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Yoji Onaka
Saga University

Akio Miyara
Saga University

Koutaro Tsubaki
Saga University

Shigeru Koyama
Kyushu University

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Analysis of Heat Pump Cycle Using CO_2/DME Mixture Refrigerant

Yoji ONAKA[1], Akio MIYARA[2*], Koutaro TSUBAKI[2], Shigeru KOYAMA[3]

[1] Saga University, Graduate school of engineering,
1 Honjomachi, Saga-shi, 840-8502, Japan
[2] Saga University, Department of Mechanical Engineering,
1 Honjomachi, Saga-shi, 840-8502, Japan
Phone: (81) 952 28 8623, Fax: (+81) 952 28 8587, E-mail: miyara@me.saga-u.ac.jp
[3] Kyushu University, Interdisciplinary Graduate school Engineering Science,
6-1 Kasuga-koen, Kasuga, 816-8580, Japan

ABSTRACT

In this study, the performance analysis of heat pump cycle using carbon dioxide (CO_2) and dimethyl ether (DME) zeotropic mixture has been carried out by cycle calculation in order to clarify the characteristics and coefficient of performance (*COP*) of CO_2/DME heat pump cycle. The calculation conditions were established as a hot-water supply system and the calculations were conducted by considering the heat transfer between the refrigerant and heat source/sink water. The heat pump cycle is formed around the critical point for high CO_2 concentration mixtures and it is formed under the critical point for low CO_2 concentration mixtures. The *COP* has the maximum at a certain pressure for each mixture and the *COPs* of the mixture and pure DME are higher than that of pure CO_2. Operating pressure and refrigerant mass flow rate decreases with increase of DME concentration. The effects of concentration on characteristics of the cycle have also been discussed.

1. INTRODUCTION

Natural refrigerants which have zero ozone depletion potential (ODP) and low global warming potential (GWP) such as carbon dioxide (CO_2), ammonia (NH_3), and hydrocarbons (HCs) have attracted attention as alternative to fluorocarbons (CFCs, HCFCs, HFCs). Since CO_2 is nonflammable and nontoxic, it is especially focused as refrigerant of heat pump water heater and car air-conditioner. In the case of heat pump water heater, CO_2 shows higher coefficient of performance (*COP*) than other refrigerants because the CO_2 cycle forms around the critical point, called as trans-critical cycle, and the water is heated effectively by the super-critical fluid, where the heat exchanger is referred as gas cooler. However, the operating pressure of heat pump using CO_2 becomes very high, over the critical pressure 7.34MPa. The *COP* of the trans-critical cycle as an air-conditioner is lower than that of the cycle operated under the critical point, which is the conventional cycle using fluorocarbons and is called as conventional cycle in this paper. On the other hand, dimethyl ether (DME) has some good thermal properties, such as higher thermal conductivity and large latent heat, and it is acceptable to the environmental problems. The DME has zero ODP and low GWP. The defects of DME are flammability and low pressure. So mixing DME with CO_2 may reduce the defects of the high operating pressure of CO_2 and the flammability of DME. Koyama *et al.* (2007) compared experimentally the system performance of pure CO_2 and CO_2/DME mixture. They showed the CO_2/DME system could reduce the operating pressure than pure CO_2 with same system *COP* level. Afroz *et al.* (2008) reported on heat transfer coefficients and pressure drops during in-tube condensation of CO_2/DME mixture. Kim *et al.* (2007) compared the system performance of CO_2 and CO_2/propane mixture experimentally and showed that CO_2/propane system could reduce the operating pressure.

The *COP* and cycle characteristics of heat pump using zeotropic mixture refrigerant change with concentration of refrigerant. In experiment, however, it is difficult to clarify the characteristics and *COP* over a wide range of concentration. An analysis by cycle calculations is convenience in this case. Although many investigations on the cycle calculation were carried out, most of studies using zeotropic mixture refrigerants are focused on the conventional heat pump cycle.

In this study, the calculation method on the trans-critical and the conventional cycle using CO_2/DME mixture has been discussed and the characteristics and *COP* of CO_2/DME mixture heat pump cycle have been clarified by the cycle calculation.

