THEORETICAL STUDY OF HEAT PUMP SYSTEM USING CO_2/DIMETHYLETHER AS REFRIGERANT

by

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Nowadays, HCFC22 is widely used in heat pump systems in China, which should be phased out in the future. Thus, eco-friendly mixture CO_2/dimethylether is proposed to replace HCFC22. Compared with pure CO_2 and pure dimethylether, the mixture can reduce the heat rejection pressure, and suppress the flammability and explosivity of pure dimethylether. According to the Chinese National Standards on heat pump water heater and space heating system, performances of the subcritical heat pump system are discussed and compared with those of the HCFC22 system. It can be concluded that CO_2/dimethylether mixture works efficiently as a refrigerant for heat pumps with a large heat-sink temperature rise. When mass fraction of dimethylether is increased, the heat rejection pressure is reduced. Under the nominal working condition, there is an optimal mixture mass fraction of 28/72 of CO_2/dimethylether for water heater application under conventional condensation pressure, 3/97 for space heating application. For water heater application, both the heating coefficient of performance and volumetric heating capacity increase by 17.90% and 2.74%, respectively, compared with those of HCFC22 systems. For space heating application, the heating coefficient of performance increases by 8.44% while volumetric heating capacity decreases by 34.76%, compared with those of HCFC22 systems. As the superheat degree increases, both the heating coefficient of performance and volumetric heating capacity tend to decrease.

Key words: *carbon dioxide, dimethylether, heat pump system, subcritical, pinch point*

Introduction

With increasing requirements for environmental protection and the strict situation of energy shortage all over the world, the environment-friendly and energy saving technologies have been given much closer attention by researchers [1]. Meanwhile, heat pump, as an efficient and energy conservation technology, presents unique advantages for environmental protection and energy usage [2]. Nowadays, the mainly used working fluids in China for heat pump applications are HCFC22, HFC134a, R410A, and R407C, *etc.*, of which HCFC22 system holds a dominant percentage [3, 4]. All of these working fluids are freons which should be phased out in the near future. With the sustainable development in consideration, natural refrigerant is ideal to replace HCFC22 in a long run. However, there still is no any satisfacto-

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ry natural refrigerant to substitute HCFC22 even now. Hence this paper selected the natural refrigerants CO_2 (or R744) and DME (or RE170, dimethylether) as the potential components to form a competitive binary mixture to replace HCFC22. Both CO_2 and DME, with an ozone depletion potential (ODP) of zero and a global warmth potential (GWP) of 1.0, present excellent environmentally-friendly properties. However CO_2 has a high heat rejection pressure up to 10.0 MPa while DME has flammable and explosive disadvantages [5, 6].

