Chapter 15
Low GWP Refrigerants for Energy Conservation and Environmental Sustainability

Kutub Uddin, Bidyut Baran Saha, Kyaw Thu and Shigeru Koyama

Abstract Refrigerant significantly influences the performance of air-conditioning and refrigeration system as well as it has some environmental issues that need to be considered before selection. These systems can be made eco-friendly, if it is powered by solar energy or low-grade thermal energy and they use environment-friendly refrigerants. In this chapter, low GWP (global warming potential) refrigerants have been explored for the domestic air-conditioning applications. Refrigerants with high GWP are mostly used in environment control applications such as heating, ventilation, air-conditioning (HVAC), and refrigeration systems. Some refrigerants contribute to significant environmental issues and the Montreal Protocol and Kyoto Protocol have been signed to address the threats of ozone layer depletion and global warming potential. To fulfil the commitments of Kyoto Protocol, meanwhile, governments in many countries instituted phase-out plan for the use of environmentally harmful gasses in heat pump systems. For instance, EU MAC Directives, F-gas regulation, and Japan METI directives, which clearly declared their target year to use new refrigerant of GWP below 150 for mobile air conditioner and GWP below 750 for the residential air conditioner. Research interest has been stimulated to find alternative refrigerants with low or

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K. Uddin · B. B. Saha (✉) · K. Thu
International Institute for Carbon-Neutral Energy Research (WPI-I2CNER),
Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
e-mail: saha.baran.bidyut.213@m.kyushu-u.ac.jp

K. Uddin
Faculty of Physics, Jagannath University, Dhaka 1100, Bangladesh

B. B. Saha · K. Thu
Kyushu University Program for Leading Graduate School, Green Asia Education
Center Interdisciplinary Graduate School of Engineering Sciences, Kyushu University,
Kasuga-Koen 6-1, Kasuga-Shi, Fukuoka 816-8580, Japan

B. B. Saha
Mechanical Engineering Department, Kyushu University, 744 Motooka, Nishi-ku,
Fukuoka 819-0395, Japan

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ultra-low GWP for energy conservation and environmental sustainability. Hydrofluoroolefins (HFOs) have a very low environmental impact, and thus HFOs are considering as potential candidates to replace the hydrofluorocarbon (HFC) refrigerants such as R410A, a near-azeotropic mixture of difluoromethane (R-32) and pentafluoroethane (R-125) and is commonly used refrigerant in air-conditioning applications. The limited number of pure fluids sometimes cannot meet the excellent heat transfer criteria due to their low volumetric capacity and moderate flammability or toxicity. Mixing of HFOs and HFCs refrigerants, in this case, allows the adjustment of the most desirable properties of the refrigerant by varying the molar fraction of the components. Different combination of mixture presented here cannot be claimed as the best mixture, but it might be a good choice for further study. This chapter focuses on the research trend in finding low GWP refrigerants and its application in different heat pump system considering the system performance, safety, and the overall environmental impact. The conventional vapor compression system, thermally driven adsorption system, and sorption-compression hybrid system have been taken into consideration.

Keywords Global warming potential · Hydrofluoro-olefins (HFOs)
Refrigerant blend · Temperature glide · Volumetric capacity

15.1 Introduction

The air-conditioning and refrigeration system are widely used in a domestic and industrial application for providing thermal comfort and storage facilities (Calm and Didion 1998). According to the Japan Refrigeration and Air Conditioning Industry Association (JRAIA), the demand for room air conditioners (RAC) is estimated to reach 88.81 million units in 2016 which is 2.9% higher than the previous year. Figure 15.1 presents the huge demand of RAC and in a country or region which reflect the significance of environmental concern in this sector in terms of greenhouse gas emission and electrical energy consumption.

Refrigerants as heat carrier substance significantly influence the performance of the RAC and refrigeration systems. Thermophysical properties of such refrigerants are crucial in designing such a system. Additionally, flammability, toxicity, and environmental friendliness are equally important. From the beginning of commercial production of the system, most of the popular refrigerants such as CFCs and HCFCs possess show excellent system performance. These refrigerants are not flammable and toxic but possess higher ODP and GWP characteristics. Following the Montreal Protocol (1987), a gradual phase-out of refrigerants that deplete the ozone layer has been implemented and are substituted with more environment-friendly refrigerants which have almost zero ODP (UNEP 2016; Benhadid-Dib and Benzaoui 2012). The air-conditioning and refrigeration industry have taken many initiatives after signing the Montreal Protocol to overcome challenges in developing suitable refrigerants to replace the popular CFCs and

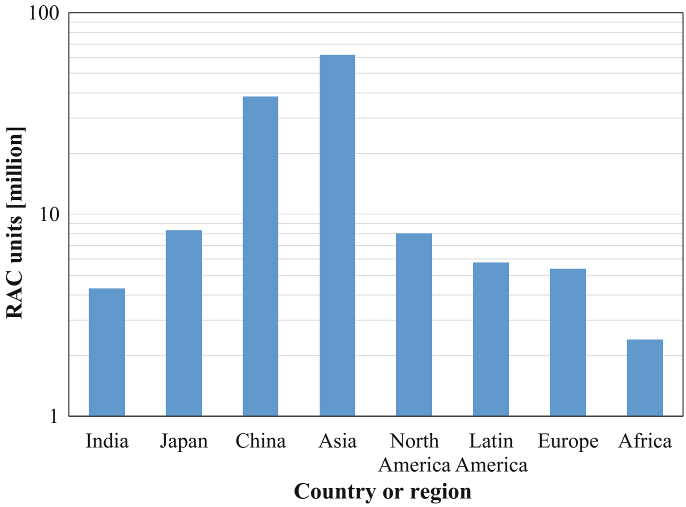

Fig. 15.1 World room air-conditioning demand (RAC) in 2016 (JRAIA 2017)

HCFCs refrigerants (Calm and Didion 1998; McMullan 2002). Remarkably, the CFCs phase-out has been accomplished in 1996 in the developed countries whilst the targeted deadline for the developing countries is the year 2010 whereas HCFCs phase-out will be accomplished in 2030 or earlier (Powell 2002). Today, most acceptable choice of refrigerants as an alternative to the ozone-depleting refrigerants (CFCs and HCFCs), includes R410A, R134a, R407C, etc., particularly, for residential and automobile air-conditioning systems.

However, the global warming potential (GWP) of these refrigerants are considered very high. For example, hydrofluorocarbon refrigerant R134a and R410A have zero ODP but their GWP values are 1300 and 1900, respectively (Cabello et al. 2015; Xu et al. 2013). Refrigerant R410A has good thermal and transport properties with high volumetric capacity for air-conditioning applications, but it has an unfavorable effect on the environment in case of leakage that might be resulted during maintenance and unavoidable wear and tear. The Kyoto Protocol in 1997 (COP3-1997) (Parties to the Protocol 1998) commits the state parties will reduce the greenhouse gas emission to the atmosphere at least 5% below 1990 levels in the first commitment period, i.e., from 2008 to 2012. In the second commitment period, from 2013 to 2020 (agreed in 2012, known as Doha Amendment to the protocol), 37 countries including the European Union agreed to reduce 18% greenhouse gas emission. According to the European Environment Agency report (2016), the emission of F-gas, which includes HFCs, PFCs, and SF6, will be reduced by two-thirds of its 2014 value by 2030. In the USA, the Montreal Protocol is amended and now is implementing as the Clean Air Act via the US Environment Protection Agency (EPA). The EPA (1990) decided to limit the use of R134a in a newly manufactured light-duty vehicle from the model year 2021 and HVAC units using

HCFC-22 can continue to be serviced until 2020. After the model year 2025, R134a will not be accepted in MVAC system although its production will continue for servicing older vehicles contain R134a. The Australian government has imposed 50 $/kg carbon tax for R410A (Pham and Rajendran 2012).

Finding low GWP refrigerants with excellent energy efficiency has become an urgent task of the present generation whilst the total climate impact associated with refrigerants consists of direct and indirect contributions. Realizing the long-term environmental commitments and to comply with global regulations, the auto industry began to look for new, low GWP air conditioner refrigerants in approximately 2011. There are a number of refrigerants available which have a low environmental impact but not suitable to replace the existing halogenated refrigerants. The phase-out plan of high GWP refrigerants used in domestic and automobile application is listed in Table 15.1.

