Thermodynamic performance assessment and application feasibility analysis of small heat pump water heater using CO₂/R41 azeotropy mixture as refrigerant for sustainable development

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In order to improve the application possibility of CO₂/R41 azeotropy mixture in the refrigeration industry, the optimum mass ratio of composition is defined and determined according to the thermodynamic properties and safety. On the basis of the first and second laws of thermodynamics, a model is proposed to evaluate the performance of CO₂/R41 single-stage transcritical cycle (CO₂/R41 cycle) in which a throttling valve is integrated and CO₂/R41 azeotropy refrigerant is adopted. The performance of CO₂/R41 cycle at the optimum mass ratio of CO₂/R41 azeotropy mixture is then compared with that of a CO₂ two-stage transcritical cycle with throttling valve (CO₂ two-stage cycle) and that of a CO₂ single-stage transcritical cycle with expander (CO₂ expander cycle). The results show that the optimum mass ratio of CO₂/R41 azeotropy mixture is 0.583/0.417. Compared with CO₂ two-stage cycle and CO₂ expander cycle, CO₂/R41 cycle has the advantages of a simpler structure, lower optimum high pressure, appropriate discharge temperature of the compressor, and higher COP. Therefore, the CO₂/R41 azeotropy mixture with the mass ratio of 0.583/0.417 is eco-friendly and can be considered as a good alternative refrigerant for application in the refrigeration industry. The simple CO₂/R41 cycle shows great feasibility to replace the complex CO₂ two-stage cycle and CO₂ expander cycle.

1 Introduction

In line with the Kigali Amendment of the Montreal Protocol, a drastic phase-down of hydrofluorocarbons (HFCs) has been imposed from 2019 due to the high global warming potential (GWP) (Astrain et al., 2019; Wang et al., 2019). Because of this, one of the urgent tasks in the refrigeration industry is to search for alternative refrigerants with less influence

on the environment (Zhao et al., 2019; Dai et al., 2023). Natural working fluid CO_2 is considered to be a promising refrigerant because of its eco-friendly properties, such as having zero ozone depleting potential (ODP), low GWP, and high thermodynamic performance and being nonflammable, non-toxic, and cheap (Cecchinato et al., 2005; Dai et al., 2023). CO_2 refrigeration systems have been widely applied in air conditioning and heat pumps (Wang et al., 2017). However, several defects (i.e., higher operating pressure, lower efficiency, and overheating of discharge refrigerant gas) existing in the CO_2 systems should be solved to develop the application fields (Wang et al., 2017; Nemati et al., 2018; Wang et al., 2020). Three approaches are frequently employed to improve the comprehensive performance of CO_2 systems: adopting two-stage compression with inter-cooling between the stages (Srinivasan, 2011), using an expander to replace throttling valve (Joneydi Shariatzadeh et al., 2016), and using mixture refrigerant instead of pure refrigerant (Wang et al., 2017). However, the two-stage compression system and the single compression system with an expander are complex. Moreover, it is difficult to design a satisfactory CO_2 expander at present. Therefore, there is an obvious need to develop CO_2-based blends as a refrigerant. In recent years, several CO_2-based zeotropic refrigerants, such as CO_2/R290, CO_2/R600, and CO_2/R32, have been studied and applied (Sugiyama et al., 2011; Dai et al., 2014). However, the high temperature glide and mass transfer resistance in nucleate boiling of zeotropic mixture cause a lower heat transfer coefficient compared with pure refrigerant and azeotropy mixture (Kundu et al., 2014). In addition, it is difficult to overcome the inherent problem of composition shift arising in the leaking or recharging processes in application aspects of zeotropic mixture (Morrison and McLinden, 1993). So, the azeotropy mixtures have been attracting increasing attention and are preferred as refrigerants among different types of mixtures, because the azeotropy mixtures have good performance similar to the pure fluids (Aslam and Sunol, 2004; Zhao et al., 2019). Moreover, the systems with azeotropy refrigerants would have higher coefficient of performance (COP), higher refrigeration capacity, and lower energy consumption than those with zeotropic refrigerants (Zhao et al., 2016).

