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Assessment of blends of CO_2 with butane and isobutane as working fluids for heat pump applications

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ABSTRACT

In the present study, blends R744/R600 and R744/R600a are being proposed as working fluids in heat pumps for medium and high temperature heating applications. COP based performances have been evaluated for zeotropic mixtures of both working fluid pairs for various compositions and compared against that of pure working fluids. Effect of internal heat exchanger on blend based system performance is also presented and finally heat transfer issues in evaporation and condensation are discussed. Results show that due to gliding temperature during evaporation and condensation, the zeotropic blends, instead of pure counterparts, can be employed very effectively in heat pumps for variable temperature or simultaneous cooling and heating applications (e.g., dairy plants) at conventional high side pressure. The blend R744/R600a can be the best alternative refrigerant to R114 for high temperature heating due to superior COP (more than twice) over R600 and R600a and eliminating the requirement of extremely high side pressure of R744 systems.

1. Introduction

Due to the negative effects of synthetic refrigerants on the environment, the eco-friendly natural refrigerants such as ammonia, propane, butane, isobutane, propylene and carbon dioxide [1] have gained interest lately as alternative refrigerants for heat pump applications because of their zero ODP and negligible GWP. Hydrocarbons and its mixtures have been emerging as popular alternative refrigerants either by replacing the synthetic refrigerants in most of the existing refrigeration and heat pump systems or by developing new systems [2]. To overcome a few individual deficiencies, such as toxicity of ammonia, flammability of hydrocarbons and high pressure and low COP of CO_2, blends may be more effective alternatives. Zeotropic mixture can improve the overall performance over appropriate azeotropic and pure fluids for temperature gradient heating and cooling processes in the food and pharmaceutical industries where the one-pass nature of the process is required to meet their health and safety standards.

Mongey et al. [3] examined hydrocarbon mixtures for high temperature heat pump applications. Performances of hydrocarbon mixtures as drop in replacement for R22, R12 and R134 were measured in heat pump and refrigeration systems [4,5]. Chang et al. [6] experimentally investigated the performance of a heat pump system using binary mixtures of propane/isobutane and propane/butane as working fluids and compared with R22 system. Hewitt et al. [7] proposed an ammonia and water mixture for high temperature heat pumps, capable of reaching temperatures of 120 °C while maintaining conventional pressures. Nanxi et al. [8] tested a ternary mixture of R124/R142b/R600a, named HTR01, for moderately high temperature heat pumps. Park et al. [9] measured the performances of two pure hydrocarbons and seven mixtures composed of propylene, propane, HFC152a, and dimethylether as substitute for R22 in residential air-conditioners and heat pumps.

After the reinvention of CO_2 as a refrigerant, the mixtures of CO_2 with hydrocarbons gained interest due to superior heat transfer properties and compactness with reduced cycle pressure and significantly reduced flammability compared to individual hydrocarbons. Kim and Kim [10] investigated the performance of an auto-cascade refrigeration system using zeotropic refrigerant mixtures of R744/134a and R744/290 to keep the highest pressure of the system within a limit, and through test and simulation, they showed that as the composition of R744 in the refrigerant mixture increases, cooling capacity is enhanced, but COP tends to decrease while the system pressure rises. Recently CO_2/propane mixtures have been studied experimentally in refrigeration [11] and air-conditioning [12] applications. Several alternative refrigerant technologies have been established for low and medium temperature heating, but no established technology for replacement of R114 for high temperature heating has been offered.

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Nomenclature

COP_h	heating coefficient of performance	w	compressor work ... kJ/kg
h	specific enthalpy ... kJ/kg	η_{II}	second law efficiency
I	component irreversibility		
P_2	discharge pressure ... bar	*Subscripts*	
q	specific cooling/heating effect ... kJ/kg	c	condenser or gas cooler
r_p	compressor pressure ratio	comp	compressor
s	specific entropy ... kJ/kg K	e	evaporator
t/T	temperature ... °C, K	ex	expansion device
T_o	reference temperature ... K	si	secondary fluid inlet
v	specific volume ... m^3/kg	eso	secondary fluid at evaporator outlet
V_h	volumetric heating capacity ... kJ/m^3	cso	secondary fluid at condenser/gas cooler outlet