This chapter will focus both the pure and blend refrigerants which have ultra-low and low GWP but system performance equivalent or better to the existing refrigerant in domestic and automobile air-conditioning application. According to the taxonomy of RTOC 2014 Assessment Report (UNEP 2016), the 100 year GWP levels are classified in five levels which is shown in Table 15.2.

Table 15.1 Target GWP value for designated product and year of implementation (European Environment Agency 2016; EPA 1990; Pham and Rajendran 2012; Meno 2015; Fukushima and Hashimoto 2015)

	Designated products	Current Refrigerant and GWP_{100} (IPCC5)		Targeted GWP	Year of implementation
Japan	Room air-conditioning	R410A R32	1900 675	750	2018
	Mobile air-conditioning	R134a	1300	150	2023
USA	Mobile air-conditioning	R12 R134a	10900 1300		2021
	Residential air-conditioning/ refrigerator	R22 R410A R134a R407C	1760 1900 1300 1600		2020 NA 2025 NA
EU	Mobile air-conditioning	R134a	1300	150	2017
	Room air-conditioning			750	2021
Canada	Domestic refrigeration			150	2025
	AC-chillers			700	2025

Table 15.2 Classification of 100 year GWP levels (UNEP 2016)

100 year GWP	Classification
<30	Ultra-low or negligible
<100	Very low
<300	Low
300–1000	Medium
>1000	High

15.2 Refrigerant Selection

Currently, the widely used refrigerant in the domestic air-conditioning system is R410A which has no ODP but higher GWP. Alternative refrigerant with low GWP is desirable to fulfil the directive of Kyoto Protocol and some countries local guideline. Low GWP refrigerant mixture is being studied by many authors around the world considering the system performance, flammability, and toxicity. The refrigerants R32, R1234yf, R1234ze(E), R744, R152a, and hydrocarbon (HC) possesses very low GWP and within safety limit. Sometime refrigerant blend is found suitable to replace the widely used R410A. Blend is usually a mixture of two or more refrigerants. Some characteristics features of the pure refrigerants are furnished in Table 15.3. Along with the GWP and safety limit, the volumetric capacity and cycle performance are equally important. For blend, the temperature glide needs to be under consideration.

15.2.1 Global Warming Effect

GWP_{100} is measured by the amount of heat traps in a refrigerant compared to the heat trap by the same mass of CO_2 over 100-year horizon. A clear definition of GWP calculation is to be found in the IPCC’s 2001 Third Assessment Report. The widely used refrigerants in domestic and automobile applications are R410A and R134a, have the GWP of 1900 and 1300, respectively. After Kyoto Protocol, research interest on low GWP refrigerant intensified. Initially, HFCs and HFOs are put into the domain. But in most of the cases, single component low GWP cannot meet the requirements to drop-in replacement of R410A. Now refrigerant blend is considering as an alternative refrigerant. Blend are formed by mixing two or more single component refrigerants, the GWP of a refrigerant mixture is calculated as the mass weighted average of GWPs of individual components in the mixture. To respond the international guideline, refrigeration industry is looking for ultra-low GWP refrigerant either pure or blend. The GWP value of the mixture can be adjusted varying the composition of constituents in a mixture. Table 15.4 lists the most widely used refrigerants with respective ODP and GWP in the residential and automobile applications.

Table 15.3 Main characteristics of some individual refrigerants (Fukushima and Hashimoto 2015; Lemmon et al. 2013; Higashi and Akasaka 2016; Takizawa et al. 2009)

Refrigerant name	R32	R1234yf	R1234ze	R1123	R744	R152a	R134a	R410A
Molar mass (kg/kmol)	52.02	114.04	114.04	82.03	44.01	66.05	102.03	72.59
Normal boiling point (°C)	−51.7	−29.5	−19.0	−59.1	−78.5	−24.02	−26.07	−51.5
Critical temperature (°C)	78.2	94.7	109.37	58.55	30	113.26	101.06	71.34
Critical pressure (MPa)	5.78	3.38	3.64	4.55	7.38	4.52	4.06	4.9
GWP (UNEP 2016)	677	<1	<1	<1	1	138	1300	1900
Atmospheric lifetime	4.9 yr	11 d	18 d	1.6 d	–		14.6 yr	17 yr
Flammability range (vol%)	13.3–29.3	6.2–12.3	7.0–9.5	10.4–29.3	–			None
Burning velocity (cm/s)	6.7	1.5		7				–
Safety class (ASHRAE classification)	A2L	A2L	A2L	–	A1	A2	A1	A1

GWP values taken from the IPCC AR5 report (IPCC 2014)

Following the number of components in the blend the GWP can be calculated as:

$$
\begin{aligned}
\text{GWP of Blend} = {} & \text{Proportion by \% mass of component A} \times \text{GWP of A} \\
& + \text{Proportion by \% mass of component B} \times \text{GWP of B} \\
& + \text{Proportion by \% mass of component C} \times \text{GWP of C}
\end{aligned}
$$

15.2.2 Volumetric Capacity

Volumetric capacity is defined by the cooling capacity per unit of vapor volume at the exit of evaporator. It is calculated by the product of evaporation enthalpy (Δh_{eva}) and vapor density at evaporator outlet (ρ_v). A refrigerant with high volumetric capacity gives high cooling capacity for a given swept volume in compressor (Granryd 2001). Generally, low GWP HFOs have found low volumetric capacity also compared to HFCs. By mixing HFOs with higher volumetric HFCs can solve the problem of low volumetric capacity. So the mixture of high GWP HFCs with low GWP HFOs increases the volumetric capacity but it reduces the GWP. Table 15.5 shows the volumetric capacity of some pure refrigerant at a temperature −3 °C.

Table 15.4 Most widely used refrigerants with respective ODP and GWP

	Mostly used refrigerant in the system	Mostly adopting regions	ODP	GWP_{100} (IPCC5)	Comments
Residential air-conditioning	R22 (Park et al. 2007; Chen and Yu 2008; Park et al. 2008; Park et al. 2009; Park et al. 2009; Joudi and Al-Amir 2014; Devotta et al. 2001) [retrofitting R22 are R134a (GWP-1300), R407C (GWP-1600), R407A (GWP-1900) and R404A (GWP-3900)]	Developing countries	0.034	1760	Will be banned on January 1, 2020
	R410A (Yun et al. 2006; Mota-Babiloni et al. 2017; Spatz et al. 2004)	Developed countries	0	1900	
	R32 (n.d.)		0	677	DAIKIN Tec. introduced
Automobile air-conditioning	R134a (Brown et al. 2002; Vaghela 2017; Minjares 2011)	Developed and developing	0	1300	Replacing R12 and will be banned very soon (Tiwari and Gupta 2011)
	R1234yf (Sciance 2013; Navarro-Esbrí et al. 2013; Zilio et al. 2011)	Developed country	0	<1	

GWP_{100} (IPCC5)-values are taken from the IPCC AR5 report (IPCC 2014) for pure fluids; for mixtures, values are calculated based on the values for pure fluids

Volumetric capacity,

$$VC = h_{\text{eva}} + \rho_v \tag{15.1}$$

15.2.3 Flammability and Toxicity

Most potential refrigerant having lower GWP and toxicity possess higher flammability, which is a problem to replace HCFC refrigerants. A special security arrangement is required to make the system when flammable refrigerant is used. The LFL and UFL (lower and upper flammable limit) range the basic combustion

Table 15.5 Volumetric capacity of some widely known refrigerant at −3 °C

Refrigerant	R32	R1234yf	R1234ze	R1123	R744	R152	R134a	R410A	Propane
Volumetric capacity (MJ/m^3)	5.17	1.94	1.49	5.34	12.34	2.34	2.61	4.78	3.59

Table 15.6 The flammability limit and burning velocity of the refrigerants

Property	R1234yf	R1234ze (E)	R32	Propane (R-290)	R152a	Ammonia (R717)	Ethanol	Gasoline
Lower flammable limit (vol% air)	6.2	7	14.4	2.2	3.9	15	3.3	1.4
Upper flammable limit (% vol. air)	12.3	9.5	29.3	10	16.9	28	19	7.6
Minimum ignition energy (mJ)	>5000, $<1\times10^4$	61,000–64,000	>30, <100	0.25	0.38	100–300	0.65	0.29
Heat of combustion (kJ/g)	10.7	–	9.4	46.3	16.5	18.6	29.8	47
Burning velocity (cm/s)	1.5	–	6.7	46	23	7.2	58	34
Safety class (ISO 817 and ASHRAE 34)	A2L	A2L	A2L	A3	A2	B2L	A3	A3

A—lower chronic toxicity, have an occupation exposure limit of 400 ppm or greater
B—higher chronic toxicity, have an occupation exposure limit of less than 400 ppm
2L—lower flammability, burning velocity not higher than 10 cm/s, the energy of combustion below 19 MJ/kg and not flammable below 3.5% volume concentration

characteristics of flammable refrigerants. ASHRAE (American Society of Heating, Refrigeration and air conditioning) updated two standards, NSI/ASHRAE standard 15 Safety Standard for Refrigeration Systems and standard 34 Designation and Safety Classification of Refrigerants. In the latest version, classification “2L” was added to highlight the lower flammability refrigerants with a maximum burning velocity <10 cm/s which benefit the promotion of HFOs and R32 (Yang and Wu 2013). The burning velocity and safety group of some refrigerants are presented in Table 15.6.