CO_2 mixed with DME is expected to overcome the shortcomings of high discharge pressure of pure CO_2 and flammability, explosivity of pure DME [7]. DME has a much higher critical temperature than that of CO_2, which is supposed to reduce the high rejection pressure of CO_2 heat pump system on mixing. On the other hand, CO_2 can suppress the flammability, explosivity of pure DME. Afroz *et al.* [8] experimentally measured local heat transfer coefficients and pressure drops inside a horizontal smooth tube of CO_2/DME mixture (39/61, 21/79, mass %) during condensation. They found that with the increase of mass fraction of CO_2, the heat transfer coefficient decreased and the pressure drop decreased significantly. By changing the two-phase frictional multiplier in existing condensation prediction method of binary refrigerant mixtures, it is improved to predict the present experimental data. They also measured in-tube evaporation heat transfer coefficient of CO_2/DME mixtures (10/90, 25/75, mass %) and compared with that of pure DME [9]. They concluded that on mixing CO_2 with DME, the heat transfer coefficient of mixture tends to decrease. And existing correlations can well predict the heat transfer coefficients of CO_2/DME mixture with 10% CO_2, but could not well predict that of mixture with 25% CO_2. Nicola *et al.* [10] theoretically analyzed the performance of a cascade refrigeration cycle operated with blends of CO_2 and natural refrigerants including DME as the low-temperature working fluid. Liu *et al.* [11] set up the physical models and governing equations of CO_2/DME mixtures in the horizontal tube to numerically simulate the flow and heat transfer characteristics. Bi *et al.* [12] theoretically analyzed the performance of transcritical refrigeration cycle with CO_2/DME mixture, and compared to pure CO_2 system, the discharge pressures are lowered by about 3.0 MPa while the refrigerating COP is increased by about 4.3 percent for CO_2/DME mixture. Koyama *et al.* [7] experimentally investigated the performances of CO_2/DME (90/10, mass %) and pure CO_2 transcritical systems under the conditions of constant heating/cooling capacity and superheat. They found that the CO_2/DME can reduce the discharge pressure by about 2.0 MPa in the heating mode and about 1.9 MPa in the cooling mode under the maximum COP condition. Hydrocarbon refrigerants have the same high critical temperature as DME, and so are able to lower the high pressure. The previous studies on the CO_2/DME mixtures aimed to the performances of transcritical system or the cascade refrigeration system. However, the investigations on the heating performance for CO_2/DME mixtures applied to subcritical heat pump system are scarce in the published literature.

Based on the previous researches on pure CO_2 heat pump by our research team, CO_2/DME mixture is proposed as a potential alternative refrigerant used in heat pump systems for water heating and space heating [13, 14]. Then it is essential to confirm which composition of mixture is optimum, or at least appropriate, for a certain heat pump application. Based on the Chinese National Standards involving in water heater and space heating system, the heating coefficient of performance, compressor power consumption, condensation pressure, compression ratio, discharge temperature, mass and volumetric heating capacities have been analyzed for different CO_2/DME mixtures in the subcritical cycle. And the performance comparisons with that of HCFC22 system have been presented. Finally, the influences of superheat on performances of system using CO_2/DME mixture as the working fluid have been studied for the optimum composition under the specific conditions.

Methodology

Mathematical modeling of subcritical heat pump system

Using the newest REFPROP 9.0, the critical pressure and temperature of CO_2/DME mixtures are shown in fig. 1 [15]. It can be seen that on mixing with DME, the critical pressure of CO_2/DME increases first and then decreases. In this research, the cycle is subcritical one, and the temperature-entropy diagram of heat pump system is shown in fig. 2.

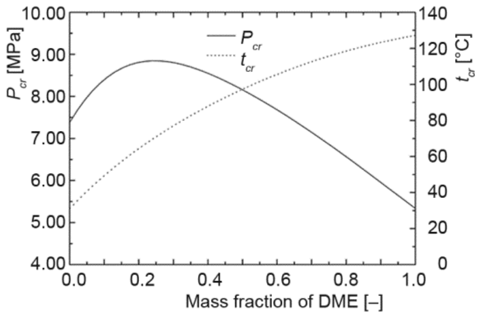

Figure 1. Critical pressure and temperature of CO_2/DME mixture

The theoretical heating *COP* of the cycle is defined as:

$$COP = \frac{q_\mathrm{h}}{w_\mathrm{c}} = \frac{h_2 - h_3}{h_2 - h_1} \tag{1}$$

where q_h [kJkg^{-1}] is the unit mass heating capacity, w_c [W] – the compressor electric power, and h [kJkg^{-1}] – the specific enthalpy.

The unit volumetric heat capacity, $q_{\upsilon\mathrm{h}}$ [kJm^{-3}] is given by:

$$q_{\upsilon\mathrm{h}} = \frac{q_\mathrm{h}}{\upsilon_1} = \frac{h_2 - h_3}{\upsilon_1} \tag{2}$$

where υ_1 [m^{3}kg^{-1}] is the specific volume at state point 1.