Up to now, only two CO_2-based azeotropy refrigerants (CO_2/R170 and CO_2/R41) have been reported and analyzed in the published literature. In our previous study, the performance of a heat pump water heater with CO_2/R170 azeotropy refrigerant was studied, and a lower discharge temperature was observed for the system with CO_2/R170 azeotropy refrigerant compared with the system with pure CO_2 and R134a, indicating that the lifetime of a compressor can be significantly prolonged (Wang et al., 2019; Wang et al., 2020). Under supercritical conditions, Kravanja et al. (2018) measured the heat transfer coefficient of CO_2, R170, and CO_2/R170 azeotropy mixture in a double-pipe and countercurrent flow tube. The experimental results indicated that the heat transfer coefficient value of CO_2/R170 mixture fell between that of pure CO_2 and R170 near the critical point. Then, the COP of a simple system with pure CO_2 and CO_2/R170 mixture as a refrigerant was evaluated by a thermodynamic model. The comparison data showed that the COP values of CO_2/R170 cycle were more than 50% higher than those of the pure CO_2 cycle when the evaporation temperature was above 0°C, which could help to reduce the operational cost by a significant amount. For CO_2/R41 azeotropy mixture, as a refrigerant, the performance of the refrigerated cabinet and heat pump water heater

was analyzed under various working conditions in our previous study (Wang et al., 2017). The results showed that the comprehensive performance of CO_2/R41 cycle was significantly better than that of CO_2 cycle. Dai et al. (2015) developed a thermodynamic model to evaluate the performance of a heat pump water heater with ten CO_2-based mixtures as a refrigerant. They found that the CO_2/R41 mixture could be recommended as a suitable candidate to replace the pure CO_2. Yu et al. (2019) conducted an experiment to comprehensively study the overall performance of CO_2/R41 used in automobile air conditioning and heat pump systems. The experimental results demonstrated that the performance of the CO_2/R41 system could be significantly improved with the increase of R41 mass fraction (from 0% to 100%). Under the condition of optimum charge, the COP of pure R41 system was 14.5% and 25.7% higher than that of pure CO_2 system in the heating and cooling modes, respectively. Meanwhile, the operation pressure of the pure R41system significantly decreased with the increase of R41 mass fraction (from 0% to 100%) under the same gas cooler outlet temperature.

As was shown in the above-mentioned studies, both CO_2/R41 and CO_2/R170 can be used in refrigeration and heat pump systems as a refrigerant because of the higher COP and lower discharge temperature. However, CO_2/R170 azeotropy refrigerant has an unfavorable effect in the operating pressure of systems (Wang et al., 2019). The results were compared with those obtained from references (Wang et al., 2019) and (Wang et al., 2017); it was found that the low/high pressures of the studied air-source heat pump water heater system using CO_2/R170 azeotropy mixture are higher than those using pure CO_2 refrigerant. In contrast, the CO_2/R41 system has an obviously lower operating pressure than the CO_2 system under the same conditions. So, the CO_2/R41 azeotropy refrigerant is preferable and needs to be studied in further detail.

The mass fraction of CO_2/R41 azeotropy refrigerant has a significant effect on the comprehensive performance of the system. It is important to identify an optimum mass ratio of CO_2/R41 azeotropy refrigerant for its practical application in the refrigeration industry. In general, the optimum mass ratio is defined as the mass ratio of mixture composition corresponding to the maximum COP of the system. From the above literature analysis, it is observed that the thermodynamic performance of CO_2/R41 system is improved continuously with an increasing R41 mass fraction. Hence, the COP of the system cannot be the only parameter to determine the optimum mass ratio in CO_2/R41 azeotropy mixture.

For a refrigerant, the issues of safety and its thermodynamic properties must be considered. R41 can improve the COP of a refrigerating system with pure CO_2, although it can also reduce the safety due to its flammability. Therefore, pure R41 cannot be directly recommended to replace CO_2 in refrigeration systems.