2. CALCULATION METHOD

The cycle calculation is taken into account heat exchanges between heat sink/source water and refrigerant at heat exchangers. By considering a heat pomp water heater, heat sink/source water conditions, such as inlet/outlet temperatures, t_{cin}, t_{cout}, t_{ein} , t_{eout}, and heating rate Q_c, are required as calculation conditions. The other calculation conditions are the CO_2 concentration y_B, compressor discharge pressure P_1, overall heat transfer coefficient of the heat exchanger K, and heat transfer area of the heat exchanger A. The heat pump cycle is assumed to apply water heating, and the operating conditions as shown in table 1 have been given. In addition the above mentioned conditions, the following assumptions are given for simplicity.

(1) Refrigerant is saturated vapor at inlet of compressor
(2) Compression process is isentropic process
(3) Expansion process at expansion valve is isenthalpic process
(4) Pressure drops are neglected at gas cooler/condenser and evaporator

Table 1: Heat pump cycle operating condition

y_B[mass%]	0~100
Q_c[kW]	3.0
KA[kW/K]	0.2
t_{cin}[ºC]	20
t_{cout}[ºC]	65
t_{ein}[ºC]	20
t_{eout}[ºC]	5

Figure 1 shows a trans-critical cycle of CO_2/DME mixture refrigerant on *T-s* diagram. The number of 1, 2, 3, and 4 on this diagram mean state points of refrigerant at a compressor outlet, a gas cooler/condenser outlet, an expansion valve outlet, and an evaporator outlet, respectively. CO_2/DME mixture refrigerant is zeotropic mixture with large gliding temperature due to large different boiling points. The boiling points at 1 atm are -78.4ºC for CO_2 and -25.1ºC for DME. A saturation temperature at evaporator (3-4) changes as shown in figure 1. In trans-critical cycle, a refrigerant in gas cooler (1-2) becomes supercritical fluid. Since the specific heat of the supercritical fluid changes significantly with temperature, the temperature variation in cooling process is not linear as shown in figure 1. In this case, applying the logarithmic-mean temperature difference (*LMTD*) to the total heat exchanger is not appropriate because the *LMTD* was derived for constant specific heat condition. A similar problem is indicated by Utamura *et al.* (2007). Consequently the heat exchanger was divided into 100 subsections from inlet to outlet in this calculation as shown in figure 2. Therefore the problem was avoided. The division number 100 is large enough to cancel the effect of specific heat variation on the calculated *COP*. The parenthetic numbers in figure 2 mean the subsection numbers. $T_c(0)$, $T_c(100)$, $tw_c(0)$, $tw_c(100)$, $T_e(0)$, $T_e(100)$, $tw_e(0)$, and $tw_e(100)$ in figure 2 are equal to T_1, T_2, t_{cout}, t_{cin}, T_3, T_4, t_{eout}, and t_{ein} in figure 1, respectively. Thus, the following relations are worked out in the cycle calculation.

At gas cooler/condensation process (1-2)

$$Q_c = W_R(h_1 - h_2) \tag{1}$$

$$Q_c = W_c C_{pc}(t_{cout} - t_{cin}) \tag{2}$$

$$\Delta Q_c(i) = \frac{Q_c}{100} \tag{3}$$

$$\Delta Q_c(i) = W_R[h_c(i-1) - h_c(i)] \tag{4}$$

$$\Delta Q_c(i) = W_c C_{pc}[tw_c(i-1) - tw_c(i)] \tag{5}$$

$$\Delta Q_c(i) = \Delta KA(i)\Delta T_{mc}(i) \tag{6}$$

$$\Delta T_{mc}(i) = \frac{[T_c(i-1) - tw_c(i-1)] - [T_c(i) - tw_c(i)]}{\ln[\frac{T_c(i-1) - tw_c(i-1)}{T_c(i) - tw_c(i)}]} \tag{7}$$

At evaporation process (3-4)

$$Q_e = W_R(h_4 - h_3) \tag{8}$$

$$Q_e = W_e C_{pe}(t_{ein} - t_{eout}) \tag{9}$$

$$\Delta Q_e(i) = \frac{Q_e}{100} \tag{10}$$

$$\Delta Q_e(i) = W_R[h_e(i) - h_e(i-1)] \tag{11}$$

$$\Delta Q_e(i) = W_e C_{pe}[tw_e(i-1) - tw_e(i)] \tag{12}$$

$$\Delta Q_e(i) = \Delta KA(i)\Delta T_{me}(i) \tag{13}$$

$$\Delta T_{me}(i) = \frac{[tw_e(i) - T_e(i)] - [tw_e(i-1) - T_e(i-1)]}{\ln[\frac{tw_e(i) - T_e(i)}{tw_e(i-1) - T_e(i-1)}]} \tag{14}$$

