



Environment friendly refrigerant options for automobile air conditioners: a review

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Abstract

In this paper, the environment friendly refrigerant options suitable for automobile air conditioners are reviewed. Initially, the thermophysical, thermodynamic and chemical characteristics of the environment friendly refrigerant options are presented. Then, the reviews of research investigations reported on environment friendly refrigerant options (such as hydrofluorocarbons, hydrofluoroolefins, hydrocarbons, carbon dioxide, composite mixed refrigerants and nanorefrigerants) are presented. The limitations and further research needs with environment friendly refrigerant options are identified and listed. The paper concludes that the hydrocarbon refrigerants will dominate the automobile air conditioning sector due to their good thermodynamic, thermophysical and environmental properties. Secondary loop configurations are recommended for the use of hydrocarbon refrigerants to reduce the flammable risk. The carbon dioxide is identified as a good option for electrical vehicles operating at low ambient conditions. The hydrofluoroolefins have short atmospheric life and get decomposed in the atmosphere and form tri-fluoro-acetic acid, which is harmful to the aquatic environment. Hence, hydro-fluoro-olefins are identified as an interim option. The outcome of this review is more helpful to the manufacturers and researchers working in the field of automobile air conditioners.

Keywords Environment friendly refrigerants · Automobile air conditioners · Nanorefrigerant

Abbreviations

AAC	Automobile air conditioner
COP	Coefficient of performance
GWP	Global warming potential
ODP	Ozone depletion potential
HC	Hydrocarbon
HFC	Hydrofluorocarbon
HFO	Hydrofluoroolefins
MO	Mineral oil
PAG	Polyalkylene glycol
POE	Polyolester
TEGWI	Total equivalent global warming impact
TFA	Trifluoroacetic acid

Introduction

Nowadays, the air conditioners become standard equipment of modern automobiles to ensure passenger comfort [1]. The cooling loads of an automobile air conditioner (AAC) includes: (a) solar heat gain through the cabin roof and wind screens; (b) heat gain by infiltration and ventilation of air; (c) heat gain by passengers; and (d) heat gain by electrical accessories inside the cabin. The air conditioners in automobiles provide ventilation and thermal comfort environment to the passengers [2]. The compression refrigeration cycle is the good option for automobile air conditioners due to its compactness and less mass with high coefficient of performance (COP) [3]. The halogenated refrigerants have been widely used in AAC systems. After the phase-out of R12, the AAC manufacturers start using R134a due to its good thermodynamic, thermophysical and chemical properties with zero ozone depletion potential (ODP) [4]. But, the R134a has high global warming potential (GWP) of 1430 [5]. As per Paris environmental protocol 2016, the consumption of R134a in AAC systems should be reduced. More than 195 countries have signed in Kigali agreement (Paris protocol

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2016) to reduce the consumption of halogenated refrigerants with high GWP [6]. The AAC systems have major share in R134a emissions due to frequent refrigerant leakages [7]. It is possible to phase out R134a in AAC systems during its servicing. Hence, it is an urgent need to identify a sustainable alternative to phase out R134a in automobile air conditioners (AACs).

Some of the earlier reviews in the field of environment friendly refrigerants have reported the standards for using hydrocarbon refrigerants [8], alternative options to halogenated refrigerants [9], new refrigerant mixtures [10], replacement policy of non-ecological refrigerants [11], hydrocarbon refrigerant mixtures [12] and energy performance of low GWP refrigerants [13]. Similarly, the earlier review reports on AACs highlights the developments of adsorption air conditioners [14], energy-efficient AAC systems [15], solutions for air conditioning of electrical vehicles [16] and developments of AAC systems [17]. All these reported reviews are consolidated in Table 1. It is noticed that the research attention on environment friendly refrigerants and AAC systems are getting increasing during last two decades. Ensuing earlier reported reviews, it is understood that no specific review has been reported on environment friendly refrigerant options for AACs. Thus, the present review consolidates the research investigations reported on environment friendly refrigerant options suitable for AACs.

The remaining part of this review has following sections: Sect. 2 highlights the characteristics of environment friendly refrigerant options; Sect. 3 summarizes the reviews of reported investigations on environment friendly refrigerants for AACs; Sect. 4 presents the limitations and further research needs; and Sect. 5 concludes with major outcomes of the review.

Characteristics of environment friendly options

The characteristics of environment friendly options for phasing out of R134a in AACs are presented in this section.

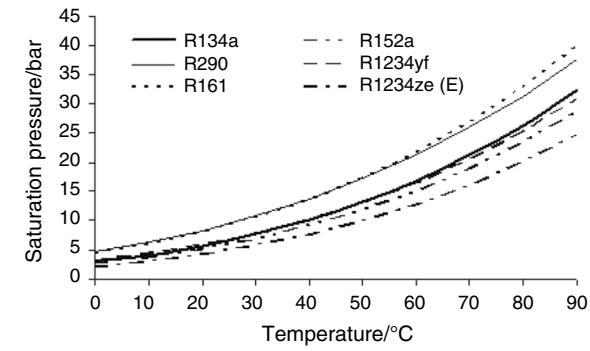
Thermophysical properties

The thermophysical properties (such as vapour pressure, latent heat, liquid density and liquid viscosity) of R134a and its possible pure substitutes are compared in Fig. 1 for the temperature range between 0 and 90 °C. From Fig. 1a, it is observed that the saturation pressure of R152a, R1234yf and R1234ze is 9–11%, 1–5%, 23–26% and lower than R134a, respectively. The R290 and R161 are having higher saturation pressure compared to R134a. The R1234yf, R1234ze and R152a are used as drop-in substitutes to phase out R134a due to its similar vapour pressure. The R290 and R161 are not possible to use as a drop in substitute due to mismatch in operating pressure. In Fig. 1b, the latent heat variations of R134a and its pure substitutes are depicted. It is noticed that the latent heat of R152a, R290 and R161 was found to be 35–50%, 37–47% and 47–49% higher than R134a, respectively. The high latent heat results in good refrigeration effect and faster cooling rate. The R1234yf and R1234ze are having 17–38% and 1–7% lower latent heat compared to R134a, which results in lower refrigeration effects and COP. The COP and refrigeration effect were improved using internal heat exchanger (IHX). From Fig. 1c, it is observed that the liquid densities of all the drop-in substitutes were found to be lower than R134a. The liquid densities of R152a, R290, R1234yf, R1234ze and R161 are 25%, 60%, 10%, 5% and 47% lower when compared to R134a, which results in lower refrigerant quantity. The R152a and R1234yf are having about 40% and 10% reduction in refrigerant mass-charge when compared to R134a due to lower liquid density. From Fig. 1d, it is observed that all the drop-in substitutes are having lower liquid viscosities compared to R134a, which results in better heat transfer coefficients and less irreversibility due to friction in all the components of AAC.

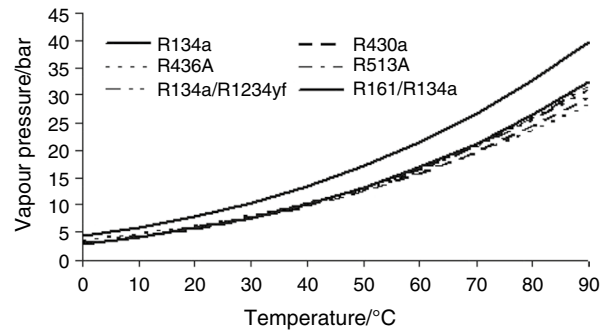
The thermophysical properties of R134a and possible environment friendly refrigerant mixtures reviewed in this paper are compared in Fig. 2 for the temperature range between 0 and 90 °C. From Fig. 2a, it is observed that the vapour pressures of refrigerant mixtures such as

Table 1 Earlier studies on review of environment-friendly refrigerants and AAC

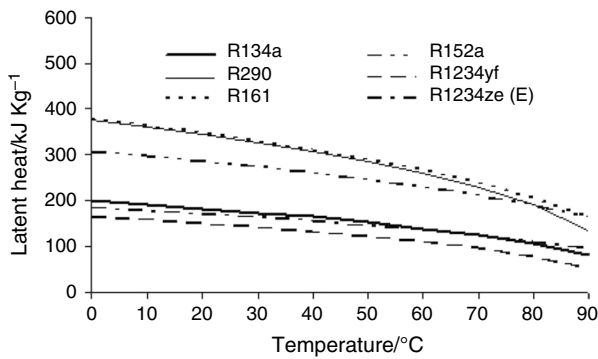
Authors [Ref.]	Year	Country	Topic of review
Corberán et al. [8]	2008	Spain	Standards for use of hydrocarbon refrigerants
Mohanraj et al. [9]	2009	India	Environment-friendly alternative refrigerants
Mohanraj et al. [10]	2011	India	Refrigerant mixtures
Sarbu [11]	2014	Romania	Replacement policies of alternative refrigerants
Harby [12]	2017	Egypt	Hydrocarbons and their mixtures
Mota-Babiloni et al. [13]	2018	Spain	Energy performance and environmental impacts
Abdullah et al. [14]	2011	Malaysia	Automobile adsorption air conditioning system
Sukri et al. [15]	2015	Malaysia	Energy efficient automobile air conditioning system
Zhang et al. [16]	2018	China	Solutions for air conditioning of electrical vehicles
Bentrcia et al. [17]	2018	Saudi Arabia	Developments of alternative automobile systems