In order to promote the industrial application of CO_2/R41 mixture, the optimum mass ratio of composition should be determined. Under the premise of safety, the CO_2/R41 systems should have an optimal thermodynamic performance when the mixture composition reaches an optimum mass ratio. So, the optimum mass ratio of CO_2/R41 mixture is defined as the maximum R41 mass fraction corresponding to the A1 security level in this paper. In this situation, the mixture can be assured to be a non-combustible gas and correspond to the maximum COP of the system.
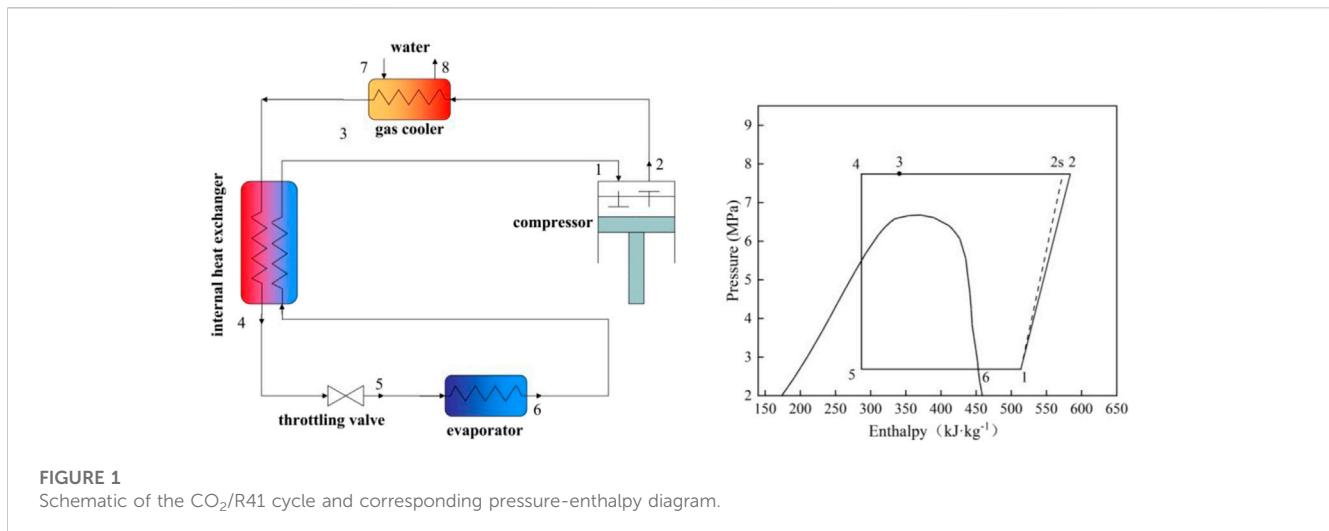
FIGURE 1
Schematic of the CO_2/R41 cycle and corresponding pressure-enthalpy diagram.

In this study, the optimum mass ratio of CO_2/R41 mixture is firstly calculated and determined. On the basis of the first and second laws of thermodynamics, a model is proposed to evaluate the performance of three different cycles, namely, a single-stage compression transcritical cycle with a throttling valve when CO_2/R41 mixture with the optimum mass ratio is used (i.e., CO_2/R41 cycle), a single-stage compression transcritical cycle with an expander when pure CO_2 is used (i.e., CO_2 expander cycle), and a two-stage compression transcritical cycle with a throttling valve when pure CO_2 is used (i.e., CO_2 two-stage cycle). Finally, the feasibility of using simple CO_2/R41 cycle to replace complex CO_2 two-stage cycle and/or CO_2 expander cycle is comprehensively evaluated in terms of COP, optimum high pressure, and discharge temperature.