At compression process (4-1)

$$s_4 = s_1 \tag{15}$$

At expansion process (2-3)

$$h_3 = h_2 \tag{16}$$

Where W_R is mass flow rate of refrigerant, W_c is mass flow rate of heat sink water, C_{pc} is specific heat at constant pressure heat sink water, ΔT_{mc} is *LMTD* for each subsection in gas cooler/condenser, W_e is mass flow rate of heat source, C_{pe} is specific heat at constant pressure of heat source, ΔT_{me} is *LMTD* for each subsection in evaporator, h is

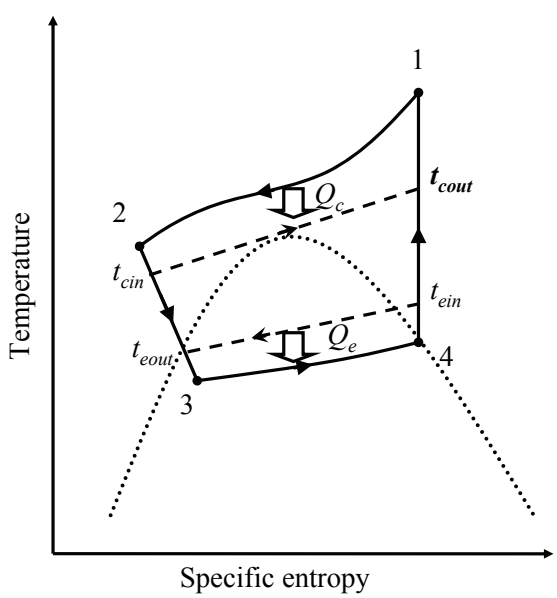


Figure 1: *T-s* diagram of trans-critical CO_2/DME

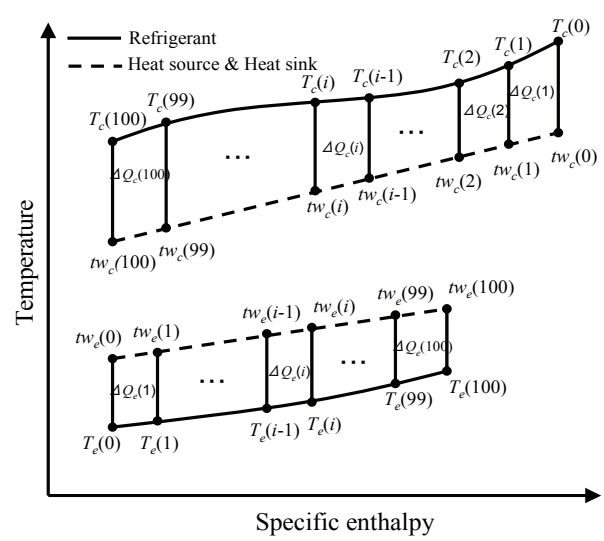


Figure 2: Temperature profile at heat

refrigerant specific enthalpy, s is refrigerant specific entropy. Thermal properties of refrigerant are calculated from Benedict-Web-Rubin equation of state (BWR EoS) (Benedict *et al*., 1940, Miyara *et al.*, 2007).
The *COP* of heat pump is

$$(COP)_H = \frac{h_1 - h_2}{h_1 - h_4} \tag{17}$$

The Irreversible loss L_c at gas cooler/condenser is given by

$$L_c = \sum_{i=1}^{100} \frac{\{(T_c(i-1) - tw_c(i-1)) + (T_c(i) - tw_c(i))\}(s_c(i-1) - s_c(i))}{2} \tag{18}$$

The irreversible loss L_e at evaporator is given by

$$L_e = \sum_{i=1}^{100} \frac{\{(tw_e(i-1) - T_e(i-1)) + (tw_e(i) - T_e(i))\}(s_e(i) - s_e(i-1))}{2} \tag{19}$$