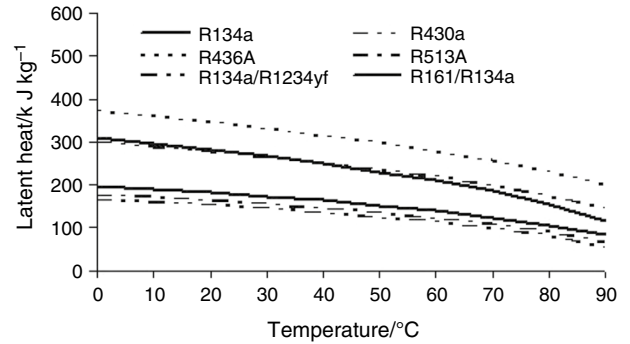
(a) Saturation pressure



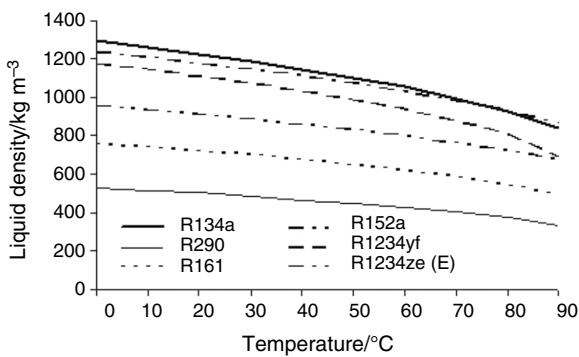
(a) Saturation pressure



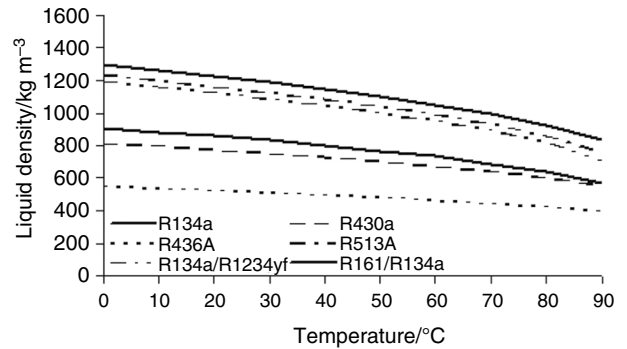
(b) Latent heat



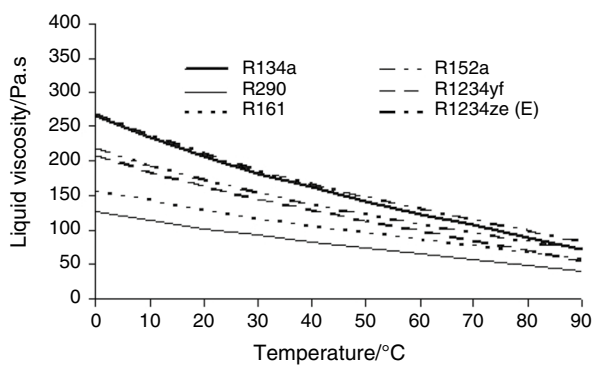
(b) Latent heat



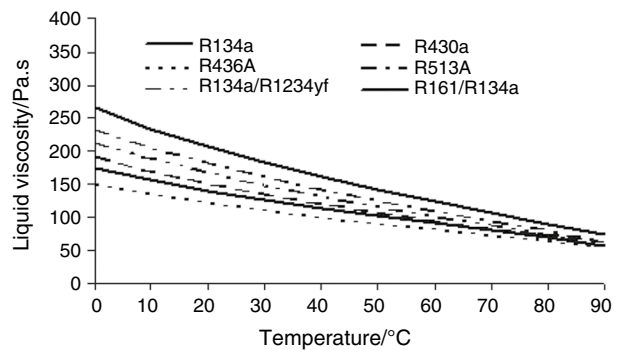
(c) Liquid density



(c) Liquid density



(d) Liquid viscosity



(d) Liquid viscosity

Fig. 1 Thermophysical properties of R134a and its possible pure alternatives

Fig. 2 Thermophysical properties of R134a and possible mixed alternatives

R430A, R436A, R513A and R134a/R1234yf are found to be closer to R134a. As a result, the compressor modification is not required for retrofitting with these mixtures. The R161/R134a mixture has high pressure compared to R134a, which needs modifications in compressor design. From Fig. 2b, it is observed that the R430A, R436A and R161/R134a mixtures are having higher latent heat compared to R134a, which results in better refrigeration effect. However, the R513A and R134a/R1234yf mixture has lower latent heat compared to R134a, which results in poor refrigeration effects and COP. From Fig. 2c, it is confirmed that the liquid densities of mixtures are found to be lower compared to R134a, which ensures less refrigerant quantity compared to R134a. The exact refrigerant charge requirement for an AAC system has been optimized using exergy analysis [18]. In Fig. 2d, the liquid viscosities of R134a and its possible refrigerant mixtures are compared. It is noticed that all the mixtures are having lower liquid viscosity compared to R134a, which results in better heat transfer coefficients with less irreversibility in all the system components.

The R744 has low critical temperature when compared to R134a. In Fig. 3, the variations of thermophysical properties of R744 and its mixtures in the range between $-40\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$ are compared. From Fig. 3a, it is noticed that the vapour pressure of R744- and R744-based mixtures was found to be significantly higher than R134a. Hence, the replacement of R134a with R744 and its mixtures are not possible due to mismatch in operating pressure. Moreover, the condenser should be replaced with a gas cooler and to withstand high operating pressure. In Fig. 3b, the liquid density variations of R744 and its mixtures are compared with R134a. It is observed that all the liquid density variations of R744-based mixtures are found to be lower compared to R134a, which results in lower refrigerant quantity. From Fig. 3c, it is observed that R744 and its mixtures are having high latent at low temperatures. However, at high temperatures above $30\text{ }^{\circ}\text{C}$, the latent heats of R744 and its mixtures are found to be lower compared to R134a. As a result, the R744 and its mixtures are having poor performance at high ambient temperatures. The liquid viscosities variations of R134a, R744 and its mixtures are compared in Fig. 3d. It is noticed that the R744 and R744 based mixtures are having lower viscosities compared to R134a, which results in improved heat transfer coefficients and reduced irreversibly. The high latent heat, low liquid density and low viscosity of environment friendly refrigerants have ensured better heat transfer coefficients in the condensers and evaporators with less thermal irreversibility in all the components of AAC. The presence of irreversibility in AAC systems is due to thermophysical properties of refrigerants, which are quantified using exergy analysis [19].

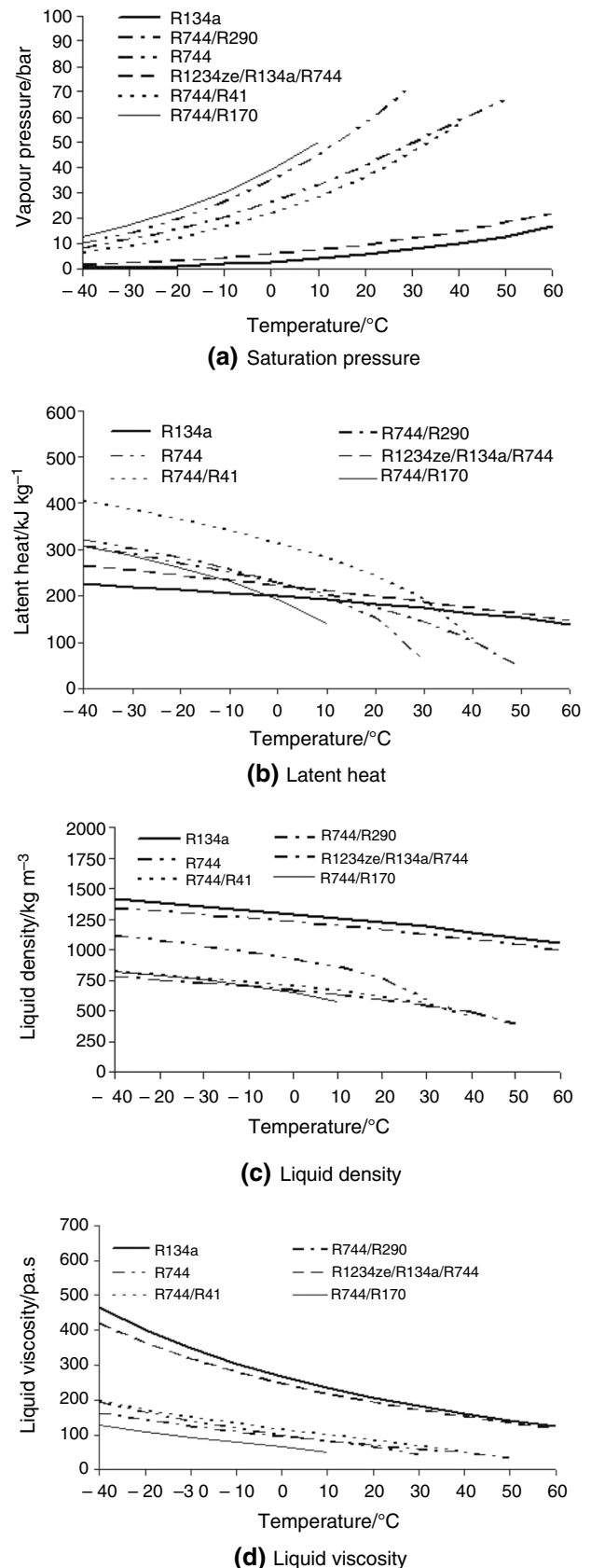


Fig. 3 Thermophysical properties of R744 and its mixtures

Thermodynamic properties

The thermodynamic properties of R134a and environment friendly refrigerant options reviewed in this paper are shown in Tables 2 and 3. The new refrigerants mixtures not listed by American Society of Heat Refrigeration and Air Conditioning Engineers (ASHRAE) are designated as NRM in Table 3. The refrigerants with high critical temperature are required to achieve good performance. Except R744 and its mixtures, all the alternatives listed in Tables 2 and 3 are having critical temperatures closer to R134a within 10 K differences. The R744 and its mixtures have significant performance degradation at high ambient temperatures due to its lower critical temperatures. The refrigerants with lower critical pressures compared to R134a are preferred to achieve low compressor discharge temperature. The critical pressure of refrigerants such as R152a, R161, R744, R161/R134a, R430A and R445A is significantly higher than R134a, which results in high compressor discharge temperatures. The refrigerants with high molecular mass affect the compressors size. Hence, the refrigerants with low molecular mass are recommended for AAC (using reciprocating compressors). The refrigerants with low boiling point are essential for heating applications in automobiles operating in low ambient temperatures. The R290 and R744 are having low boiling points, which are suitable for automobile heating systems. For cooling applications, the refrigerants with boiling points similar to R134a are preferred. The refrigerants such as R1234yf, R152a, R290/R600a, R430A, R436A, R445A, R450A and R513A are having boiling points similar to R134a, which are suitable for automobile cooling applications.

Chemical properties

During retrofitting, the refrigerant should be compatible with all the components of the system and also with the

lubricant. The halogenated refrigerants are compatible with all the components of AACs. However, the fluorine-based refrigerants are not miscible with mineral oil, which is conventionally used lubricant [20]. Hence, the synthetic lubricants are preferred, which are hygroscopic in nature. The miscible behaviours of hydrofluoroolefin (HFO) refrigerants with lubricants are similar to the hydrofluorocarbons (HFC) refrigerants. The HFO refrigerants are mildly flammable with an ASHRAE flammable index of A2L [21]. The hydrocarbon refrigerants are miscible with both mineral oil and synthetic lubricants. The ASHRAE classifications of toxicity and flammability of R134a and environment friendly refrigerant options are listed in Tables 2 and 3.

Mixtures and their behaviour

Presently, the refrigerant mixtures are getting much research attention due to the limited availability of pure refrigerants as environment friendly alternatives. The mixture of two or more refrigerants provides a chance to vary the required thermophysical and thermodynamic properties to match with existing halogenated refrigerants. The refrigerant mixtures are categorized as azeotropes, near azeotropes and zeotropes [22]. The azeotropic mixtures behave like a single substance during its evaporation and condensation with negligible temperature glide. The thermodynamic and thermo-physical properties of azeotropic mixtures are found to be better than its constituents. The near azeotropic mixtures extend the alternative options beyond its single compounds with a low-temperature glide between 0.2 and 0.6 °C. The compositions of near azeotropic mixtures are not influenced during leakage. Zeotropic refrigerant mixtures are not behaving like single substance during its phase change. Instead, it evaporates and condenses with a temperature glide of 4–7 °C. The phase change behaviors of zeotropic mixtures are non-isothermal. The composition of zeotropic mixtures may vary during leakage.

Table 2 Thermodynamic properties of R134a and its alternatives

Refrigerant	Molecular weight	Critical properties		Boiling point /°C	ASHRAE code	ODP R11 = 1	GWP 100 yr
		Temperature /°C	Pressure M Pa				
R41	34.03	44.1	5.90	−78.1	A1	0	97
R134a	102.03	101.1	4.06	−26.1	A1	0	1300
R152a	66.05	113.3	4.52	−24	A2	0	120
R161	48.06	102.2	4.70	−34.8	A1	0	12
R290	44.1	96.7	4.25	−42.2	A3	0	20
R600a	58.12	134.7	3.64	−11.7	A3	0	20
R744	44.01	31.1	7.38	−78.4	A1	0	1
R1234yf	114	94.7	3.38	−29.5	A2L	0	<4
R1234ze	114	109.4	3.63	−19.0	A2L	0	<4

Table 3 Thermodynamic properties of R134a and selected refrigerant mixtures

ASHRAE designation	Composition	Ratio (by mass)	Boiling point /°C	Molecular weight	Critical properties		ASHRAE code	ODP R11 = 1	GWP 100 yr
					Temperature /°C	Pressure MPa			
R134a	Pure fluid	–	–26.1	102.03	101.1	4.06	A1	0	1430
R430A	R152a/R600a	0.76:0.24	–21.4	64.14	118.4	4.3	A3	0	107
R436A	R290/R600a	0.5:0.5	–27	49.33	115.0	4.2	A3	0	<20
R444A	R32/R152A/ R1234ze	0.12:0.05:0.83	–23.3	96.696	101.2	4.23	A1	0	92
R445A	R744/R134A/ R1234ze	0.06:0.09:0.85	–21.5	103.11	104.7	4.49	A1	0	130
R513A	R134a/ R1234yf	0.44:0.56	–29.9	108.43	97.7	3.85	A1	0	573
NRM	R744/R290	0.6:0.4	–61	44.085	54.5	6.8	A1	0	<20
NRM	R744/R41	0.7:0.3	41	40.4	35.9	7.00	A3	0	<20
NRM	R1234yf/ R134a	0.9:0.1	–30.71	112.71	95.4	3.40	A1	0	144
NRM	R161/R134a	0.6:0.4	–30	60.95	98.5	4.69	A1	0	575
NRM	R290/R600a	0.45:0.55	–23.5	50.1	118.2	4.23	A3	0	<20