2 Calculation of the optimum mass ratio

The CO_2/R41 mixture is non-toxic; the safety issues stem from its flammability. For pure R41, the flammability limit is 6.8%/20.3% (volume fraction). The lower flammability limit (volume fraction, LFL_V) and the upper flammability limit (volume fraction, UFL_V) of CO_2/R41 mixture can be calculated with the following expression (Niu, 2006).

$$C_{CO_2/R41} = C_{R41} \frac{\left[1 + B_{CO_2}/\left(1 - B_{CO_2}\right)\right] \times 100}{100 + C_{R41}B_{CO_2}/\left(1 - B_{CO_2}\right)} \quad (1)$$

Where $C_{CO2/R41}$ and C_{R41} are the flammability limit of CO_2/R41 and pure R41 respectively and B_{CO2} is the volume fraction of CO_2 in the CO_2/R41 mixture.

3 System modeling

3.1 System description

Three transcritical cycles are studied based on an air-source heat pump water heater (ASHPWH) system with optimal control strategy in the paper. Schematics and corresponding pressure-

enthalpy diagrams of the systems with the three cycles analyzed in this study are shown in Figures 1–3.

The isentropic and actual compression processes are respectively illustrated by the dashed line ″1–2s″ (and ″3–4s″ in Figure 3) and the solid line ″1–2″ (and ″3–4″ in Figure 3) in the pressure-enthalpy diagrams. Similarly, the lines ″4–5s″ and ″4–5″ express isentropic and actual expansion processes respectively in Figure 3. On the basis of the first and second laws of thermodynamics, a model is proposed to evaluate and compare the performance of the three cycles carefully. The studied ASHPWH systems are assumed to operate based on optimal control strategy during simulation.

3.2 Assumptions for the model

The thermodynamic model is conducted based on the following assumptions:

(1) The three studied cycles are all operated under steady conditions.
(2) The heat loss and pressure drop of refrigerant flowing inside the heat exchangers and connecting pipes are ignored.
(3) The compression and expansion processes are adiabatic.
(4) The compression and expansion processes are non-isentropic.
(5) The refrigerant is in a saturated state at the evaporator outlet.
(6) The lubricant oil does not flow with the refrigerant.

3.3 Establishment of the thermodynamic model

The parameters of external conditions have a significant effect on the system performance. The external environment temperature and hot water inlet/outlet temperature of the studied ASHPWH systems in this paper are specified based on the Chinese standards GB/T 21362-2008 (GB/T 21362-2008, 2008) and GB/T 23137-2008 (GB/T 23137-2008, 2008), which are shown in Table 1.