15.2.4 Refrigerant Mixture

To use pure refrigerant in a system is always easy because of its azeotropic nature and the available thermophysical properties. Nowadays, HFO refrigerants get attention due to its suitable properties like extremely low GWP, lower toxicity, and moderate flammability (A2L). But some researcher reported that pure HFOs are not

Table 15.7 Currently used popular blend refrigerants (UNEP 2016)

Refrigerant designation	Refrigerant composition (mass %)	Molecular weight	Boiling point (bubble/dew)	Safety class	ODP	GWP_{100}
R404	R125/143a/134a (44/52/4)	97.6	−46.6/−45.8	A1	0	3900
R407A	R-32/125/134a (20/40/40)	90.1	−45.2/−38.7	A1	0	1900
R407C	R32/125/134a (23/25/52)	86.2	−43.8/−36.7	A1	0	1600
R407F	R32/125/134a (30/30/40)	82.1	−46.1/−39.7	A1	0	1700
R410A	R32/125 (50/50)	72.6	−51.6/−51.5	A1	0	1900
R507A	R125/143a (50/50)	98.9	−47.1/−47.1	A1	0	4000

Safety classification follows ANSI/ASHRAE Standard 34-2010
GWP values are calculated based on the values of pure refrigerant from IPCC AR5 report (IPCC 2014)

good choice as an alternative of R410A in residential scale air-conditioning due to their low vapor pressure (Kojima et al. 2015; Barve and Cremaschi 2012; Koyama et al. 2011). The improvement of overall system performance is achieved by many researchers when added with HFC or natural refrigerant (Han et al. 2007; Mota-Babiloni et al. 2015; Maczek et al. 1997; Wu et al. 2009). Refrigerant mixture can solve the problem of very limited number of fluids which have suitable properties. But there is a chance to alter the other properties of mixture. There are three categories of mixtures which can be used as working fluids: azeotropes, near-azeotropes, and non-azeotropes. This chapter highlighted some important parameters of binary and ternary mixture which need to be considered during mixture formation such as temperature glide, volumetric capacity, GWP, and cycle performance. In this chapter, few new mixture properties are presented keeping in mind the performance of widely used R410A (Table 15.7).

15.2.5 Temperature Glide

During the evaporation process, refrigerant begins to boil at a saturated liquid temperature, called bubble point, and ended with saturated vapor pressure, called dew point. At constant pressure, the difference between dew point and bubble point is called temperature glide. Pure refrigerant boils and condenses at a constant temperature so it has no gliding temperature. A mixture of two or more different fluids is classified as azeotropes and has long been used in the refrigeration industry; this refrigerant behaves like a pure refrigerant so it has no gliding temperature. The boiling point and condensation point curves unite at a point at which vapor and liquid have the same concentration. Near-azeotropes have a much greater

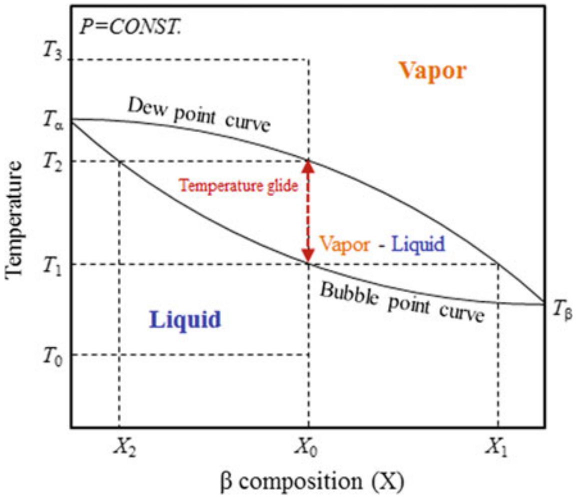

Fig. 15.2 Phase equilibrium diagram of zeotropic mixtures with the state points of the vapor compression cycle superimposed

potential for drop-in alternatives to HFCs (Morrison and McLinden 1993). The temperature change during evaporation and condensation is negligible (1–2 K) for near-azeotropic mixture. Non-azeotropic (zeotropic) mixtures have a separate curve for bubble point and dew point over the full concentration range. During the evaporation, a more volatile component of the mixture starts to boil first where less volatile component boils at last, so there is a concentration change with temperature, that creates temperature glide (3–20 K). Sometime leakage may alter their composition and properties so as to T_{glide}. At composition X_0 in Fig. 15.2, the refrigerant begins to boil at T_1 and ended at T_2 ($T_{\text{glide}} = T_2 - T_1$), the temperature varies because the evaporating liquid continuously changing its composition and thus the boiling point.

Temperature glide

$$\Delta T_{\text{glide}} = T_{\text{dew}} - T_{\text{bulb}} \tag{15.2}$$

15.2.6 Cycle Performance

The cycle performance of the refrigerant is very important and can be calculated theoretically and experimentally. The coefficient of performance (COP) can be evaluated theoretically employing thermophysical properties of refrigerant from REFPROP database which contain so many refrigerants. Considering the application area, cycle simulation requires operating condition for the system. As the mixture shows temperature glide during evaporation and condensation, so pressure selection for simple calculation is difficult. Sometimes average values for temperature are considered for evaporation and condensation in the simulation process.

Table 15.8 Parameter considered for cycle performance calculation

Condensation temperature (average)	30 °C
Evaporation temperature (average)	−3 °C
Degree of subcool	0 °C
Degree of superheat	3 °C
Adiabatic compression efficiency	0.85
Thermophysical properties	REFPROP V9.1

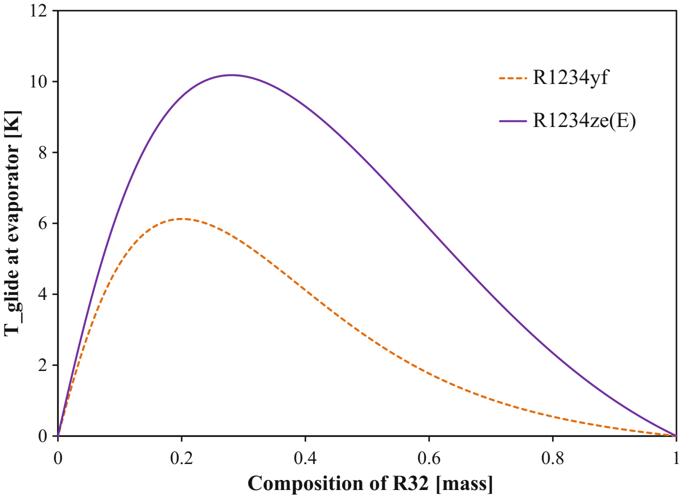

Fig. 15.3 Temperature glide of two binary mixtures R32/R1234ze and R32/R1234yf

In this chapter, mixture performance are shown using constant operating parameters which are shown in Table 15.8. The following equations can be used where suffix 1, 2, 2a, 3, and 4 are picked from Fig. 15.3.

