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Cycle performance studies on a new HFC-161/125/143a mixture as an alternative refrigerant to R404A*

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Abstract: In this paper, a new ternary non-azeotropic mixture of HFC-161/125/143a (0.15/0.45/0.40 in mass fraction), as a promising mixed refrigerant to R404A, is presented. The ozone depletion potential (ODP) of the new refrigerant is zero and its basic thermodynamic properties are similar to those of R404A, but its global warming potential (GWP) is much smaller than those of R507A and R404A. Meanwhile, theoretical calculations show that, under the working condition I (the average evaporation temperature: −23 °C, the average condensing temperature: 43 °C, the superheat temperature: 28 °C, the subcooling temperature: 5 °C), the volumetric refrigerating effect and specific refrigerating effect of the new mixture are 2.33% and 15.48% higher, respectively, than those of R404A. The coefficient of performance (COP) of the new mixture is 5.19% higher than that of R404A and the pressure ratio of the new mixture is 0.82% lower than that of R404A. Equally, under the working condition II (the average evaporation temperature: −40 °C, the average condensing temperature: 35 °C, the superheating temperature: 30 °C, the subcooling temperature: 5 °C), the volumetric refrigerating effect and specific refrigerating effect of the new mixture are 2.24% and 20.58% higher, respectively, than those of R404A. The COP of the new mixture is 4.60% higher than that of R404A and the pressure ratio of the new mixture is similar to that of R404A. The performances of the new mixture and R404A are compared in a vapor compressor refrigeration apparatus originally designed for R404A under several working conditions (condensing temperatures: 35–45 °C, evaporation temperatures: −40–−20 °C). Experimental results show that the new mixture can obtain a higher COP, by 6.3% to 12.1%, and a lower pressure ratio, by 1.8% to 6.6%, compared to R404A; although the discharge temperature of the new mixture is slightly higher than that of R404A. The advantages of the new mixture will be further verified in the actual system.

Key words: Alternative refrigerant, Mixture, Cycle performance, R404A, HFC-161
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1 Introduction

R502 is the mixture of chlorodifluoromethane (R22) and chloropentafluoroethane (R115), with the mass fractions being 0.488 and 0.512. Its normal boiling point is −45 °C and is an important refrigerant in low temperature applications due to its good thermodynamic performance. The provisions of the Montreal protocol have prohibited the use of R115 and were to be phased out by the year 1996 in developed countries, and before 2010 in developing countries. The deadline for the use of R22 is year 2020 in developed countries and year 2030 in developing countries (Jiang, 1997; Arora and Kaushik, 2008). Concerning the ozone depletion potential (ODP) and global warming potential (GWP) of R22 and R115, the research on refrigerant replacement for R502 has been one of the key focuses in the refrigeration and air-conditioning industry.

Some research has been done to develop the new alternative refrigerants to R502 (Aprea and Mastrullo, 1996; Riffat *et al.*, 1997; Doring *et al.*, 1997; Swinney *et al.*, 1998; Granryd, 2001). Two important substitutes of R502 are R507A and R404A. R507A is a binary azeotropic refrigerant composed of

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HFC-125/R143a (0.50/0.50 in mass fraction), and its normal boiling point is slightly lower than that of R502. Thus, it is commonly selected for low temperature applications at a temperature range of −40–−45 °C, such as low temperature freezers. R404A is a ternary-mixture refrigerant composed of HFC-125/R143a/R134a (0.44/0.52/0.04 in mass fraction) and its normal dew point and bubble point temperatures are very close to those of R502. Thus, R404A is commonly used for cold storages at a temperature range of −35–−40 °C. Performance evaluation of R404A and R507A refrigerant mixtures in an experimental double-stage vapour compression plant is developed by Llopis *et al.* (2010). However, the GWP of R507A and R404A are high (Calm and Hourahan, 2007).