The irreversible loss L_{ep} at expansion valve is given by

$$L_{ep} = \frac{(T_3 + T_2)(s_3 - s_2)}{2} \tag{20}$$

3. RESULT AND DISCUSSION

Figure 3 shows the variation of $(COP)_H$ with compressor discharge pressure. For each concentration, $(COP)_H$ shows the maximum at a certain discharge pressure. For trans-critical cycle, it is well known that there is a optimum pressure where the $(COP)_H$ becomes maximum. In the case of high CO_2 concentration mixture refrigerant, the cycle is a trans-critical cycle. On the other hand, the cycle of low CO_2 concentration refrigerant, which is less than 85mass%CO_2, becomes a conventional cycle. The calculation was carried out in the same way for both the trans-critical cycle and conventional cycle. Under the present calculation method, the $(COP)_H$ of conventional cycle also shows the peak value. Figure 4 shows the cycles of 70mass%CO_2 on *P-h* diagram. Not only the refrigerant saturation temperature but also the subcooling temperature at condenser outlet change with the discharge pressure. For low pressure condition, the state point of condenser outlet enters two phase region. Increasing the pressure from 5.0MPa, the heating capacity (h_1-h_2) shows larger increase than compression work (h_1-h_4). However, the increasing rate of (h_1-h_2) becomes small in high pressure region. This is the reason that $(COP)_H$ shows the maximum.

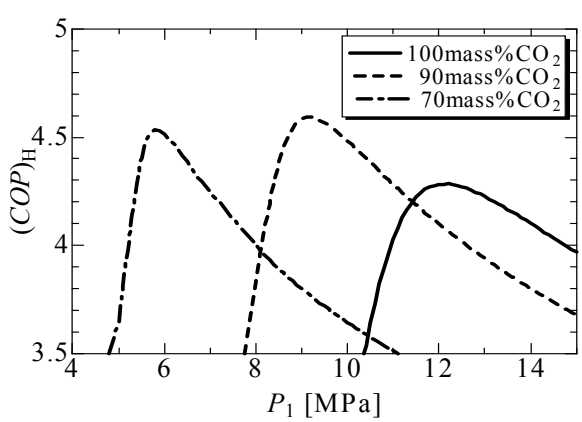


Figure3: Variation of $(COP)_H$

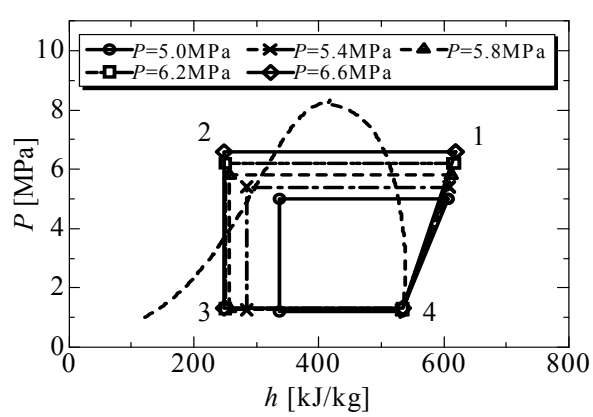


Figure 4: P-h diagram of conventional cycle of 70mass% of CO_2

Figure 5 shows the variation of optimum pressure with the DME concentration. The optimum pressure decreases with increase of the DME concentration. Decreasing rate is more remarkable in low DME concentration region. Figure 6 shows the variation of mass flow rate of refrigerant at optimum pressure with the DME concentration. The mass flow rate of refrigerant also decreases with increase of the DME concentration. The decrease of mass flow rate is caused by increase of heating capacity (h_1-h_2). These results show effectiveness of adding DME into CO_2.