Coefficient of Performance (COP) for heating of an ideal cycle is presented in Eq. 15.3.

$$COP_\mathrm{h} = \frac{h_{2a} - h_3}{h_{2a} - h_1} \tag{15.3}$$

where

$$h_{2a} = \frac{h_2 - h_1}{0.85} + h_1 \tag{15.4}$$

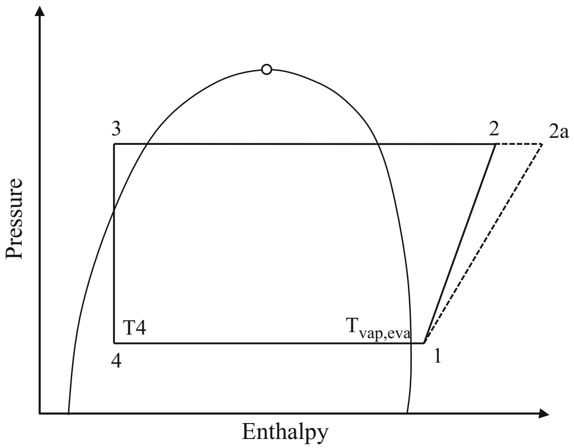

Fig. 15.4 Basic thermodynamic cycle

For refrigeration or cooling COP,

$$\mathrm{COP_r} = \frac{h_1 - h_4}{h_{2a} - h_1} \tag{15.5}$$

Volumetric capacity during evaporation can be calculated as

$$\mathrm{VC_{eva}} = (h_1 - h_4) \times \rho_1 \tag{15.6}$$

Temperature glide at evaporator can be calculated as shown in Eq. 15.7, where the temperatures are shown in Fig. 15.4. Basic thermodynamic cycle.

$$T_{\mathrm{glide\_eva}(T_4)} = T_{\mathrm{vap,eva}} - T_4 \tag{15.7}$$

15.3 Low GWP Refrigerants

There is an urgent need to find a low GWP refrigerant to develop sustainable technologies. The current single component low GWP refrigerant may increase energy consumption, introduce safety risk and sometimes require significant system modification. Refrigerant blend can be an effective alternative to achieve sustainable building technology reducing energy consumption and greenhouse gas emissions by 50% compared to the current best refrigerants. This section discusses the ongoing research activities about some pure and blend refrigerants which are considered as a promising alternative.

15.3.1 Pure Refrigerants

15.3.1.1 R1234yf

The R1234yf (CF3CF = CH2) is a refrigerant of GWP < 1. It is low in toxicity and mildly flammable (A2L) (Minor et al. 2010; Honeywell Technical Bulletin 2012). It has no ODP but has excellent life cycle climate performance (LCCP) compared to R134a and R744 (Spatz and Minor 2008). The critical temperature and critical pressure of the refrigerant are 94.7 °C and 3.38 MPa, respectively (Tanaka and Higashi 2010; Akasaka et al. 2010; Lai et al. 2011). In 2007, the SAE International launched CRP 1234 program to investigate the safety and performance of HFO 1234yf for the use in mobile air-conditioning. It has got attention as a prospective alternative candidate of R134a, the mostly used refrigerant in automobiles (Spatz and Minor 2008; SAE-CRP 1234 2009; Lee and Jung 2012) though the performance of R11234yf is slightly lower than R134a (Navarro-Esbrí et al. 2013; Zilio et al. 2011; Qi 2015). General Motors started using R1234yf for vehicles in 2012 (Sciance 2013). However, when this refrigerant is used as an alternative to R410A, it shows lower coefficient of performance (COP) and also it requires larger unit bodies related to R410A (Barve and Cremaschi 2012; Fukuda et al. 2016). Figure 15.5 shows that thermodynamic cycle of R1234yf positioned much lower than R410A. The volumetric capacity of R1234yf is lower compared to R410A. Insufficient production capacity and higher price are another constraints to use this refrigerant in the larger scale.

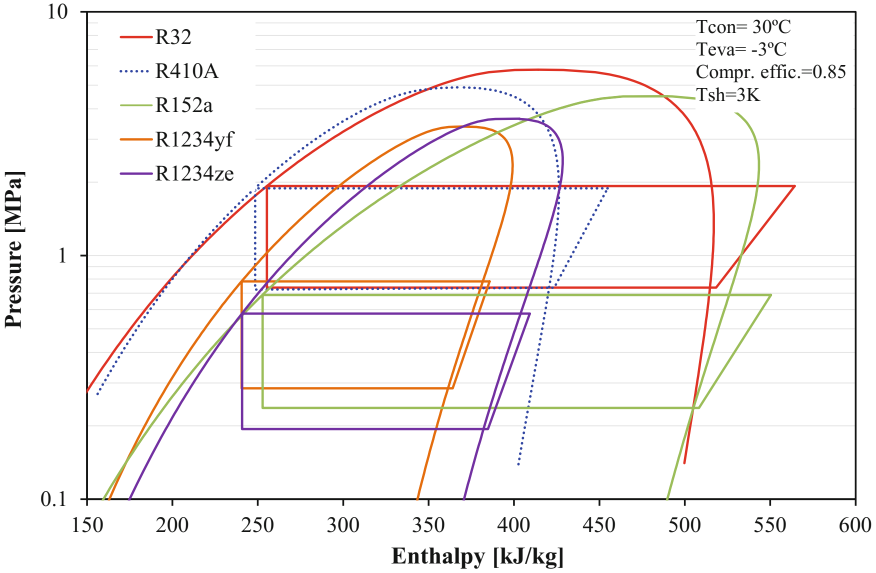

Fig. 15.5 Comparison of P-h diagram of some pure refrigerant along with thermodynamic cycle

15.3.1.2 R1234ze(E)

The (R1234ze(E) (CF3CH = CHF) got attention due to its ultra-low GWP (<1) and it is investigated as a candidate refrigerant for industrial centrifugal chillers (Ueda et al. 2011; Yang et al. 2015). The critical temperature and critical pressure of the refrigerant are 109.3 °C and 3.63 MPa, respectively (Higashi et al. 2010; Brown et al. 2010). It is a potential refrigerant for high-temperature heat pumps which works as hot dryers and steam generators for industrial purposes, such as the concentration of beverages, sterilization of foods, drying lumber, solvent recovery and distillation of petrochemical products. The possibility of using the refrigerant R1234ze(E) and R1234ze(Z) into high-temperature heat pump system has been investigated by Fukuda et al. (2014). The flammability of the refrigerant was studied by the same authors and found all the properties are suitable for the future application. Brown et al. (2009) predicted the performance potential of R1234ze(Z) in high-temperature heat pumping applications and suggested for further research as a possible alternative of R114. Experimental studies revealed that due to its low volumetric capacity, pure R1234ze(E) is not suitable as an alternative for R410A (Koyama et al. 2011) but it is suitable for turbo refrigeration system if the impeller size of the compressor is enlarged as compared to that of R134a (Koyama et al. 2010a). The energy saving potential of the refrigerant is found to 9–15% compared to R134a (Kabeel et al. 2016; Lai 2014). Figure 15.6 shows the schematic diagram of water-cooled experimental set up which is used to study the performance of new refrigerants and their blends (Fukuda et al. 2016).

Figure 15.7 shows the coefficient of performance (COP) of R1234ze(E) compared to R410A and R32, where it is found that the COP of R1234ze(E) is lower than other two. The COP is the ratio of heat transfer in the condenser or evaporator to the compressor/inverter input and can be estimated based on the cycle level and system level. The $\mathrm{COP}_{\mathrm{cycle}}$ and the $\mathrm{COP}_{\mathrm{system}}$ are calculated using the following equations.