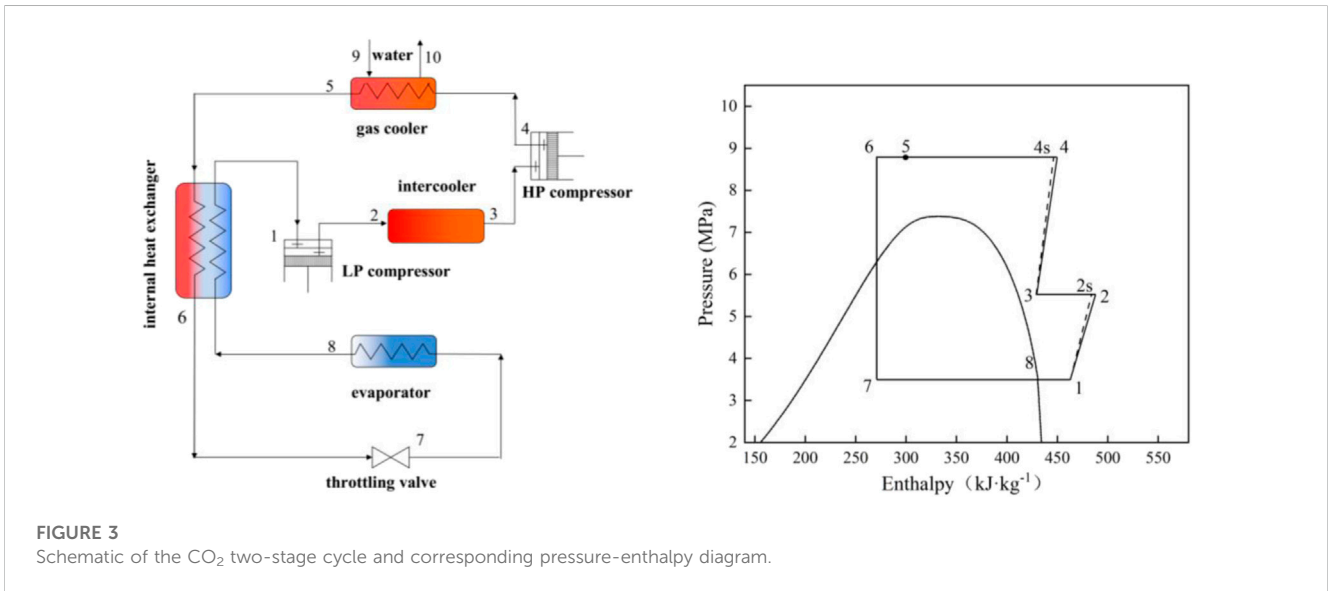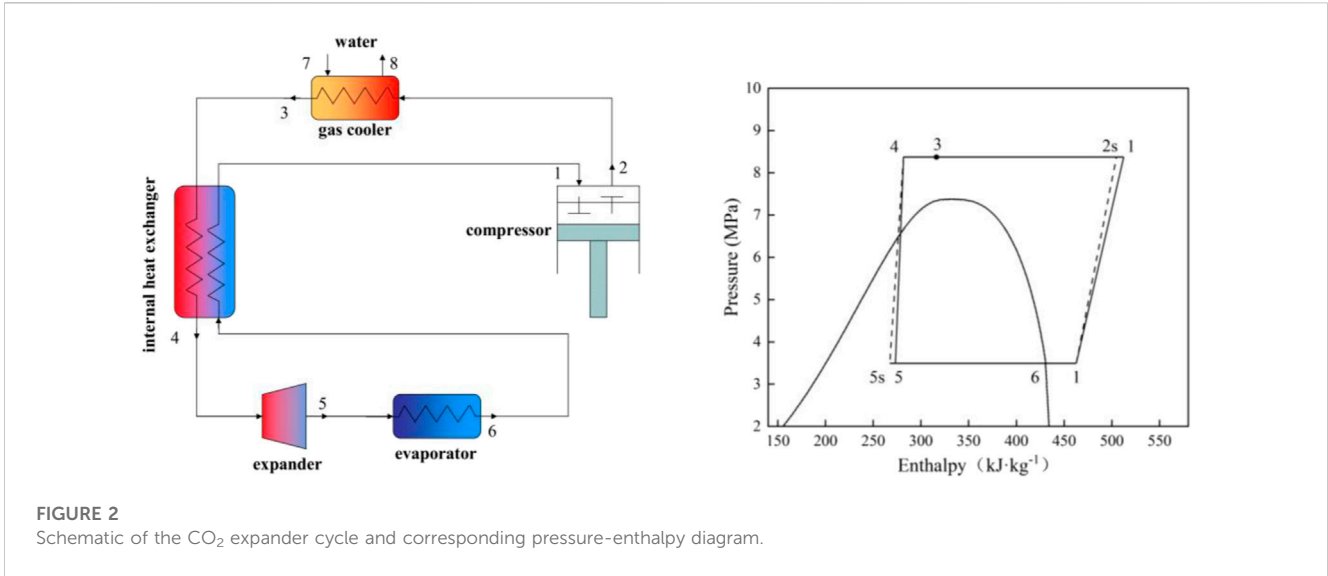(1) Isentropic efficiency of the compressor (Sarkar et al., 2004):

FIGURE 2
Schematic of the CO_2 expander cycle and corresponding pressure-enthalpy diagram.

FIGURE 3
Schematic of the CO_2 two-stage cycle and corresponding pressure-enthalpy diagram.

TABLE 1 Standard rating condition of ASHPWH.

