factor. The second term represents indirect emissions, which comprise the yearly energy consumption of the system, E_a, and the country-dependent emission factor, β. The β value for India is taken from Alba *et al.*[32] The capital cost (CAPEX) of the proposed blends is obtained from the following expression:

$$\text{CAPEX (\$ per year) } \Sigma C_k = (C_k \times \varphi/3600 \times \text{AOT}) \times \text{CRF} \quad (2)$$

$$\text{CRF} = \{i(1+i)^n/(1+i)^n - 1\} \quad (3)$$

The capital cost of the vapor compression refrigeration cycle (VCRC) consists of the installation cost of the equipment, and the recovery factor is assumed to be 14% with annual interest rate, i, lifetime of the system, n, and annual operating time (AOT) of 8760 h and maintenance factor, φ with a value of 1.06.[23,29] The AOT of 1200 h per year used for both the E_a in the TEWI calculations and the operating cost component in the CAPEX assessment, represents the typical usage pattern of residential air conditioners in Indian climatic conditions. This value corresponds to an average of about 3–4 hours of operation per day during the cooling season and aligns with data reported in the ICAP and by Khosla *et al.* (2021),[12] which estimate residential AC usage of 1000–1500 hours annually, depending on the region and climate zone. By applying the same AOT across both environmental and economic evaluations, it ensures internal consistency between indirect emission ($E_a \times \beta$) and cost calculations, reflecting realistic residential behaviour.

The environmental cost (C_{env}) is calculated from the following relation:

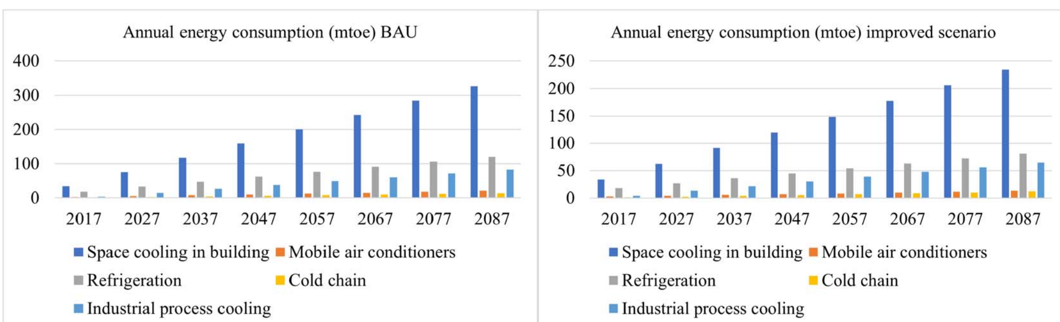
$$C_{env} = m_{CO_{2eq.}} \times C_{CO_2} = (\beta \times E_a) \times C_{CO_2} \quad (4)$$

C_{env}, which accounts for the CO_2 penalty cost rate based on the annual GHG emissions ($m_{CO_{2eq.}}$), is taken from Alba *et al.* for India.[32] The country-dependent average costs of CO_2 emission avoidance (C_{CO_2}) are also included in the C_{env} estimation.

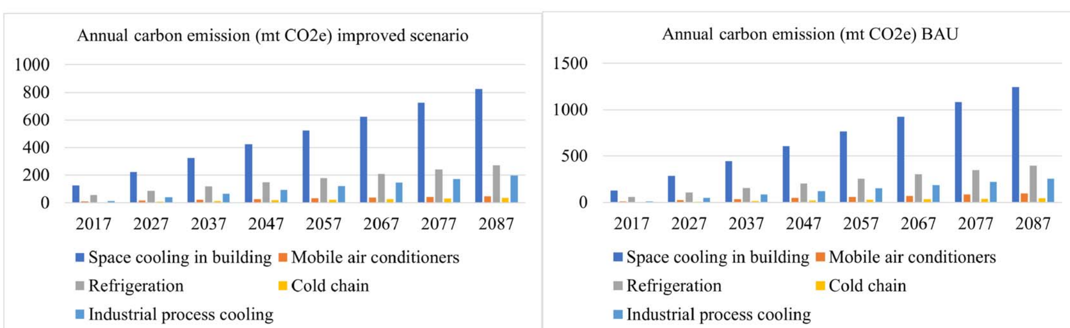
3. Results and discussion

3.1 Energy consumption in the cooling sector

The annual energy consumption from five different sectors in India, such as space cooling in buildings, mobile air conditioners (MAC), refrigeration, cold chain and industrial process cooling, is obtained from earlier studies.[13] The methodology is discussed in the SI. The annual energy consumption in the BAU and improved scenarios from different sectors, and the corresponding CO_2 emissions are shown in Fig. 2, where the projection of energy consumption with the year 2020 as baseline is shown. The improved scenarios are obtained with the improvisation in energy efficiency with respect to the policy interventions in terms of building performance standards and increasing the energy efficiency of RAC appliances.[13] As shown in Fig. 2, space cooling in buildings consumes more energy



(a)



(b)

Fig. 2 (a) Annual energy consumption (mtoe) and (b) annual CO_2 emission ($mtCO_{2eq.}$) from different cooling sectors.

when compared to the other sectors. In 2017, the annual energy consumption for space cooling in buildings was 33.8 Mtoe. Over the years, there is a consistent increase in energy consumption, reaching up to 326.4 mtoe in 2087 in the BAU scenario. In the improved scenario, the energy consumption for space cooling in buildings will reduce by ∼22% and reach 234.7 mtoe. Due to the population growth centered on the tropics and the rise in temperature in most parts of the country, the energy consumption in space cooling is higher than in other sectors, and there will also be an increase in the demand for space cooling.[11] It is quite obvious that the energy consumption from space cooling in buildings that comprise both residential and commercial sections is the highest, due to their prolonged usage. In cities such as Delhi, during the hot summer season, half of the electricity consumed is due to the use of air conditioners in residential and commercial buildings.[33] Space cooling is followed by refrigeration and then industrial cooling processes. The MAC and cold chain systems are the least energy-consuming sectors among the cooling sectors considered. R134a is the commonly used refrigerant in MACs in India, and MACs in cars consume around 10–20% of the fuel used. However, on a comparative scale, the energy consumption from MACs is the lowest. The projections shown in Fig. 2 also reveal that energy consumption from MACs will not change much in the next 60 years in the Indian context. Nevertheless, on a global scale, MAC-related HFC emissions contribute about one-third of GWP-weighted global HFC emissions.[34] In accordance with the global commitment to phase down HFCs under the Kigali Amendment, the replacement of R134a by R1234yf may act as a potential refrigerant.