Thermodynamic cycle COP for heating,

$$\mathrm{COP}_{\mathrm{h\_cycle}} = \frac{h_{\mathrm{R,COND\_in}} - h_{\mathrm{R,COND\_out}}}{h_{\mathrm{COMP\_out}} - h_{\mathrm{COMP\_in}}} \tag{15.8}$$

Thermodynamic cycle COP for refrigeration,

$$\mathrm{COP}_{\mathrm{r\_cycle}} = \frac{h_{\mathrm{R,EVA\_out}} - h_{\mathrm{R/EVA\_in}}}{h_{\mathrm{COMPR,out}} - h_{\mathrm{COMPR,in}}} \tag{15.9}$$

System COP for heating,

$$\mathrm{COP}_{\mathrm{h\_system}} = \mathrm{COP}_{\mathrm{h\_cycle}} \times (\eta_{\mathrm{inv}} \cdot \eta_{\mathrm{COMPR}}) \tag{15.10}$$

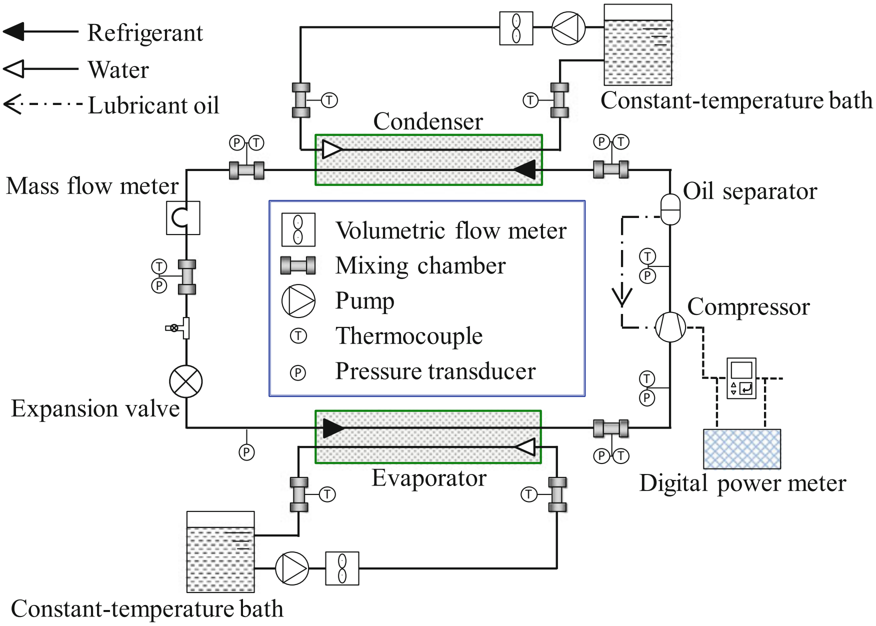

Fig. 15.6 Experimental set up to test new refrigerant (Koyama et al. 2010a)

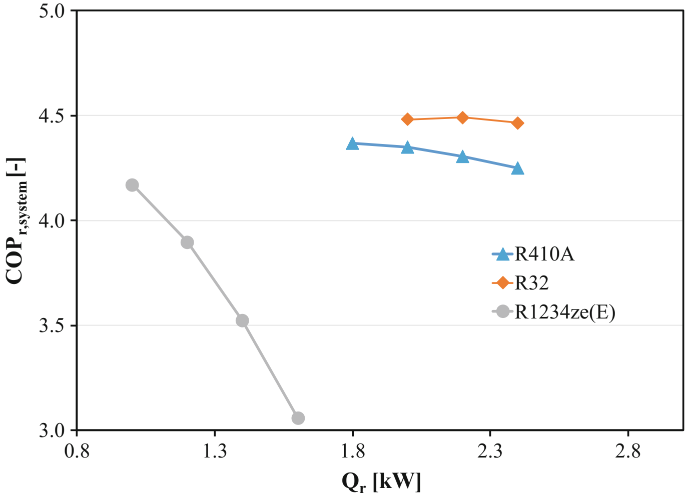

Fig. 15.7 Variation of coefficient of performance with cooling load

System COP for refrigeration or cooling,

$$\mathrm{COP}_{\mathrm{r\_system}} = \mathrm{COP}_{\mathrm{r\_cycle}} \times (\eta_{\mathrm{inv}} \cdot \eta_{\mathrm{COMPR}}) \tag{15.11}$$

15.3.1.3 R152a

HFC-152a (1,1 difluoroethane, C2H4F2) has been used for many years as a component in refrigerant blends but not as a single compound. The critical temperature and pressure of the refrigerant are 113 °C and 4.52 MPa, respectively (Higashi et al. 1987; Tamatsu et al. 1993; Van Poolen et al. 1997). It has zero ODP. The special advantage of this refrigerant is the low global warming potential (=138, Stocker et al. 2013) and reduced price compared to other HFC and HFO refrigerants. Compared to R134a, R152a possesses very similar volumetric cooling capacity and pressure levels, while the energy efficiency, the mass flow, and the vapor density are even more favorable (SAE-CRP 1234 2009). Bolaji (2010) and Cabello et al. (2015) reported superior system performance of R152a in a vapor compression system while comparing to the experimental result with R134a. Their test results revealed an improvement in COP ranges from 4.7 to 13% with a decrease in cooling capacity of about 0–10%. This refrigerant has been used for a long time as an aerosol spray propellant and foam blowing agent, as well as a component in some refrigerant blends (R401A, R415A, R430A, R500, etc.). However, its flammability is ranked as A2 by ASHRAE (Wilson et al. 2010), and hence flammable hazards could be the major reason in hindering its usage as a pure refrigerant until now.

15.3.1.4 R744

R744 (Carbon dioxide, CO_2) is a natural refrigerant used in vapor compressor systems of many types for over 130 years (Pearson 2005; Austin and Sumathy 2011; Bolaji and Huan 2013). The cost of this refrigerant is low and it is not necessary for recovery or disposal but it requires extremely high pressure as it operates at transcritical refrigeration cycle. There is a renewed interest in R744 as it is free of toxicity and flammability (Austin and Sumathy 2011; Maina and Huan 2015). Gustav Lorentzen was the pioneer of the revival of R744 in the early 1990s. Lorentzen and Pettersen (1994) developed a laboratory prototype of car air-conditioning system to evaluate the cycle performance of R744 and R12. Authors suggested that the higher energy density of high-pressure refrigerants may give considerable advantages in terms of cost and practicality due to the reduced dimension and weight. Xue et al. (2010) developed a steady state model of the R744 transcritical cycle for air-conditioning to estimate the heating and cooling performance. The performance of R744 both theoretically and experimentally as well as the comparison with other refrigerants has been conducted by many authors as a viable alternative of synthetic fluids (Brown et al. 2002; Jing-yang et al. 2003; Girotto et al. 2004; He et al. 2016; Pitarch et al. 2016; Chen et al. 2017). Hwang et al. (2004) measured the performance of different two-stage compressor R744 cycles and found 18–35% improved COP over the basic cycles at 7.2 °C evaporating temperature. Girotto et al. (2004) found a possibility to improve the efficiency of the CO_2 system approaching the efficiency of the R404A system though the installation cost is 20% higher. Maina and Huan (2015), and Nekså (2002) reviewed numerous area of applications for R744 including hot water production, commercial refrigeration, and heat pump dryers.

15.3.1.5 HC

HC (hydrocarbon) is a natural refrigerant which offers in general, high efficiency, good miscibility with mineral oils, lower compressor discharge pressure and good heat transfer criteria, but its highly flammable behavior limits the usage of this refrigerant in a larger scale. The use of HCs as refrigerant is confined to Europe because many other countries elsewhere banned the use of flammable gas in the presence of public. Lampugnani and Zgliczynski (1996) studied the performances of R290 in comparison with R22 theoretically and experimentally. The experimental result showed that R290 is an excellent candidate to replace R22 from the thermodynamic point of view. Granryd (2001) reviewed the possibilities and problems of using hydrocarbons as the refrigerant for refrigeration and heat pump applications. It is found a number of HC have favorable characteristics as refrigerants from the thermodynamic and heat transfer point of view. Halimic et al. (2003) concluded in their study that R290 is an attractive alternative to R12 in small domestic refrigerators after correcting technical operation and safety factors. Bjerre and Larsen (2006) evaluated the potential of R600 for household applications and found 10% better performance than R134a. Palm (2008) reviewed the excellent performance of HC comparing R134a, R22, and ammonia. The author suggested that the safety risk can be reduced by designing the systems as hermetic type with the minimum number of connections and a minimum charge of refrigerant or it can be used as an indirect system. Corberán et al. (2008) reviewed the standard of using HC in vapor compression system. It is stated that the IEC355.2.20 standard allows up to approximately 150 g of HC sealed in the typical refrigerator and small freezers are permitted to be located anywhere regardless of the room size incorporating a few special safety measures. This standard has opened the way for some European refrigerator manufacturers to produce household refrigerator with flammable HCs.

15.3.1.6 R32

R32 is a difluoromethane having GWP of 677. The critical temperature and pressure of this refrigerant is 78.2 °C and 5.8 MPa, respectively. Though the safety class of this refrigerant is 2L, it is higher hazardous than R1234yf due to its faster flame propagation. The volumetric capacity (VC) of R32 is higher than R410A (see Table 15.4) which shows the potentiality of higher COP than R410A. The larger VC reduces the charging amount even to achieve similar COP of that of R410A. The direct equivalent greenhouse gas emission of R32 is also lower due to low charging. But the higher compressor discharge temperature of R32 adversely affects its vast application (Mota-Babiloni et al. 2017; Bolaji 2010; Leck 2010).