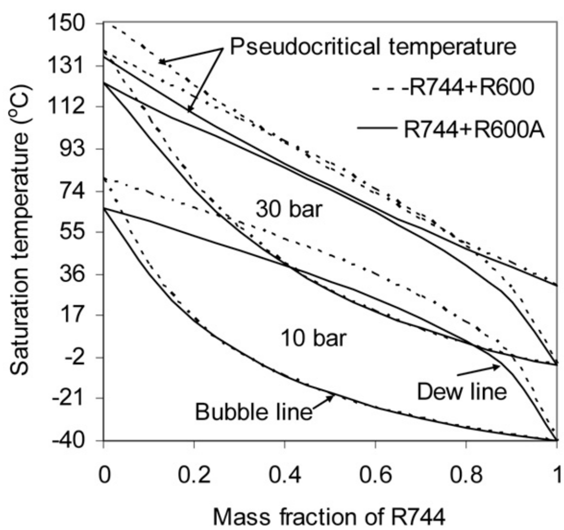

Fig. 1. T–x diagram of CO_2/isobutane and CO_2/butane mixtures.

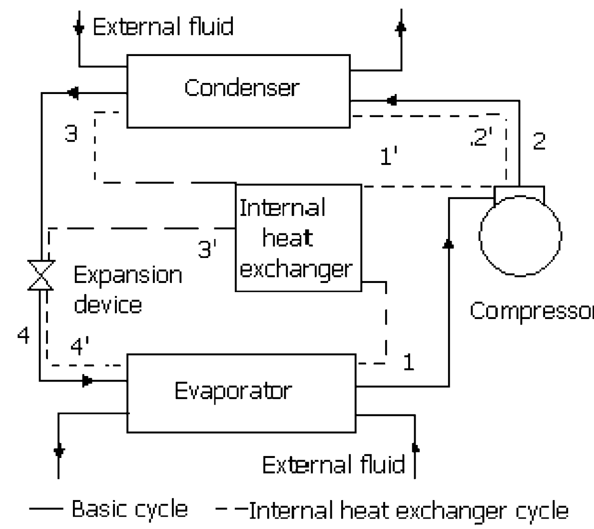

Fig. 2. Schematic diagram of mixture based heat pump.

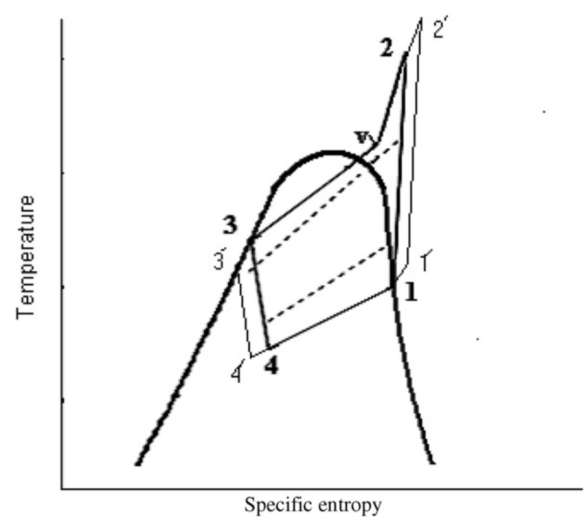

Fig. 3. Representative T–s diagram of a mixture based heat pump.

In the present study, blends of CO_2/butane and CO_2/isobutane are proposed as working fluids in heat pump for both space heating and industrial process heating. Performances have been evaluated for the zeotropic mixtures of both working pairs with various compositions and comparisons based on COP, compressor pressure ratio, volumetric heating effect, throttling loss and exergetic efficiency with R744, R600 and R600a are presented for both applications and various heating outlet temperatures. Effect of internal heat exchanger on mixture based heat pump and heat transfer aspects are studied as well for 50/50 compositions. Finally, performance comparison has been presented with respect to R114 for high temperature heating at 120 °C.

2. Mixture properties

Although the R600/R600a blend is an azeotropic mixture, blends of R744 with R600 and R600a will form zeotropic mixtures [13], whose gliding temperature condensation and evaporation can be very useful for single phase heating and cooling. The variations of saturation temperature with mixture composition at pressures of 10 bar and 30 bar along with the critical temperature are illustrated in Fig. 1. At any composition and pressure, the difference between dew point temperature and bubble point temperature of R744+R600 blend is higher than that of R744+R600a blend. Hence the R744+R600 blend can yield better performance for higher temperature glide cooling/heating applications compared to R744+R600a blend at the same composition.

