A RECENT REVIEW OF REFRIGERANT R-1234YF AND R-1234ZE (E)

[1] Prof.Pragnesh D. Kandoliya, [2] Prof.Nirajkumar C Mehta
[1] A.P.M.E., [2] A.P.M.E.
[1] Mechanical Engineering,
[1] Vadodara Institute of Engineering, Vadodara, India

Abstract*— In the present study, recent research is considered about new generation refrigerant R-1234yf and R-1234ze (E). Chlorofluorocarbons (CFCs) had been phased out under the Montreal Protocol; CFC alternative refrigerants are searching for based on the condition of no chlorine atoms because of zero ODP. It seemed that conversion from CFC refrigerant to HFC refrigerant or natural refrigerant had progressed smoothly in the two decades. As for the low GWP refrigerants, hydrofluoric-olefins (HFOs), especially, HFO-1234yf (CF3CF=CH2: 2, 3, 3, 3-tetrafluoropropene) and HFO-1234ze (E) (CF3CH=CHF: trans-1, 3, 3, 3-tetrafluoropropene) are recently focusing in the world. Both of these HFOs have low GWP values (HFO- 1234yf is 4 and HFO-1234ze (E) is 6), and expecting as the next generation refrigerant. R-1234yf and R-1234ze (E) can used in mobile air conditioning and ejector refrigeration system.

***Keywords*—R1234yf, R1234ze, R134a, Ejector**

I. INTRODUCTION

Scientific research on hydro fluorocarbons (HFC's) refrigerants in the last few years has devoted great efforts on the retrofitting processes applicable for refrigerants which have high global warming potential (GWP). The European Union has approved a regulation which prohibits the use of fluorinated gases with a GWP above than 150 in domestic refrigerators and freezers by January 1, 2015, and in new types of mobile air-conditioning systems by January 1, 2017.[1] HFOs are synthetic fluids that contain a carbon–carbon double bond. They are characterized by very low GWP values (under 10), low flammability and non-toxicity and similar properties to HFC (and materials and lubricants compatibility). R1234yf was the first HFC launched as a low-GWP alternative. It is used as R134a drop-in replacement in mobile air conditioning (MAC) systems [1]. R1234ze (E) is another alternative to R134a proposed in new systems of medium temperature applications: air-cooled and water-cooled chillers, heat pumps, refrigerators, vending machines and CO_2cascade systems. Other HFOs as R1243zf are still being studied prior to being commercialized [2].

II. NEW GENERATION REFRIGERANTS WITH LOW GWP

The greatest environmental effect is the destruction of the ozone layer by the chemical gases. Decrease or removal of this layer which functions as a filter against harmful ultra violet rays can damage life on earth profoundly. After the exploration of the damage caused on the ozone layer by chlorine based gases, removal of this type of gases has been planned with Montreal Protocol. ODP of R11 gas, which is in CFC group, has been accepted as 1 and used as a reference value. ODP of R22 gas, which is in HCFC group, is 0.055 [3].

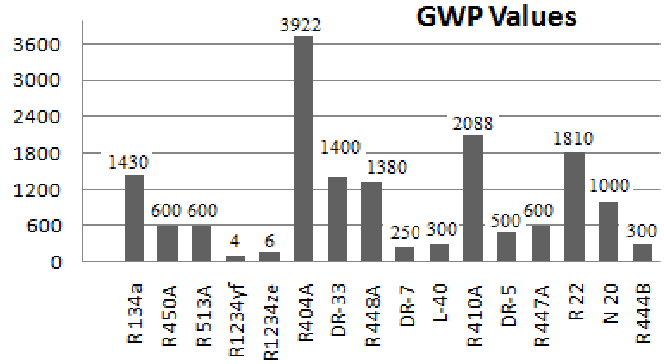

Figure 1 GWP Values of Refrigerant

GWP

Another environmental impact is high GWP value which is used to measure greenhouse effect of a gas based on its radioactive properties relative to CO_2 in a given time frame. The GWP of CO_2 is 1 [4]. Refrigerants having high GWP are not preferred since they stimulate sera gas formation and increase global warmth [5]. The GWP depends on the infrared radiation absorption of the refrigerant, gas lifetime in the atmosphere, and the selected time frame. Thus, the same gas can have different GWP for different time frames with 100 years normally used as the standard time frame [4]. Comparison n of GWP values of the refrigerants used in this study is shown in Figure 1 which illustrates the comparison of four main refrigerating fluids and the fluids that could be used instead of them. In Figure 1, it is clear that 58% decrease of GWP can occur by using R513A instead of R134a.