15.3.2 Refrigerant Blend

Pure refrigerants for vapor compression systems can be considered convenient due to azeotropic nature and mostly well-developed thermophysical properties. For pure refrigerants, HFOs are good choices in terms of toxicity, flammability, and ultra-low GWP. Bella and Kaemmer (2011) reported that pure HFOs are not efficient alternatives for R410A from the viewpoint of system performance because redesigning the system is required with larger compressor, piping, and heat exchangers. Mixing HFOs with some other refrigerants is one approach to solve the aforementioned problems. Generally, the addition of two or more single component refrigerants is termed as blend, which can be of two types: azeotropic and zeotropic. Azeotropic blends behave like a single component refrigerant, in that they boil and condense at respective constant temperature at any given pressure. Whereas zeotropic blends boil and condense through a range of temperatures at a given pressure. Such temperature range is called “temperature glide” which it is basically the difference between the bubble point and the dew point of the refrigerant compound.

15.3.2.1 Binary Mixtures

The addition of two single component refrigerants is termed as binary mixtures. Figure 15.8 shows the temperate glides of R32/R1234ze(E) binary mixtures at a constant pressure. It can be seen that the temperature glide depends on the mixture component. About 20–30% of R32 in the mixture provides maximum temperature glide.

R32/R1234ze(E)

Figure 15.7 shows that the COP of R1234ze(E) is lower than that of commonly used refrigerant, i.e., R410A and R32, mainly due to the low volumetric capacity and higher pressure drop (Mota-Babiloni et al. 2016). To increase vapor density as well as the performance of R1234ze(E), R32 is normally mixed using various ratios (Koyama et al. 2010a; Wang and Amrane 2014). The various refrigerants mixture and their respective GWP values, typically less than 300. In the cycle performance

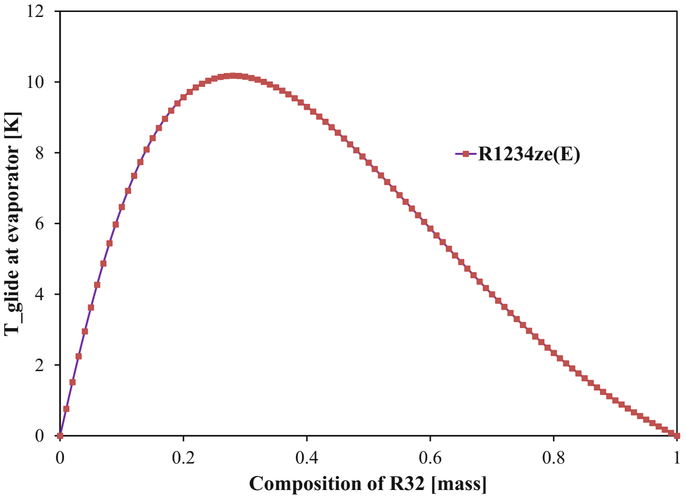

Fig. 15.8 Temperature glide of a binary mixtures R32/R1234ze(E)

analysis, Koyama et al. (2010b) showed that the addition of R32 (50% mass) with R1234ze(E) improved the volumetric capacity keeping COP higher than that of R410A which suggested this mixture is a strong candidate to replace R410A.

R32/R1234yf

The refrigerant R1234yf can be considered as a promising next-generation refrigerant with its ultra-low GWP and comparable performances with R134a. Hitherto, some shortcomings of R1234yf, especially the volumetric capacity, which is considerably lower than that of R134a. On the other hand, pure R32 is a good choice for residential air-condition but it shows very high temperature at the compressor outlet and considerably higher GWP. So mixing of these two refrigerants offers solutions to overcome their individual shortcomings. In a drop-in experiment, Kojima et al. (2016) studied the performance of this mixture considering the GWP values 300 and 200. The experimental results show the performance of R32/R1234yf binary mixture of 42/58 (by mass) is considerably higher than that of R410A. An irreversible loss by parts and total irreversible loss for different mixtures are also compared where results show that the irreversible loss for R32/R1234yf (42/58) mixture is lower than R32/R1234ze(E) (28/72). Figure 15.9 shows that after mixing with R32, the cycle operation area for binary mixture match with R410A. It seems these mixtures can replace R410A.

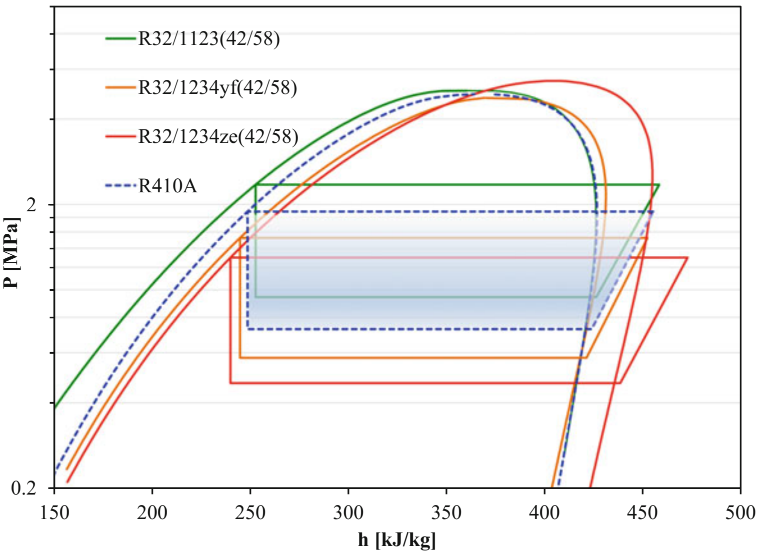

Fig. 15.9 P-h diagram with thermodynamic cycle for binary mixtures

R32/R1123

In 2014, AGC (Asahi Glass Co., Ltd.) developed a new refrigerant for air-conditioning systems that can reduce GWP further, which adopts hydrofluoroolefin R1123 as a main component. R1123 (trifluoroethylene) is strongly attractive because of its performance, which is equivalent to that of conventional refrigerants, along with extremely low GWP (=0.3) (Tanaka et al. 2014). Considering the safety and stability, the mixture of R1123 and R32 is considered as an alternative to R410A. According to Asahi Glass Co. Ltd., the new refrigerant mixture is azeotropic and can achieve good performance when replacing R410A for domestic and commercial air-conditioning system (Fukushima and Hashimoto 2015).

HC Mixtures

HC mixtures are environment-friendly natural refrigerants and can be used in the existing systems. Due to high flammable (A3) properties, HC mixtures are preferred to use in a small system where the charged amount is very small compared to halogenated refrigerants. Many researchers studied R290/R600a mixture as a substitute for R12 and found higher COP and refrigeration capacity of the hydrocarbon mixture than R12 (Richardson and Butterworth 1995; Dalkilic and Wongwises 2010; Mani and Selladurai 2008; Jung et al. 2000). Kim et al. (2007, 2008) experimentally studied the mixture of R744/R290 with three different compositions and found the ratio of 3:1 (by mass) enhanced the COP or 12.8% than that of R744 when the temperature glide matches with the change in fluid temperature. Tian et al. (2015) studied the performance of R32/R290 mixtures (68/32) as a drop-in replacement for R410A and found the COP of the mixture is 6–7% lower than that of R410A, whereas the charge amount is reduced by 30–35%. Mohanraj et al. (2011) reviewed the development of HC mixtures and identified that these mixtures can be suitable alternatives to phase-out halogenated based refrigerants in vapor compression systems.

15.3.2.2 Ternary Mixtures

R744/R32/R1234ze(E)

The binary mixture of R32/R1234yf and R32/R1234ze(E) show better performance than R410A when the mass fraction of R32 is above 50% in the mixtures. The mass fraction of R32 is below 50% in the binary mixture gives the GWP value less than 300; however, the COP drastically decreases as a consequence of the insufficient volumetric capacity. Fukuda et al. (2014, 2016), added R744 into the binary mixture to increase the volumetric capacity. In a drop-in experiment, authors studied the performance of R744/R32/R1234ze(E) mixtures having GWP 300 and GWP 200 and found the COP of GWP 300 mixture is comparable to that of R410A in both heating and cooling modes.