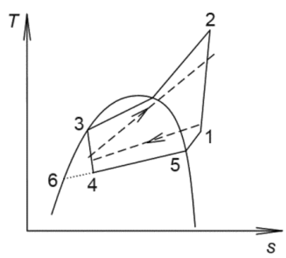

Figure 2. *T–s* diagram showing the CO_2/DME based subcritical heat pump

In order to develop a model close to the practical cases, taking heat transfer temperature pinch point into consideration during evaporation and condensation is reasonable. Due to zeotropic mixture's unique characteristics of large non-linear variation of two-phase enthalpy against temperature during the phase change process, the Distributed Parameter model is used in this study, which will be provided a good agreement with the real conditions and therefore improve its prediction [16]. The condenser and evaporator are divided into a number of segments. Based on the continuity equations of working fluid and the secondary fluid, the outlet state of the former element is the inlet state of the latter element under the steady condition. For an element, lumped parameter approximation is employed. Then mass conservation equation, energy conservation equation and constraint conditions are used to develop the model.

In the evaporator, when inlet temperature of heat source is given, then the outlet temperature for fluid at point 1 is equal to inlet temperature of heat source minus designed pinch point temperature difference. If a certain value for pinch point is wanted, the outlet temperature for fluid at point 1 has to be iteratively determined using element method stated above.

In the condenser, when inlet temperature of heat sink is given, the outlet temperature at point 3 is equal to inlet temperature of heat sink plus designed pinch point temperature difference. The pinch point can be controlled by the same method as what used in the evaporator. The element method can expect to develop more instructive results than the estimated method assuming the CO_2 based mixtures has a linear curve of enthalpy with temperature during phase change.

Simulation conditions

Based on the energy balance of individual components of the system, steady flow energy equations have been employed in each case.

In order to simplify the analysis, the following assumptions have been made.

– The system operates at a steady-state.
– The CO_2 and DME are all taken as pure fluid, and the lubricant effect upon their properties or the mixtures properties is negligible.
– Pressure drops in condenser, evaporator and connecting pipes have been neglected; heat transfer between the system and the ambient are not taken into account.
– Compression process is adiabatic, but non-isentropic and the isentropic efficiency is assumed to be 0.70 for each case; evaporation process and heat rejection process for mixtures are isobaric.
– The pinch point temperature differences for both evaporator and condenser are designed as a constant value of 7 °C. Due to the neglect of heat transfer resistance, the pinch point is set to a value a little higher than the normal value of 5 °C with a consideration that heat transfer will deteriorate in practical case.
– Based on Chinese National Standard GB/T23137-2008, the heat sink and heat source temperatures are determined [17]. The heat sink inlet and outlet temperatures are 15 °C and 55 °C while the heat source temperatures of different kind are shown in tab. 1.
– Based on the national standard, the heat sink inlet and out temperatures are set to 40 °C and 45 °C which are the typical temperatures for space heating, and the heat source inlet and out temperatures are 15 °C and 7 °C [18], respectively.

Table 1. Temperatures of different kinds of heat sources

Heat source	Water-loop[a]	Ground-water[b]	Ground-loop[c]
Inlet temperature [°C]	20	15	10
Outlet temperature [°C]	15	10	5

Notes: [a] water-loop heat source is the circulated water in the public pipeline; [b] ground-water heat source is the water from well, lake or lake; [c] ground-loop heat source is the circulated water in the ground coil

Based on the above assumption, a simulation code for subcritical CO_2/DME heat pump systems using Engineering Equation Solver (EES) was developed [19]. The property subroutines in the code have been linked with an interface program EES_REFPROP which calls REFPROP 9.0 to carry out the necessary property calculations [20].

Results and discussions

Water heat pump application

The variation of CO_2/DME performance with mass fraction of DME for heat pump water heater application is shown in fig. 3. Under the given working conditions, the minimum mass fractions of DME should be greater than 5.0%, below which the mixture will have a lower critical temperature than 40.6 °C and therefore fails to obtain the higher heat sink outlet temperature of 55 °C by subcritical cycle. Compressor ratio r is increased gradually and gently as mass fraction of DME is increased. The system performance shows the similar characteristics for different kinds of heat sources. Therefore, unless otherwise specified, the heat source in the following discussion is water-loop.