In this study, refrigerants widely used in vapor compression refrigeration systems were investigated. Although each gas is used for different processes, R134a gas is used in small capacity refrigerators and chiller equipment generally, R404A is used in cool-store equipment, R410A is used in air conditioning equipment (cooling and heating), and R22 is used in both refrigerating and air conditioning devices. The properties of four main refrigerating fluids according to different application fields and the alternative refrigerants with low GWP values are given in Table 1. Some properties were determined by Refprop [6]. When critical temperatures and pressures of main refrigerant and alternative gases are reviewed, it is clear that the values are similar. It is seen that some of the candidate gases are mildly flammable according to ASHRAE safety class [7, 8]. This property will be limiting for usage in some applications.

Table 1 Properties of investigated Refrigerant

Refrigerant	ASHRAE Safety class	Boling Temperature (°C)	Critical Temperature (°C)	Critical Pressure (MPa)
R 134a	Al	-26.07	101.06	4.06
R 450A	Al *	-25.6	100.18	3.74
R 513A	Al *	-27.9	97.51	3.67
R 1234yf	A2L	-29.45	94.7	3.38
R 1234ze(E)	A2L	-18.97	109.36	3.63
R 404A	Al	-46.5	72.12	3.73
DR-33	Al *		85.02	4.48
R448A	Al *	-38.5	84.63	4.47
DR-7	A2L*	-37.9	89.17	4.55
L40	A2L*	-22	89.89	4.84
R410A	Al	-51.4	71.34	4.9
DR-5	A2L*	-45.4	83.11	5.4
R447A	A2L*		80.45	5.35
R22	Al	-40.81	96.14	4.99
N20	Al *	-31.7	91.87	4.19
R444B	A2L*	-36.7	90.56	5.07

A2L: Mildly Flammable, Al: Non Flammable , [10]

P-h diagrams shown in Figure 2 were plotted with respect to thermodynamic properties in Refprop program. As it is clear in Figure 2a, where R134a gas is compared with the alternatives, specific refrigerating effect of R134a for the same phase change temperature is higher than that of other gases. The refrigerants observed as most close to R134a are R450A and R1234ze (E). With the same perspective, it can be stated that L40 and DR-7 in Figure 2b are much better thanR404A. It is obvious that R448A and DR-33 refrigerants having better specific refrigerating effect in comparison to R404A have almost similar characteristics. In Figure 2c, comparison of R410 with DR-5 and R447A gases are considered, and it is evident that specific refrigerating effects of low GWP refrigerants are higher than that of R410A. The investigation of R22, R444B and N20 in Figure 2d presents that specific refrigerating effect of R444B is higher than that of R22[11].In the same plot, it can be stated that N20 having low GWP has similar properties as R22. Cooling capacity of the refrigerating fluid with high specific refrigerating effect can be high as well [9].

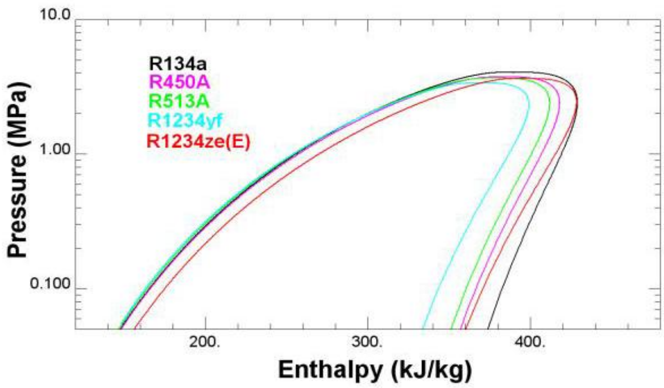

Figure 2a Pressure-enthalpy diagram of the refrigerating fluids R134a and its alternatives