Environmental properties

The halogenated refrigerants are the chemical substance derived from methane and ethane by replacing the hydrogen with chlorine and fluorine. The emissions of chlorine and fluorine atoms in atmosphere are responsible for ODP and GWP. In 1974, Molina and Rowland [23] have identified that chlorine in halogenated refrigerants acts as a catalyst for depleting the ozone layer. Moreover, the chlorine refriger-

Environment impact assessments

Total equivalent global warming impact (TEGWI) is an indicator for estimating the direct emissions due to refrigerant leakage (during servicing, damage of components and disposal of equipment after its life cycle) from the system and indirect emissions due to power consumption (during combustion of fuels to power the air conditioner) [26]. The TEGWI is given by following equation:

$$TEGWI = GWP \times L \times N \times m + (GWP \times m \times (1 - \alpha) + \left(\frac{q_f}{10,000} \times km/year + \frac{q_f}{10,000 \times 100} \times m_{AC} \times km/year \right) \frac{COP_{reference}}{COP_{alternative}} \beta) \quad (1)$$

ants are also responsible for GWP. The Montreal protocol 1987 restricts the consumption of R12 in AACs due to its high ODP. After the phase-out of R12, the AAC manufacturers have shifted to R134a during the year 1995. The Kyoto protocol 1997 has identified six greenhouse gases influencing the global warming, which includes HFC refrigerants [24]. The Paris protocol 2016 has restricted the consumption of halogenated refrigerants, which are responsible for GWP. The phase-out schedule as per the Paris protocol (Kigali agreement) is shown in Fig. 4. The scenario of refrigerant usage is depicted in Fig. 5. Presently, the AAC manufacturers have shifted to HFO refrigerants due to their low GWP of less than 5. However, the HFO refrigerants are unsaturated organic compounds, which are destroyed quickly in the atmosphere and produced trifluoro acetic acid (TFA). The formation of TFA is more harmful to the aquatic systems [25]. The environmental properties of R134a and its possible alternatives are listed in Tables 2 and 3.

The following assumptions are used for estimating TEGWI:

- The GWP values of refrigerants are assumed as listed in Tables 2 and 3.
- The mass of accessories and basic components of AAC systems are 15 kg based on the manufacturers specifications [26].
- The system life is 15 years approximately.
- The refrigerant mass-charges were assumed as per the recommendation given by the manufacturer.
- On average, the annual leakage rate of AAC systems is in the range between 20% and 30%.
- The average COP of AAC systems is to be assessed based on experimental trials.

Fig. 4 Kigali agreement—HFC phase out schedule

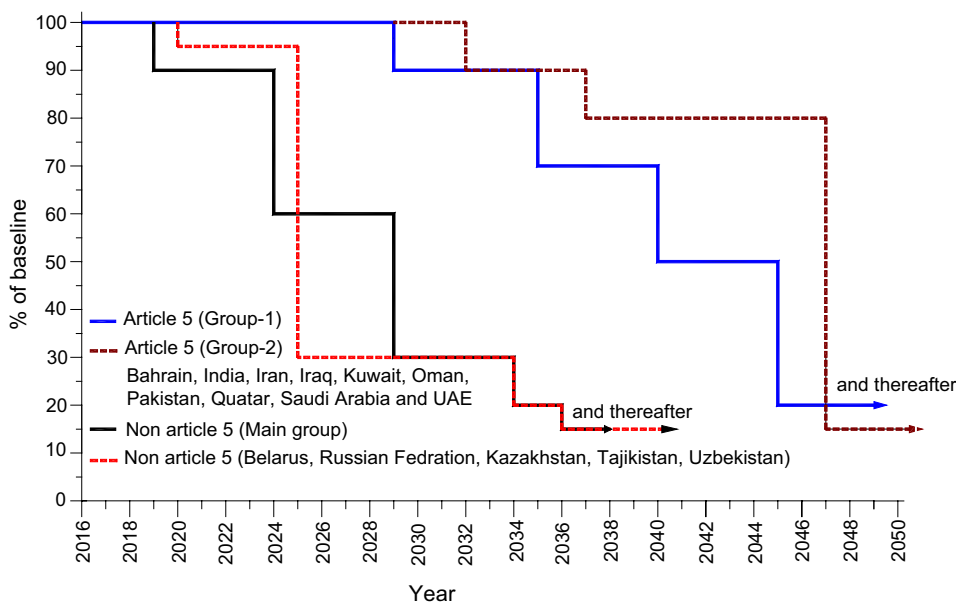
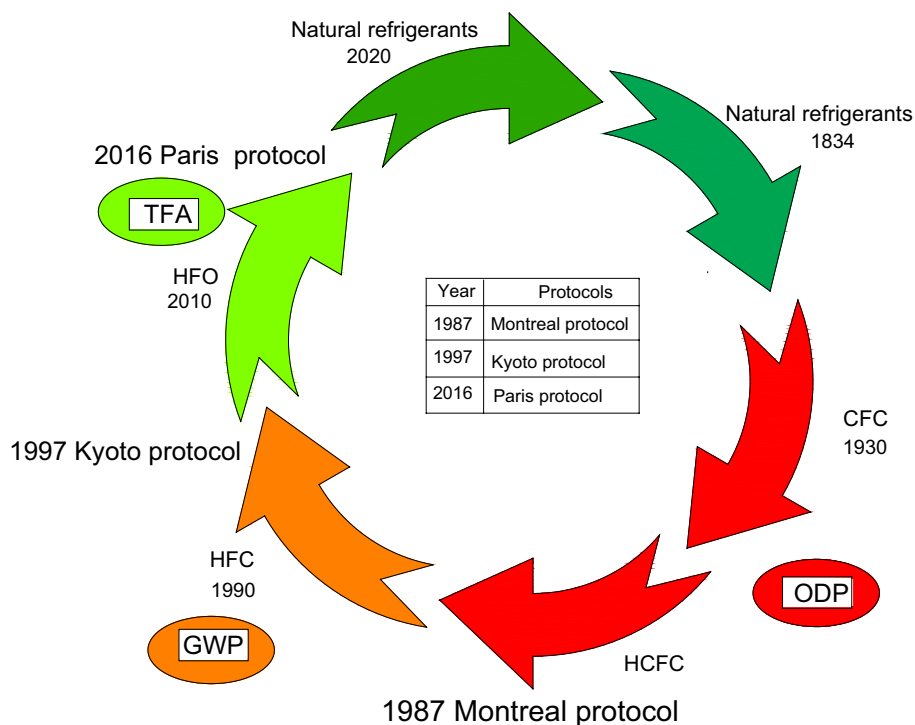


Fig. 5 Scenario of refrigerant usage**Table 4** Carbon dioxide emissions for different automobiles

Fuel	Petrol	Diesel	LPG
Vehicle carbon dioxide emissions (kg of CO ₂ per litre)	2.31	2.68	1.64

- The average fuel consumptions observed in petrol, liquefied petroleum gas and diesel operating with and without air conditioners are to be evaluated.
- The carbon dioxide emission factors for various fuels are given in Table 4.

Review of research investigations

Many research and development investigations have been made on environment friendly refrigerant options for AAC systems. The reported research investigations have been grouped as follows: (a) hydrofluorocarbons (HFC); (b) hydrofluoroolefins (HFO); (c) hydrocarbons; (e) carbon dioxide (R744) and (f) composite mixtures. A summary of selected research investigations reported in open literature is described in this section.

Hydrofluorocarbon refrigerants

The HFC refrigerants with low GWP have been reported as possible alternatives to R134a in AACs. The summary of

Table 5 Research highlights of HFC alternatives for AAC systems

Authors [Ref.]	Refrigerant	Research highlights
Mohmoud [27]	R152a	The COP of R152a was improved by 11% compared to R134a under driving conditions
Bryson et al. [29]	R152a	Refrigeration effect and COP were improved by 2% and 9%, respectively
Li et al. [30]	R152a	Compressor discharge temperature was found to be 2–6 °C higher than R134a
Han et al. [38]	R161/R134a	The refrigeration capacity and power consumption of compressor were increased by about 32% and 30%, respectively, compared to R134a. Operating pressure is higher than that of R134a
Wu et al. [39]	R161	The refrigeration capacity and power consumption were increased by about 56% and 47%, respectively, compared to R134a. Compressor discharge temperature is significantly higher than R134a
Wang et al. [40]	R407C	Not suitable for AAC systems due to its zeotropic behavior
Wu et al. [42]	R32	Recommended for new electrical vehicles

selected research investigations reported on HFC refrigerants is summarized in this section, and the research highlights on HFC alternatives are given in Table 5.

Mohmoud [27] investigated the possibility of using R152a and hydrocarbon refrigerants such as RC270, R290 and R600a as possible alternatives to R134a in an AAC. It was reported that the COP of the AAC operating with R152a and RC270 were 11% and 9% higher compared to R134a systems under driving conditions. The R290 and R600a are not possible to use as a drop-in substitute due to its mismatch in volumetric cooling capacity. The R152a is having higher compressor discharge temperature compared to R134a. During the year 2009, Yoo and Lee [28] investigated the performance of an AAC using R134a and R152a as working fluids. It was reported that R152a has similar refrigeration effect with higher COP compared to R134a due to its lower compressor power consumption. Moreover, they also reported that the R152a has better thermodynamic and thermophysical properties compared to R134a. The R152a has GWP of about 140, which is significantly lower than R134a. Similarly, the performance of an AAC using R152a as a drop-in substitute to R134a was investigated and reported with 2% improved refrigeration effect with 9% higher COP compared to R134a [29].

Li et al. [30] investigated the performance of an AAC using R134a and R152a as working fluids. Secondary loop configuration was used in their work to reduce the flammability risk. Their studies reported that the R152a has 28% reduced refrigerant quantity compared to R134a due to its lower liquid density. The COP of an AAC using R152a was improved by 5% and 10% in highway driving and idling conditions, respectively, with 9.6% reduced exergy destruction compared to R134a due to its favourable thermophysical properties. Similarly, the performance of an AAC was investigated using R134a and R152a [31]. It was reported that R152a can be used as a drop-in substitute to R134a in an AAC due to its similar compressor pressure ratio and volumetric efficiency. In another work, the performance of AAC systems using R134a and R152a as working fluids was compared [32]. The COP of R152a was found to be about 4.2–13.5% higher than R134a due to its lower compressor power consumption. However, the refrigeration capacity of R152a was found to be lower than R134a. The compressor discharge temperature of R152a was found to be 10–19 °C due to its higher critical pressure compared to R134a. Ma et al. [33] experimentally investigated the performance of a gas engine operated heat pump working with R134a and R152a as an alternative. It was reported that the primary energy ratio, isentropic efficiency and volumetric efficiency of heat pump using R152a were increased by 2.6–10.4%, 3.5–10.7% and 5.8–7.3%, respectively, when compared to R134a with the increase in engine speed from 1200 rpm to 1600 rpm. They also reported that R152a is having better

heating performance compared to R134a. The refrigerant R152a has 7% lower TEGWI when compared to R134a due to its lower GWP with improved energy efficiency [34].

Bolaji [35] experimentally studied the performance of a small capacity refrigeration system using R134a and R152a as working fluids and reported 4.7% improvement in COP compared to R134a. Moreover, it is also reported that the R152a has about 4% lower energy consumption compared to R134a. Bhatkar et al. [36] investigated the performance of a compression refrigeration cycle working with R134a and R152a using micro-channel condenser. Their results reported that the refrigerant requirement of R152a was reduced by about 40% compared to R134a due to its lower liquid density. The compressor discharge temperature of R152a was reported to be higher in the range of 6–10 °C than R134a. The refrigeration capacity of R152 and R134a was reported to be similar. The performance of an AAC using R134a and its possible alternatives such as R152a and R444A under the influence of internal heat exchanger (IHX) was experimentally investigated [37]. It has been reported that the highest COP was observed with R152a followed by R134a and R444A without IHX. However, the AAC systems using R444A under the influence of IHX have significant performance improvement over R134a and R152a. The R152a can be used as a drop-in substitute to R134a without modifications. The use of R444A needs addition of IHX for performance improvement.