HFC-161 is an environmentally friendly refrigerant (ODP=0, GWP=12 and the atmospheric lifetime is 3 years). However, its flammable characteristic limits its application as a pure working fluid for refrigeration and air-conditioning systems. Thus, the mixture of HFC-161 with flame retardants, such as HFC-125 can be proposed for practical applications. Some research has been conducted on the new alternative refrigerants with HFC-161 for replacing R22 and R502 (Chen *et al.*, 2005; Guo *et al.*, 2005; Xuan and Chen, 2005; Han *et al.*, 2007; Wang *et al.*, 2009). Xuan *et al.* (2005) proposed M2 (HFC-161/HFC-125/HFC-143a (0.10/0.45/0.45 in mass fraction)) as the replacement of R502. However, from analysis results, there are some shortcomings. For example, an increase of coefficient of performance (COP) is not obvious in two working conditions, but the GWP of M2 is still high. Also, there are a few experimental results that need to be verified to confirm the merits of the cycle performances within a wide range of temperatures. Therefore, the mixture HFC-161/125/143a, with new mass fractions, is proposed in this work, and the cycle performances of it and R404A are tested and compared in an experimental apparatus to verify its potentials as an alternative refrigerant for R404A, as well as R502.

2 Proposed mixed refrigerant

2.1 Physical and environmental characteristics

The HFC-161/125/143a mixture has a composition of 0.15/0.45/0.40 in mass fraction, and is named "M4". Nonflammable HFC-125 is added in consideration of the flammability of HFC-161. The basic physical characteristics of the new ternary alternative refrigerant M4 are compared with R502, R507A, and R404A in Table 1 and Fig. 1 (Calm and Hourahan, 2007; McLinden *et al.*, 2007).

From Table 1, it can be seen that the normal bubble boiling point temperature and normal dew boiling point temperature of M4 are similar to those of R502, but a little higher than those of R507A and R404A. The critical temperature of M4 is lower than that of R502 and a little bit higher than those of R507A and R404A, but the critical pressure of M4 is the highest among these refrigerants. It can also be seen that the GWP of the M4 is smaller than the other three refrigerants, with an ODP of zero.

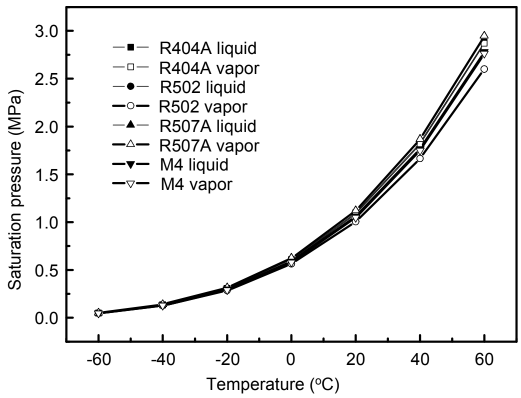

Fig. 1 Bubble and dew pressures of R502, R404A, R507A and M4

Table 1 Physical and environmental characteristics of R502, R507A, R404A and M4

Refrigerant	Molar mass (g/mol)	Bubble point temperature (°C)*	Dew point temperature (°C)*	Critical temperature (°C)	Critical pressure (MPa)	ODP	GWP
R502	111.63	−45.10	−45.10	80.70	3.92	0.25	4700
R507A	98.86	−46.70	−46.70	70.50	3.70	0	4000
R404A	97.60	−46.20	−45.47	72.00	3.72	0	3900
M4	84.04	−45.16	−44.54	78.85	4.13	0	3300

* Bubble point and dew point are saturation temperatures under standard atmosphere pressure, 101.325 kPa

Fig. 1 shows that the saturation pressure of M4 is similar to those of R502, R507A, and R404A at the temperature range of −60 to 0 °C. Therefore, there is no modification required for the structure of refrigeration systems for R404A, if M4 is supplied as a retrofit refrigerant.

2.2 Theoretical cycle performances at nominated working conditions

The cycle performances of M4 and R404A are calculated at nominated working conditions I and II listed in Table 2, and the calculated results are shown in Table 3. The thermodynamic properties of the refrigerants required in the calculations were supplied by REFPROP routines (McLinden *et al*., 2007). In the calculations, the total efficiency of compressor is 0.65 (the total efficiency mainly consists of the isentropic efficiency (about 0.8), the mechanical efficiency (about 0.9), and the electric efficiency (about 0.9)) (Wu, 2004).

From Table 3, it can be seen that, under the working condition I, the volumetric refrigerating effect and specific refrigerating effect of M4 are 2.33 % and 15.48% higher, respectively, than those of R404A, the COP of M4 is 5.19% higher than that of R404A, and the pressure ratio of M4 is 0.82% lower than that of R404A. Under the working condition II, the volumetric refrigerating effect and specific refrigerating effect of M4 are 2.24% and 20.58% higher, respectively, than those of R404A. The COP of M4 is 4.60% higher than that of R404A and the pressure ratio of M4 is similar to that of R404A. These results indicated that M4 can be a promising alternative refrigerant to R404A, as well as R502.