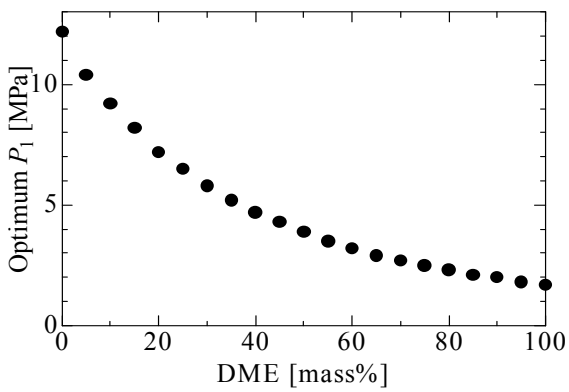


Figure 5: Optimum P_1 versus DME concentration

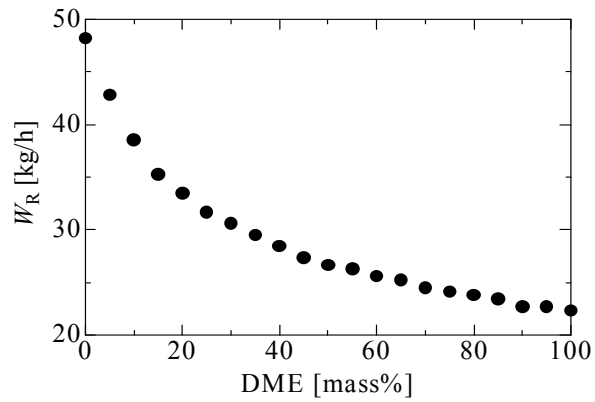


Figure 6: Mass flow rate W_R versus DME concentration

Figure 7 shows the variation of the maximum $(COP)_H$ with DME concentration. Increasing concentration of DME tends to increase $(COP)_H$. However, in the low DME concentration region, where the cycle is trans-critical, $(COP)_H$ has a peak at 10mass%DME. It is reduced slightly from 10mass%DME to 30mass%DME. The cycle of 30mass%DME is a conventional cycle.

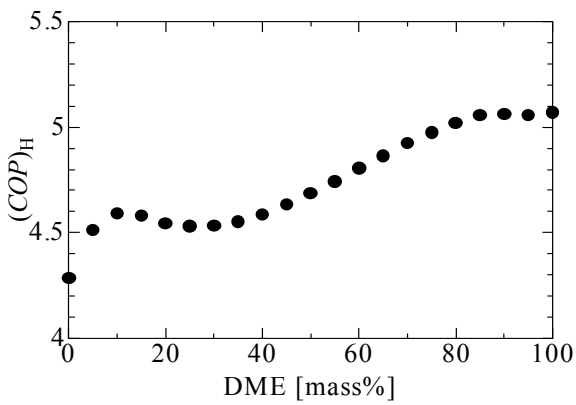


Figure 7: $(COP)_H$ versus DME concentration

Figure 8 shows the variations of irreversible loss ratio with DME concentration. The Irreversible loss ratio defined as the ratio of irreversible loss to the heating capacity (h_1-h_2). In figure 9, the variation of irreversible loss is shown. Since the irreversible loss affects on the $(COP)_H$ and decreasing the irreversible loss gives higher $(COP)_H$, it is important to investigate the irreversible loss in each component. As shown in figure 8, total irreversible loss ratio $L/(h_1$-$h_2)$ has a minimum value at 10mass%DME where $(COP)_H$ has a peak value and has the maximum at 30mass%DME where $(COP)_H$ has a minimum peak. On the other hand, the irreversible loss shown in figure 9 has no peak vale at 10mass%DME. On the whole, the irreversible loss of gas cooler/condenser is lager than that of evaporator and expansion valve though the loss of expansion valve is largest for pure CO_2.

The major cause of the decrement of total irreversible loss ratio and the increment of $(COP)_H$ with DME concentration is decrement of irreversible loss ratio at expansion valve. The decrement is caused by the increment of latent heat at evaporating pressure, which makes larger heating capacity (h_1-h_2). Figure 9 shows the relation of the

heating capacity and latent heat at evaporating pressure with DME concentration for the cycle which has the maximum $(COP)_H$ of each concentration.