CO_2 emissions from the five cooling sectors associated with energy consumption for the years 2017–2087 are presented in Fig. 2b. As most energy is consumed by the space cooling sector, the highest CO_2 emissions are also from this sector and are projected to increase rapidly over the years. In 2017, the space cooling sector emitted 124 $mtCO_{2eq.}$ of carbon emissions, which will reach up to 1244 $mtCO_{2eq.}$ by 2087 in the BAU scenario. In the improved scenario with the sustainable cooling technologies, the emissions will reduce and could be limited up to 824 $mtCO_{2eq.}$ by 2087. Similarly, the CO_2 emissions from other sectors also vary in accordance with energy consumption.

While improving energy efficiency can substantially reduce indirect greenhouse gas emissions from cooling systems, the choice of refrigerant primarily affects direct emissions resulting from leakage and disposal. Therefore, prioritizing low-GWP refrigerants in high-energy-use sectors can yield synergistic climate benefits, addressing both direct and indirect emissions simultaneously. In this case, drop-in replacements will be more promising, and designing low-GWP refrigerants with blends of synthetic and natural refrigerants may be more effective. HFOs, which are fourth-generation synthetic refrigerants, possess very low GWP and therefore can serve as suitable alternatives. However, HFOs have a few shortcomings, which are discussed in the following section. The blending of natural refrigerants with HFOs may fulfil refrigerant blend requirements such as: (i) minimize flammability, (ii) possess low GWP, (iii) zero ozone-depleting potential and non-toxicity, (iv) improved efficiency, and (v) possess equivalent volumetric cooling capacity (VCC).[35] The discussions below explore the possibilities of blending synthetic R1234yf with R290 and CO_2 natural refrigerants to achieve sustainability in the cooling sector.

3.2 Atmospheric oxidation pathways of HFOs and propane

The atmospheric oxidation of the studied HFOs, R1234yf, R1225yez, R1234ze, R1234zee and R1243zf by OH radicals can proceed either by H-atom abstraction or F-atom abstraction from the HFO, leading to a C-centered radical along with H_2O/HFO as co-products. The enthalpy of the reactions for the abstraction by an OH radical at different reactive sites is shown in Fig. 3.

As noted from Fig. 3, the H-atom abstraction from different C-sites is thermodynamically more favorable than the F-atom abstraction reactions. The electronegativity difference between carbon and fluorine atoms is relatively large ($\Delta\chi^P = 1.5$), whereas that between carbon and hydrogen atoms is comparatively small ($\Delta\chi^P = 0.4$). Consequently, C–F bonds differ substantially from C–H bonds in their chemical nature. Notably, the C–F bond is the strongest single bond that carbon forms with any element. As a result, the reactivity of OH radicals toward C–F bonds is significantly lower than toward C–H bonds. The R1234ze(Z) and R1234ze(E) are isomers with different thermophysical[36] and reactive properties. In the case of H-atom abstraction reactions, the *trans* isomer R1234ze(E) shows higher reactivity when compared to its counterpart. In order to better understand the reactivity of these HFOs in the atmosphere, the PES of the reaction of HFOs with OH radicals is further explored, as illustrated in Fig. 4. The PES is characterized through a pre-reactive complex (RC), where the initial non-bonded interactions between the reactants take place; the transition state (TS), through which the reactants have to pass as an energy barrier; and the product complex (PC), which is an intermediate formed before the complex breaks into the final products.

In the case of R1234yf, the reactants are stabilized through hydrogen-bonding interactions in the RC; the H-atom

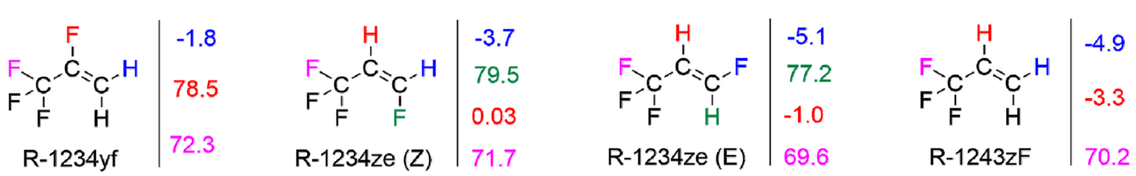


Fig. 3 Enthalpy (ΔH_{298}, kcal mol^{-1}) for H-/F-atom abstraction by an OH radical at different sites of the studied HFOs.