Table 2 Parameters of the nominated working conditions

Working condition	t_e (°C)	t_c (°C)	t_{suph} (°C)	t_{subc} (°C)
I	−23	43	28	5
II	−40	35	30	5

t_e, t_c, t_{suph}, and t_{subc} are the average evaporation temperature, average condensing temperature, the degree of superheat, and the degree of subcooling, respectively

3 Experiment

3.1 Materials

R404A is supplied by Honeywell Company, HFC-125, HFC-143a, and HFC-161 are supported by Zhejiang Lantian Environment Protection Hi-Tech Co., Ltd. with a minimum mass fraction purity of 99.99%, 99.99%, and 99.74%, respectively. There is no further purification to be done for these refrigerants before use. Each sample of the HFC-161/125/143a (0.15/0.45/0.40 in mass fraction) new mixture is mixed in a cylinder, with a volume of 5 L, by charging the three pure refrigerants in turn according to their calculated weights. The liquid in the cylinder is analyzed by gaseous chromatography to ensure the correct composition.

3.2 Experimental apparatus

An experimental apparatus was built to investigate the cycle performance of this new refrigerant and R404A. The schematic diagram of the refrigeration system is shown in Fig. 2, similar to that described in detail by Han *et al.* (2007; 2012). In the experimental apparatus of this work, the compressor used in the experiment is a reciprocating piston, hermetically sealed type with a displacement volume of 20.9 cm^3, originally designed for R404A (Danfoss SC21CL, China). The condenser is tube-in-tube type and water-cooled, as well as the subcooler. A receiver is used between the condenser and subcooler to ensure the tested refrigerant entering the subcooler is in a liquid state. The calorimeter includes a Dewar, an evaporator, an electric heater, and heat transfer fluid. The Dewar is used for heat insulation. The evaporator

Table 3 Theoretical cycle performances of M4 and HFC-404A at nominated working conditions I and II

Refrigerant		COP	t_{dis} (°C)	q_v (kJ/m^3)	q_0 (kJ/kg)	p_e (MPa)	p_c (MPa)	PR
Working condition I	HFC-404A	1.35	109.5	1113	96.8	0.27	1.96	7.34
	M4	1.42	114.7	1139	117.3	0.26	1.89	7.28
Working condition II	HFC-404A	1.09	104.1	602.9	99.6	0.13	1.62	12.4
	M4	1.14	110.3	616.4	120.1	0.13	1.56	12.4

t_{dis} is the discharge temperature,, q_v is the volumetric refrigerating effect, q_0 is the specific refrigerating effect, p_e is the average evaporation pressure, p_c is the average condensing pressure, and PR is the pressure ratio, PR=p_c/p_e

and the electric heater are installed in the upper part and bottom of the calorimeter respectively, and the electric heater is submerged by the second refrigerant.

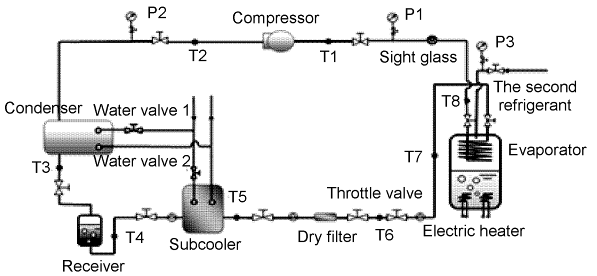

Fig. 2 Schematic diagram of experimental apparatus

Two digital wattmeters (Qingzhi ZW1403, single phase, China) are used to measure the electrical power input to the compressor and the heating power of the electrical heaters. The overall uncertainties of wattmeters measured for the compressor power (full scale is 2 kW) and heater power (full scale is 4 kW) are within ±10 W and ±20 W, respectively. The relative deviation of COP is within 1.8%. The temperatures and pressures of the refrigerants are measured at different locations in the experimental apparatus, shown in Fig. 2. The suction and discharge pressures and temperatures of the compressor are measured by two precision pressure gauges (YB-150, China) (p_1, p_2) and two thermocouples (T_1, T_2) located at the inlet and outlet of the compressor, respectively. The condensing and subcooling temperatures are measured by two thermocouples (T_4, T_5) located at the outlets of the receiver and the subcooler, respectively. The evaporation temperature is measured by a thermocouple (T_7) located at the outlet of the expansion valve. These thermocouples are calibrated by a four-head 25-platinum resistance thermometer (WZPB-2, China) with an uncertainty of ±10 mK (ITS) in a high accuracy thermostat bath. Agilent 34970A data acquisition/switch unit is used to record the temperatures. The overall uncertainty of temperature measured is within ±0.05 K. The precision pressure gauges (the accuracy: 0.25%; full scale: 2.0 MPa for the evaporation pressure, 4.0 MPa for the condensating pressure) are calibrated by an oil-piston type dead-weight pressure gauge (YS-6·60·250·600, China). The pressure measurement systems or the evaporation pressure and the condensing pressure have the uncertainties of ±7 and ±10 kPa, respectively.