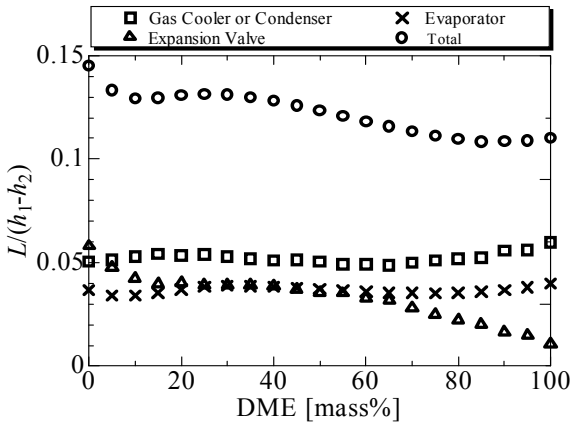


Figure 8: Variation of irreversible loss ratio with DME concentration

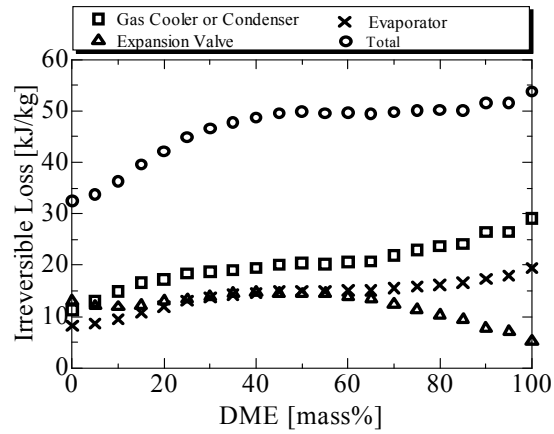


Figure 9: Variation of irreversible loss with DME concentration

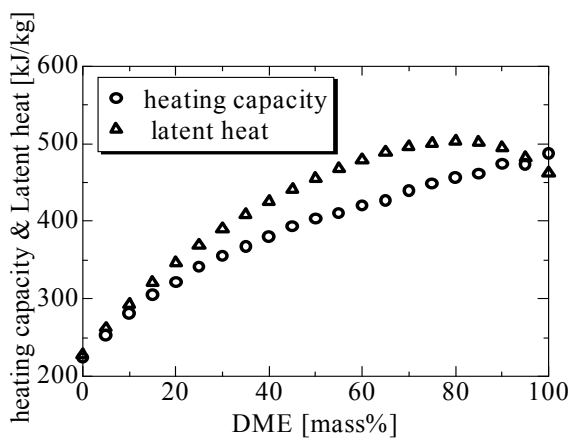
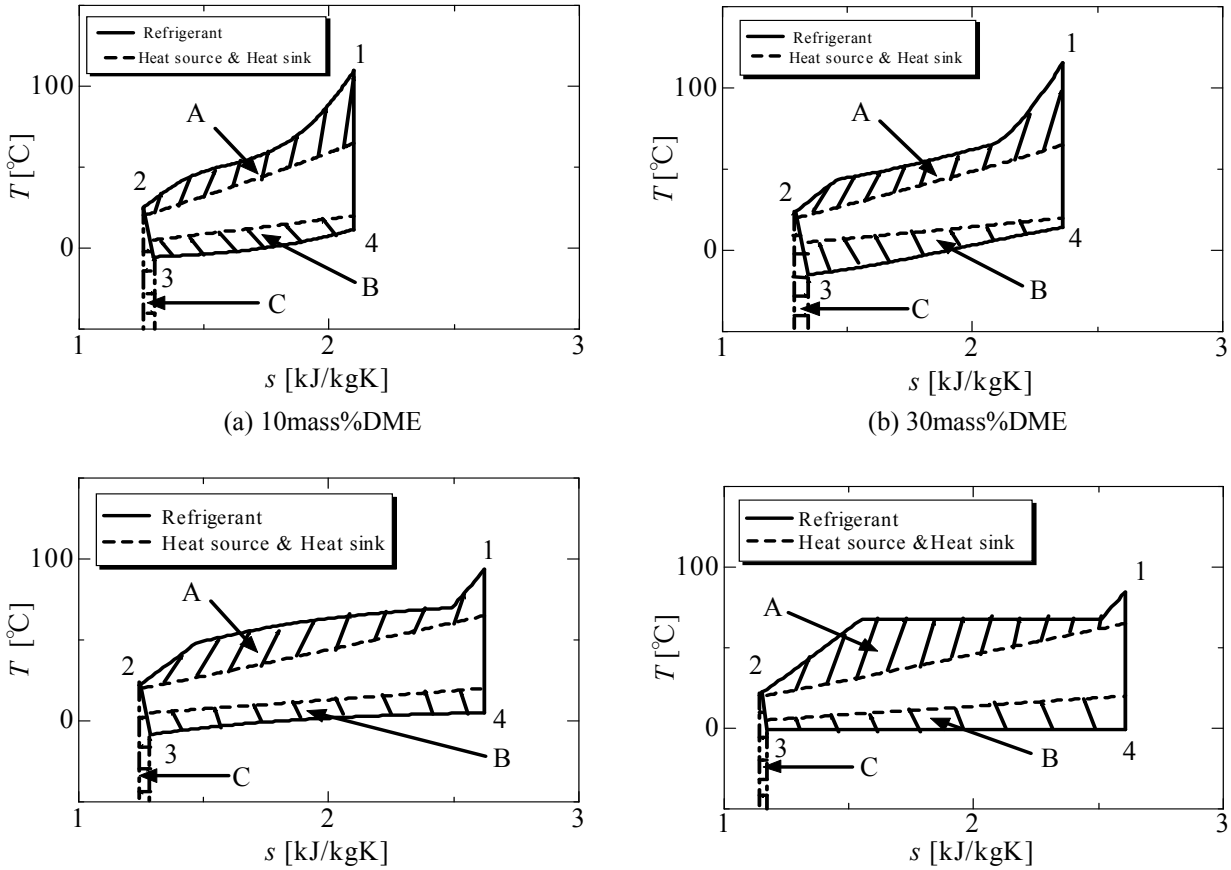