Han et al. [38] experimentally studied the performance of AAC systems using R134a and the mixture composed of R161 and R134a (in the ratio of 0.6:0.4, by mass) as working fluids. The experiments have been conducted at the condensing temperatures ranging from 50 °C to 65 °C and the evaporator temperatures ranging from –5 °C to 10 °C. The experimental results reported that refrigeration capacity and compressor power consumption were increased by about 32% and 30%, respectively. The COP of AAC systems using R161/R134a mixture is similar to R134a. The pressure ratio of the mixture was observed to be about 10.9% higher compared to R134a, which results in lower volumetric efficiency. The high compressor power consumption was observed with the mixture due to high operating pressure of R161. Similarly, the performance of an AAC using R161 (having low GWP of 12) as a possible alternative to R134a was studied [39]. The performance was evaluated at the evaporator temperature ranging from –5 to 10 °C and the condensing temperature ranging from 50 to 65 °C. It has been reported that the refrigeration capacity and compressor power consumption were increased by 56% and 47%, respectively, compared to R134a. The saturation pressure of R161 was found to be significantly higher compared to R134a. The compressor discharge temperature of R161 was 20–35 °C higher due to its higher critical pressure compared to R134a. As a result,

R161 cannot be used as an alternative to R134a, which needs compressor modifications.

Wang et al. [40] evaluated the performance of a heat pump used in an electrical vehicle working with R134a and R407C. It has been reported that the heating capacity and compressor power consumption of heat pump using R134a and R407C were increased with the increase in compressor speed. But, the energy efficiency of R407C was reduced significantly. Moreover, the R407C is a zeotropic mixture, with high GWP and higher pressure than R134a. The composition of R407C mixture may vary under the influence leakage. Hence, the R407C is not recommended for AAC. The environmental impacts of AAC systems using R134a and R152a, R1234yf and R744 as alternatives were assessed by Yuan et al. [41]. It has been reported that the carbon dioxide emissions were reduced by 8.74%, 0.28% and 0.07% for the system retrofitted with R152a, R1234yf and R744, respectively, when compared to R134a. The R152a has good thermophysical properties compared to R1234yf and R744. The R1234yf has lower cooling capacity, which influences the indirect carbon dioxide emissions due to excess compressor operating time.

Wu et al. [42] assessed the heating and cooling performance of AAC systems using R134a and R152a, R1234yf, R290, R410A, R32 and R744 as possible alternatives. It was reported that the R290 has the lowest and R744 has the highest TEGWI compared to other investigated refrigerants. However, the flammability issues with R290 restrict its usage in AAC systems. The refrigerant R32 was suggested in their work as a possible replacement in terms of cooling and heating performance. However, R32 and R290 cannot be used as a drop-in replacement to R134a due to mismatch in operating pressure. Hence, it is recommended for the new AAC systems.

The reported studies on HFC alternatives confirmed that the R152a can use as a drop-in substitute to replace R134a in AAC systems. However, the R152a has high compressor discharge temperature due to higher critical pressure, which affects the characteristics of lubricant used in compressors. Hence, the systems using R152a needs additional cooling arrangement to control the compressor operating temperature. The refrigerants R161 and R32 are not possible to use as drop-in substitutes to replace R134a in AAC systems. The R32 and R161 are recommended for new ACC systems.

Hydrofluoroolefins

Many researchers have investigated the performance of hydrofluoroolefins (HFO) such as R1234yf and R1234ze as drop-in substitutes to R134a. The summary of selected research investigations reported on the use of R1234yf in AAC systems is presented in this section. The research highlights on HFO refrigerants are given in Table 6. The AAC systems using R1234yf has lower CO₂ emissions compared to R134a [43].

Mathur [44] studied the performance of an AAC using R1234yf as a drop-in substitute to R134a. The condenser air temperatures was maintained between 25 and 50 °C, air velocities approaching the condenser were maintained between 2 and 10 m s⁻¹, and the compressor speed was maintained between 800 and 3000 rpm. The cabin temperature and relative humidity were maintained at 20 °C DBT and 50%, respectively. The R1234yf refrigerant charge was reduced by 10% due to its lower liquid density. It was reported that the COP of AAC using R1234yf was found to be lower due to its poor latent heat when compared to R134a. The compressor discharge temperature using R1234yf was found to be lower by 5–9 °C, which ensures better compressor life. Similarly, Zilio et al. [45] conducted experiments in AAC systems using R134a and R1234yf. The

Table 6 Research highlights of HFO alternatives for AAC systems

Authors [Ref.]	Refrigerant	Research highlights
Mathur [44]	R1234yf	The refrigerant charge requirement was reduced by 10% compared to R134a
Zilio et al. [45]	R1234yf	The COP and cooling capacity were increased by increasing the condenser and evaporator face areas
Lee and Jung [46]	R1234yf	The performance enhancement of AAC using R1234yf is possible by changing the condenser and evaporator areas
Cho et al. [48]	R1234yf	Cooling capacity and COP of R1234yf were significantly improved using an IHX compared to R134a
Qi [50, 51]	R1234yf	The cooling capacity of R1234yf using micro-channel parallel flow evaporator was improved up to 6.5% compared to R134a
Lee et al. [52]	R1234yf	The R1234yf shows the maximum COP improvement by 29.8% with 17% reduced power consumption compared to R134a using saturation cycle concept
Junye et al. [55]	R1234yf	the cooling capacity and COP were increased by 11.3% and 8%, respectively
Golzari et al. [57]	R1234yf	Compressor has more exergy destruction compared to other components
Prabakaran et al. [70]	R1234yf	The energy and exergy performance of AAC using R1234yf were improved by turning expansion device
Lee and Hwang [74]	R1234yf	Compatible with synthetic lubricants used in R134a systems

AAC experimental setup consists of variable displacement compressor, mini-channel condenser and evaporator and thermostatic expansion. It was reported that R1234yf has lower performance when compared to R134a. The simulation results reported that the COP and the cooling capacities were improved significantly by increasing the condenser area by 20% and evaporator face area by 10% and also by tuning the expansion valve for the AAC system using R1234yf.

Lee and Jung [46] studied the performance of R134a-based AAC system using R1234yf as a drop-in substitute. It was reported that the COP and cooling capacity of R1234yf were 2.7% and 4.0% lower when compared to R134a, respectively. The compressor discharge temperature of R1234yf was observed to be about 6.5 °C lower due to its lower critical pressure compared to R134a. The mass-charge of R1234yf was reduced by 10% due to its reduced liquid density when compared to R134a. It is suggested that the performance of AAC systems was improved by modifying the condenser and evaporator area. Zhao et al. [47] experimentally investigated the performance of AAC systems using R1234yf as a drop-in replacement for R134a. The refrigerant quantity of R1234yf was reduced by 10% compared to R134a due to its lower liquid density. It was reported that R1234yf has 12.4% lower cooling capacity and 9% lower COP when compared to R134a. The performance of the system was enhanced by modifying the area of the condenser and evaporator. The performance of AAC using R1234yf was improved by changing the design of thermostatic expansion valve. In another work, the performance of AAC systems using R134a and R1234yf as refrigerants with and without IHX was investigated [48]. It was reported that the cooling capacity and compressor power consumption of an AAC using R1234yf were reported lower by 7% and 4%, respectively, compared to R134a. The compressor discharge temperature of R1234yf was found to be 4.9–8.3 °C lower compared to R134a, which ensures better compressor reliability while using R1234yf. The cooling capacity and COP of the system working without IHX using R1234yf were dropped by about 7% and 4.5%, respectively. However, the integration of IHX has reduced the drop of cooling capacity and COP to 1.8% and 2.9%, respectively.

Navarro et al. [49] investigated the performance of an AAC using R134a and R1234yf. It was reported that the R1234yf has 10 K lower compressor discharge temperature when compared to R134a due to its lower critical pressure compared to R134a. The R1234yf has 10–15% lower cooling capacity with lower COP when compared to R134a due to its lower latent heat. The volumetric efficiency of R1234yf was found to be 5% lower than R134a due to its more compressor pressure ratio. Qi [50] studied the performance of an AAC working with R134a and R1234yf system under three typical vehicle operation conditions (idle, city and high speed). It was reported that the COP and cooling capacity

of R1234yf system were lower compared to R134a by 4.8% and 7.7%, respectively, in idle operating conditions. Further, in city driving conditions, the COP and cooling capacity were dropped by 5.8% and 9.1%, respectively. The COP was dropped by 7%, and cooling capacity was dropped 10.6% in high-speed operating conditions. The cooling capacity and COP were increased by 15% by increasing the sub-cooling from 1 to 10 K. The performance of an AAC using R1234yf was improved by introducing IHX. Further, the performance of an AAC working with R1234yf and R134a using laminated plate and micro-channel parallel flow evaporators was investigated [51]. The cooling capacity of R1234yf using laminated plate evaporator was reduced up to 8% compared to R134a, whereas the cooling capacity of R1234yf using micro-channel parallel flow evaporator was improved up to 6.5% compared to R134a. The air side pressure drops in both evaporator configurations are found to be similar. The refrigerant R1234yf has more pressure drop than R134a in both the evaporator configurations.

Lee et al. [52] applied saturation cycle concept for the performance improvement of an AAC using R134a and its possible alternatives such as R152a, R445A and R1234yf. It was reported that the COP of AAC using R134a was improved by 23.9% with 19.3% reduction in compressor power consumption. The R1234yf shows the maximum COP improvement by 29.8% with 17% reduced power consumption compared to R134a. The refrigerant R445A shows the lowest COP improvement by 12.64%. The COP improvements of other investigated refrigerants are lower compared to R134a. Pottker and Hmjak [53] experimentally investigated the performance of an AAC using R134a and R1234yf under the influence of sub-cooling in the condenser and IHX. The COP R134a and R1234yf systems with condenser sub-cooling were improved up to 9% and 18%, respectively. The use of sub-cooling in condenser and in IHX has improved the system performance using R1234yf.

Sotomayor and Parise [54] simulated the performance of open type compressor used in AAC systems. It was reported that the shaft power of R1234yf was reduced by 2% due to its similar thermophysical and thermodynamic properties with R134a. The pressure drops in the suction and discharge of compressors using R1234yf were reported to be higher compared to R134a. The refrigeration mass flow rate of R1234yf was found to be 16% higher when compared to R134a. Similarly, Junye et al. [55] experimentally studied the performance of an AAC using R1234yf as drop-in substitute by turning the expansion valve. It was reported that the cooling capacity and COP were increased by 11.3% and 8%, respectively. Cho and Park [56] compared the thermodynamic performance of AAC systems working with R134a and R1234yf as working fluids with and without the IHX. The R1234yf system has 4–7% lower cooling capacity with 3.6–4.5% lower COP compared to the R134a system. The

exergy efficiency of the R1234yf system was reported as 3.4–4.6% lower when compared to R134a systems at all the compressor speeds. The COP of R1234yf was improved by 0.9% at 2500 rpm with IHX. The exergy efficiency of an AAC using R1234yf was improved by 1.5–4.6% when compared to the AAC using R1234yf without IHX.