The gaseous chromatograph (GC112A, China), equipped with a Flame Ionization Detector, analyses the composition of the tested refrigerant, calibrated with pure components of known purity and mixtures of known composition gravimetrically.

Table 4 presents the specifications of measuring apparatus and their uncertainties.

Table 4 Specifications of measuring apparatus

Parameter	Measuring apparatus	Range	Accuracy
Temperature (°C)	Thermocouple thermometer	−100–100	0.1
Suction pressure (MPa)	Precision manometer	0–1.0	0.25%FS
Discharging pressure (MPa)	Precision manometer	0–2.5	0.25%FS
Compressor power (kW)	Digital wattmeter	0–2.0	0.4%
Heater power (kW)	Digital wattmeter	0–4.0	0.4%
Composition	Gas chromatography	0–1.0	0.3%

FS: full scale

3.3 Experimental procedure

The experimental procedure is as follows:

(1) The system is evacuated by the vacuum pump first;

(2) An estimated amount of liquid sample of R404A or the new mixture (about 2 kg) is charged into the system;

(3) The system is started;

(4) The heaters are turned on to compensate for the cooling capacity of the system and heating powers of the heaters are adjusted to control the suction temperature T_1;

(5) The opening degree of throttle valve is adjusted by the flow rate of refrigerant to control the evaporation temperature T_7;

(6) The flow rates of water in the condenser and the subcooler are adjusted to control the condensing temperature T_4 and subcooling temperature T_5, respectively;

(7) It is shown that 1 h or more is sufficient to obtain thermal stability state at thermal balance. Measurement deviations of experimental data during the experiment are listed in Table 5;

(8) The pressures, temperatures, compressor power and heater power are recorded after the system is at thermal balance, respectively;

(9) The experimental data at thermal balance are

measured at least four times (1 time/0.5 h) to ensure repeatability.

4 Results and discussion

During the experiment, the ambient temperature is maintained at (20±1) °C, the total heat leakage is about 0.082 W/K, which is estimated to be less than 1% of the cooling capacity of the system. Therefore, it is ignored in the experiment.

Table 5 Permitted deviation for experimental parameters

Experimental parameter	Maximum deviation between each measured data and rated data
T_4 (°C)	±0.1
T_5 (°C)	±0.1
T_7 (°C)	±0.1
T_1 (°C)	±3.0

According to the working conditions of R502 in low temperature range, the ranges of condensing temperatures (T_4) and evaporation temperatures (T_7) were selected, respectively, to be about 35–45 °C and −40–−20 °C, respectively. The degree of subcooling, i.e., the temperature difference between condensing temperature (T_4) and subcooling temperature (T_5) was maintained at 5 °C. The superheat, i.e., the temperature difference between evaporation temperature (T_7) and suction temperature (T_1) was also maintained at 30 °C.

Table 6 gives the experimental data in different working conditions, and Figs. 3–7 summarizes the experimental results of cycle performances of M4 and R404A.