Figure 10: Variation of heating capacity and latent heat at evaporating pressure with DME concentration

In order to investigate the details of irreversible losses, *T-s* diagrams at 10, 30, 80, and 100mass%DME, are shown in figure 11 (a)~(d), respectively. Areas of region A and B in these figures indicate the irreversible losses caused by heat transfer in gas cooler/condenser and evaporator. Area C shows the irreversible loss at the expansion valve. In the case of 10mass%DME, which has a peak of the $(COP)_H$, temperature variations of refrigerant and heat source water are almost same and constant temperature difference is fairly kept. The area of C is smaller in comparison with that of pure CO_2 though it is not shown. For 30mass%DME, which has a minimum peak of the $(COP)_H$, the temperature difference between refrigerant and heat source water in evaporator is large at evaporator inlet of refrigerant (point 3) and the irreversible loss becomes larger. Although the temperature difference in condenser is kept constant in the condensing region, it is large at condenser inlet (point 1). In the case of 80mass%DME, which has higher $(COP)_H$ than 10 and 30mass%DME, the temperature difference is almost constant in the evaporator and it is middlingly constant. The superheat at the condenser inlet is small and the irreversible loss becomes small. For pure DME, temperature difference is large at the end point of condensation. Because the condensing temperature is constant and heat sink water is heated with large temperature rise to make hot water, the temperature difference is largest at this point. On the other hand, the temperature difference in the evaporator is not so large in spite of the constant evaporating temperature because the temperature drop of heat source water is small. The irreversible loss at expansion valve of pure DME is especially small.



(a) 10mass%DME (b) 30mass%DME

(c) 80mass%DME (d) 100mass%DME

Figure 11: Irreversible losses on *T-s* diagram

4. CONCLUSION

The cycle calculation considered heat transfer has been carried out on a heat pump operated with CO_2/DME mixture refrigerant where the cycle of rich CO_2 mixture is formed around the critical point, called trans-critical cycle, and that of rich DME mixture is under the critical point. In the case of super critical fluid, the specific heat capacity varies significantly during the heat transfer process and the logarithmic mean temperature difference is not applicable to the whole of heat exchanger. A method that the heat exchanger is divided into sufficiently small part and the heat transfer of the small part is calculated has been proposed. Cycle calculations have been conducted under a hot-water supply condition and following results have been obtained.

(1) The *COP* of the mixture and pure refrigerants of CO_2 and DME has the maximum value at a certain pressure for each concentration.
(2) The maximum *COP* varied with the concentration. On the whole, it increases with increase of DME concentration though it has a peak value at 10mass%DME.
(3) The optimum pressure, where the *COP* becomes the maximum, can be reduced by adding DME into CO_2.

From the analysis of irreversible loss at the gas cooler/condenser, evaporator, and expansion vale, following results have also been obtained.

(4) The irreversible loss at gas cooler/condenser is lager than other losses except the loss at expansion valve of pure CO_2.
(5) The irreversible loss at expansion valve is decrease with decrease of DME concentration.

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