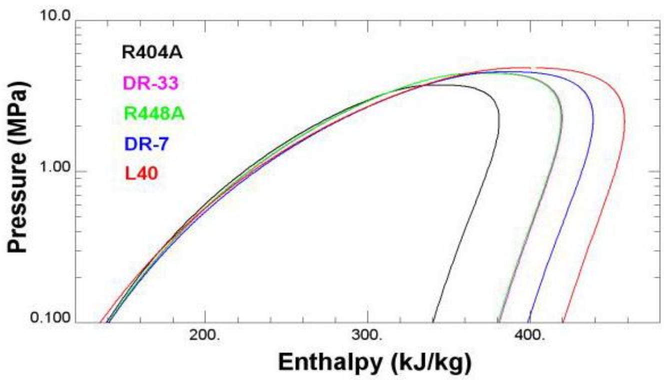

Figure 2b Pressure-enthalpy diagram of the refrigerating fluids R404A and its alternatives

In the selection of refrigerating fluids, in addition to low GWP consideration, gases with better energy characteristics should be preferred because of their limiting characteristics. The study represents that all new alternative gases are better regarding their lower GWP values. Although they have some differences in terms of energy parameters, it can be stated that R1234yf, L40, DR-5 and R444B refrigerants can be good alternatives to R134a, R404A, R410A and R22, respectively. Since there is no system to take place of vapor compression refrigeration cycles in the medium term, proper gas search should be conducted and test of gases commercially provided to the market should be carried out [11].

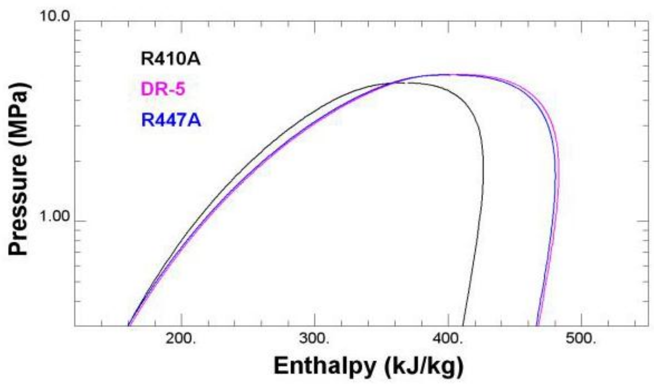

Figure 2c Pressure-enthalpy diagram of the refrigerating fluids R410A and its alternatives

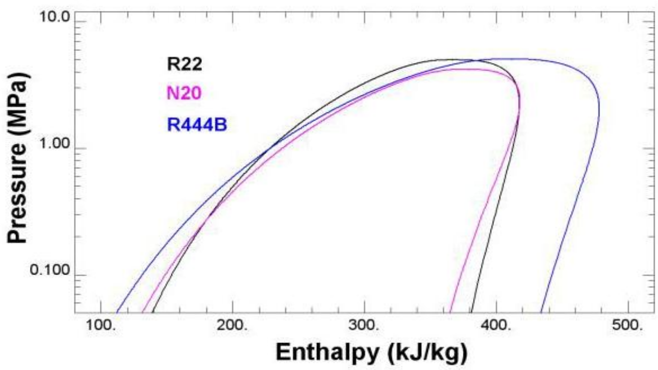

Figure 2d Pressure-enthalpy diagram of the refrigerating fluids R22 and its alternatives

III. R1234YF MOBILE AIR CONDITIONING SYSTEMS

The performance improvement potentials of R1234yf mobile air conditioning (MAC) system under various operation conditions were studied in this research based on thermodynamic cycle analysis. The effects of superheat at evaporator outlet, subcooling at condenser outlet and compressor efficiencies on system performance were analyzed. It was found that superheat was few benefits for both system coefficient of performance (COP) and cooling capacity. Increasing sub cooling from 1K to 10K at condenser outlet, system cooling capacity and COP could be improved by 15% if compressor consumption power was fixed [15]. The isentropic efficiency of the compressor was a key factor in system COP improvement. By adding an internal heat exchanger and improving compressor efficiencies would be good options for the future R1234yf MAC system enhancement.

