THERMODYNAMIC COMPARISION OF R744/R600A AND R744/R600 USED IN MID-HIGH TEMPERATURE HEAT PUMP SYSTEM

by

Xiao-Wei FAN [*a], ***Fu-Jun JU*** [a], ***Xian-Ping ZHANG*** [b], ***and Fang WANG*** [a]

[a] School of Energy and Environment, Zhongyuan University of Technology, Zhengzhou, China
[b] School of Civil Engineering, Henan Institute of Engineering, Zhengzhou, China

Original scientific paper
DOI: 10.2298/TSCI1405655F

The mid-high temperature heat pump provides hot water at a relatively high temperature using some industrial waste heat as its source. Now, the main refrigerants in this application are CFC114, HCFC123, and HCFC142b, etc., which are scheduled to be phased out due to their high ozone depletion potential and global warmth potential. Some studies have been conducted to find an eco-friendly alternative. In this paper, the natural non-azeotropic mixtures R744/R600a and R744/R600 are analyzed as alternatives. The performance of the heat pump system using new mixture is discussed and compared with those with CFC114, HCFC123, and HCFC142b. Under the given operating conditions, the maximum heating COP should occur at the mass fractions of 18/82 for R744/R600a and 10/90 for R744/R600. Both of their COP are higher than those with the refrigerants of CFC114, HCFC123, and HCFC142b. The COP and volumetric heating capacity of the system with R744/R600a are superior to those with R744/R600.

Key words: *carbon dioxide, butane, isobutene, heat pump, mid-high temperature*

Introduction

The proper choice of an appropriate working fluid for a given heat pump application is very important, but it is not straightforward. For mid-high temperature heat pump system which is commonly used in medical, dry, food, wood, and chemical industries, R114 was once widely used as the working fluid [1, 2]. Some studies on alternative refrigerant for mid-high temperature heat pump have been carried out for many years, such as R123, R142b, R22/R141b [3], R124/R142b/R600a [4], R22/R236ea, R22/R236ea/R141b [5], and R600, R600a [6]. The literature on mid-high temperature heat pump similarly focuses on the choice of refrigerant [7]. However, due to the multiple factors which would influence the selection of working fluid for mid-high temperature heat pump, there is still no satisfactory refrigerant to substitute R114. In the long term consideration, natural alternative refrigerant should be the best choice.

Sarkar *et al.* [8] theoretically investigated the system performances of heat pump using mixtures of R744/R600 and R744/R600a with various compositions as working fluids, respectively and compared performances of 50/50 mixtures with those of R744, R600a, and R600. Performance comparisons of R600, R600a, R744, and R744/R600 and R744/R600a with R114 for high temperature heating at a heating outlet temperature of 120 °C are presented. Based on the requirement in China and our research group works in heat pump using pure R744 and R744-based mixture as refrigerants, R744/R600a (MZ1) and R744/R600 (MZ2) are proposed as the candidate alternative for mid-high temperature heat pump [9, 10]. In this pa-

* Corresponding author; e-mail: xwfan@zut.edu.cn

per, the heating *COP*, compressor power consumption, condensation pressure, compression ratio, discharge temperature, mass and volumetric heating capacities have been analyzed for different MZ1 and MZ2 mixtures at the operating conditions.

Thermodynamic analysis

The heat pump system

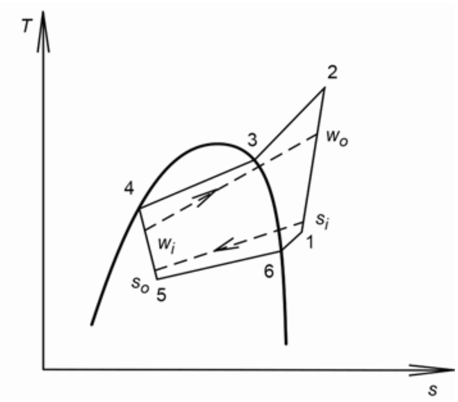

Figure 1. Schematic of subcritical heat pump using MZ1 or MZ2 as refrigerant

The heat pump consists of a compressor (process 1-2), a condenser (2-3-4), an expansion valve (4-5), and an evaporator (5-6-1) as shown in fig. 1. The heat exchangers are all of the counter flow type, and working fluid of one side is refrigerant while the other is water.