Hot water inlet/outlet temperature (℃)	External environment temperature (℃)
17/65	16

$$\varepsilon_{is} = 0.815 + 0.022\left(p_o/p_i\right) - 0.0041\left(p_o/p_i\right)^2 + 0.0001\left(p_o/p_i\right)^3 \tag{2}$$

(2) Energy balance in the internal heat exchanger:

$$\Delta h_H = \Delta h_C \tag{3}$$

(3) The effectiveness of the internal heat exchanger is given by Eq. 4, as 0.6 (Sarkar et al., 2004):

$$\beta_{IHE} = \frac{\Delta T_C}{T_{gc,o} - T_K} \tag{4}$$

(4) The effectiveness of the intercooler is given by the following expression, as 0.8 (Yari and Sirousazar, 2008):

$$\beta_{IC} = \left(T_2 - T_3\right)/\left(T_2 - T_{en}\right) \tag{5}$$

(5) The inter-stage pressure is given by the following expression (Nemati et al., 2018):
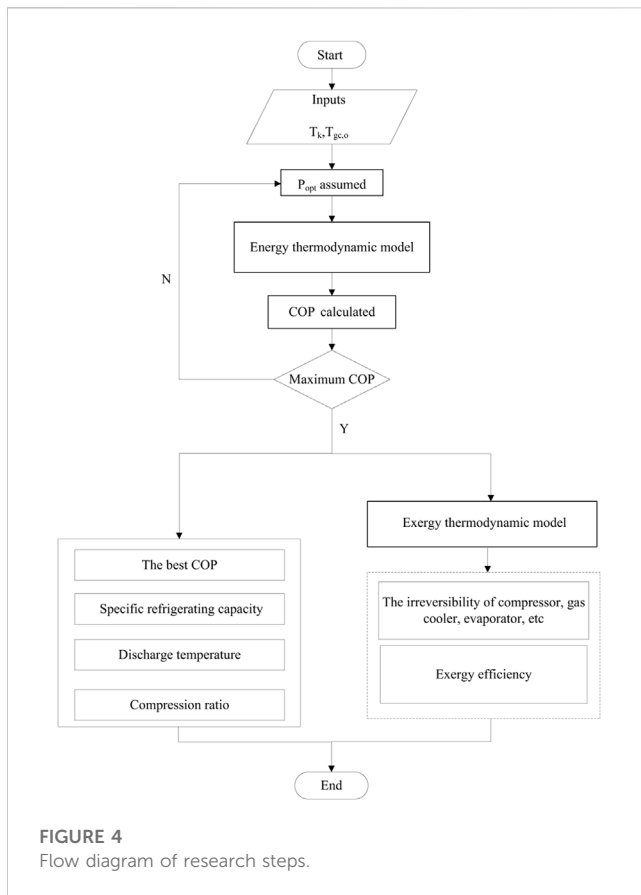
FIGURE 4
Flow diagram of research steps.

$$p_2 = \sqrt{p_1 \times p_4} \qquad (6)$$

(6) The isentropic efficiency of the expander is given by the following expression (Wang et al., 2020):

$$\varepsilon_{EXP} = 1.0094 - 0.0504\left(p_4/p_5\right) \qquad (7)$$

(7) The compression ratio of the cycle is given by:

$$R = \frac{p_{gc}}{p_K} \qquad (8)$$

(8) COP is given by:

$$COP = \frac{q}{w} \qquad (9)$$

(9) The irreversible loss of the adiabatic component is given by:

$$I = T_{en}\Delta s_r \qquad (10)$$

(10) The irreversible loss of the component exchanging heat with the external fluid is given by:

$$I = T_{en}\left(\Delta s_r + \Delta s_{ef}\right) \qquad (11)$$

(11) The exergy efficiency for the overall system is given by:

$$\eta = 1 - \frac{I_{tot}}{w} \qquad (12)$$

4 Research steps

The research steps are provided in Figure 4. For a transcritical cycle, the outlet temperature of gas cooler ($T_{gc,o}$) and the evaporation temperature (T_k) are critical parameters effecting the cycle performance (Hu et al., 2018), and they are set to initial conditions in the present model. It is widely known that the system applying the transcritical cycle has an optimum high pressure (p_{opt}) that yields the best COP under the specific operation conditions. However, there is no existing correlation that can be used in the case of the three studied transcritical cycles. In the present thermodynamic model, the ever-increasing high operating pressure (1 kPa step) is assumed to calculate the performance of the analyzed system until the maximum COP is reached. Then, the optimum high pressure and the corresponding performance indicators can be obtained.