Golzari et al. [57] made an exergy analysis of an AAC using R1234yf as a working fluid. It has been reported that R1234yf has higher exergy efficiency compared to R134a. The highest exergy destruction of about 53% was observed in compressor. The exergy destructions in other components are about 21%, 15% and 11% for the condenser, expansion device and evaporator, respectively. The exergy destructions and entropy generations of R1234yf cycle are lower compared to R134a. The maximum exergy destructions of about 49% and 50% were observed in the compressor of the system operating with R134a and R1234yf, respectively, and the lowest exergy destructions of about 9% were observed in evaporator for both the fluids. The exergy efficiency of R1234yf was reported to be higher when compared to R134a, and the COP of the system working with R1234yf was reported to be about 15.5% and 19.8% higher when compared to R134a using energy method and entropy method, respectively. Sanchez et al. [58] evaluated the energy performance of R1234yf and R1234ze as low-GWP alternatives to phase out R134a. It was reported that the cooling capacity of R1234yf was dropped by 4.5–8.6%, with an increase in compressor power consumption of 1.6–6.7%. As a result, the average COP was reduced by about 10%. The cooling capacity and power consumption of R1234ze (E) were reduced by 24.9% and 17.8%, respectively. The R1234yf was reported as good drop-in substitutes to replace R134a in compression-based systems than R1234ze.

Vaghela [59] compared the performance of an AAC system using R134a and R152a, R290, R600a, R404A, R407C, R410A, R1234yf and R1234ze as possible alternatives to R134a. It was reported that R1234yf is identified as a good drop-in substitute to replace R134a due to its negligible GWP with similar thermodynamic and thermophysical properties. Moreover, all the components of the AAC using R134a are compatible with R1234yf. Similarly, Direk et al. [60] investigated the performance of an AAC working with R1234yf as drop-in substitute under the influence of an IHX. It was reported that the cooling capacity and COP of AAC systems were found lower when compared to R134a by about 17.1% and 12.4%, respectively. The influence of IHX has enhanced the system performance using R1234yf by about 7.9% and 4.1%. The refrigerant R1234yf has about 7% reduced CO₂ emissions in AAC due to its lower GWP with improved energy savings when compared to R134a [61].

Daviran et al. [62] simulated the performance of an AAC using R1234yf as a drop-in alternative to R134a. The performance was simulated with constant evaporator capacity

and constant mass flow rate conditions. It was reported that the R1234yf has 18–21% lower heat transfer coefficients compared to R134a with 24% lower pressure drop in the condenser and 20% lower pressure drop in the evaporator. The COP of R1234yf system was reported to be 1.3–5% lower compared to R134a for constant cooling capacity. The COP of R1234yf was reported to be about 18% higher than that of R134a at constant refrigerant mass flow rate conditions. Devecioglu and Oruc [63] compared the performance of an AAC working with R134a, R1234yf, R444A (composed of R1234ze, R152a and R32, with 0.83:0.5:0.12, by mass) and R445A (composed of R1234ze, R134a and R744 with 0.85:0.09:0.06, by mass) as possible alternatives. It was reported that the refrigeration capacities of the mixtures (R444A and R445A) were found to be higher than R1234yf. Moreover, the compressor power consumptions of the mixtures (R444A and R445A) are also found to be higher. As a result, the COPs of mixtures were found to be lower than that of R1234yf. The R444A and R445A mixtures are having lower flammability than R1234yf due to the presence of HFC refrigerants. Direk et al. [64] experimentally investigated the performance of an AAC in terms of exergy analysis using R1234yf as drop-in substitute to R134a. It was reported that the exergy destruction in the system using R1234yf was reduced by integrating with IHX. Similarly, Direk and Kelesoglu [65] investigated the performance of AAC systems using IHX under the influence of condenser and evaporator temperatures. The refrigerant R1234yf was used. It has been reported that the COP of the AAC was improved by about 4–6% and the system exergy destruction was reduced by 13–16% under the influence of an IHX.

Navarro-Esbri et al. [66] experimentally studied the performance of compression refrigeration cycle using R134 and R1234yf with and without IHX. It has been reported that R1234yf has 9% and 19% lower cooling capacity and COP when compared to R134a in compression refrigeration systems. The energy performance was significantly improved by integrating with IHX. Similarly, Navarro-Esbri et al. [67] experimentally investigated the performance of compression refrigeration cycle working with R134a and R1234yf under the influence of IHX. It was reported that the COP and cooling capacity were reduced by 6–13% without the IHX. The internal heat exchanger has reduced the drop of COP and cooling capacity by 2%.

Moles et al. [68] studied the performance of compression refrigeration cycle using R134a and its possible alternatives such as R1234yf and R1234ze under the influence of expanders or an ejector instead of expansion valve. The COP of the system was improved by 9–15% and 11–20% for R1234yf and R1234ze, respectively, when compared to conventional refrigeration cycle using R134a as a working fluid. Jankovic et al. [69] made thermodynamic and heat transfer analysis of R134a and R1234yf and R1234ze as

possible alternatives in small-capacity refrigeration systems. It has been reported that R1234yf has 5–9% lower cooling capacity with 7–10% lower COP than R134a. The refrigerant R1234ze has 25% lower cooling capacity with 4–7% a higher COP due to lower compressor power consumption due to poor thermophysical properties when compared to R1234yf and R134a.

Prabhakar et al. [70] made experimental studies on thermodynamic performance of R134a AAC working with R1234yf an alternative. The performance of an AAC using R1234yf was improved by turning the thermostatic expansion valve. After tuning, the COP and cooling capacity were improved by 4.3–8.6% and 6.5–10.2%, respectively. The exergy efficiency of the system was improved by 3.7–5.1%. The TEGWI of the system using R1234yf was reduced by 28% and 25% lower when compared to R134a for tuned and un-tuned positions of thermostatic expansion valve, respectively. The performances of an AAC using R134a and R1234yf as working fluids were experimentally investigated [71]. It was reported that the system COP working with R1234yf was found to be 2–11% lower compared to R134a. The compressor power consumption was found to be about 11.2% higher than R134a. The exergy efficiency of the system using R1234yf was found to be 2.4–12.6% lower when compared to R134a.

Alkan et al. [72] reported the performance of an automobile heat pump system using R1234yf as a possible alternative to R134a. It was reported that the R1234yf has 9.2–15.4% lower heating capacity with 1.6–7.1% lower COP and 3.1–19.2% higher system exergy destruction due to its good thermophysical properties when compared to R134a. The R1234yf has a significantly lower TEGWI compared to R134a due to its lower GWP and reduced compressor power consumption. Li et al. [73] compared the performance of an automobile heat pump used in electrical vehicles working with R134a and R1234yf under cold climatic conditions. It was reported that the performance of an automobile heat pump using R1234yf operating at low ambient temperatures was improved using economized vapour injection

technology. The heating capacity and COP of a heat pump using R1234yf were improved more than R134a by increasing the air mass flow rate by 10%, which influences sub-cooling in the condenser.

The studies reported in open literature confirmed that R1234yf is identified as a good drop in substitute to phase out R134a. The lubricants used in R134a systems are compatible and miscible with HFO refrigerants such as R1234yf and R1234ze [74]. The performance of HFO refrigerants is improved using IHX, ejectors, expanders and turning of expansion valve [75]. The R1234yf has less environmental impact due to its low GWP. The HFO refrigerants are destroyed faster than R134a and forms TFA, which is more harmful to aquatic systems. As a result, the environmental impacts of HFO refrigerants become more significant than R134a. Hence, HFO refrigerants are identified as interim options to extend the life of existing R134a-based AAC systems.

Hydrocarbon refrigerants

The hydrocarbon refrigerants are reported as the promising alternatives to R134a due to its lower GWP [76]. The hydrocarbon refrigerants have 20% improved energy efficiency due to its good thermophysical properties compared to R134a [77]. The pure hydrocarbon refrigerants such as R1270, R290 and R600a are not possible to use as a drop-in replacement to R134a due to mismatch in volumetric cooling capacity and operating pressure, which requires compressor modifications. Hence, the binary hydrocarbon mixtures composed of R290 and R600a are preferred as drop-in replacement for R134a. The research highlights reported with hydrocarbon refrigerants are given in Table 7.

Jung et al. [78] reported that the hydrocarbon refrigerant mixture composed of R290 and R600a (in the ratio of 0.6:0.4, by mass) has shown the maximum COP of 3.36 with minimum compressor discharge temperature of 72.3 °C when compared to R12, which has the COP of 3.3 and the compressor discharge temperature of 76 °C. However, the

Table 7 Research highlights of HC alternatives for AAC systems

Authors [Ref.]	Refrigerant	Research highlights
Jung et al. [78]	R290/R600a	The R290/R600a mixture has the maximum COP of 3.36 with 4 °C lower compressor discharge temperature compared to R12. The R290/R600a mixture has 7.4 K temperature glide
Wongwises et al. [82]	R290/R600/R600a	The COP of the system using hydrocarbon mixture is 14.2% higher than R134a. The compressor power consumption and refrigeration capacity of the mixture were 21% and 41% higher than those of R134a, respectively
Li et al. [30]	R290	The R290 has about 8% higher COP compared to R134a at highway driving conditions. At idling conditions, the COP of R290 was dropped by 15% compared to R134a
Liu et al. [84]	R290	Recommended for electrical vehicles
Zhang et al. [85]	R290	Secondary loop system was recommended to avoid the flammable risks with hydrocarbon refrigerants

proposed hydrocarbon mixture is a zeotropic mixture with a temperature glide of 7.43 K. They also proposed R134a/RE170 mixtures to replace R12 as a drop-in substitute in an AAC. It was reported with 4% improved COP compared to R134a. Maclaine-Cross [79] investigated the flammable risk of using hydrocarbon refrigerant mixtures composed of R290 and R600a (in the ratio of 0.55:0.45, by mass) in AAC systems at Australia and USA during the time interval between 1993 and 2003. The accident frequencies of using hydrocarbon refrigerants in cars are much lower. It is confirmed that the leakage of hydrocarbon refrigerant mixtures in the compartment will not form a flammable mixture. The environmental impacts of hydrocarbon refrigerants are found to be lower when compared to R134a due to its negligible GWP and improved energy efficiency [80].

Joudi et al. [81] simulated the performance of AAC systems using R12, R134a, R290, R600a and the hydrocarbon mixture composed of R290 and R600a (in the ratio of 68:32, by mole fraction). It was reported that the hydrocarbon refrigerant mixture has improved performance with 2–6 °C lower compressor discharge temperature when compared to R12. The outlet air temperature of an AAC using R290/R600a mixture was observed to be about 1–3 °C lower when compared to R12 due to its higher latent heat. Wongwises et al. [82] compared the performance of AAC systems using R134a with the ternary hydrocarbon refrigerant mixture composed of R290, R600a and R600 (with a mass fraction of 0.5:0.10:0.4). It was reported that the COP of the system using R134a and the hydrocarbon refrigerant mixture are 1.33 and 1.55, respectively. The compressor discharge temperatures for the hydrocarbon refrigerant mixtures were found to be significantly lower when compared to R134a, which ensures better compressor life. The compressor power consumption and refrigeration capacity of the proposed hydrocarbon refrigerant mixture were found to be higher by about 21% and 41%, respectively, when compared to R134a. Karthikeyan et al. [83] experimentally studied the performance of binary hydrocarbon mixture composed of R290 and R600a in the ratio of 0.5:0.5 (by mass fraction) as a possible alternative to R134a in an AAC. It was reported that the hydrocarbon refrigerant mixture has improved energy performance when compared to R134a. The compressor discharge temperature was reported to be about 7 °C lower when compared to R134a, which ensures compressor reliability. However, the binary hydrocarbon refrigerant mixture has a temperature glide of 5–7 °C. Due to high temperature glide, the performance of AAC system using hydrocarbon mixtures was significantly degraded at high ambient conditions. The composition of the hydrocarbon mixtures is not possible to maintain under leakage conditions.