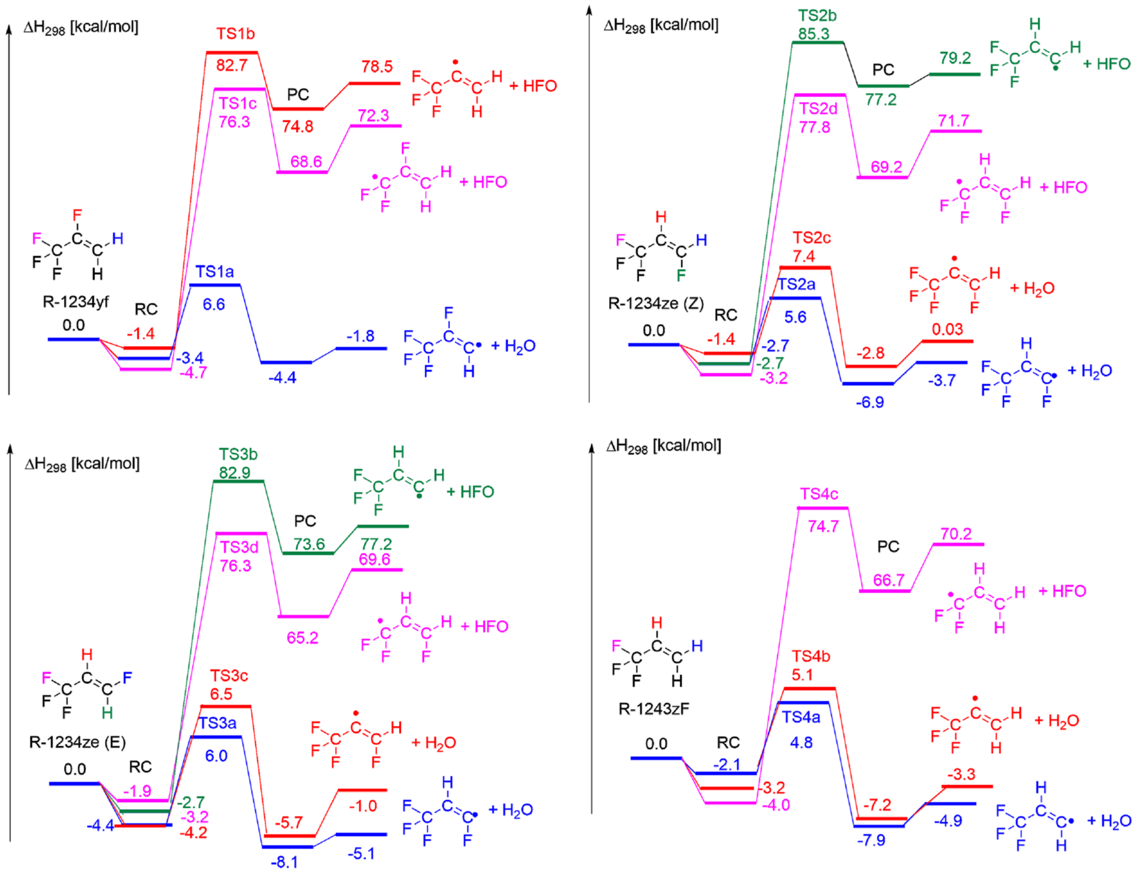


Fig. 4 PES of the OH-initiated reactions of the studied HFOs, calculated at the M06-2X/6-311++G(d,p) level of theory.

abstraction from the –CH_2 group is more favorable, with an enthalpy barrier of 10 kcal mol^{-1} that passes through TS1a. The TS1a proceeds to the hydrogen-bond-stabilized PC, which further dissociates into a C-centered radical and H_2O. The F-atom abstraction from R1234yf proceeds through transition states TS1b and TS1c, with high energy barriers, through highly endothermic reactions, making the pathways less feasible. In the cases of R1234ze(*Z*) and R1234ze (*F*), the H-atom abstraction from the –CHF group is more favorable than that from the –CH group, passing through the RCs and TS2a and TS2b, and TS3a and TS3c, respectively. This is in agreement with an earlier direct dynamics study that revealed that H-atom abstraction from –CHF is the major product channel in HFCs that have a –CHF group.[37] The enthalpy barrier associated with TS2a is 8.3 kcal mol^{-1}, that with TS2b is 8.8 kcal mol^{-1}, and those with TS3a and TS3c are 10.4 and 10.7 kcal mol^{-1}, respectively. In contrast to these HFOs, in the case of R1243zf, the H-atom abstraction from the –CH group is more favorable than that from the –CH_2 group. The respective energy barriers through TS4b and TS4a are 8.3 and 6.9 kcal mol^{-1}. As noted in Fig. 4, the F-atom abstraction reactions are less feasible in terms of energy barriers as well as reaction enthalpies for all the studied HFOs. Overall, among the four HFOs studied, the energy barrier for the initial H-atom abstraction reaction by the OH radical differs by only 1 to 2 kcal mol^{-1}. This reveals that HFOs can oxidize favorably in the atmosphere upon OH oxidation. The atmospheric oxidation pathways of propane were also studied, and the PES is shown in Fig. 5.

In the case of propane, there are three sites for H-atom abstraction by OH radicals, of which two are symmetrical. As shown in Fig. 5, the OH-initiated reaction with propane proceeds through H-atom abstraction from either the –CH_3 or –CH_2 group, forming a C-centered radical and H_2O. The –CH_3 H-

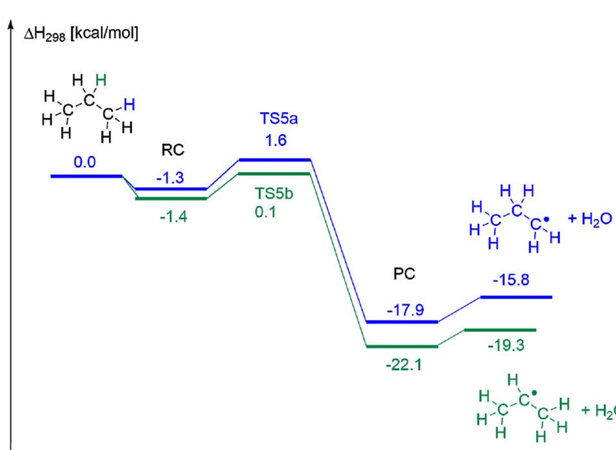


Fig. 5 PES of the OH-initiated reactions of propane calculated at the M06-2X/6-311++G(d,p) level of theory.

atom abstraction proceeds through TS5a, with an enthalpy barrier of 2.9 kcal mol^{-1}, leading to the products in an exothermic reaction with a reaction enthalpy of −15.8 kcal-mol^{-1}. The $-CH_2$ H-atom abstraction reaction through TS5b exhibits an enthalpy barrier of 1.5 kcal mol^{-1}, leading to an exothermic reaction with an enthalpy of −19.3 kcal mol^{-1}. This reveals that both reactions are energetically favored in the atmosphere and undergo oxidation favorably.