3. Theoretical modelling and simulation

3.1. Mathematical modelling

As shown in the schematic diagram (Fig. 2) and corresponding T–s diagram (Fig. 3) of a mixture based heat pump, the saturated vapour at state 1 is compressed to state 2 in the compressor and then cooled in the condenser/gas cooler to state 3 by rejecting heat to the external fluid (useful heating effect). Saturated liquid (except pure R744) at state 3 is expanded through the expansion device to state 4 and then it evaporates in the evaporator by extracting heat from the external fluid (useful cooling effect). It may be noted that evaporation and condensation are at constant temperature for pure fluids. The broken line below process 2–3 represents the external fluid being heated and that above the evaporating process represents the external fluid being cooled. The entire system has been modelled based on energy balance of individual system components to yield the conservation equations that follow. Steady flow energy equations based on first law of thermodynamics have been employed in each case and the following assumptions have been made for the simplified theoretical analysis:

1. Heat transfer with the ambient is negligible.
2. Evaporation and condensation/gas cooling processes are isobaric.
3. Refrigerant at the evaporator outlet is dry saturated.
4. Refrigerant at the condenser outlet is wet saturated
5. The temperature approaches for both evaporator and condenser/gas cooler are a fixed value of 7 °C.
6. The compression process is adiabatic but non-isentropic with an isentropic efficiency of 75% for all cases.

Performance of the heat pump has been evaluated based on heating COP given by,

$$\mathrm{COP}_h = \frac{h_2 - h_3}{h_2 - h_1} \tag{1}$$

Volumetric heating effect, related to the compressor size for certain heating output, can be evaluated by,

$$V_h = q_c/v_1, \quad \text{where, } q_c = h_2 - h_3 \tag{2}$$

Percentage of irreversibility due to expansion is expressed as,

$$I_{\mathrm{ex}} = T_o(s_4 - s_3)/w, \quad \text{where, } w = h_2 - h_1 \tag{3}$$

Similarly, irreversibility in compressor is given by,

$$I_{\mathrm{comp}} = T_0(s_2 - s_1)/w \tag{4}$$

Evaporator and condenser irreversibilities for simultaneous cooling and heating applications are, respectively, given by:

$$I_e = T_0\left[(s_1 - s_4) - \frac{q_e}{T_{es}}\right]\Big/w, \quad \text{where, } q_e = h_1 - h_4 \tag{5}$$

$$I_c = T_0\left[\frac{q_c}{T_{\mathrm{cs}}} - (s_2 - s_3)\right]\Big/w \tag{6}$$

Hence, the second law efficiency for combined cooling and heating is expressed as:

$$\eta_{\mathrm{II}} = 1 - \sum I = (\mathrm{COP}_h - 1)\left(\frac{T_o}{T_{\mathrm{es}}} - 1\right) + \mathrm{COP}_h\left(1 - \frac{T_o}{T_{\mathrm{cs}}}\right) \tag{7}$$

where, T_{es} and T_{cs} are the thermodynamic average temperatures of secondary fluids for cooling and heating, respectively:

$$T_{\mathrm{es}} = \frac{(T_{\mathrm{si}} - T_{\mathrm{eso}})}{\ln(T_{\mathrm{si}}/T_{\mathrm{eso}})}; \qquad T_{\mathrm{cs}} = \frac{(T_{\mathrm{cso}} - T_{\mathrm{si}})}{\ln(T_{\mathrm{cso}}/T_{\mathrm{si}})} \tag{8}$$

It may be noted that the same inlet temperature is taken in case of both secondary fluids for simplicity, although it may not be identical usually for air-conditioning systems and heat pumps. In the evaporator, $T_1 = T_{\mathrm{si}} - \mathrm{AT}$ for constant temperature cooling and the following condition must be satisfied for variable temperature situations:

$$\min\left[(T_{\mathrm{si}} - T_1), (T_{\mathrm{eso}} - T_4)\right] = \mathrm{AT} \tag{9}$$

In the condenser, $T_3 = T_{\mathrm{si}} + \mathrm{AT}$ for constant temperature heating and the following condition must be satisfied for variable temperature situations:

$$\min\left[(T_3 - T_{\mathrm{si}}), \left(T_v - \left\{T_{\mathrm{si}} + \frac{h_v - h_3}{h_2 - h_3}(T_{\mathrm{cso}} - T_{\mathrm{si}})\right\}\right), (T_2 - T_{\mathrm{cso}})\right] = \mathrm{AT} \tag{10}$$

where, T_v is the saturated vapour temperature at condenser pressure and corresponding temperature of secondary fluid can be estimated from an energy balance.