Assumptions

The assumptions are made to simplify the modelling: the heat pump system operates at a steady state; the refrigerants are all taken as pure substances without consideration of the effect of lubricant upon the properties of working fluid; pressure drops in all components and connecting pipes have been neglected; the heat transfer efficiency of condenser and evaporator are 1.0; compression process is adiabatic but non-isentropic, and the isentropic efficiency is assumed to be 0.70; the heat transfer pinch point temperature for heat exchangers is set at 7 °C [8].

Main equations

The heat pump system performances have been assessed on the basis of heating *COP* which is defined as:

$$COP_{\mathrm{h}} = \frac{h_2 - h_4}{h_2 - h_1} \tag{1}$$

The heat transfer pinch point in condensation process is defined as:

$$PP_{\mathrm{co}} = \min\left\{ t_2 - t_{\mathrm{wo}},\quad t_3 - \left[t_{\mathrm{wi}} + \frac{h_3 - h_4}{h_2 - h_4}(t_{\mathrm{wo}} - t_{\mathrm{wi}}) \right],\quad t_4 - t_{\mathrm{wi}} \right\} \tag{2}$$

The heat transfer pinch point in evaporation process is calculated in the same way.

The thermal properties of MZ1 and MZ1 mixtures are calculated by REFPROP 9.0 [11]. A modelling code using engineering equation solver (EES) was developed.

Operating conditions

Considering the industrial waste heat available in China and heat pump user's demand, the heat sink inlet temperature is set at 30 °C and the hot water outlet temperatures should exceed 85 °C [2, 12]. The heat source inlet and outlet temperatures are 30 °C and 10 °C, respectively, by which the evaporation temperature can be determined.

Results and discussions

It should be pointed out that the maximum mass fraction of R744 in the mixtures should be 55% for MZ1 and 35% for MZ2, above which the pseudo-critical temperature of MZ1 and MZ2 will be low and therefore the system will fail to achieve the expected mid-high temperature. Figure 2 illustrates the variation of heat pump system performances with the mass fraction of R744 for MZ1 and MZ2 when the hot water outlet temperature is 85 °C. The heating *COP* increases firstly and then decreases with the mass fraction of R744. The optimum mass fractions of MZ1 and MZ2 are 18/82 and 10/90, respectively, at which the heating *COP* attains the maximum. MZ1 has a higher system performance at optimum mass fraction than MZ2 under the given conditions. It can be seen that the compressor power consumption of MZ2 system is larger than that of MZ1 within the mass fraction range of R744. The compressor power consumption decreases at first and then increases.

The variations of mass heating capacity and volumetric heating capacity with the mass fraction of R744 are shown in fig. 3. When the mass fraction of R744 is increased, the mass heating capacities of MZ1 and MZ2 system all increase at first and then gradually decrease, but the volumetric heating capacity always augments. The relationships of condensation pressure, compression ratio, and the mass fraction of R744 are shown in fig. 4. For MZ1 and MZ2, the tendency of condensation pressure indicates the similar change with the mass fraction of R744. Compression ratio for MZ2 decreases first and then increases with the mass fraction of R744. Near the maximum mass fraction, the compression ratio increases flat, and then decreases again, which is more obvious for MZ1. At the optimal mass fraction, MZ1 has a smaller compression ratio than MZ2.

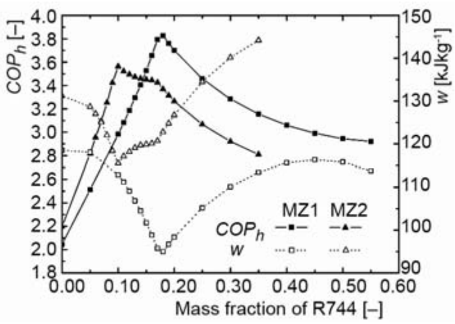

Figure 2. COP_h and compressor power of MZ1 and MZ2 *vs.* mass fraction of R744

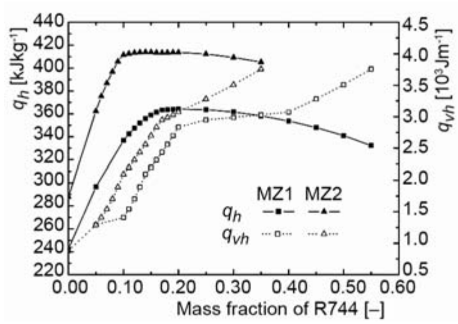

Figure 3. q_h and volumetric heating capacity of MZ1 and MZ2 *vs.* mass fraction of R744