The resulting C-centered radicals from both the HFOs and propane further undergo molecular transformation upon reacting with O_2, forming a peroxy radical, which is the key intermediate in the atmosphere. The peroxy radical further reacts with other atmospheric oxidants, leading to new products through radical chain, propagation and termination reactions. Therefore, the initial reaction is the key step in determining the atmospheric oxidation potential. An in-depth analysis of the oxidation pathways reveals that R1234yf has the lowest oxidation potential towards the OH radical in terms of having a higher energy barrier; hence, this can render the gas more stable and increase its lifetime in the atmosphere. As earlier studies revealed, trifluoroacetic acid (TFA) is one of the secondary products formed from HFOs that is persistent in the environment.[38] In the case of R1234yf, the possibility of TFA formation is through secondary reaction from the C–F site of R1234yf. Modelling studies indicate that nearly 100% of R1234yf degradation results in $CF_3C(O)F$, which further converts to TFA *via* hydrolysis. While TFA is not considered acutely toxic, it is recognized as a highly persistent environmental degradation product whose accumulation in aquatic systems may have potential long-term ecological implications.[38] As discussed above, the initially formed radical will subsequently react with O_2, forming a peroxy radical. The peroxy radical will have sufficient energy to react with NO, leading to its oxidation, thereby resulting in an alkoxy radical. The intermolecular H-shift process of the alkoxy radical is the only possible pathway for the formation of TFA, where the O atom is eliminated. However, with the substantially higher energy barrier in the initial step for the F-atom abstraction reaction, the reaction is not possible. Therefore, the formation of TFA from R1234yf is least possible. Further, in the case of propane, the H-atom abstraction takes place at relatively less energy barriers (1.6 and 0.2 kcal mol^{-1}), which reveals that propane can oxidize easily in the atmosphere. Taken together with the atmospheric oxidation potential of both compounds, it is clear that neither compound is persistent in the atmosphere, and, even if leaked into the atmosphere, they have less potential to form toxic compounds. In order to achieve a trade-off between their atmospheric impacts and considering the best suitability of the R1234yf refrigerant, the refrigerant blends of R1234yf with propane are studied further. Furthermore, the CO_2 + R1234yf blends are studied to compare the environmental suitability of natural and fourth-generation synthetic refrigerants.

3.3 HFOs and natural refrigerant blends

3.3.1 Propane (R290) and R1234yf blends. Although propane (R290) has flammability issues, a recent study reported that propane in split ACs up to 7 kW can be classified as a potential alternative to HFC-driven split ACs.[39] Furthermore, a very recent study reported that a switch to propane in split ACs could avoid a 0.09 °C increase in global temperature by the end of the century.[40] Thus, the use of propane as an alternative refrigerant may lead to sustainable cooling. The blending of natural and synthetic refrigerants was initially screened in ratios of 50 : 50, 60 : 40, 70 : 30, 80 : 20 and 90 : 10. The vapor–liquid equilibrium (VLE) data for the binary system of propane + R1234yf were obtained at 273 and 298 K, as shown in Fig. S1. Here, the mole fractions of propane in the liquid and vapor phases *versus* the pressure are plotted. The binary mixture exhibited azeotropic behavior at a mole fraction of 0.75 at both temperatures. This value is consistent with the azeotropic behavior of propane, which occurs at a mole fraction near 0.76.[41]

The compatibility of the propane and R1234yf blends in the refrigerant system is assessed by considering their VCC and COP values. The VCC and COP values for propane, R1234yf and their blends in different proportions are summarized in Table 1, along with the glide temperature (TG), condenser pressure (P_{cond}) and normal boiling point (NBP) values. The VCCs of pure propane and R1234yf are higher and are almost double that of the standard refrigerant R134a (VCC 1.7 kJ L^{-1}).[32] In the case of blends, the VCC is in line with that of propane in all the proportions. Even with half of the proportion of R1234yf in the blend, the VCC is enhanced because R1234yf, which, as a pure working fluid, has been proven to be a better alternative for R134a in many applications.[42] Furthermore, the VCCs of the designed blends are also comparable to that of R410ac,[32] which is a replacement for R22 in residential air-conditioners. The VCC of propane : R1234yf in a 90 : 10 ratio is less than the VCC of R410a by 10%, which is within the assessment criteria of a maximum of 25% for potential drop-in replacements.

From Table 1, it is clear that both propane and R1234yf have higher and a closer COP values. In the case of blends, the COP values for all the proportions range from 5.1 to 5.2, revealing their compatibility in the designed proportions. Taking into account both VCC and COP, the increase in the propane content in the blends leads to technically compatible refrigerants. The simulated COP of the propane : R1234yf blend in the 90 : 10 ratio is around 6.7% above the COP of R134a operating under the same conditions.[43] Also, the COP of R32, which is used commonly in split ACs in India, is 4.4,[44] and this is ∼15% less than that of the propane : R1234yf blend. On looking into the T_G, the propane : R1234yf blends with 80 : 20 and 90 : 10 proportions show T_G values below 0.3 K, which classifies them as azeotropic or near-azeotropic.[44] Further, T_G values higher than 10 K are not suitable for cooling systems. The 90 : 10 ratio has the lowest T_G and the highest COP. The condenser pressure (P_{cond}) increases as the proportion of propane in the blend increases, and the value is ∼3% to 4% less than those of R32 and R410a.[32] The mass flow rate of R1234yf is 0.056 kg s^{-1} and that of propane is 0.023 kg s^{-1}, whereas for blends with propane to R1234yf ratios of 90 : 10 and 50 : 50, the mass flow rates are 0.027 kg s^{-1} and 0.042 kg s^{-1}. This reduction in mass flow rate in the blends compared to that of R1234yf may reduce the