When heat source inlet temperature increases, heating coefficient of performance (COP_h) tends to rise because of the higher evaporation temperature. It may be seen that the COP_h slightly decreases when the mass fraction of DME increases in the beginning. The reason is that the ratio of specific heating capacity gain to specific heating capacity, $\Delta q_h/q_h$ is lower than that of compressor power, $\Delta w_c/w_c$. So COP_h drops first. After the minimum point, they are going in the opposite direction. As shown in fig. 4, the compressor power curve w_c shows a flat

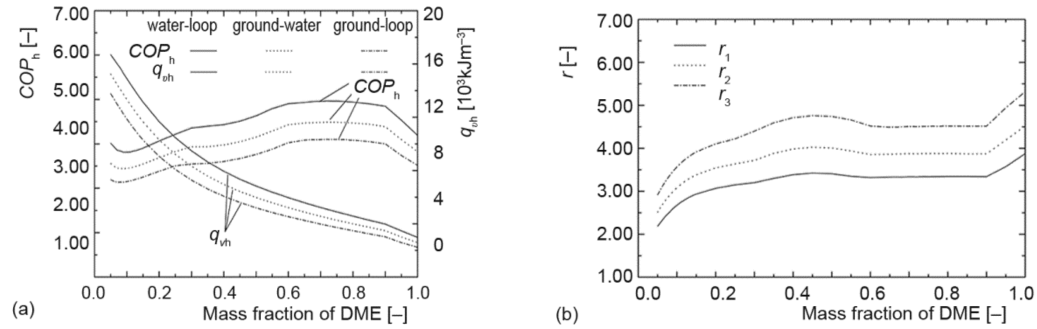

Figure 3. System performances *vs*. mass fraction of DME for water heater application

increase while the specific heating capacity q_h rises sharply, thus resulting an increase in COP_h. At the point of mass fraction CO_2/DME of 28/72, COP_h reaches a peak. Because mixture with different composition has different temperature glide characteristics during evaporation and condensation, under the given heat sink conditions, it may exists an optimum composition to achieve the optimum temperature matching between working fluid and the secondary fluids. Figure 4 also shows that near the maximum COP_h, the line is flat, which is a benefit to practical operation. It can be seen that in a large range of mass fraction of DME, the COP_h of mixture is higher than HCFC22 system. Compared with the pure DME based system, the mixture system has the higher volumetric heating capacity which is useful for system compactness.

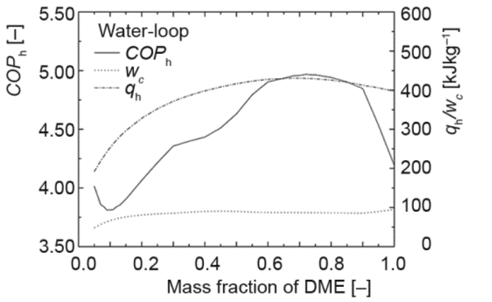

Figure 4. System performances *vs*. mass fraction of DME for water-loop water heater

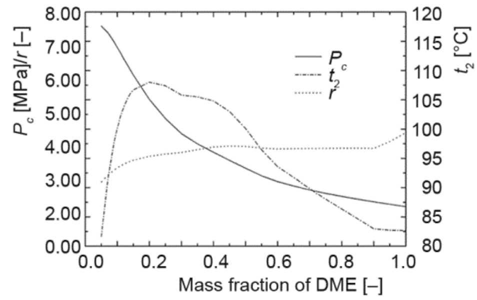

Figure 5. P_c, *r*, and t_2 *vs*. mass fraction of DME for water-loop water heater

As shown in fig. 5, the discharge pressure of CO_2/DME mixture is reduced when mass fraction of DME is increased. The system can work with the optimum COP_h for CO_2/DME of 28/72 under the conventional condensation pressure of 1.872 MPa. It is clear that the compressor discharge temperature increases firstly and then decreases. For optimum fraction of 28/72, the mixture temperature values are slightly higher than that of HCFC22, which can still guarantee a steady operation of compressor.