5 Results and discussion

5.1 Security level analysis of CO_2/R41 azeotropy mixture

In order to overcome the shortcomings discussed in the literature and improve the application possibility of CO_2/R41 azeotropy mixture in the refrigeration industry, the optimum mass ratio of composition is defined and determined in this study.

According to the Standard of the U. S. Department of Transportation DOT 173 .115 (Wang et al., 2002), working fluid with the LFLv higher than 13% or the difference between UFLv and LFLv less than 12% can be identified as non-flammable fluid (i.e., A1 security level). Table 2 shows the UFLv and LFLv of the CO_2/R41 mixture with various volume fractions of composition. It is obvious that the increase of volume fraction of R41 can decrease the UFLv and LFLv and their difference. Under the condition of A1 security level, the maximum volume fraction of R41 is 48% in a CO_2/R41 mixture. As can be observed from the existing literature, the thermodynamic performance of a refrigeration/heat pump system with CO_2/R41 refrigerant can be improved continuously by increasing the fraction of R41. Therefore, when the safety and thermodynamic property are considered comprehensively, the optimum volume ratio of CO_2/R41 azeotropy refrigerant is identified to be 0.52/0.48, which can be converted into the optimum mass ratio, i.e., the optimum mass ratio is 0.583/0.417.

The main thermo-physical properties of the CO_2/R41 mixture with the optimum ratio can be obtained, as shown in Table 3. Therefore, the CO_2/R41 mixture (0.583/0.417, mass ratio) is eco-friendly and particularly strong for a transcritical cycle because of its low critical temperature (i.e., 37.67°C).

5.2 Verification of the model accuracy

It is well known that the COP of a refrigeration/heat pump system can be directly affected by the high pressure. So, the optimum high pressure (p_{opt}) should be accurately determined to ensure the accuracy of the simulation results from the proposed thermodynamic model. For a single-stage transcritical cycle with a throttling valve when pure CO_2 refrigerant is used, there are several correlations that can be employed to

TABLE 2 The UFLv and LFLv of the CO_2/R41 mixture.

Volume fraction of R41 (%)	LFLv (%)	UFLv (%)	Security level
10	42.2	71.8	A1
20	26.7	56.0	A1
30	19.6	45.9	A1
40	15.4	38.9	A1
48	13.2	34.7	A1
49	13	34.2	A2L
50	12.7	33.7	A2L
60	10.8	29.8	A2L
70	9.4	26.7	A2L
80	8.4	24.1	A2L
90	7.5	22.1	A2L
100	6.8	20.3	A2L

TABLE 3 The main thermo-physical properties of the CO_2/R41 mixture (0.583/0.417, mass ratio).

ODP	GWP	T_{cri} (°C)	p_{cri} (Mpa)	ρ_{cri} (kg. m^{-3})
0	41	37.67	6.8538	388.68

TABLE 4 The results of the optimum high pressure using Eq. 13 and the proposed iterative method.