Table 1 VCC and COP of propane and R1234yf blends

Blends and individual refrigerant	Composition	VCC (kJ L^{-1})	COP	Glide temperature T_G (K)	Pressure condenser P_{cond} (Mpa)	Normal boiling point NBP (°C)
R290 : R1234yf	50 : 50	3.684	5.152	2	1.375	−35.55
	60 : 40	3.776	5.165	1.1	1.406	−36.86
	70 : 30	3.875	5.189	0.42	1.432	−38.17
	80 : 20	3.840	5.178	0.09	1.425	−39.48
	90 : 10	3.882	5.2	0.01	1.427	−40.79
R1234yf	Pure	2.895	5.236			
R290	Pure	3.863	5.212			

operational costs, as it has been reported that an increase in mass flow rate has a direct impact on operational costs.[45] Thus, by blending with propane, the increased operational costs of R1234yf may be reduced. The NBP of the blends at 1 bar is within the range of −35 to −41 °C, making them suitable for use in low-temperature refrigeration.

The above technical parameters reveal the compatibility of propane and R1234yf blends in the 90 : 10 ratio as suitable alternatives for use in split ACs in residential cooling. The addition of R1234yf provides the advantage of improved VCC and low glide temperature. The COP is not much affected, as both propane and R1234yf have better COP values. Furthermore, the mass flow rate of pure R1234yf is reduced on blending with the propane without affecting the VCC, showing that the blend is attuned for refrigerant systems.

The GWP of propane for 20- and 100-year THs are 3 and 7, respectively. As given in Table 2, the GWP of R1234yf is 1 for both THs. The GWP for 20- and 100-year THs for R290 + R1234yf blends for different molar compositions of propane and HFO are illustrated in Fig. 6. It is clear that as the mole fraction of R1234yf in the blend decreases, the GWP of the blend increases. In a mole composition of 90 : 10 of propane and R1234yf, the GWP20 is 2.5, and that of GWP100 is 5.8. When compared to the GWP of propane, the GWP of the blend is decreased. Also, it is interesting to note that, in the 50 : 50 composition of propane and R1234yf, the GWP is drastically reduced, with a value of 1.6. Note that, as per the EU guidelines, the acceptable GWP for a blend combination is <150.[46]

The proposed blends are well below the GWP threshold, as both propane and R1234yf possess relatively low GWPs. Although the 50 : 50 composition leads to significantly lower GWP, the adoption of HFOs in developing countries like India is quite difficult due to their large initial costs. On the other hand, split ACs utilizing propane are commercially available in the Indian markets and contribute ~2% to the annual sales of split ACs in India.[39] With the refrigerant compatible thermodynamic properties and efficiency properties discussed above, the 90 : 10 blend of propane and R1234yf can serve as a better alternative for residential cooling; *i.e.* in split ACs. In terms of flammability issues of propane, there will certainly be a trade-off between the lower flammability of R1234yf and the higher flammability of propane, with a marginally higher GWP, as evidenced in Fig. 6. This is the case for blending R1234yf with R134a, where the flammability of the overall mixture is reduced.[44] Even a 10% blending of R1234yf with R134a reduces the overall flammability of R134a.[43] Although R1234yf exhibits a lower flammability compared to propane, the small fraction (10 wt%) used in the present R290/R1234yf blend is insufficient to completely mitigate the flammability hazard. Propane (R290) has an extremely low flash point (−104 °C) and remains highly flammable even in dilute mixtures. Previous studies (41) indicate that the transition from an A3 to a lower flammability classification (A2L or A1) generally requires more than 50% of the low-flammability component. Therefore, while blending R1234yf can reduce the heat of combustion and slow flame propagation, it does not overcome the flammability issue at the 90 : 10 ratio. This blend should still be regarded as flammable (A3) and handled with appropriate safety measures. Further optimization of the mixing ratio or incorporation of flame-suppressing additives may be necessary to improve safety without compromising thermodynamic performance.

3.3.2 CO_2 (R744) and R1234yf blends. CO_2 (R744) is an environmentally friendly refrigerant with zero ODP and low GWP. Furthermore, it is widely and inexpensively accessible both as a component of the atmosphere and as a result of industrial processes, particularly those involving fuel. However,

Table 2 VCC and COP for CO_2 and R1234yf blends

Blends and individual refrigerant	Composition	VCC (kJ L^{-1})	COP	Glide temperature T_G (K)	Pressure condenser P_{cond} (Mpa)	Normal boiling point NBP (°C)
R744 : R1234yf	50–50	5.698	2.947	35.4	3.681	−53.75
	60–40	6.705	2.863	33.9	4.358	−58.7
	70–30	8.567	2.922	31.08	5.268	−63.65
	80–20	10.468	3.118	26.51	5.936	−68.6
	90–10	13.963	3.619	18.81	6.923	−73.55
R1234yf	Pure	2.895	5.236			
R744	Pure	3.863	6.378			