Table 2 presents the system properties under the identical conditions for HCFC22 based system, and for comparison the corresponding properties of optimum composition of mixture are also listed in the table. For water-loop, ground-water and ground-loop heat sources, the COP_h of CO_2/DME mixture system are enhanced by 18.97%, 17.76% and 16.97%, respectively. Furthermore, the volumetric heating capacities are increased by 3.65%, 2.56% and 2.00%, respectively. Each of the three compressor discharge temperatures t_2 for mixture system is nearly equal to the corresponding value of HCFC22 based system under same condition, which makes the system works steady and durably. The condensation pres-

Table 2. Performance comparison for HCFC22 and mixtures with optimum composition

Refrigerant / Parameters	Water-loop		Ground-water		Ground-loop	
	HCFC22	CO_2/DME	HCFC22	CO_2/DME	HCFC22	CO_2/DME
COP_h [–]	4.176	4.968	3.813	4.490	3.507	4.102
q_h [kJkg^{-1}]	181.4	430.3	185.9	438.6	190.6	447.1
w_c [kJkg^{-1}]	43.44	86.63	48.75	97.68	54.37	109
q_{vh} [kJm^{-3}]	4910	5089	4333	4444	3798	3874
P_c [MPa]	2.161	1.872	2.132	1.848	2.099	1.824
P_e [MPa]	0.6389	0.5615	0.5484	0.4777	0.4664	0.4051
r [–]	3.382	3.334	3.887	3.869	4.500	4.503
t_2 [°C]	87.89	89.05	91.42	92.85	95.17	96.82

sure P_c and evaporation pressure P_e for mixture are all lower than those of HCFC22 system, which is good for safe operation and economy of component manufacture. It can be concluded that CO_2/DME with the optimum composition is a competitive alternative for HCFC22.

Space heating application

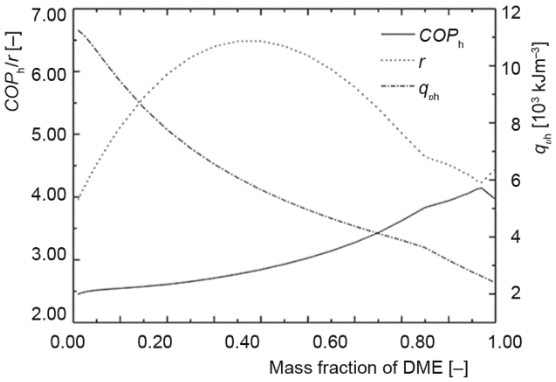

Figure 6. System performances *vs*. mass fraction of DME for space heating application

As that in water heater heat pumps, it is essential to provide a minimum DME composition of about 11.0% under the given working conditions. The variation of CO_2/DME system performance with mass fraction of DME is shown in fig. 6. It can be seen that the COP_h increases with the mass fraction of DME. At mass fraction of 3/97, there exists a maximum COP_h, which is increased by 8.44% compared to HCFC22 showed in tab. 3, and 4.67% to pure DME. Then COP_h tends to decrease with the mass fraction of DME. In the range of 15/85 and 1/99, the system COP_h is higher than that of HCFC22. The condensation pressure for mixture of 3/97 is 1.221 MPa, which is lower than HCFC22 system.

One disadvantage of optimum mixture in such application is that its volumetric heating capacity is decreased by 34.76% in comparison with HCFC22. Results clearly show that the zeotropic mixture CO_2/DME is also suitable for constant space heating application.