R744/R32/R1234yf

Fukuda et al. (2016) experimentally studied two ternary mixtures by adding R744 into R32/R1234yf mixture to increase the volumetric capacity and then compared the cycle performance with R410A. It is also found that the addition of R744 decreases the GWP but increases the temperature glide. But when the temperature glide of mixtures matches with the temperature changes in the heat sink and heat source during condensation and evaporation, they found that the irreversible loss is minimum. The ternary mixture of GWP nearly 300 show very good performance in both heating and cooling modes which means the ternary mixture of 4/44/52 (by mass) can be used as a drop-in alternative of R410A (Fukuda et al. 2016). Figure 15.10 shows the COPs of the ternary mixtures at optimum charge condition which are comparable with R410A.

Other Ternary Mixture

Maczek et al. (1997) studied R744/R32/R134a (7/31/62) mixture theoretically and experimentally to compare the performance with R22. Authors found the mixture is promising as a drop-in replacement of R22 with 10% better COP suggested using in

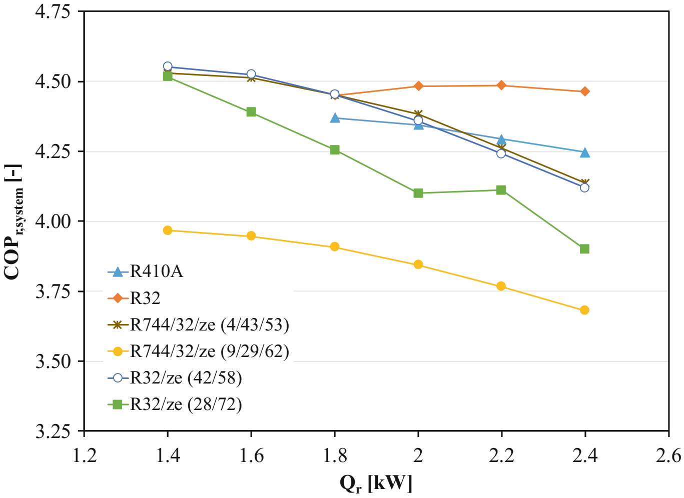

Fig. 15.10 COP value with cooling load for binary and ternary mixtures

low-temperature heat pump because of its excessive condensing pressure. Hakkaki-fard et al. (2014) theoretically compared the performance of R744/R32/Propane (10/80/10, GWP ~ 540) mixture with R410A and found the heating capacity of the mixture is higher than that of R410A.

15.4 Environmental Sustainability

The conventional vapor compression air-conditioning and refrigeration technology are responsible for both direct and indirect greenhouse gas emission. The warming potential of heat transfer fluid and the input electrical energy to run the system are accountable for environmental sustainability. Here, the emission is calculated considering system lifetime 10 years. Other related data are taken from the "Kyushu Electric Power Environmental Action Report 2013".

15.4.1 Direct Emission

The direct emission is a function of GWP, the charge amount, and the emission due to leakages from the air-conditioning system and those associated with the servicing and equipment disposal. Leakage can be reduced by using a small and tight system with sealed compressor but the servicing and equipment disposal cannot be stopped. Figure 15.11 shows the comparison of GWP for newly proposed binary and

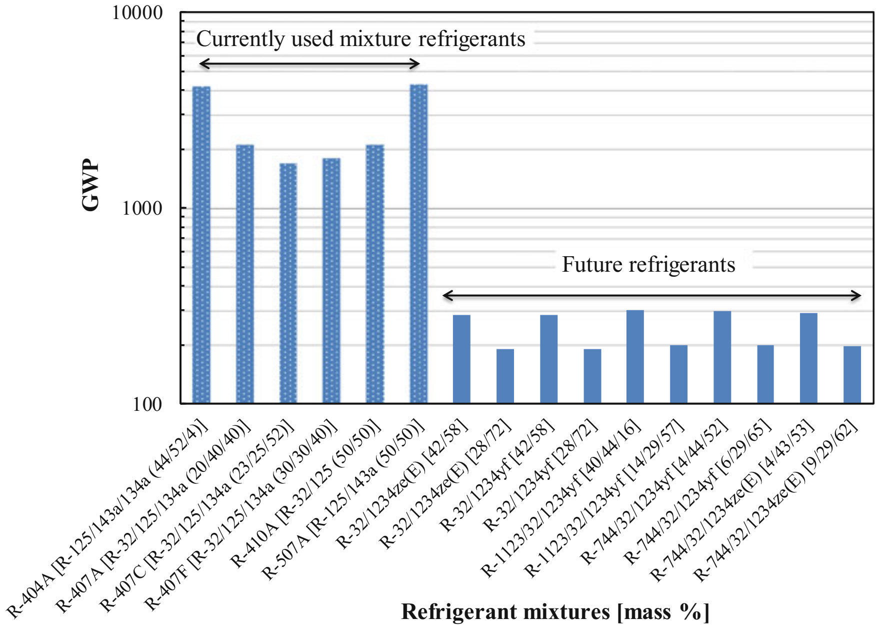

Fig. 15.11 GWP of some binary and ternary mixtures

ternary mixtures with currently used blend refrigerants. Figure 15.12 shows the direct equivalent CO_2 emission for pure refrigerant considering different application area. Figure 15.13 shows the comparison of direction emission among the widely used R410A with newly proposed binary and ternary mixtures when applied in domestic air condition system. It can be seen from these two figures that direct emission significantly reduced when blend refrigerants are considered as an alternative.

$$\text{Direct Emission} = \text{Emission due to leakage} + \text{Emission due to disposal}$$

15.4.2 Indirect Emission

The conventional air-conditioning and refrigeration devices are run by the electricity. The indirect emission is related to the operational activities of the system such as the emission during the production of electricity in a power plant, i.e., kg CO_2-equivalent emission generated during production of electrical energy which is consumed by the air-conditioning system. Usually, the higher performance of the

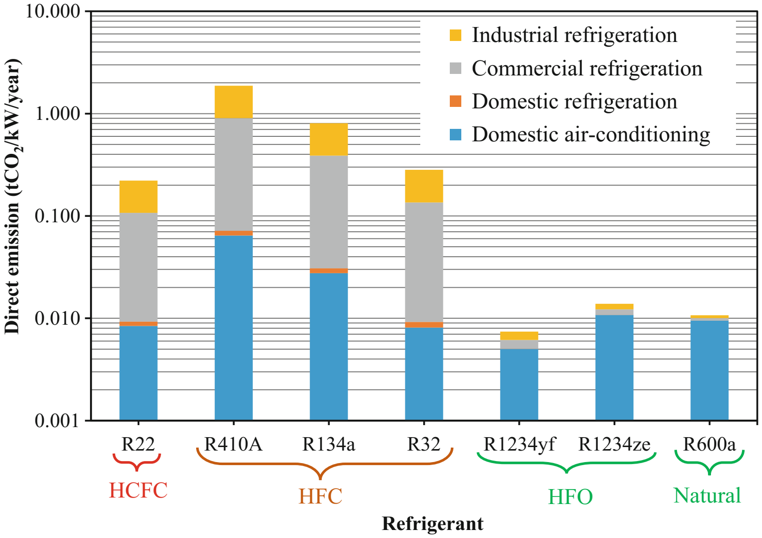

Fig. 15.12 Direct CO_2 equivalent emission for some popular pure refrigerant (Pal et al. 2018)

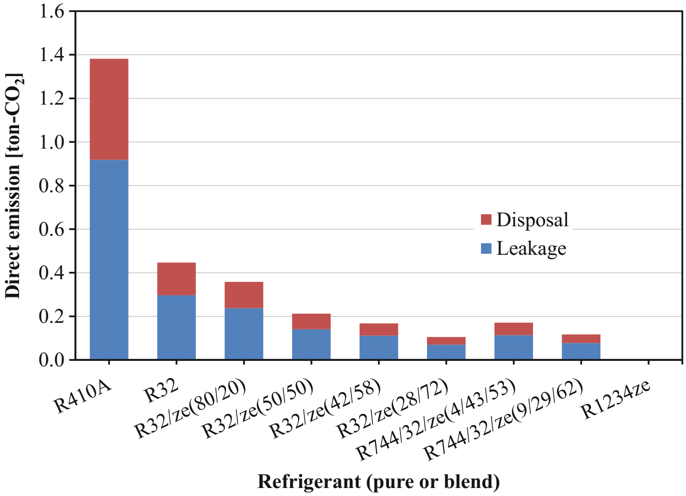

Fig. 15.13 Direct CO_2 equivalent emission for pure and mixture refrigerants

system means lower electricity consumption. The proposed refrigerant blend is attractive not only due to its very low GWP but also its excellent system performance. Figure 15.14 shows the indirect emission considering the annual use for heating is 1183 h and for cooling 1008 h.