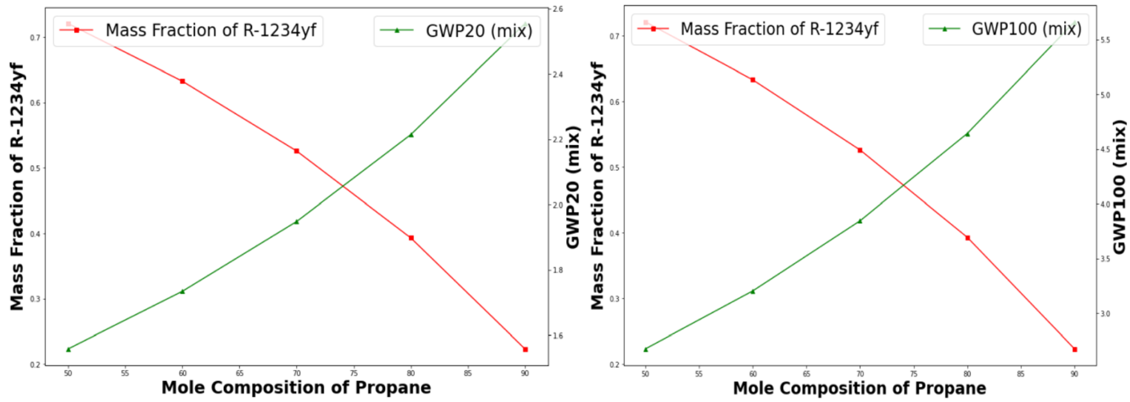


Fig. 6 GWP20 and GWP100 for propane and R1234yf blends in different proportions.

its threshold temperature stands at 31.1 °C. The low critical temperature means that R744 cannot be used effectively in a convectional (subcritical) refrigeration cycle because the condenser will not transfer heat above the critical temperature. As a result, the condenser will fail, leading to extensive losses. Furthermore, at temperatures that are close to but below the critical temperature, there is a significant decrease in the vaporization enthalpy, which results in a diminution in heating capacity and diminished system performance. As Lorentzen has suggested, R744 is only effective when applied in a *trans*-critical cycle.[47] Owing to the relatively excellent properties of CO_2 other than the operating conditions, blends of CO_2 with R1234yf are designed and investigated to determine whether R1234yf has a positive influence on the performance of CO_2. As discussed above for propane blends, the CO_2 and R1234yf are blended in ratios of 50 : 50, 60 : 40, 70 : 30, 80 : 20 and 90 : 10. The VLE diagram of CO_2 : R1234yf, shown in Fig. S2, reveals that at a mole fraction of 1, the system reaches near azeotropy at 273 and 298 K.

The technical criteria of the CO_2 : R1234yf blends, such as VCC, COP, T_G, P_{cond} and NBP, are summarized in Table 2. The VCC values for the mixture show a drastic increase in the 90 : 10 proportions, which is more than double that of the 50 : 50 mixture. The COP is higher in the 90 : 10 ratio, but it is less than that of the pure R1234yf and half that of CO_2. The COP is much less than the corresponding COP of propane and R1234yf blends. The T_G, which should be below 10K, is not satisfied for the CO_2-R1234yf blend. The minimum of 18 K T_G is achieved when the ratio is 90 : 10. The NBP is greater than 50 °C for all ratios, making them unsuitable for operation in refrigeration conditions.

Although the thermodynamic properties of the simulated CO_2 : R1234yf blends are good enough, the blends do not meet the technical compatibility requirements. In terms of environmental compatibility, since both CO_2 and R1234yf exhibit a GWP of 1, the GWP of the blends is also 1.

3.4 Comparison between propane + R1234yf and CO_2 + R1234yf blends

A comparative analysis of the thermodynamic properties, technical compatibility and GWP of the propane, CO_2, propane + R1234yf and CO_2 + R1234yf blends was performed through fixed criteria, as schematically shown in Fig. 7. The rating is given based on the performance of the simulated blends with reference to that of propane in the case of propane + R1234yf, and CO_2 in the case of CO_2 + R1234yf blends. In the case of propane, except for its flammability issue, all the other properties make it suitable for split ACs in residential cooling. As discussed in the earlier section, the flammability issue of propane can be overcome by blending with R1234yf; although it remains mildly flammable, it is technically more compatible. The blending of propane + R1234yf improved the thermodynamic properties, VCC and COP of R1234yf. Although the properties of propane are much better than those of the blends, its combination with the attractive fourth-generation synthetic refrigerant R1234yf will lower the upward operational costs of R1234yf. This may be achieved through the higher NBP of the blends at the 90 : 10 ratio, and the lower refrigeration effect of the R1234yf[42] can be overcome by the propane, thereby reducing

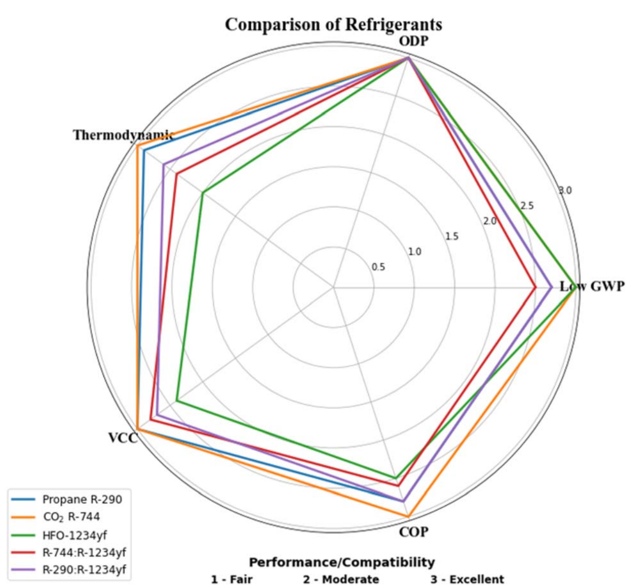


Fig. 7 Comparison of the thermodynamic, technical and environmental compatibility of propane, CO_2, propane + R1234yf and CO_2 + R1234yf blends.

the operational cost incurred by R1234yf. That is, the low operating costs of propane can balance the high operating costs of R1234yf. The GWP is slightly increased in the blends when compared with R1234yf, but it is a very mild change, which will not have a major impact. Owing to the thermodynamic, technical and GWP advancements, propane-R1234yf blends can be a suitable alternative to R32, which is widely used in split ACs as a replacement for R410A.