Liu et al. [84] evaluated the performance of R290 heat pumps using in electrical vehicles. It was reported that R290 has good performance over R744 at ambient temperatures

above –10 °C. The compressor heating capacities were increased with the increase in compressor speed. However, the COP of heat pump was dropped significantly with the increase in compressor speed. The maximum COP of about 2.26 was observed in R290 system for outdoor air velocity of 2 m s⁻¹. The R290 has high operating pressure and flammability compared to R134a. Hence, it is suggested to use safety connections for the use of R290 in AACs. Zhang et al. [85] investigated the flammability risk of R290 in AAC systems. It was reported that the leakage of R290 inside the passenger compartment is the highly risk situation than leakage in engine compartment. The secondary loops were used in AAC systems to eliminate the direct use of flammable refrigerants inside the vehicle compartment. The non-flammable anti-freeze solutions were used in secondary loop with plate type evaporators recommended to reduce the refrigerant inventory. Li et al. [30] studied the performance of an AAC using secondary loop to avoid the flammable risks of hydrocarbon refrigerants. The largest exergy destruction was observed in compressor. It was reported that the R290 has about 8% higher COP when compared to R134a at highway driving conditions. At idling conditions, the COP was reduced by 15% compared to R134a. The exergy destruction of the system using R290 was found to be 12.5% lower than R134a. The R290 has improved energy performance and compressor volumetric efficiency compared to R134a.

The hydrocarbon refrigerant mixtures were reported to be good drop-in substitutes to R134a due to their similar thermophysical properties. However, the hydrocarbon refrigerant mixtures are having temperature glide in the range of 4–7 °C, which results in high-performance degradation at high ambient temperatures. Moreover, the compositions of hydrocarbon refrigerant mixtures are not possible to maintain uniform under the leakage conditions. The R290 has improved energy performance over R1234yf, R744 and R134a due to its negligible GWP [86]. The R290 is not possible to use as a drop-in substitute due to mismatch in volumetric cooling capacity and operating pressure of R134a. Hence, R290 is a recommend only for new systems. The flammable risk of the hydrocarbon refrigerants in AAC systems is tackled by introducing secondary loop circuit using anti-freezing solutions [87]. The safety sensors are recommended in AAC systems using hydrocarbon refrigerants.

Carbon dioxide

The carbon dioxide is a natural refrigerant with negligible GWP. Many researchers have tried with R744 as a possible environment friendly option for compression cycles used for cooling and heating applications [88]. The summaries of selected research investigations reported on use of R744 for AAC are presented in this subsection, and the research highlights are given in Table 8.

Table 8 Research highlights of R744 for AAC systems

Authors [Ref.]	Refrigerant	Research highlights
Brown et al. [89]	R744	The COP of R744 systems will degrade more with increase in compressor speed and ambient temperature
Liu et al. [90]	R744	The synthetic lubricants are preferred for R744 systems. High air flow rates over the evaporator and condenser need to be maintained to attain maximum performance
Tamura et al. [91]	R744	The R744-based AAC heating system has significant energy savings compared to R134a
Kim et al. [92]	R744	The heating capacity and COP of the system were improved up to 54% and 22%, respectively, while using preheated air through the condenser
Apra et al. [95]	R744	The R744 is not suitable for AAC systems due to its poor thermodynamic performance
Salim [96]	R744	The R134a systems have recover only 18% of work in the expander. The COP of the expander cycle without IHX was 30–45% higher than the conventional cycle and 10–12% higher than expander cycle with IHX
Chen et al. [97]	R744	The refrigeration capacity and COP were improved by 19.8% and 12.8%, respectively, under the influence of IHX
Peng et al. [102]	R744	The performance of R744 under the influence of vapour injection has 30.7–38.6% improved heating capacity than conventional trans-critical heat pump

Brown et al. [89] evaluated the performance of an AAC working with R134a and R744. The R744-based AAC was additionally fitted with liquid line suction heat exchanger. It was reported that the R744 AAC system has 21% and 34% lower COP when compared to 134a system at 32.2 °C and 48.9 °C condenser inlet air temperatures, respectively. At higher compressor speeds and high ambient temperatures, the COP degradation is more due to more entropy generation in the gas cooler. Liu et al. [90] investigated the performance of an AAC under the influence of synthetic lubricants (PAG and POE), evaporator pressure, refrigerant mass-charge, inlet air temperature to the gas cooler, air flow rate through the evaporator and compressor speed. It was reported that the performance of R744 AAC using PAG has better performance over POE lubricant. The viscosity of POE was significantly degraded at high ambient temperatures. The high air mass flow rate over the evaporator and gas cooler is to be maintained to control the condenser pressure for achieving good performance. Tamura et al. [91] experimentally investigated the performance of R744-based AAC systems for cooling and heating applications. In their system, the heat recovered during dehumidification of incoming air was used as a heat source instead of using an electrical resistance heating. The proposed heating system has significant energy savings due to its high energy efficiency when compared to R134a.

Kim et al. [92] investigated the performance of an electrically driven R744-based heat pump used for cooling and heating applications in fuel-cell-powered vehicles. The heat pump unit consists of basic components such as electrically driven semi-hermetically sealed compressors, micro-channel gas cooler, micro-channel evaporator and an IHX. The heating capacity and COP of the system were improved up to 54% and 22%, respectively, while using preheated air through the condenser. The heating performance of the system was improved by changing the locations of evaporator

and radiator. The cooling capacity and COP were dropped by 40–60% and 43–65%, respectively. An increase in compressor speed has increased the cooling capacity by about 35% with 86% increase in compressor power consumption. As the result, the COP was dropped by 28%. Further, Kim et al. [93, 94] experimentally studied the performance of R744-based AAC systems under the influence of inlet refrigerant pressure of the gas cooler, compressor speed, air temperatures at the entry of evaporator and gas cooler. It was reported that the cooling capacity and the COP were reported as 4.9 kW and 2.4 during idling conditions. The cooling capacity was increased to 7.5 kW with drop in COP to 1.7 during driving conditions when condenser inlet temperature was maintained at 45 °C and evaporator inlet was maintained at 35 °C. Apra et al. [95] evaluated the TEGWI of AAC systems using R134a and R744 as working fluids. It has been reported that the TEGWI of R134a was lower when compared to R744 for the refrigerant leakage rates below 20%. At 25% leakage rate, the environmental impact of both R134a and R744 are the same. At 30% leakage rate, the environmental impact of R134a was found to be 4% higher when compared to R744. The results confirmed that R744 is not suitable for AAC systems due to its poor thermodynamic and thermophysical properties.

Salim [96] studied the performance of three AAC configurations using R744 as a working fluid (i) conventional cycle with IHX, (ii) conventional cycle with expander without IHX and (iii) conventional cycle with an IHX and an expander. It was reported that the COP was improved by 30–45% in the cycle integrated with expander followed by the cycle with expander and IHX and the conventional cycle. It is possible to recover 57% of the compressor work input from in the cycle with expander without IHX, and 30% of the compressor work was recovered from the cycle with IHX and the expander. The R134a systems have recover only 18% of work in the expander. The COP of the expander cycle

without IHX was 30–45% higher the conventional cycle and 10–12% higher than expander cycle with an IHX. Chen et al. [97] improved the refrigeration performance of trans-critical cycle by integrating with IHX using R744 as a working fluid. It was reported with 19.8% improvement in refrigeration capacity and 12.8% improvement in COP when compared to the conventional system without IHX.

Wang et al. [98] investigated the performance of a R744-based heat pump used in electrical vehicles at continental climatic conditions. Their results reported with a COP and heating capacity of 3.1 and 3.6 kW, respectively, at low ambient temperature of -20°C . The use of secondary loop has reduced the system COP by 19% compared to conventional heat pump. The COP was dropped to 1.7 when the air inlet and outlet air temperatures were maintained at 20 and 40°C , respectively, with -20°C ambient temperature. Further, the performance of a R744-based heat pump was tested using series gas coolers in electrical vehicles [99–101]. It was reported that the series gas coolers have improved the heating capacity and COP by 33% and 32% compared to the system using single gas cooler, respectively. At low ambient temperature of -20°C , the heat pump has attained the COP of 1.8 and heating capacity of 5.6 kW. The heating capacity was improved by 42% (4.2 kW to 6.4 kW) by increasing the depth from 32 mm to 128 mm. Peng et al. [102] numerically simulated the performance of a trans-critical heat pump using R744 as working fluid. It has been reported that the vapour injection trans-critical heat pump has 30.7–38.6% higher heating capacity than conventional trans-critical heat pump. The compressor discharge temperature of the vapour injection trans-critical heat pump was found to be lower when compared to conventional trans-critical heat pump. Similarly, the COP of R744 compression systems was improved by 30% using expanders and other refrigerants were improved by 10% [103].

The reported research investigations confirmed that R744 can be used as a possible refrigerant in new AAC systems with necessary precautions. The R744 has negligible environmental impact and improved heating performance, which can be used in automobile heat pumps operating under continental climates [104]. The R744 cannot be used as a drop-in substitute in the existing R134a systems due to mismatch in thermophysical and thermodynamic properties. Moreover, R744 has 20% higher green house gas emissions due to increased compressor power consumption compared to R134a. The overall performances of R744-based compression systems are lower than that of R134a due to its poor thermophysical properties. Hence, it is suggested to use R744 in heating systems used in electrical vehicles at low ambient temperatures to reduce the carbon dioxide emissions.

Composite mixtures

The composite mixtures provide flexibility in matching the thermophysical and thermodynamic properties of refrigerants with R134a and to improve the chemical properties and reducing the environmental impacts. Many research and developments have been made on composite mixtures composed of HFC, HFO, HC and carbon dioxide. The summary of reported investigations suitable for AAC systems is described in this section and the research highlights are given in Table 9.

Kiatsirirrot and Euakit [105] studied the performance of an AAC using ternary mixture composed of R22, R124 and R152a at different mass fractions. It was reported that the COP of the system was increased with increase in mass fraction of R22. The maximum COP was observed for the mixture having R22 mass fraction in the range between 0.2 and 0.3. In 2009, Ravikumar and Lal [106] investigated on

Table 9 Research highlights of composite alternatives for AAC systems

Authors [Ref.]	Refrigerant	Research highlights
Meng et al. [109]	R1234yf/R134a (0.89:0.11, by mass)	The flammability of R1234yf was reduced by adding 10% of R134a. The mixture has 4–9% and 4–16% lower COP than R134a in cooling and heating modes, respectively
Shin et al. [110]	R134a/R1234yf (0.7:0.3, by mass)	The COP and exergy destruction of the mixtures were dropped by 5.2% and 25.8%, respectively, with 21.8% improved exergy efficiency when compared R134a
Andrew and Mohanraj [114]	R430A	The R430A has 6–11% lower compressor power consumption, 12–20% higher COP with 2–6 $^{\circ}\text{C}$ higher compressor discharge temperature compared to R134a
Lee et al. [116]	R444	The COP, capacity and compressor discharge temperature of R1234yf/R134a mixture are similar to R134a. The addition of 10% of R134a has reduced the flammable risk of R1234yf
Yu et al. [125]	R744/R290 (0.6:0.4, by mass)	The COP was improved 29.4% compared to R744, which is R134a
Yu et al. [126]	R744/R41	The COPs were increased by 8% and 21% at 4000 rpm and 6000 rpm, respectively, with the increase in mass fraction of R41 from 0.5 to 1.0

road performance of an AAC working with R12 and the ternary mixture composed of R134a/R290/R600a (in the ratio of 0.91:0.04:0.05, by mass) as possible drop-in substitute. It was reported that the proposed refrigerant mixture has 25–33% higher refrigeration effect when compared to R12. The compressor discharge pressure was observed to be about 7% higher when compared to R12. The COP of the system was dropped by about 5–15% when compared to R12 due increased compressor power consumption. The proposed refrigerant mixture has 5% of low volatile component (R600a), which is miscible with mineral oil lubricant used in R12-based systems. The R600a takes back the lubricant to the compressor as expected [107]. However, the mixture composed of R134a/R290/R600a is zeotropic mixture with composition shift during leakage conditions.