Table 6 Experimental data in different working conditions

Refrigerant	Working condition				COP	Q (W)	P_0 (W)	t_{dis} (°C)
	t_c (°C)	t_e (°C)	t_{subc} (°C)	t_{suph} (°C)				
M4	35	−20	5	30	1.51	954	634	108.4
		−25			1.28	751	583	112.1
		−30			1.07	561	520	117.5
		−35			0.89	392	443	122.1
		−40			0.65	230	350	124.0
	40	−20	5	30	1.38	887	652	111.0
		−25			1.22	705	580	116.2
		−30			1.01	511	505	122.3
		−35			0.81	366	450	126.6
		−40			0.55	200	362	127.1
	45	−20	5	30	1.23	829	675	117.7
		−25			1.04	643	620	121.0
		−30			0.88	480	544	127.9
		−35			0.68	291	426	130.0
		−40			–	–	–	–
	43	−23	5	28	1.17	730	625	117.4
HFC-404A	35	−20	5	30	1.41	930	660	106.4
		−25			1.18	732	620	109.0
		−30			0.99	541	547	115.4
		−35			0.81	394	478	121.5
		−40			0.61	230	380	124.2
	40	−20	5	30	1.28	886	694	110.1
		−25			1.07	690	647	114.4
		−30			0.89	493	555	120.0
		−35			0.73	350	478	124.5
		−40			0.55	213	390	126.8
	45	−20	5	30	1.14	826	726	114.0
		−25			0.96	640	661	119.6
		−30			0.81	477	590	124.4
		−35			0.61	285	470	128.3
		−40			–	–	–	–
	43	−23	5	28	1.10	745	675	114.3

Q is the cooling capacity, and P_0 is the power consumption

Fig. 3 shows the variation of the cooling capacity with the evaporation temperature of the refrigerants M4 and R404A. From Fig. 3 and Table 6, it can be seen that with the increase of the evaporation temperature, the cooling capacities of two refrigerants increase. Under the same working condition, the cooling capacity of R404A is smaller than that of M4, and the cooling capacity of M4 increases up to 3.7%.

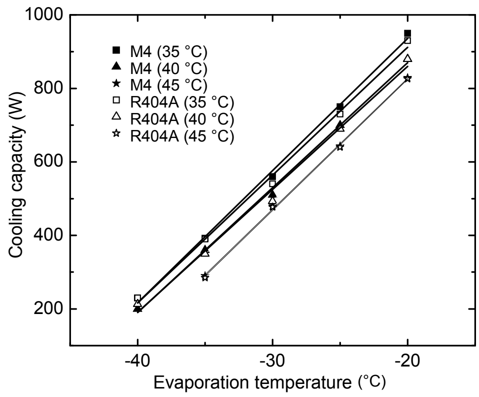

Fig. 3 Variation of cooling capacity at different working conditions

Fig. 4 gives the variation of the compressor power consumption with the evaporation temperature of the refrigerants M4 and R404A. From Fig. 4 and Table 6, it can be found that with the increase of the evaporation temperature, the power consumption of two refrigerants increases. Under the same working condition, the power consumption of M4 is smaller than that of R404A. The maximum drop of the power consumption of M4 is nearly 11%.

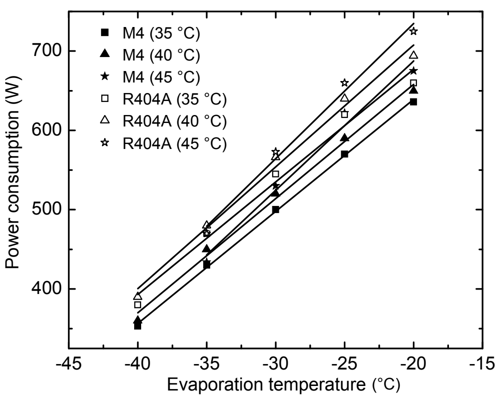

Fig. 4 Variation of compressor power consumption at different working conditions

Fig. 5 shows the variation of the COP with the evaporation temperature of the refrigerants M4 and R404A. From Fig. 5 and Table 6, it can be seen that, at a lower evaporation temperature (−40 °C), the cooling capacity of M4 is almost equal to that of R404A, while the compressor power consumption is less than that of R404A. Therefore, the COP of M4 is higher than that of R404A by a minimum of 6.3%. With the increase in evaporation temperature, the increase of COP becomes even more obvious, with a maximum lift of 12.1%. These experimental results verified the theoretical calculation results about the advantage of the new refrigerant on COP. It can be seen that the experimental COPs for the two refrigerants are lower than theoretical ones, which indicates that the actual overall efficiency of the compressor is far below 0.65, which has been used in theoretical calculations, especially at the low evaporation temperature region. The difference between the theoretical and experimental results can also result from the accuracy of the experimental measurement and from the thermodynamic property calculation of the ternary mixtures.