In the case of CO_2 + R1234yf blends, the CO_2 and R1234yf as standalone refrigerants perform much better than their blends. The thermodynamic properties of R1234yf are improved well through blending, but the other properties are moderately improved in them. The CO_2 has excellent properties in terms of its VCC and COP, but blending with R1234yf does not enhance the properties of R1234yf. The blending of CO_2 with HFCs may be viable at this point because the GWP of HFCs can be reduced by blending with CO_2.

3.5 Environmental and economic analysis of propane + R1234yf blends

Owing to the technical compatibility of propane and R1234yf blends in the 90 : 10 ratio, the total equivalent warming impact (TEWI) and the economic analysis for the blends in the Indian scenario were evaluated, as discussed in the methodology section. In obtaining the TEWI metric, in addition to the contribution from direct and indirect GHG emissions, the atmospheric oxidation potential (AOP) was also included. Fig. 8.

Since both compounds can undergo oxidation easily in the atmosphere, the AOPs of the compounds are assumed to be 0, and, including this factor, the TEWI of the propane + R1234yf blend is 5.1 $tCO_{2eq.}$ per year, which is around 22 times lower than that of the reference refrigerant R32 (ref. 32) and R1234yf as a sole refrigerant. Thus, the environmental burden of using R32 in split ACs in India can be reduced by 96% by the use of the propane and R1234yf blends. Furthermore, along with the higher technical compatibility of the designed blends, these can be attractive alternatives for R32. The sharp (∼22×, ≈95–96%) reduction in TEWI for the R290 : R1234yf (90 : 10) blend relative to R32 is primarily attributable to a two-order-of-magnitude reduction in refrigerant GWP (direct TEWI), together with a modest (≈15–20%) decrease in electricity consumption (indirect TEWI) and negligible atmospheric persistence of the blend. In the TEWI formulation, the replacement collapses the direct term to near-zero because GWP falls from hundreds (R32) to a few units for the blend, while the indirect term is only slightly reduced by improved cycle performance. Consequently, systems with significant refrigerant charge or leakage exhibit very large total CO_2-equivalent benefits, consistent with recent experimental and assessment studies of low-GWP alternatives. These findings are in agreement with prior TEWI and refrigerant-selection analyses.[15,32,40] Furthermore, the similar TEWI values observed for R32 and R1234yf (Fig. 8) arise from the combination of the assumed charge size, leakage rate, and lifetime recovery fraction used for the parameters of both systems, which cause the indirect (energy-related) term to be large (≈5153 kg CO_2-eq. for R32 and ≈4380 kg CO_2-eq. for the blend) and dominate the total TEWI, so, the total TEWI reduces by ≈38% in the base case rather than 95%. This explains the apparent similarity between R32 and R1234yf bars in Fig. 8. The total TEWI depends mainly on energy consumption, and thus the blend consistently exhibits values that are two orders of magnitude lower than the direct CO_2-equivalent impact.[48,49]

In terms of the economic benefits of the designed blends, the capital costs (CAPEX) are evaluated, since this has the largest contribution to the economic assessment of the newly designed blends. Based on the data given in the SI (Table S1), the CAPEX and environmental cost (C_{env}) are given in Fig. 8. The CAPEX and C_{env} for the propane + R1234yf blend in a 90 : 10 ratio are found to be 129 and 29.89 $ per year, respectively. The numerical values used were drawn from industrial cost benchmarks and techno-economic assessments: specifically, we adopted values from Albà *et al.* (2023)[32] and Sanguri *et al.* (2021).[50]

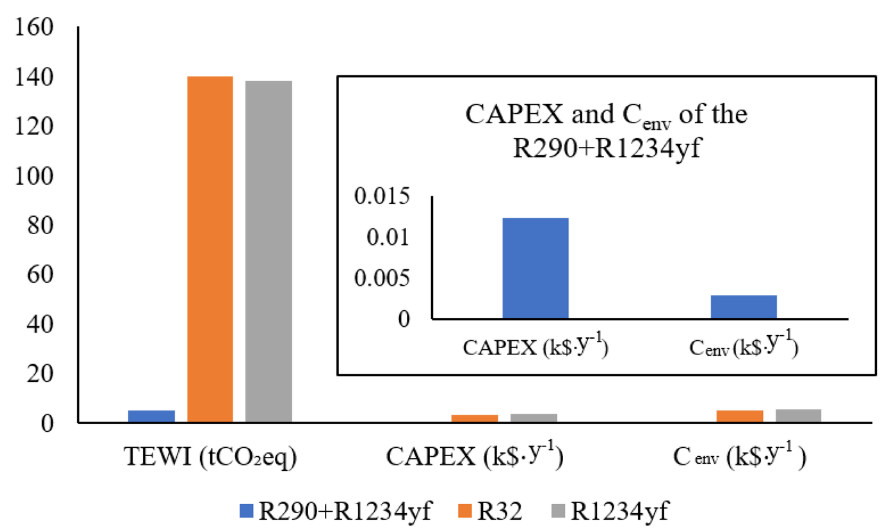


Fig. 8 TEWI, CAPEX and C_{env} of R1234yf, propane and the blends compared with those of R32. The inset details the CAPEX and C_{env} components for R290 + R1234yf blend.

Although it is true that pure R290 systems are typically somewhat higher in upfront cost than R32 systems due to safety requirements, in the study, the R290 + R1234yf (90 : 10) blend shows lower normalized CAPEX because:

(1) The system design using the blended refrigerant required a smaller refrigerant charge mass (≈20–25% less than the R32 baseline) owing to its higher volumetric cooling capacity in the cycle simulation.