Gill and Singh [108] investigated the performance of compression refrigeration cycle working with the mixture composed of R134a and LPG (in the ratio of 0.28:0.72, by mass). It was reported that the new proposed mixture has 15–17.8% higher COP and 1–6% lower pull-down time with lower compressor discharge temperature when compared to R134a. The R134a/LPG mixture is miscible with mineral oil. The flammable risk of LPG mixture was reduced by blending with R134a. Similarly, the performance of an AAC using R134a and the binary mixture composed of R1234yf and R134a (in the ratio of 0.89:0.11, by mass) as working fluids was investigated [109]. It was reported that the capacities of the proposed mixture in both heating and cooling modes are similar. The COP of the system working with the proposed mixture was reported to be lower by 4–9% and 4–16% in cooling and heating modes, respectively. The compressor discharge temperature was observed to be about 10 °C lower when compared to R134a in both the cooling and heating modes. The mixture becomes non-flammable by adding 11% of R134a in the mixture. The mixture has GWP less than 150. The mixture is compatible with all the components used for R134a systems. The GWP of R1234yf/R134a mixture is lower compared to R134a with low temperature glide. The addition of R134a with R1234yf has reduced the flammability risk of R1234yf. The critical pressure of R1234yf/R134a mixture was found to be lower when compared to R134a, which confirms low compressor discharge temperature. In a similar work, Shin et al. [110] investigated the thermodynamic performance of AAC systems working with R134a and the binary mixture composed of R134a and R1234yf (with mass fraction of 0.7:0.3). It was reported that the COP of the proposed mixture has 5.2% lower than R134a. The exergy destruction of AAC using R134a/R1234yf was reduced by 25.2% with 21.9% improved exergy efficiency when compared R134a. The exergy efficiency of the AAC systems using R134a and R134a/R1234yf mixture was dropped by 52.7% and 52.5%, respectively.

The composite binary mixture consisting of R152a and 600a (with the mass fraction of 0.76:0.24) was reported as a possible alternative to R134a. Park and Jung [111] tested the performance of a small capacity refrigeration system using R430A as drop-in substitute and compared with R134a. It was reported with 19% improved COP, and 13.4% reduced compressor power consumption compared to R134a. The compressor discharge temperature was found to slightly higher than R134a. Further, Mohanraj [112, 113] compared the performance of R134a and R430A in a small-capacity refrigeration system. The thermophysical and thermodynamic properties of R430A were found to be better than R134a. The presence of R600a in the mixture is miscible with both mineral oil and synthetic lubricants. Hence, lubricant change is not required for using R430A. The R430A has 2–4 °C higher compressor discharge temperature compared to R134a due to its higher critical pressure. Andrew and Mohanraj [114] investigated the performance of AAC systems using R134a and R430A as working fluids. It was reported that the R430A mixture has 6–11% lower compressor power consumption with 12–20% higher COP compared to R134a. The R430A mixture has higher compressor discharge temperature in the range of 2–6 °C compared to R134a. The presence of R600a in the mixture has significantly reduced the compressor discharge temperature compared to R152a. The R430A mixture has about 47%, 35% and 32% lower TEGWI for liquefied petroleum gas, petrol and diesel vehicles, respectively.

Schulze et al. [115] investigated the performance of R445A (composed of R1234ze, R134a and R744 with a mass fraction of 0.85:0.09:0.06) as an alternative to R134a in a bus air conditioning system. It was reported that the R445A has lower COP and cooling capacity compared to R134a. The cooling capacity and COP were improved by 5.5% and 12% by reducing the mass fraction of R744. In another work, Lee et al. [116] investigated the performance of R1234yf and three binary mixtures composed of R1234yf/R134a (with 5%, 10% and 15% mass fractions of R134a). It was reported that the COP, capacity and compressor discharge temperature of R1234yf/R134a mixture are similar to R134a. The main advantage of adding 10% (by mass) of R134a with R1234yf is to reduce the flammable risk of R1234yf. The mass-charge requirement of the proposed refrigerant mixture was reduced by about 10% when compared to R134a. Their results confirmed that R134a is an environment friendly alternative to phase out R134a in AAC systems without modifications.

The performances of a refrigeration system using R134a and R450A mixture (composed of R134a and R1234ze, in the ratio of 42:58, by mass) were investigated [117]. It was reported that R450A mixture has about 6% lower cooling capacity with 1% higher COP due to lower compressor power consumption. The compressor

discharge temperature was found to be about 2 K lower than R134a. Mendoza-Miranda et al. [118] compared the performance of a variable speed compression refrigeration system using R134a and its possible alternatives such as R1234yf, R1234ze and R450A. It was reported that the COP of using R1234yf, R1234ze and R450A was lower by 8–13%, 4–11% and 4–6% lower compared to R134a. The refrigerant mixture R450A was reported as good alternative to R134a due to its improved performance when compared to R1234yf and R1234ze. Similarly, the R450A was tested in a small capacity compression refrigeration system as a drop-in replacement to R134a [119]. It has been reported that the power consumption, cooling capacity and COP of R450A were lower than R134a by 7.2%, 9.9% and 2.9%, respectively. The lower refrigeration effect observed with R450A is due to lower latent heat compared to R134a. Similarly, the performance of a compression refrigeration system working with R450A as a drop-in substitute to R134a was investigated by Gill et al. [120]. The maximum exergy destructions for both the refrigerants were observed in the compressor and the least exergy destruction was observed in the evaporator. The exergy destruction in the system working with R450A was found to be lower by 15–27.5% with 10–131% higher exergy efficiency compared to R134a.

Makhnatch et al. [121] studied the performance of compression refrigeration cycle using R450A and R513A mixture (composed of R1234yf and R134a, in the ratio of 0.56:0.44, by mass) with negligible temperature glide as alternatives to R134a. The experiments were carried out in the evaporator temperature range between -10 and 15 °C and the condensing temperature range between 40 and 60 °C. The maximum compressor discharge temperature was reported as 98.6 , 93.1 and 88.4 °C for R134a, R450A and R513A, respectively. The refrigerant mass flow rate of R450A was reduced by about 9.2%, and the R513A mass flow rate was increased by 19.3%. The COP of R450A was found to be about 5.3% lower than R134a, and the COP of R513A was found to be similar to R134a for the considered range of operating conditions. Mota-Babiloni et al. [122] studied the performance of compression refrigeration cycle with R134a and R513A as working fluids. It was reported that the COP of compression refrigeration cycle using R513A was improved by 5% compared to R134a by turning the expansion valve. The R513A has lower compressor discharge temperature compared to R134a. Further, the exergy performance of a refrigeration system was investigated with R134a and R513A mixture as an alternative [123]. The performance was evaluated in the evaporator temperatures ranges from -15 to 5 °C with 30 and 35 °C condensing temperatures. It has been reported that R513A has 0.4% higher exergy efficiency than R134a. The maximum exergy destruction was reported in the compressor

followed by evaporator, condenser and expansion valve. Further, the performance of the refrigeration system working with R134a and R513A under the influence of IHX was investigated [124]. It was reported that the COPs of R513A and R134a were improved by 8% and 4%, respectively, with 2% reduced compressor power consumption. The cooling capacity of the system using R513A was improved by about 5.6% compared to R134a.

Yu et al. [125] studied the performance of an AAC using binary mixture composed of R744 and R290 with different mass fractions of R290 between 0 and 1. The R744/R290 composition was optimized to 0.6: 0.4 (by mass fraction). The COP of the optimum composition was improved by 29.4% when compared to system using pure R744, which is equal to R134a. The compressor discharge temperature was significantly reduced with increase in R290 mass fraction. Further, the possibility of using R744/R41 mixtures (with different mass fractions of R41) in an AAC was investigated [126]. It was reported that the heating and cooling COPs of the mixture were improved by 14.5% and 25.7%, respectively, when compared to R744 system. The refrigerant mass-charge was optimized to 0.8 and 1.0 kg in heating and cooling modes, respectively. The cooling capacities were reduced by 21.7% at 4000 rpm and 24.8% at 6000 rpm with the increase in mass fraction of R41 from 0 to 1.0. The compressor power consumption was increased by 31% at 4000 rpm and 59% at 6000 rpm with the increase in mass fraction of R41 from 0 to 1.0. The COPs were increased by 8% and 21% at 4000 rpm and 6000 rpm, respectively, with the increase in mass fraction of R41 from 0.5 to 1.0.

The composite mixtures have several advantages such as improved thermodynamic, thermophysical and chemical properties with reduced environment impacts. The miscibility issues of HFO and HFC refrigerants with mineral oil were improved by blending with hydrocarbon refrigerants. The performance assessments of R450A and R513A as possible replacements to R134a for AAC applications need further research. The flammable risk of HFO refrigerants was reduced by blending with R134a. Similarly, the compressor discharge temperature of R744 was reduced by blending with R290.

Nanorefrigerants and lubricants

The addition of nanoparticles with the base refrigerants or lubricants is called nanorefrigerant or nanolubricant, respectively [127–129]. The lubricants used in AAC compressors are: mineral oil (MO) and synthetic lubricants like polyalkylene glycol (PAG) and polyolester (POE) [130]. The synthetic lubricants PAG and POE are hygroscopic in nature. Hence, the compressors using synthetic lubricants are not exposed to atmosphere. The addition of nanoparticles with refrigerants has improved both boiling and condensation

characteristics of refrigerants, which reduces the size of evaporators and condensers, respectively [131–133]. The thermophysical properties of refrigerants are also improved significantly by addition of nanoparticles. Moreover, the refrigeration effect has been significantly improved with reduced compressor power consumption [134]. The refrigerant pressure drops have been increased due to increase in viscosity [135]. The nanoparticles have improved the interaction between the refrigerant and lubricant reduced the compressor wear rate in compressors [136]. The summaries of selected research investigations reported on nanorefrigerants and nanolubricants are presented in this section, and the research highlights are given in Table 10.

The thermophysical properties of R134a (such as thermal conductivity, dynamic viscosity and density) were improved by adding 5% (by volume) of aluminium oxide (Al_2O_3) with R134a [137]. The thermal conductivity of nanorefrigerant was improved by 28.58% with 13.68% improvement in dynamic viscosity and 11% improvement in density when compared to R134a. The thermal conductivity improvement has enhanced the system COP by 15%. Jwo et al. [138] experimented in a compression refrigeration cycle using Al_2O_3 nanoparticle (at 0.05%, 0.1% and 0.2%, by mass) with R290/R600a mixtures. It was reported that the system using nanorefrigerant with 0.1% (by mass) has 2.4% reduced compressor power consumption with 4.4% improved COP when compared to the system using R134a. However, the oxide-based nanoparticles have flammable risk during their usage with hydrocarbon refrigerants. Similarly, Redhwan et al. [139] investigated the performance of an AAC system using Al_2O_3 nanolubricant. The nanoparticle concentration was optimized to 0.010% (by volume). It was reported with 31%

improved COP, 26% reduced compressor power consumption, and 32% improved cooling capacity when compared to the conventional lubricant. Soliman et al. [140] experimentally studied the performance of a compression refrigeration cycle using R134a with two nanolubricants (mineral oil with 0.1% of Al_2O_3 and POE with 0.1% of Al_2O_3). It was reported that the system using POE with Al_2O_3 has 19.5% improved COP when compared to the mineral oil with Al_2O_3 . The addition of nanoparticles with the lubricant has reduced the energy consumption of the system by about 10% when compared to the system without addition of nanoparticles. Aminullah et al. [141] investigated the performance of an AAC using 0.010% of Al_2O_3 nanoparticle (by volume) with PAG lubricant. It was reported with 7.59% of energy savings compared to the conventional PAG lubricant with 33.39% of reduced wear rate when compared to the conventional PAG lubricant. Kedzierski [142] improved the boiling heat transfer coefficient of a refrigerant-lubricant mixture (composed of R134a and POE) by adding Al_2O_3 particle (by 0.5% mass fraction). The viscosity of nanolubricant is sharply increased for the concentrations more than 0.3% (by volume) [143]. It is suggested to use to Al_2O_3 nanoparticle with less than 0.3% (by volume) for AAC applications to reduce the irreversibility due to viscosity. Subhedar et al. [144] improved the performance of R134a-based compression refrigeration cycle using Al_2O_3 nanolubricant. It was reported that the COP of the system was improved by about 85% for 0.075% volume fraction of Al_2O_3 with 27% reduced compressor power consumption.