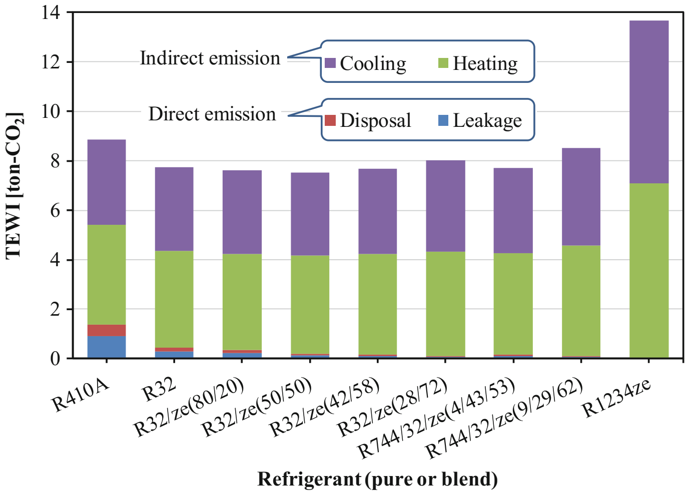

Fig. 15.14 TEWI for few blend refrigerants in comparison with R410A

$$\text{Indirect Emission} = \text{System run in cooling mode} + \text{System run in heating mode}$$

The environmental impacts of the air-conditioning and refrigeration system for its lifetime can be calculated by LCCP (Life Cycle Climate performance) or TEWI (Total Equivalent Warming Impact) (Mohanraj et al. 2011; Islam et al. 2017). LCCP accounts the energy embodied in product materials, greenhouse gas emissions during chemical manufacturing, and end of life disposal of the unit which is ignored for the case of TEWI. The small sources of emissions generated over the course of the lifetime of the unit are explicitly accounted for in LCCP. This study compared the TEWI value of blend with widely used R410A to avoid the emission related to the manufacturing of the component of the system.

$$\text{TEWI} = \text{Direct emission} + \text{Indirect emission} \tag{15.12}$$

$$\begin{aligned}\text{DE} = {} & \text{GWP} \times M \times \left[1 - (1 - \text{a}/100)^{Y}\right] + \text{GWP} \times M \\ & \times (1 - \text{a}/100)^{Y} \times (1 - \text{b}/100)\end{aligned} \tag{15.13}$$

$$\text{IDE} = c \times Y \times (\text{HC} \times t_{\text{h}}/\text{COP}_{\text{h}} + \text{CC} \times t_{\text{c}}/\text{COP}_{\text{r}}) \tag{15.14}$$

where

a	Annual refrigerant leak rate [%/year]
b	Refrigerant recovery rate (based on residual refrigerant at disposal) [%]
c	Carbon dioxide emission coefficient [kg-CO$_2$/kWh]
CC	Rated cooling capacity [kW]
HC	Rated heating capacity [kW]

LE	Refrigerant leakage during disposal [kg-CO_2]
LL	Lifetime refrigerant leakage [kg-CO_2]
M	Refrigerant charge amount [kg]
t_c	System use in cooling mode [h/year]
t_h	System use in heating mode [h/year]
Y	System lifetime [year]

15.4.3 Energy Efficiency

Energy efficiency for a refrigeration system is related to the selection of refrigerant, system configuration, and component efficiencies. For a specific refrigerant, there is need of suitable configuration of evaporator, condenser, and compressor to achieve maximum performance. There is different approach to assess the energy efficiency for a specific refrigerant, which are theoretical or semi-theoretical cycle simulations, detailed equipment simulation models and laboratory test of the system. The operating condition, system capacity, and system hardware also influence the energy efficiency. In practice, the cost of the system is another important parameter as the success in the market depends on a cost-performance trade-off.

15.4.4 Nonconventional System

There is another approach to building a sustainable environment by changing the design of the vapor compression system. The adsorption cooling/heating system is one of them. This system is able to use natural refrigerants and is driven by renewable or waste energy. Water, ethanol, ammonia, and methanol known as natural refrigerants, are getting attention in domestic and automobile heat pump applications (Saha et al. 1995; El-Sharkawy et al. 2014; Tamainot-Telto et al. 2009; Wang et al. n.d.). These refrigerants have no GWP and toxicity. As the system is driven by waste energy so it is free from direct and indirect greenhouse gas emission. Water (R-718) and ethanol are not familiar refrigerant in vapor compression systems due to poor volumetric efficiency, but they can be considered as popular refrigerants in sorption-based systems (Wang et al. 2014; Uddin et al. 2014). Adsorption cooling systems can be operational utilizing low-temperature heat sources such as solar energy and low-grade process waste heat, e.g., engine exhaust, industrial waste heat (Khan et al. 2006; Kai and Edward 2011). When the system is applied in automobiles, the exhausted heat can be utilized without compromising any mechanical energy output from the engine. Hybrid vapor compression–adsorption system is also feasible when low-grade heat is available (Banker et al. 2008; Uddin et al. 2013). Figure 15.15 shows the conventional mechanical system and nonconventional adsorption heat pump system. The thermal

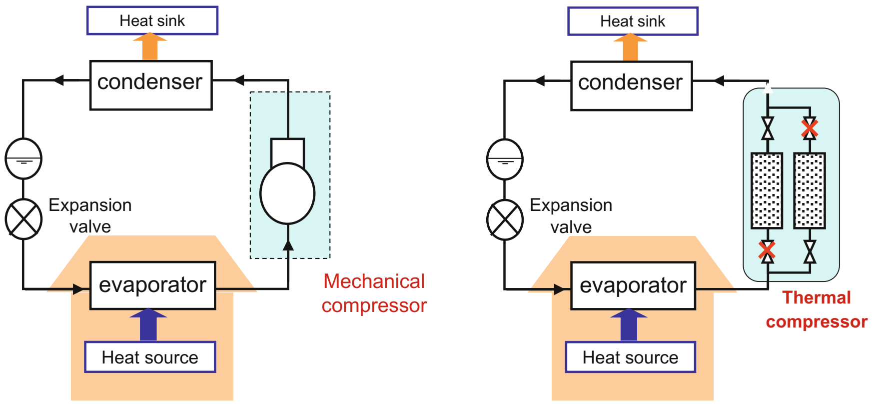

Fig. 15.15 Conventional mechanical compression system and nonconventional adsorption system

compressor in nonconventional system works based on adsorption and desorption phenomenon.

15.5 Summary

To summarize, the most important factors determining the environmental sustainability are the low GWP refrigerant with higher volumetric capacities. Figure 15.16 shows the progression of refrigerants from the beginning of commercial production to current condition. The fourth generation refrigerant should be zero ODP, ultra-low GWP, should have a shorter lifetime in atmosphere, and high efficiency. The HFOs and their mixture can be a good solution to reduce the direct and indirect greenhouse gas emission. The study presented here will help the reader to find a suitable composition of the mixture that is desirable for a specific application.

The adsorption cooling system using natural refrigerant is also a promising alternative to traditional vapor compression system, in terms of primary energy source diversification and reducing the overall environmental effect. Vapor compression and adsorption hybrid system can also be a promising alternative of current mechanical vapor compressor system using conventional refrigerants.

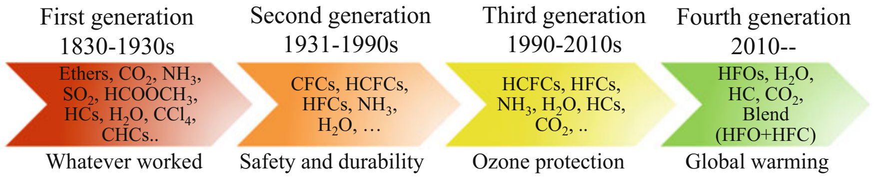

Fig. 15.16 Refrigerant progression toward sustainable environment

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