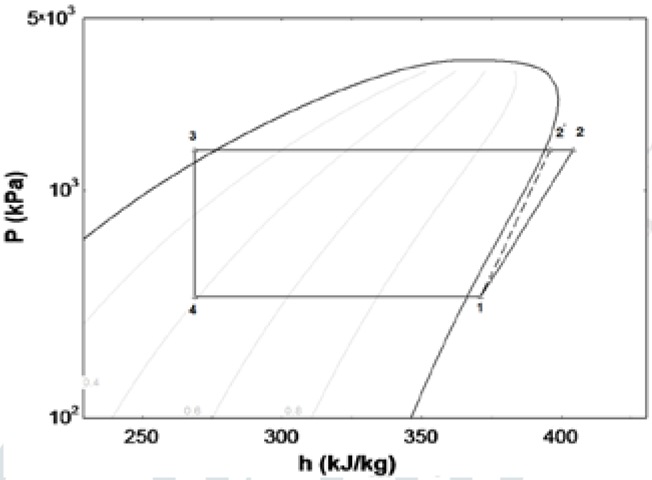

Figure 3 R1234yf basic thermodynamic cycle in logP-h diagram

The simplified thermodynamic cycle was shown as Figure 3 which was composed of four processes. There were some assumptions which are following

- The superheat at evaporator outlet and subcooling at condenser outlet were 5K if it was not a variable, respectively.
- The pressure drops in evaporator, condenser and connection tubes were ignored.
- The throttle process in expansion valve was isenthalpic.
- The compressor had a constant displacement (120×10^{-6} $m^3 rev^{-1}$).
- The compressor efficiencies changed with vehicle operation conditions.
- The evaporation temperature was constant (5^oC) for all vehicle operation conditions and the temperature difference between condensation and ambient air was constant (20K).
- The above parameters could be a variable during the following analysis.

The cooling capacity, compressor consumption power, system COP and refrigerant mass flow rate were calculated by Eqs. (1-4):

$$Q_{evap} = m\,(h_1 - h_4) \quad \ldots\ldots\ldots\ldots 1$$
$$W_{comp} = m\,(h_{2'} - h_1) \quad \ldots\ldots\ldots 2$$
$$COP = \frac{Qevap}{Wcomp} \ldots\ldots\ldots\ldots\ldots\ldots 3$$
$$m_{ref} = V_{cyc}\eta_{vol}\rho_1\left(\frac{N}{60}\right)m \ldots\ldots\ldots 4$$

All the above equations and calculations were carried out using Engineering Equation Solver (EES, F-Chart Software, 2014 [16]. The thermodynamic properties of R1234yf and R134a were from the data provided by Richter et al. (2011) [13] and Tillner-Roth and Baehr (1994), [14] respectively.

The theoretical R1234yf system performance was compared with that of R134a system as shown in Table 2 [15]. It was implied that both system COP and cooling capacity of R1234yf system were smaller than that of R134a for all the vehicle operation conditions. The gap ranges of system COP, cooling capacity and compressor consumption power were 4.8~7.0%, 7.7~10.6% and 3.1~3.8%, respectively. The following discussions were explained from the effect of superheat, sub cooling and compressor performance on the system performance improvement potentials.

Table 2 R1234yf and R134a MAC System performances under three typical conditions

	Idle		City		High Speed	
	R1234yf	**R134a**	**R1234yf**	**R134a**	**R1234yf**	**R134a**
Q_{evp}(kW)	2.488	2.696	4.503	4.952	5.852	6.544
W_{comp}(kW)	0.802	0.828	1.946	2.015	3.466	3.604
C.O.P.	3.1	3.257	2.314	2.457	1.689	1.816

If compressor isentropic efficiency (η_{isen}) was increased, system cooling capacity would be constant when the compressor volumetric efficiency and cycle state points were constant as shown in Figure 4. The benefit from compressor isentropic an efficiency (ηisen) improvement was the system COP increasing which resulted from the compressor consumption power reduction. Under high speed condition, R1234yf system COP could be lifted to the same level as R134a system when compressor isentropic efficiency (η_{isen}) was increased from 0.55 to 0.59. From the theoretical analysis, R1234yf system COP could be improved by 72.7% if compressor isentropic efficiency (η_{isen}) was increased from 0.55 to 0.95. The biggest gain from compressor isentropic efficiency (η_{isen}) improvement was compressor consumption reduction as shown in Figure 5.