On the other hand, in case of the gas cooler (heating application), to confirm a certain value of AT, the heat exchanger is discretised into 50 sub-ranges yielding 50 sub-zones of temperature between T_{si} and T_{cso}. The temperature difference between the refrigerant and the secondary fluid at any location should be more than or equal to AT. Temperature at the corresponding boundary of a zone of the refrigerant is found by conserving the heat exchanged between the two fluids in the gas cooler only for that length of the gas cooler. Thus temperature difference at each boundary is evaluated and restricted to be greater than or equal to the temperature approach (AT) with the help of an iterative technique. In this context, it is important to note that performance of transcritical R744 cycles has been analysed to obtain an optimum compressor discharge pressure (in bar) to yield maximum COP and is given by (temperature in °C) [14]:

$$P_2 = \frac{t_3 - 16.73}{0.32453 + 0.0011366t_1} + \frac{1044.3}{t_3} \tag{11}$$

3.2. Simulation code and validation

To investigate the heat pump performance, a simulation code was developed which was integrated with REFPROP [15] property subroutines for mixtures, R600, R600a and R114, and CO2PROP property subroutine [16] for R744 to compute relevant thermodynamic parameters. For given secondary fluid temperatures, the code searches for evaporation and condensation temperatures and pressures as well as all the state point properties using an effective iteration technique and the assumptions made based on the procedure discussed above and subsequently evaluates the first law and second law performance parameters based on the mathematical model presented above. In the present numerical model, the following tolerances have been used for convergence in simulation for the overall satisfaction: 10^{-3} for temperature (K) and enthalpy (kJ/kg), which yield an error in energy balance below 0.01% and COP computation in the range of 10^{-4}.

Due to unavailability of experimental data for R744–R600 (R600a) mixture, the present model is validated with the reported experimental results for a R744–R290 mixture [10]. Comparison for secondary fluid inlet temperatures of 26.7 °C and 35 °C in evaporator and condenser, respectively and $T_{\mathrm{evo}} = 17.9$ °C shows that the model prediction value of COP slightly higher (about 25%) than the experimental data and results will be similar for AT = 11 K. However, reported studies in the literature show that below 3 K temperature, approach is possible for pure R744 and hence some average value (7 K) has been taken.

3.3. Operating and performance parameters

In the present comparative study of blends with its individual refrigerants and R114 for different cooling and heating applications, the following design and performance parameters are considered: compressor pressure ratio, heating coefficient of performance and

Table 1
Performance comparison at $t_1 = 0\,^\circ\mathrm{C}$ and $t_3 = 40\,^\circ\mathrm{C}$ for 50/50 mixtures.

Refrigerant	P_c (bar)	r_p	t_2 (°C)	COP_h	V_h (kJ/m^3)	I_{ex} (%)	η_{II} (%)
R600	3.793	3.668	43.15	5.5746	174.1	12.02	50.18
R600a	5.308	3.394	42.05	5.4841	649.4	13.67	49.23
R744/R600	37.01	15.67	146.1	2.4466	2269.2	15.23	19.87
R744/R600a	36.87	10.53	126.8	2.6371	3017.9	16.88	15.61
R744	102.1	2.930	91.31	3.0901	17408.9	30.08	23.82

volumetric heating effect. The throttling loss and the system exergetic efficiency are also considered to study the effect of blend on component as well as system irreversibilities. These parameters are suitably presented to illustrate the various performance trends. The reference temperature is taken as 303 K. Unless otherwise specified, the mixture mass fraction is 50/50 for both R744/R600 and R744/R600a.

4. Results and discussions

4.1. Constant temperature cooling and heating

Table 1 presents the performance comparison at $t_1 = 0\,^\circ\mathrm{C}$ and $t_3 = 40\,^\circ\mathrm{C}$. The second law efficiency has been evaluated for simultaneous space cooling at a temperature of 5 °C and heating at a temperature of 35 °C. Use of blends will deteriorate the performance significantly (use of blends instead of R600 and R600a make the performance less than half) and increase the compressor pressure ratio. The volumetric capacities for blends are higher compared to R600 and R600a and lower compared to R744. Higher absolute pressure difference across the expansion valve leads to higher throttling loss for the R744 system. Results clearly show that the zeotropic blends R744 with R600 and R600a are not suitable for constant temperature (space) cooling and heating applications.