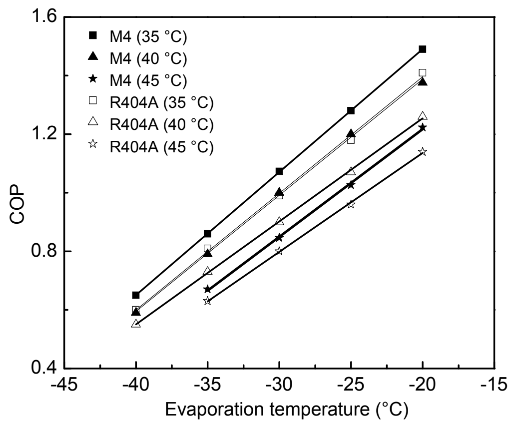

Fig. 5 Variation of COP at different working conditions

Fig. 6 shows the variation of the discharge temperature with the evaporation temperature of the refrigerants M4 and R404A. From Fig. 6 and Table 6, it can be seen that the discharge temperature of M4 is higher than that of R404A. In the high evaporation temperature range, the lift of discharge temperature is about 2–3 °C, but the gaps between the two discharge temperatures decrease in the low evaporation temperature range. When the evaporation temperature approaches −40 °C, the discharge temperatures of M4 and R404A are very close.

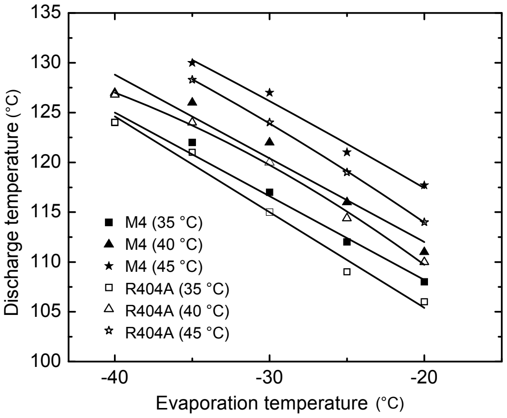

Fig. 6 Variation of discharge temperature at different working conditions

Fig. 7 gives the variation of the pressure ratios with the evaporation temperature of the refrigerants M4 and R404A. From Fig. 7 and Table 6, it can be seen that the pressure ratios of M4 apparently reduce by 1.8% to 6.6% under the tested working conditions, which may be the main reason for the reduction of the compressor power consumption.

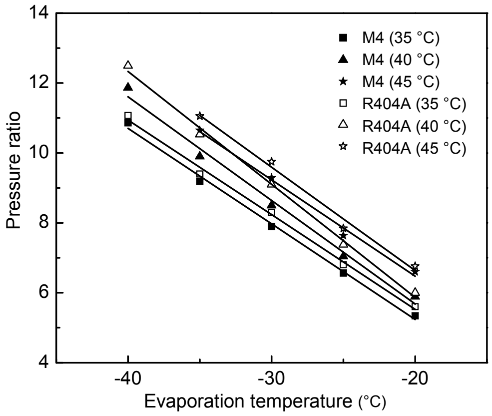

Fig. 7 Variation of pressure ratio at different working conditions

Meanwhile, from Table 6, it can be seen that the experimental data have not been included when the condensing temperature is 45 °C and the evaporation temperature is −40 °C, because the system is very unstable in the long term under this working condition.

5 Conclusions

The ODP of M4 is zero and its basic thermodynamic properties are similar to those of R502, but its GWP is smaller than those of R404A and R507A. M4 is presented as a promising alternative refrigerant to R502 in this work. From the theoretical calculation, it is shown that, under the working condition I, the volumetric refrigerating effect and specific refrigerating effect of M4 are 2.33% and 15.48% higher, respectively, than those of R404A. The COP of M4 is 5.19% higher than that of R404A, and the pressure ratio of M4 is 0.82% lower than that of R404A. Under the working condition II, the volumetric refrigerating effect and specific refrigerating effect of M4 are 2.24% and 20.58% higher, respectively, than those of R404A. The COP of M4 is 4.60% higher than that of R404A and the pressure ratio of M4 is similar to that of R404A. From the experimental test, it can be seen that, under several working conditions, with condensing temperatures of 35–45 °C and evaporation temperatures of −40–−20 °C, M4 can achieve a higher COP by 6.3% to 12.1% at a lower pressure ratio about 1.8% to 6.6%, but the discharge temperature is slightly higher than that of R404A. The experimental results show that if a compressor is specially designed for the new mixture, the merits of the new mixture on COP will be more obvious. In the future, M4 could be used as a retrofit refrigerant to R404A.

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