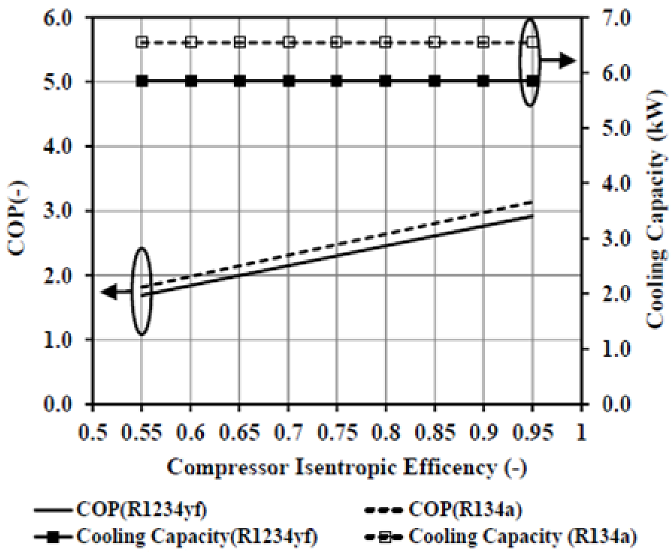

Figure 4 The effect of compressor isentropic efficiency on system COP and cooling capacity under high speed condition

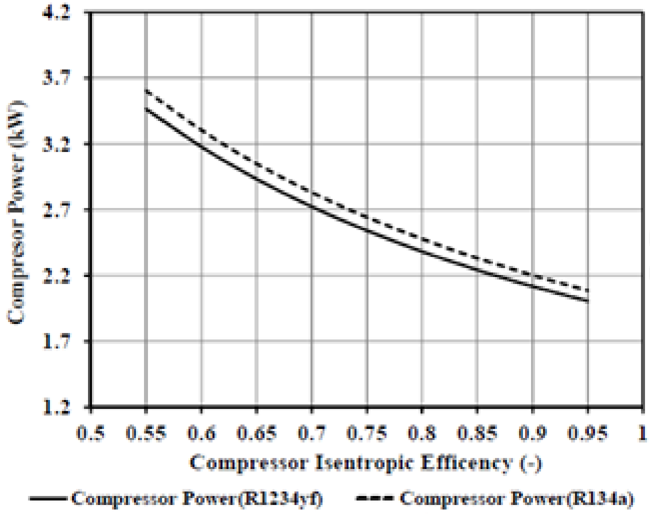

Figure 5 The effect of compressor isentropic efficiency on compressor power under high speed condition

The analysis results revealed that the R1234yf system C.O.P. and cooling capacity were lower by 4.8~7.0% and 7.7~10.6% than that of R134a system under all three conditions (idle, city and high speed), respectively. R1234yf system cooling capacity could increase by 72.8% with compressor volumetric efficiency (η_{vol}) from 0.55 to 0.95 [15]. if the other compressor efficiency and state points were fixed. On the other hand, compressor isentropic efficiency (η_{isen}) improvement could reduce the power consumption dramatically which resulted in system COP increasing. It was concluded that adding an internal heat exchanger and improving compressor efficiency would be better options in the future R1234yf MAC system enhancement.

IV. R1234YF AND R1234ZE (E) AS DROP-IN REPLACEMENTS FOR R134A IN A SMALL REFRIGERATING SYSTEM.

In this paper we present two different analyses of R1234yf and R1234ze(E) as drop-in replacements for R134a in a small power refrigeration system. The first analysis is based on equal evaporation and condensation temperatures before and after the refrigerant replacement. The second analysis is carried out for equal cooling medium conditions in the condenser, so that the transport properties and the heat transfer features in the condenser are considered for the three refrigerants. In order to perform the analyses, a simulation model was developed, that takes into account specific data, characteristics and dimensions of the main components of a small power refrigeration system. The model was validated with experimental data for R134a and later used to predict the behavior with R1234yf and R1234ze (E) [17].

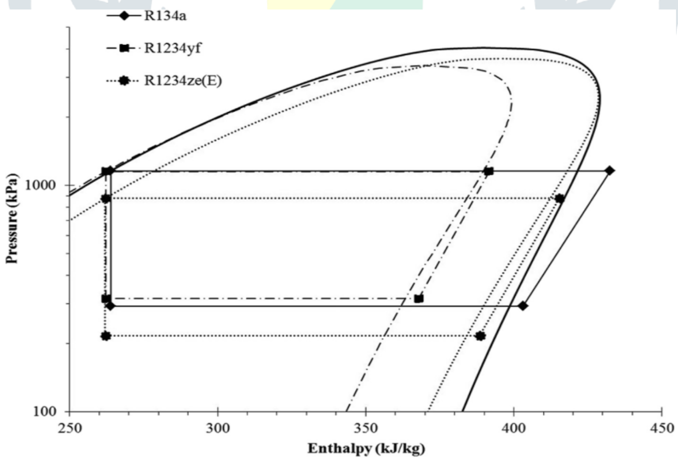

Figure 6 p-h diagram of the ideal vapor compression cycle for refrigerants R134a, R1234yf and R1234ze(E).