Table 3. System performances for HCFC22 based space heating system

Refrigerant	COP_h [–]	q_h [kJkg^{-1}]	w_c [kJkg^{-1}]	q_{vh} [kJm^{-3}]	P_c [MPa]	r [–]	t_2 [°C]
HCFC22	3.805	190.2	49.99	4025	1.9992	4.013	89.68

Influence of degree of superheat both for water heater and space heating

The influence of degree of superheat on the system performance is highly dependent on the working fluid used and the specified conditions. An appropriate degree of superheat can protect compressor from hammering by liquid refrigerant. It is still good for system performance for some refrigerants, but harmful for some other refrigerants. As analyzed above, the CO_2/DME mixture fraction of 28/72 is optimum for water heat pump application, 3/97 for space heating application. Under the given conditions in this paper for optimum fraction, the influences of degree of superheat on the system performance are illustrated in figs. 7 and 8, respectively. As the degree of superheat increases, both the COP_h and the volumetric heating capacity tend to decrease. The reason is that in order to guarantee the designed pinch point between working fluid and secondary fluid, the mean evaporation temperature is decreased as the degree of superheat is increased. For space heating application, as the superheat degree is 5 °C, both the unit mass heating capacity and the compressor power are increased. However, the increase rate of heating capacity tends to be larger than that of compressor power, then resulting in a slightly higher COP_h. With an overall consideration, it is suggested that the CO_2/DME mixture system would work with a basic degree of superheat only to defend compressor from hammering.

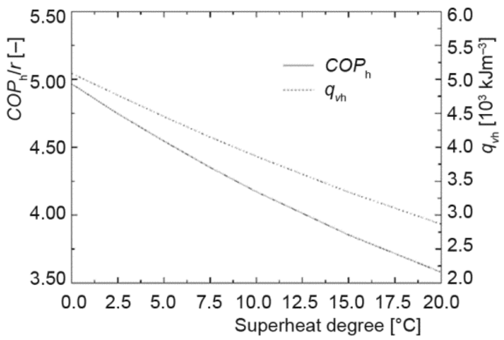

Figure 7. Superheat degree *vs.* system performance for water heater application

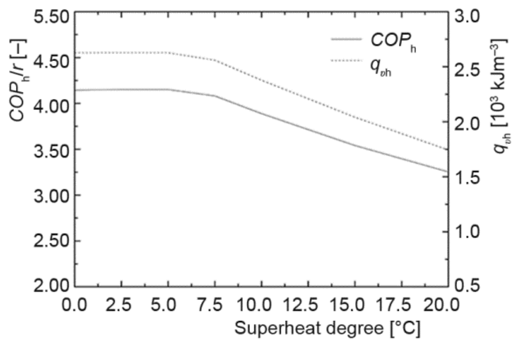

Figure 8. Superheat degree *vs.* system performance for space heating application

Conclusions

For the subcritical cycles, CO_2/DME mixtures are more efficient in heat pumps with a large heat-sink temperature rise, *e. g.* high-temperature water heater system, and superior system performances can be obtained compared with HCFC22. The heat pump using CO_2/DME mixture of 28/72 has the maximum COP_h which is enhanced by 17.90% comparison with HCFC22 system. Meanwhile, the unit volumetric heating capacity is enhanced by 2.74%. Other advantages of this application are that approximately nearly equal discharge temperature compared with that HCFC22, and lower heat rejection pressure compared to pure CO_2. For heat sink with a small temperature glide such as space heating, heat pump using CO_2/DME mixtures has the optimum mass fraction of 3/97, at which the COP_h is increased by about 8.44% while volumetric heating capacity is decreased by 34.76% compared with those of HCFC22 system. In order to obtain a high outlet temperature of 55 °C for heat sink, the mass fraction of DME should not be less than 5.0% in subcritical cycles for water heater application, 11.0% for space heating application. When heat transfer pinch point is taken into consideration, the degree of superheat has a negative influence upon system performances under the given conditions.

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