Bi et al. [145] improved the performance and reliability of the compressor by adding TiO_2 nanoparticles with mineral oil lubricant using R134a. It was reported that the system

Table 10 Research highlights on nanorefrigerants and nanolubricants

Authors [Ref.]	Nanorefrigerants/Nanolubricants	Research highlights
Mahbubul et al. [136]	Al_2O_3 /R134a	The COP was improved by 15%
Jwo et al. [137]	Al_2O_3 /R290/R600a	The COP was improved by 4.4%
Soliman et al. [139]	Al_2O_3 /POE; Al_2O_3 /MO	The COP was improved by 19.5%
Aminullah et al. [140]	Al_2O_3 /PAG	Energy saving of about 7.59% was observed
Bi et al. [144]	TiO_2 /R134a	Energy consumption was reduced by 26%
Bi et al. [145]	TiO_2 /R600a	Energy consumption was reduced by 9.6%
Gill et al. [147]	TiO_2 /LPG	The COP was improved by 3.2–18.1%
Sabareesh et al. [151]	TiO_2 /MO	The COP was improved by 3.6%
Kumar et al. [152]	ZnO/R152a	Power consumption was reduced by 21%
Kumar and Singh [153]	ZnO/R290/R600a	COP was improved by 45%
Sharif et al. [154]	SiO_2 /R134a/PAG	COP was improved by 21%
Tuomas and Isaksson [158]	Phosphate additives	To reduce the compressor wear
Wang et al. [159]	NiFe_2O_4 /R134a	To improve the miscibility of R134a with MO
Liu and Wang [160]	Fe_3O_4 /R134a	Heat transfer rate was improved by 21.23%
Kedzierski and Gong [161]	CuO/R134a	Boiling heat transfer was improved by 50–275%
Zawawi et al. [162, 163]	Al_2O_3 / SiO_2 /PAG	The COP was improved by 7.7%

has about 26% reduced energy consumption by adding 0.1% mass fraction of TiO_2 compared to the systems using conventional lubricants. Bi et al. [146] experimented in a compression refrigeration system using R600a with 0.5 g L^{-1} of TiO_2 nanoparticle (by volume) and reported with 9.6% lower energy consumption when compared to pure R600a. The irreversibility in refrigeration cycles has been reduced significantly by adding TiO_2 nanoparticles [147]. Gill et al. [148] experimented in a compression refrigeration cycle using LPG with TiO_2 (with an optimal concentration of nanoparticle is 0.4 g L^{-1})-based nanolubricant as a possible replacement to R134a. It was reported that the compressor power consumption was reduced by 3.2–18.1% with reduced compressor discharge temperature. The COP of the system was improved by 3.2–18.1%. Gill et al. [149] improved the performance of a compression refrigeration cycle using R600a by adding TiO_2 nanoparticle (with three different volume concentrations such as 0.2, 0.4 and 0.6 g L^{-1}). The volume concentration of nanoparticle was optimized to 0.2 g L^{-1} . It was reported that the power consumption was reduced by 33.33% with 21% reduced pull-down duration compared to the conventional system using LPG as refrigerant. Bobbo et al. [150] reported that TiO_2 with POE nanolubricants has good tribological behaviour (with minimum wear rate) in R134a-based compressors. Similarly, Adelekan et al. [151] improved the performance of a compression-based refrigeration system using LPG refrigerant with TiO_2 nanolubricant. It was reported that the TiO_2 nanolubricant has improved cooling capacity and COP with reduced compressor power consumption. Moreover, the compressor discharge temperature of the system using nanolubricant was observed to be lower when compared the system using conventional lubricant. Sabareesh et al. [152] experimentally investigated the performance of compression refrigeration cycle by adding TiO_2 nanoparticles with mineral oil and reported 17% improvement in COP and 3.6% improved heat transfer rate.

Kumar et al. [153] improved the performance of compression refrigeration cycle using R152a/ZnO nanorefrigerant. It was reported that the COP of system was significantly improved with 21% reduced compressor power consumption, 10.5% reduced suction pressure and 6% reduction in evaporator operating temperature for the nanoparticle concentration of 0.5% (by volume fraction) with refrigerant. Kumar and Singh [154] investigated the performance of a compression refrigeration cycle using R290/R600a refrigerant mixture with ZnO nanoparticle. It was reported with 45% improved COP when compared to the base refrigerant with 7.48% reduced compressor energy expenditure. The suction and discharge pressures were reduced by 17% and 21%, respectively.

Sharif et al. [155] experimented in an AAC using R134a/ SiO_2 /PAG nanorefrigerant. It was reported with the maximum COP at 0.05% (by volume) at all the compressor

speeds. The maximum and average COP enhancements were observed to be about 24% and 10.5%, respectively. Sharif et al. [156] investigated the performance of AAC using 0.05% of SiO_2 nanoparticle with PAG lubricant oil (by volume). The condenser pressure was reduced by 10.8% with 5.6% reduction in compressor pressure ratio. The COP was improved by 21% with 16.5% reduced compressor work. Redhwan et al. [157] reported that 0.07% of SiO_2 nanoparticle with PAG lubricant has significant reduction in compressor power consumption with significant improvement in COP. Redhwan [158] recommended to use Al_2O_3 and SiO_2 nanolubricant with less than 0.3% and 1% volume concentrations, respectively with PAG lubricant to improve the performance of AAC.

Tuomas and Isaksson [159] reported that phosphate additives with lubricants were used in the compressors and improved the lubricant film and reduced the compressor wear. The miscibility of mineral oil with HFC refrigerants has been improved by adding nanoparticles. The NiFe_2O_4 nanoparticles have been added with the mineral oil to improve the miscibility of R134a with mineral oil [160]. It is also observed that the energy efficiency ratio of refrigeration to air conditioning system have been improved by 6% using nanolubricant instead of synthetic lubricants. Liu and Wang [161] studied the performance of R134a-based compression refrigeration cycle using Fe_3O_4 nanoparticle. It was reported that the heat transfer rate was improved by 21.23% with 8.6% improved efficiency. Kedzierski and Gong [162] reported that the boiling heat transfer performance of nanorefrigerants (composed of 99.5% of R134a with 0.5% of POE/CuO nanolubricant, by mass) was improved in the range between 50% and 275% when compared to the conventional R134a/POE lubricant.

Zawawi et al. [163, 164] experimentally studied the thermophysical properties and stability of Al_2O_3 - SiO_2 /PAG nanolubricants with different nanoparticle concentrations using compressors of refrigeration and air conditioning systems. Thermal conductivity and dynamic viscosity of nanolubricants were improved by 2.41% and 9.34%, respectively. It was reported that the hybrid nanoparticles composed of Al_2O_3 and SiO_2 (with 60:40, by mass) with 0.1% volume fraction with PAG lubricants are recommended. The refrigeration capacity and COP were improved by about 60% and 7.7%, respectively, when compared to the base lubricant [165]. The compressor power consumption was reduced by 9.35% with 155 grams of refrigerant mass charge at the compressor speed of 2100 rpm. The thermal conductivity of the nanolubricant was increased with the increase in concentration of nanoparticles. Similarly, Yilmaz [166] investigated the performance of a R134a-based compression refrigeration cycle using two POE-based nanolubricants (with CuO and Cu/Ag alloy nanoparticles). It was reported that the CuO and Cu/Ag nanoparticles (with 0.5% volume) have 14.55%

and 20.88% COP improvements, respectively. The friction coefficient was reduced by 9.9% and 5.5% using CuO and Cu/Ag nanolubricants, respectively.

The use of nanorefrigerants and nanolubricants in compression refrigeration cycles has significantly reduced the compressor power consumption of with improved refrigeration effect and COP. The nanolubricants have improved tribology characteristics (reduced friction and wear rate) with improved refrigerant–lubricant interaction. Moreover, the heat transfer coefficients in condensers and evaporators have been significantly improved. The nanorefrigerants and nanolubricants have more pressure drop when compared to the base fluid. The addition of nanoparticles has increased the pressure drop in evaporator, which may drop the compressor volumetric efficiency. Moreover, the use of oxide-based nanoparticles should be avoided with A3 refrigerants.

Limitations and further research needs

The limitations and further research needs in the field of environment friendly refrigerant options for AAC systems are as follows:

- (i) The regional standards for the use of flammable refrigerants in an AAC are not established. Further research is required to explore the safety standards.
- (ii) The zeotropic mixtures are not preferred for AAC systems due to composition shift during leakage conditions [167]. Further researches on pure fluids, azeotropic mixtures and near azeotropic mixtures with minimum temperature glide are preferred for AAC systems.
- (iii) The temperature of glide of zeotropic hydrocarbon mixtures has affecting the performance of an AAC working at high ambient temperatures [168]. Hence, further research is essential to develop refrigerant mixtures with low temperature glide.
- (iv) The compatibility of environment friendly refrigerants with lubricants used in AACs needs further research [169]. The reliability of compressors using new refrigerants needs further study.
- (v) The micro-channel heat exchangers are having volume and mass reductions by 15–17% and 2.8–14.9%, respectively, compared to conventional heat exchangers. Hence, further research attention on using micro-channel heat exchangers is essential to reduce the refrigerant inventory [170].
- (vi) The charge requirements of new refrigerants are not standardized. Hence, further research on optimization of refrigerant charge is required.
- (vii) The development of R744 based AAC systems is uncertain due to continuous improvements in design.

Further research is essential to standardize the system configurations.

- (viii) The use of expanders in R744-based AAC systems needs further research to improve the energy efficiency [171].
- (ix) The use of ejectors in compression refrigeration cycle has improved the performance [172]. Further research is required to explore the possibility of using ejectors in AAC systems.
- (x) Life cycle climatic analysis of an AAC using environment friendly alternatives needs further research.
- (xi) The performance of an AAC using new refrigerant mixtures under the influence of flash gas bypass needs further study [173].
- (xii) Further research on use newly developed R134a alternatives is required.
- (xiii) The commercialization aspects of nanorefrigerants and nanolubricants for AAC.
- (xiv) The reliability of compressors using nanorefrigerant and nanolubricants.
- (xv) Thermophysical characteristics of refrigerants at different volume fraction of nanoparticles.
- (xvi) The use of oxide-based nanoparticles with hydrocarbon refrigerants has flammable risk. Hence, it is suggested to use metallic nanoparticles with flammable refrigerants.

Conclusions

Many research and development investigations have been reported on environment friendly refrigerant options for AACs. The summaries of reported investigations on environment friendly refrigerant options (with low GWP) were reviewed. The performances of about twenty environment friendly options for AACs were reported. The review of investigations confirmed that the HFO refrigerants are identified as interim options for replacing R134a in the existing systems to extend its life. The HFO refrigerants will not sustain due to the formation of TFA, which will affect the aquatic systems. The R744 was reported as another environment friendly option. But, the operating pressure of R744 is significantly high, which increases the compressor power consumption. As a result, the TEGWI of an AAC using R744 is significantly higher than using R134a. Moreover, R744 is not suitable for high ambient temperatures due to its lower critical temperature. Hence, R744 is recommended for heating applications in electrical vehicles operating at low ambient temperatures. The pure hydrocarbon refrigerants are not possible to use as drop-in substitutes for R134a systems due to mismatch in operating pressures and volumetric cooling capacity. Hence, the hydrocarbon refrigerant mixtures are preferred for R134a systems. However, the hydrocarbon

refrigerant mixtures with high temperature glide are not suitable for the AAC working at high ambient temperatures. Moreover, the R290/R600a mixtures are having zeotropic behaviour, which results in composition shift during leakage conditions. The use of nanorefrigerants is getting research attention in AAC. The use of metallic oxide nanoparticles with A3 refrigerants should be avoided to reduce to the flammability risk. The commercialization of nanorefrigerants in AAC needs further research attention. The R290 is identified as a sustainable refrigerant option for the new AAC systems due to its negligible GWP and material compatibility. Further research extensions are required to explore the safety standards for the use of hydrocarbon refrigerants in AAC systems. The secondary loop systems are required for the use of R290. The phasing out of R134a with environment friendly refrigerants plays the major role in reducing the environmental impacts caused by AAC systems. The information presented in this paper is more beneficial to the researchers and manufactures working in the field of automobile air conditioners.

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