The molecular weights (M) of refrigerants R134a, R1234yf and R1234ze(E) are similar (101, 114 and 114 kg/kmol, respectively), a closer analysis at the pressure values in Figure 6 and Table 3 yields the following conclusions [17]:

- The compression ratios (RC) for the three cycles are somehow similar, so similar volumetric efficiencies (η_{vol}) should be expected (numerical values are within 1%).
- A rough approximation for the specific volume at the suction line is given by $v_1 = T_1 R_u / (M P_E)$ (where Ru is the universal gas constant), then we should expect the specific volume to be the highest for R1234ze (E), followed by R134a and R1234yf.

$$m_{ref} = V_{cyc}\eta_{vol}\rho_1\left(\frac{N}{60}\right) \ldots\ldots\ldots\ldots\ldots\ldots 5$$

- For a specific value of the compressor supply frequency, we should expect from equation(5) that the refrigerant mass flow rate m_{ref} is the highest for R1234yf, followed by R134a and R1234ze (E).

$$Q_E = m_{ref}(h_1 - h_4) \ldots\ldots\ldots\ldots\ldots\ldots 8$$

- From equation (8) , we should expect the cooling capacity for R1234ze (E) to be lower than for R134a; however, nothing can be stated (a priori) for R134a and R1234yf due to the opposing trends observed m_{ref} and Q_E.

Table 3 Calculated variables for the cycles shown in Figure 6 [17]

Variable or Parameter	R134a	R1234yf	R1234ze(E)
Evaporator pressure (bar)	2.9	3.2	2.2
Condenser pressure (bar)	11.6	11.5	8.8
Compression ratio	3.96	3.65	4.01
Compression discharge temperature (^oC)	55.4	46.6	47
Specific volume at the suction line (m^3/ kg)	0.071	0.0582	0.0866
Specific refrigerating effect (kJ/kg)	144	113	130
Specific isentropic work (kJ/kg)	29	24	27
Refrigerant mass flow rate (kg/sec)	0.0014	0.00167	0.00111
Cooling power (w)	195	188	144
Isentropic COP	4.9	4.8	4.9

Table 3 shows the numerical results of these and some other selected variables which drop-in effect cannot be easily inferred from Figure 6, such as the isentropic compressor discharge temperature, isentropic specific work or COP. Though, these results are for specific values of the condensation and evaporation temperatures (shown in Figure 6), similar trends were observed for the range of evaporation and condensation temperature values considered in this paper.

After all, R1234yf seems as an adequate drop-in refrigerant for R134a, but R1234ze(E) may perform better when an overridden compressor can be used to match the refrigerating system cooling power. Though in this work, pressure drops were not considered relevant, they might be important in other type of similar analyses.

V. EJECTOR REFRIGERATION SYSTEM

For an ejector refrigeration system, the working fluid significantly influences the ejector behavior and system performance as well as ejector design. There are three categories of working fluids: wet fluids, dry fluids and isentropic fluids. Four wet fluids (R134a, R152a, R290 and R430A), four dry fluids (R245fa, R600, R600a and R1234ze) and one isentropic fluid (R436B) are selected in the paper. Special consideration is paid to the superheat of the ejector primary flow. This superheat is needed not only for wet fluids, but also for dry fluids and isentropic fluids at some cases, to eliminate droplets inside the ejector. A minimum superheat is found, and it is dependent on the used working fluid and the operating temperatures as well as the ejector nozzle efficiency. The comparison among these nine candidates indicates that R600 is a good candidate for the ejector refrigeration system due to a relatively high COP and its low environmental impact [18].