4.2. Variable temperature cooling and heating

Due to the temperature glide during evaporation and condensation, the zeotropic blend can yield very attractive returns in simultaneous single phase cooling and heating applications. Tables 2 and 3 show the performance comparisons of blends with pure refrigerants for secondary fluid inlet temperature of 30 °C, a temperature of 4 °C at evaporator outlet and temperatures of 73 °C and 100 °C, respectively, at condenser/gas cooler outlet. As shown in the tables, the blend based system is significantly superior in terms of lower compressor pressure ratio and throttling loss, and higher volumetric heating effect, heating COP and second law efficiency; however, it is inferior in terms of higher system pressure and compressor discharge temperature compared to R600 and R600a. On the other hand, the blend based systems are better in terms of lower system pressure, lower throttling loss, higher heating COP and higher second law efficiency, and worse with respect to lower volumetric heating effect, slightly higher compressor pressure ratio and compressor discharge temperature compared to R744. It is noted that the R744/R600a yields higher performance at a heating outlet temperature of 73 °C compared to R744/R600 whereas the trend is reverse at a heating outlet temperature of 100 °C due to higher temperature glide of R744/R600 during condensation. Results clearly show that the blends can be used very effectively in heat pumps for simultaneous cooling and heating applications and the existing system can be easily retrofitted using these blends as the high side pressure is similar to conventional systems.

4.3. Effect of mixture composition on performance

Selection of the perfect mixture composition in a refrigerant blend based heat pump is very important to obtain the best performance for certain operating conditions. It may be noted that the system performance is highly dependent on the matching of temperature glides; better fit of temperature glides of refrigerant and secondary fluid in both evaporator and condenser yields higher performance for the given requirements. The variation of heat pump performance with mixture composition are shown in Figs. 4 and 5 at secondary fluid inlet temperature of 30 °C, outlet temperatures of 4 °C in evaporator and 73 °C in condenser for R744/R600a and R744/R600, respectively. Results clearly show that the R744/R600a based heat pump exhibits the best performance for the higher R744 mass fraction compared to that for the R744/R600 based heat pump for the given operating conditions.

Table 2
Performance comparison for $t_{si} = 30\,^\circ\mathrm{C}$, $t_{eso} = 4\,^\circ\mathrm{C}$ and $t_{cso} = 73\,^\circ\mathrm{C}$.

Refrigerant	P_c (bar)	r_p	t_2 (°C)	COP_h	V_h (kJ/m^3)	I_{ex} (%)	η_{II} (%)
R600	9.70	9.742	78.0	2.6771	786.7	26.93	26.21
R600a	12.87	8.529	78.0	2.5358	1040.1	30.59	24.57
R744/R600	33.95	6.015	124.1	3.5907	4849.5	7.32	36.69
R744/R600a	33.79	4.246	106.5	4.2399	6630.0	8.19	42.98
R744	111.00	3.271	98.3	3.4306	19750.9	25.43	33.31

Table 3
Performance comparison for $t_{si} = 30\,^\circ\mathrm{C}$, $t_{eso} = 4\,^\circ\mathrm{C}$ and $t_{cso} = 100\,^\circ\mathrm{C}$.

Refrigerant	P_c (bar)	r_p	t_2 (°C)	COP_h	V_h (kJ/m^3)	I_{ex} (%)	η_{II} (%)
R600	16.80	16.877	105.0	1.7777	638.7	39.79	23.35
R600a	21.75	14.413	105.0	1.5747	782.6	46.27	20.17
R744/R600	35.50	6.289	126.9	3.4693	4808.5	8.29	49.91
R744/R600a	43.69	5.490	122.6	3.2511	5783.1	14.76	46.48
R744	141.5	4.169	121.2	3.0698	22030.9	23.93	40.21