When the hot water outlet temperature is increased from 85 °C to 95 °C, the system heating *COP* reduces due to the more compressor power consumption and the decrease of mass heating capacity, which can been observed in fig. 5. Meanwhile, the optimum mass fractions for MZ1 and MZ2 system increases slightly, which means the water temperature is one of the factors influencing the optimum mass fraction. The condensation pressure is increased with the outlet heat sink temperature. When the mass fraction of R744 is greater than 0.25, the outlet water temperature has a weak influence on the condensation pressure.

Some main parameters of the heat pump system for different refrigerants are listed in tab. 1. MZ1-opt and MZ2-opt mean the mixtures with the composition at which the maximum heating *COP* will be attained. Compared with CFC114, HCFC123, and HCFC142b, the heating *COP* is considerably increased by 95.35%, 54.88%, and 57.30% for MZ1-opt; and for MZ2-opt 81.88%, 44.19%, and 46.40%. Although the COP_h of MZ1-opt is greater than

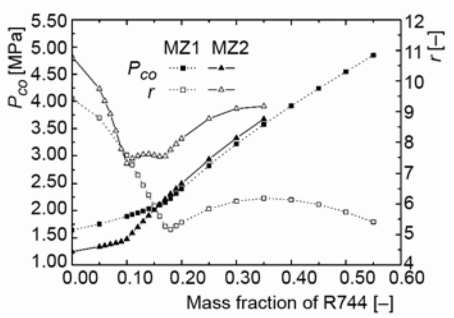

Figure 4. Condensation pressure and compression ratio *vs.* mass fraction of R744

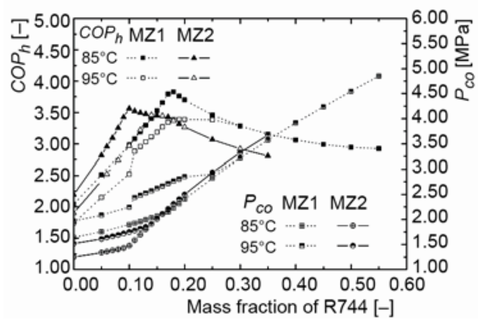

Figure 5. COP_h and P_c *vs.* mass fraction of R744 for different outlet water temperature

Table 1. Performance comparison for R114, R123, and R142b, MZ1 and MZ2 with optimal composition

Refrigerant / Parameters	MZ1-opt	MZ2-opt	R114	R123	R142b
COP_h [–]	3.827	3.563	1.959	2.471	2.433
w_c [kJkg^{-1}]	95.00	115.50	45.33	62.18	72.22
q_h [kJkg^{-1}]	363.60	411.50	88.82	153.60	175.70
q_{vh} [kJm^{-3}]	3887.0	2091.0	678.5	232.7	776.3
P_c [MPa]	2.225	1.477	1.206	0.5895	1.516
P_e [MPa]	0.431	0.202	0.099	0.037	0.162
r [–]	5.16	7.32	12.22	15.77	9.38
t_2 [°C]	100.8	99.3	92.0	102.3	104.6

that of MZ2-opt, MZ1 has a larger mass heating capacity than that of MZ2. Related to R114, R123, and R142b, the volumetric heating capacity of the system with MZ1-opt should be improved to 208%, 895%, and 195%, respectively; and with MZ2-opt it should be varied to 529%, 799%, and 169%. Both compression ratios of MZ1-opt and MZ2-opt system are lower than that of R114, R123, and R142b. For condensation pressure, compared to R114, R123, and R142b, the condensation pressure of MZ1-opt or MZ2-opt is slightly increased but below 2.3 MPa, which means heat pump using MZ1-opt or MZ2 can work under the conventional pressure. The MZ2-opt system is superior to MZ1-opt in assuring more safe and steady operation. The discharge temperatures of MZ1-opt and MZ2-opt are slightly greater than that of R114, but lower than those of R123 and R142b. Therefore, it can be concluded that the discharge temperature of MZ1-opt and MZ2-opt can ensure the steady operation of mid-high temperature heat pump.