(2) The compressor/heat-exchanger sizing was reduced relative to the pure refrigerant cases, reinforcing equipment cost savings.

(3) The high per-kg cost of R1234yf contributes only marginally because it constitutes only 10% of the blend; thus, the incremental refrigerant cost increase is small compared with equipment cost savings.

(4) The safety/containment surcharge for the blend was assumed to be intermediate between those of R32 and pure R290 (*i.e.*, a moderate surcharge, not the full R290 premium) in the benchmark cost table.

(5) The combined effect of charge reduction, compressor downsizing and a moderate safety-surcharge resulted in the estimated CAPEX for the blend being ≈8–10%, which is lower than those of R32 in the normalised cost model; however, the actual unit prices may vary with capacity and region.

Please note that the R290 + R1234yf (90 : 10) blend required a smaller compressor displacement and lower charge, reducing hardware and refrigerant costs relative to those of pure systems. The high cost of R1234yf contributes minimally because it is only 10% of the blend charge. CAPEX values represent normalized system cost; actual unit prices vary with capacity and region.

As India is the major producer of HFCs, earlier studies[32] revealed that the environmental costs are larger in India. Since R32 is the major refrigerant used in split ACs in India, the proposed alternative can be a viable option in terms of both capital and environmental costs. It is noteworthy to see from Fig. 8 that the costs associated with the blends are significantly lower than those of R32 and R1234yf as sole refrigerants. The environmental cost for HFC in India is very high due to its reliance on coal for power generation, which comes with a penalty for CO_2 emissions. However, in the case of propane + R1234yf blends, the penalty of CO_2 emissions is reduced, thereby reducing the environmental costs. Thus, the simulated blends show lower costs than the conventional refrigerants. In view of using the simulated blends as suitable alternatives of R32 refrigerant, the current cooling action plan is India needs to introduce policies promoting the use of natural refrigerants.

4. Conclusions

This work provides an in-depth analysis of the environmental impacts of natural and fourth-generation synthetic refrigerants, aiming to support the development of a sustainable cooling action plan for India using low-GWP refrigerant blends. It summarizes existing policy interventions in India's cooling sector and highlights the urgent need for alternative low-GWP refrigerants. The atmospheric oxidation pathways of four HFOs, R1234yf, R1234ze(*Z*), R1234ze(*E*), and R1243yf, as well as propane, were evaluated. A blend of propane and R1234yf was selected to achieve a trade-off between their respective atmospheric impacts and to assess its suitability for use in refrigeration systems. In India, space cooling, especially in residential buildings, is a major contributor to cooling demand, with split air conditioners (ACs) up to 7 kW being commonly used. Currently, R32 is the dominant refrigerant in this sector. The study reveals that a 90 : 10 blend of propane and R1234yf offers a viable replacement for R32 in such applications. Thermodynamic performance analysis shows that this blend demonstrates excellent VCC and COP, with values approximately 15% higher than those of R32. Blending propane with R1234yf significantly reduces the GWP of the mixture, bringing it in line with that of R1234yf alone. The performance of this blend was also compared with that of CO_2 and its blend with R1234yf. Environmental and economic analyses indicate that the total environmental impact of the propane + R1234yf blend is substantially lower than that of R32 and R1234yf when used individually. Under Indian conditions, the blend emits approximately 5.1 tCO_2 equivalent per year, about 22 times less than R32. Furthermore, both capital and environmental costs associated with the blend are significantly lower compared to those of R32. The higher cost of R1234yf can be offset through blending with propane, as reflected in the economic assessment.

In conclusion, the natural refrigerant propane and the fourth-generation synthetic refrigerant R1234yf, when blended, offer a promising alternative to conventional refrigerants currently used in India's split AC market, particularly from an environmental feasibility perspective. Further technical assessments of the blend's long-term suitability in refrigeration systems will be the focus of future research. Based on the findings of the study and the secondary literature, the following policy imperatives are recommended to support sustainable cooling in India using natural refrigerants:

4.1. Mandatory use in offices and rooms

The use of natural refrigerants should be made mandatory in all office spaces and residential rooms. Propane has demonstrated effective performance up to 7 kW, and its flammability concerns are being addressed by blending it with R1234yf.

4.2. Regulatory framework and standardization

National regulations should be established to enable a direct transition from third-generation synthetic refrigerants to natural alternatives. These should be accompanied by standards for both pure natural refrigerants and their synthetic blends.

4.3. Targeting high-temperature cities

According to iFOREST's 2025 survey[51] across major Indian metro cities, about 40% of residential ACs are refilled annually, and overall servicing accounted for ∼32 000 tonnes of refrigerant in 2024, equivalent to ∼52 Mt CO_2-eq. emissions. The high refill frequency implies significant leak rates on the order of 10% per year or more, as supported by leakage studies in

Indian residential ACs. Transitioning to natural refrigerants in these cities thus has strong potential to reduce emissions.[52]

4.4. Urgency in line with the Kigali Amendment

With the phasedown of HFCs in India in accordance with the Kigali Amendment, there is an urgent need to adopt sustainable cooling alternatives. Propane and its blend with R1234yf present a feasible solution.

4.5. Focus on space cooling in buildings and residences

The study clearly highlights that space cooling in buildings and residences is the primary sector requiring intervention. Promoting the use of natural refrigerants in this sector first allows for impact assessment and efficient resource allocation. HFCs still in use can then be reserved for applications with lower cooling demand, helping to reduce overall greenhouse gas emissions.

A multi-pronged approach, including efficiency regulations, incentive programs, awareness campaigns, and technician training for the use of natural refrigerants, will have the most significant impact in advancing India's sustainable and smart space cooling objectives.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data will be made available on request.

Supplementary information: methodology and parameters used in the study are discussed. See DOI: **https://doi.org/10.1039/d5su00597c**.

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