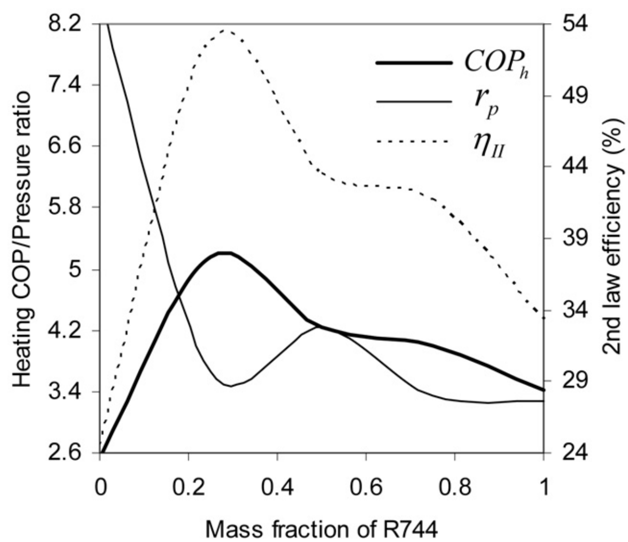

Fig. 4. Performance of R744/R600a heat pump with mixture composition at $t_{si} = 30\,^\circ\mathrm{C}$, $t_{eso} = 4\,^\circ\mathrm{C}$ and $t_{cso} = 73\,^\circ\mathrm{C}$.

4.4. Effect of using internal heat exchanger on performance

Performance improvement of R744/R600 and R744/R600a based heat pumps by use of internal heat exchanger (cycle is 1-1'-2'-3-3'-4' as given in Figs. 2 and 3, where, saturated vapour is superheated, 1'-2' by subcooling of saturated liquid, 3-3', and effectiveness is given by [16], $(T_{1'} - T_1)/(T_3 - T_1)$) for varying heat exchanger effectiveness is shown in Fig. 6 at $t_1 = 0\,^\circ\mathrm{C}$ and $t_3 = 40\,^\circ\mathrm{C}$. Results show that the use of suction line heat exchanger is more profitable in case of R744/R600a (COP improves by 4% for effectiveness of 70%) than in case of R744/R600 (COP improves by 1.5% for an effectiveness of 70%). Hence, the use of internal heat exchanger is

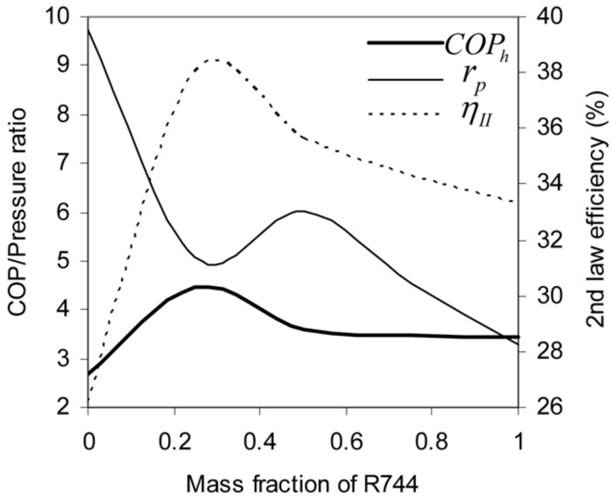

Fig. 5. Performance of R744/R600 heat pump with mixture composition at $t_{si} = 30\,^{\circ}\mathrm{C}$, $t_{eso} = 4\,^{\circ}\mathrm{C}$ and $t_{cso} = 73\,^{\circ}\mathrm{C}$.

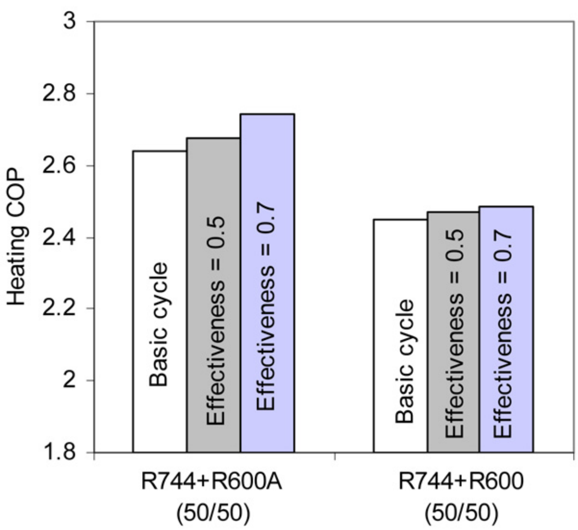

Fig. 6. Effect of internal heat exchanger on heat pump performance.

more effective for R744/R600a heat pump than for R744/R600 with respect to both performance and heat exchanger compactness. Second law analysis also shows that internal heat exchanger is more effective for R744/R600a.