Conclusions

For the mid-high temperature heat pump, both MZ1 and MZ2 mixtures are more efficient, and excellent system performances can be obtained compared with R114, R123, and R142b system under the given operating condition. By simulation, there exist the optimum mass fractions of 18/82 for MZ1 and 10/90 for MZ2, at which the heating *COP* will be 3.827 and 3.563, respectively. The MZ1 system has a higher system performance at optimum mass fraction than MZ2. Meanwhile, the unit volumetric heating capacities of the system with MZ1 and MZ2 are considerably enhanced compared with R114, R123, and R142b. The compression ratios of the system with MZ1 and MZ2 will be reduced, while the discharge temperatures changed a little. With a comprehensive consideration, MZ1 and MZ2 mixtures can work as a competitive alternative to the currently-used mid-high heat pump system.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 51176207) and Innovation Scientists and Technicians Troop Construction Projects of Zhengzhou City.

Nomenclature

P – pressure, [MPa]
PP – heat transfer pinch point, [°C]
q – heating capacity, [$kJkg^{-1}$ or kJm^{-3}]
r – compression ratio, [–]
t – temperature, [°C]

Subscripts

1-7 – state points of refrigerant
h – heating
wi – inlet of heat sink, water
wo – outlet of heat sink, water

References

[1] Chua, K. J., *et al.*, Advances in Heat Pump Systems: A review, *Applied Energy*, *87* (2010), 12, pp. 3611-3642
[2] Laue, H. J., Regional Report Europe: "Heat Pumps – Status and Trends", *International Journal Refrigeration*, *25* (2002), 4, pp. 414-420
[3] Li, T. X., *et al.*, High Temperature Hot Water Heat Pump with Non-Azeotropic Refrigerant Mixture HCFC-22/HCFC-141b, *Energy Conversion and Management*, *43* (2002), 15, pp. 2033-2040
[4] Liu, N. X., *et al*, Moderately High Temperature Water Source Heat-Pumps Using a Near-Azeotropic Refrigerant Mixture, *Applied Energy*, *80* (2005), 4, pp. 435-447
[5] Gao, P., Zhao, L., Research on Cycle Working Fluids for Moderate and High Temperature Heat Pump Systems, *Heating Ventilating & Air Conditioning*, *36* (2006), 1, pp. 24-27
[6] Pan, L. S., *et al.*, Experimental Research on Two Natural Working Fluids of Moderately High Temperature Heat Pump, *Acta Energiae Solaris Sinica*, *33* (2012), 4, pp. 827-831
[7] Minea, V., Drying Heat Pumps – Part I: System Integration, *International Journal of Refrigeration*, *36* (2013), 3, pp. 643-658
[8] Sarkar, J., Bhattacharyya, S., Assessment of Blends of CO_2 with Butane and Isobutane as Working Fluids for Heat Pump Applications, *International Journal of Thermal Sciences*. *48* (2009), 7, pp. 1460-1465
[9] Zhang, X. P., *et al.*, Theoretical and Experimental Studies on Optimum Heat Rejection Pressure for a CO_2 Heat Pump System, *Applied Thermal Engineering*, *30* (2010), 16, pp. 2537-2544
[10] Fan, X. W., *et al.*, Research on Performance of Heat Pump Systems Using R744/R600 and R744/R600a Mixtures as Refrigerants (in Chinese), *Journal of Refrigeration*, *32* (2011), 6, pp. 35-39
[11] Sun, F. T, *et al.*, New Waste Heat District Heating System with Combined Heat and Power Based on Absorption Heat Exchange Cycle in China, *Applied Thermal Engineering*, *37* (2012), 5, pp. 136-144
[12] Lemmon, E. W., *et al.*, *Reference Fluid Thermodynamic and Transport Properties (REFPROP),* NIST Standard Reference Database 23, Version 9.0, 2012

Paper submitted: October 2, 2013
Paper revised: March 6, 2014
Paper accepted: July 13, 2014