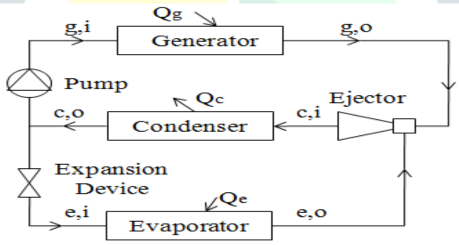

Figure 7 Ejector refrigeration systems

Figure 7 schematically shows the ejector refrigeration system. It consists of a generator, a condenser, an evaporator, an ejector, a circulation pump and an expansion valve. Low-grade heat (*Q*g) is delivered to the generator for vaporization (g,i→g,o). The high-pressure vapor out from the generator, i.e. the primary flow, enters into the ejector nozzle and draws low-pressure vapor from the evaporator, i.e. the secondary flow. The two flows undergo mixing and pressure recovery in the ejector (g,o and e,o→c,i). The mixed flow is then fed into the condenser, where condensation takes place by rejecting heat to the environment (*Q*c). Liquid from the condenser is divided into two parts. One part goes through the expansion device (c,o→e,i), and enters into the evaporator (e,i→e,o), where it evaporates and hence produces refrigerating effect (*Q*e). The rest liquid is back to the generator via the pump (c,o→g,i), and completes a cycle.The ejector is the key component in ejector refrigeration systems and fulfills the function of a compressor.

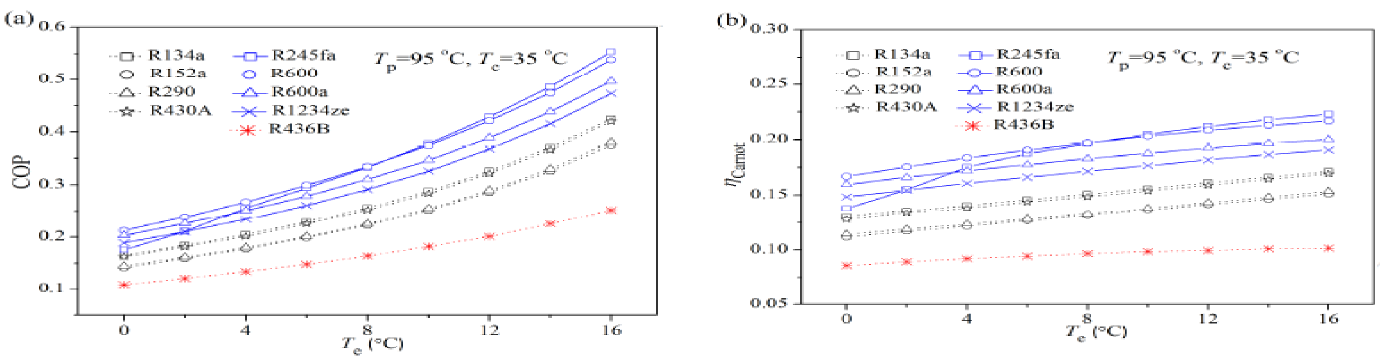

Figure 8 Effects of evaporator temperature on COP and Carnot efficiency.

Figure 8 depicts the influence of the evaporator outlet temperature *T*e on COP and Carnot efficiency η_{Carnot} at T_p=95 °C and T_c=35 °C. Obviously, both COP and η_{Carnot} increase with increasing *T*e. Similar as in Figure 8 (a), the T_e of 8 °C is the changing point for R245fa and R600. When the *T*e is lower than 8 °C, R600 shows best COP; otherwise R245fa has the highest COP. The sensitivity of COP for R600 is observed at 2% when changing one Celsius degree of *T*e. At *T*e=10 °C, R245fa and R600 have the highest COP and η_{Carnot}, in a descending order followed by R600a and R1234ze, the lower COP is found when using R134a and R430A which have similar values, then comes to R152a and R290 which also have alike values, and finally to R436B with the lowest performance.

At the reference operating condition, R245fa and R600 have the highest COP of 0.38, followed by R600a of 0.35 and R1234ze of 0.33, a lower COP of 0.28 is found for R134a and R430A, then comes to R152a and R290 with a COP of around 0.25, the lowest is observed at 0.18 for R438B. Therefore, R600 is recommended as a good candidate for the ejector refrigeration system from perspectives of system performance and environmental concern. However, its flammability requires extra considerations.

VI. CONCLUSION

Refrigeration systems are moving towards the use of low-GWP and ODP fluids. So, in future years natural refrigerants or HFO will impose, depending on the tradeoffs (performance, costs, flammability, availability etc.). One of the most promising HFO option in refrigeration and air conditioning systems is R1234ze(E) and R1234yf. In this paper, recent studies of R1234ze (E) and R1234yf (pure or mixed with other refrigerants) are reviewed. R 1234ze(E) and R 1234yf are refrigerant which can use mobile air condoning system and ejector refrigeration system but it is required more focus and research for improve performance of system.

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