4.5. Performance comparison with R114 for high temperature heating

Performance comparisons of natural refrigerants R600, R600a, R744 and natural refrigerant blends R744/R600 and R744/R600a with the synthetic refrigerant R114 (which is being used for high temperature heating) for high temperature heating at a heating outlet temperature of 120 °C are presented in Table 4 for refrigerant temperature of 25 °C at evaporator outlet and secondary fluid inlet temperature of 30 °C. As shown in the table, R114, R600 and R600a exhibit comparable performance for high temperature heating. The R744 yield superior performance compared to R114 in terms of compressor pressure ratio, volumetric capacity and heating COP, although the high side system pressure is very high compared to R114 for heat pump applications. R744/R600 exhibits better performance in term of heating COP (2 times), compressor pressure ratio, volumetric heating capacity (5 times), although the high side system pressure will be double and the discharge temperature will be slightly higher. On the other hand, the

Table 4
Performance comparison for high temperature heating at $t_{cso} = 120\,^{\circ}\mathrm{C}$.

Refrigerant	t_1 (°C)	t_{si} (°C)	P_c (bar)	r_p	t_2 (°C)	COP_h	V_h (kJ/m^3)
R114	25	30	22.77	10.620	125.0	1.4444	825.2
R600	25	30	24.16	9.909	125.0	1.7075	1130.5
R600a	25	30	30.91	8.824	125.0	1.3103	1130.7
R744/R600	25	30	45.59	8.077	142.6	2.8588	4677.2
R744/R600a	25	30	45.88	5.765	125.7	3.1027	5678.8
R744	25	30	257.9	4.024	125.9	3.1583	47036.0

Table 5
Heat transfer coefficient (W m^{-2} K^{-1}) based on saturated liquid properties (operating pressures are same as for Table 3).

Pressure (bar)	R114	R600	R600a	R744	R744/R600	R744/R600a
Evaporation	336.2	761.5	732.5	977.3	777.4	752.3
Condensation	494.3	1032.1	1087.4	1085.5	917.8	954.2

R744/R600a blend based heat pump gives superior performance in terms of lower compressor pressure ratio (nearly half), nearly 7 times higher volumetric heating effect (system compactness) and higher heating COP (115% higher) at the expense of higher cost due to doubled high side system pressure. Although the heating COP of R744 system is marginally higher than that of R744/R600a blend but the system is less attractive due to very high system pressure. Results clearly show that the blend R744/R600a can be a superior alternative to R114 for high temperature heating with conventional high side system pressure.

4.6. Heat transfer considerations

Usually mixture exhibits lower heat transfer coefficient compared to pure fluids [17] and on the other hand, the temperature approach depends on heat transfer properties of the fluids and also the design of heat exchanger in the real system, and hence the analysis with respect to heat transfer aspect is also essential. Table 5 shows the heat transfer coefficient based on saturated liquid properties (since the heat transfer coefficient of boiling or condensation is based on it [6]) for same operating pressures as in Table 3 and a tube diameter of 8 mm and a mass velocity of 200 kg/m^2 s (maximum possible mass flux for 50/50 hydrocarbon mixtures [6]). The heat transfer coefficients have been evaluated based on Dittus–Boelter correlation [6] based on saturated liquid properties. Results show that the heat transfer coefficient reduces significantly in case of the mixture (of maximum 23% compared to pure R744), however it is heartening to note that the blends exhibit superior heat transfer properties than synthetic refrigerant R114 and hence AT will be relatively lower for the same heat transfer design, which confirms the superior performance. The heat transfer performances of zeotropic mixtures in evaporator and condenser decrease so that the COP of actual system becomes lower in spite of its higher potential in the ideal condition than that with pure/azeotrope refrigerant for same heat transfer area. Hence, the performance improvement by using zeotropic mixtures, presented in Table 3, will reduce modestly for the real system; actual improvement can be measured through an experimental study only in view of the complexity inherent of the boiling and condensation processes and relatively larger property variations for the mixture.

5. Conclusions

Detailed theoretical performance analyses of heat pumps based on the zeotropic blends of CO_2/butane and CO_2/isobutene with different compositions, and comparative studies with pure refrigerants have been performed for both space and industrial process heating applications. Based on the investigations, following conclusions can be drawn:

1. Blend based systems are significantly superior in terms of compressor pressure ratio, throttling loss, volumetric heating effect, heating COP and second law efficiency, and inferior with respect to system pressure and discharge temperature compared to R600 and R600a, whereas, better in terms of system pressure, throttling loss, heating COP and second law efficiency, and worse in terms of volumetric heating effect, compressor pressure ratio and compressor discharge temperature compared to R744 for variable temperature cooling and heating.
2. The R744/R600a yields higher performance at a heating outlet temperature of 73 °C compared to R744/R600 whereas the trend is reversed at a heating outlet temperature of 100 °C for optimum secondary fluid mass flow rate due to higher temperature glide of R744/R600.
3. R744/R600a based heat pumps exhibit the best performance for higher R744 mass fraction compared to that for R744/R600 for the given operating conditions.
4. The use of internal heat exchanger is more effective for R744/R600a heat pump than R744/R600 heat pump with respect to both performance and system compactness.
5. The blends show superior performance than hydrocarbons in high temperature heating applications in terms of lower compressor pressure ratio, higher volumetric heating effect and higher heating COP.
6. Although R744 exhibits superior performance than R114 as compared to the blends, the blends do offer a better alternative to R114 in heat pumps for high temperature application due to the excessively high side pressure of R744 systems.
7. Although heat transfer properties of blends are modestly inferior to its pure refrigerant equivalent, they are significantly higher than R114, which makes the blend a promising alternative to R114.

References

[1] S.F. Pearson, Natural refrigerants for heat pumps, IEA Heat Pump Center Newsletter 20 (2004) 13–16.
[2] E. Granryd, Hydrocarbons as refrigerants – an overview, Int. J. Refrig. 24 (2001) 15–24.
[3] B. Mongey, J.T. McMullan, M.G. McNerlin, An examination of hydrocarbon mixtures for use in high temperature heat pump applications, in: Applications for Natural Refrigerants, IIR Conference, Aarhus, Denmark, 1996.
[4] A. Firth, G. Carrington, Performance of Care 50 as an R22 replacement in a domestic HPAC system, in: Proceedings of the 20th International Congress on Refrigeration, IIR/IIF, Sidney, Australia, 1999, vol. V, Paper 549.
[5] K. Mani, V. Selladurai, Experimental analysis of a new refrigerant mixture as drop-in replacement for CFC12 and HFC134a, Int. J. Therm. Sci. 47 (2008) 1490–1495.
[6] Y.S. Chang, M.S. Kim, S.T. Ro, Performance and heat transfer characteristics of hydrocarbon refrigerants in a heat pump system, Int. J. Refrig. 23 (2000) 232–242.
[7] N.J. Hewitt, J.T. McMullan, P.C. Henderson, B. Mongey, Advanced cycles and replacement working fluids in heat pumps, Appl. Thermal Engrg. 21 (2001) 237–248.
[8] L. Nanxi, L. Shi, H. Lizhong, Z. Mingshan, Moderately high temperature water source heat-pumps using a near-azeotropic refrigerant mixture, Applied Energy 80 (2005) 435–447.
[9] K.J. Park, T. Seo, D. Jung, Performance of alternative refrigerants for residential air-conditioning applications, Applied Energy 84 (2007) 985–991.
[10] S.G. Kim, M.S. Kim, Experiment and simulation on the performance of an autocascade refrigeration system using carbon dioxide as a refrigerant, Int. J. Refrig. 25 (2002) 1093–1101.
[11] N. Baolian, Z. Yufeng, Experimental study of the refrigeration cycle performance for the R744/R290 mixtures, Int. J. Refrig. 30 (2007) 37–42.
[12] J.H. Kim, J.M. Cho, I.H. Lee, J.S. Lee, M.S. Kim, Circulation concentration of CO_2/propane mixtures and the effect of their charge on the cooling performance in an air-conditioning system, Int. J. Refrig. 30 (2007) 43–49.
[13] S. Artemenko, M. Khmel'njuk, V. Mazur, Azeotropy in natural and artificial refrigerant blends, in: Sixth IIR G Lorentzen Natural Working Fluids Conference, Glasgow, 2004.
[14] J. Sarkar, S. Bhattacharyya, M. Ramgopal, Natural refrigerant-based subcritical and transcritical cycles for high temperature heating, Int. J. Refrig. 30 (2007) 3–10.
[15] REFPROP, NIST refrigerant properties database, Version 6.01.
[16] J. Sarkar, S. Bhattacharyya, M. Ramgopal, Optimization of a transcritical CO_2 heat pump cycle for simultaneous cooling and heating applications, Int. J. Refrig. 27 (2004) 830–838.
[17] L. Rajapaksha, Influence of special attributes of zeotropic refrigerant mixtures on design and operation of vapour compression refrigeration and heat pump systems, Energy Conversion Management 48 (2007) 539–545.