T_k (°C)	$T_{gc,o}$ (°C)	$p_{opt,equ}$ (Mpa)	$p_{opt,ite}$ (Mpa)	Error (%)
−10	35	8.801	8.770	0.352
−10	40	10.004	10.070	0.660
−10	45	11.217	11.345	1.141
−5	35	8.716	8.715	0.011
−5	40	9.919	9.990	0.716
−5	45	11.132	11.265	1.194
0	35	8.631	8.650	0.220
0	40	9.834	9.905	0.722
0	45	11.047	11.165	1.068

obtain the optimum high pressure with enough accuracy. However, relevant correlations are scarce for calculating the optimum high pressure in a CO_2/R41 cycle, CO_2 two-stage cycle, and CO_2 expander cycle. In our present work, one iterative method is proposed to calculate the optimum high pressure of the above cycles. Equation 13 provided in (Hu et al., 2018) is a classic correlation to obtain the optimum high pressure of a single-stage transcritical CO_2 cycle and is therefore used to verify the accuracy of the proposed iterative method.

$$p_{opt} = \left[4.9 + 2.256T_{gc,o} - 0.17T_k + 0.002T_{gc,o}{}^2\right] \times 10^{-1} \quad (13)$$

where p_{opt} is the optimum high pressure, in Mpa; T_k is the evaporation temperature, in °C; and $T_{gc,o}$ is the outlet temperature of the gas cooler, in °C.

Table 4 shows the values of the optimum high pressure that are obtained by Eq. 13 and the proposed iterative method. It is noted that the calculation results of the optimum high pressure using Eq. 13 and the iterative method are respectively marked as $p_{opt,equ}$ and $p_{opt,ite}$. It can be seen that the maximum error between Eq. 13 and the iterative method is less than 1.2%, which indicates that the proposed iterative method in this study has enough accuracy, i.e., the established thermodynamic model is reasonable.

5.3 The analysis of system thermodynamic performance

In this study, the optimum ratio of the CO_2/R41 mixture is calculated and then the performance of three different cycles

(i.e., CO_2/R41 cycle, CO_2 two-stage cycle, and CO_2 expander cycle) are evaluated and compared under the same conditions, i.e., −10°C ≤ T_k ≤ 0°C, 35°C ≤ $T_{gc,o}$ ≤ 45°C.

Figure 5 shows the optimum high pressure (p_{opt}) of the three studied cycles with various parameters of the evaporation temperature (T_k) and the outlet temperature of the gas cooler ($T_{gc,o}$). It is observed that the optimum high pressure of the CO_2/R41 cycle is more than 26.9% lower than that of CO_2 expander cycle under the same condition. In addition, the optimum high pressure of CO_2/R41 cycle is more than 32.6% lower than that of CO_2 two-stage cycles under the same condition. The decrease in operating pressure can help to improve the tightness and safety of a refrigeration system. Meanwhile, the tube thickness of the heat exchanger and connecting tubes can be appropriately reduced so as to lower the manufacturing cost of the device.

Figure 6 exhibits the effect of the evaporation temperature (T_k) and the outlet temperature of the gas cooler ($T_{gc,o}$) on the specific refrigerating capacity of the three studied cycles. It is observed that the CO_2/R41 cycle has a higher specific
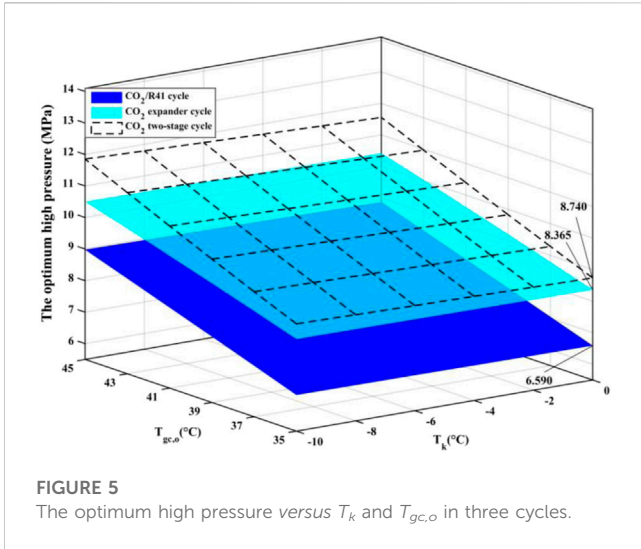
FIGURE 5
The optimum high pressure *versus* T_k and $T_{gc,o}$ in three cycles.
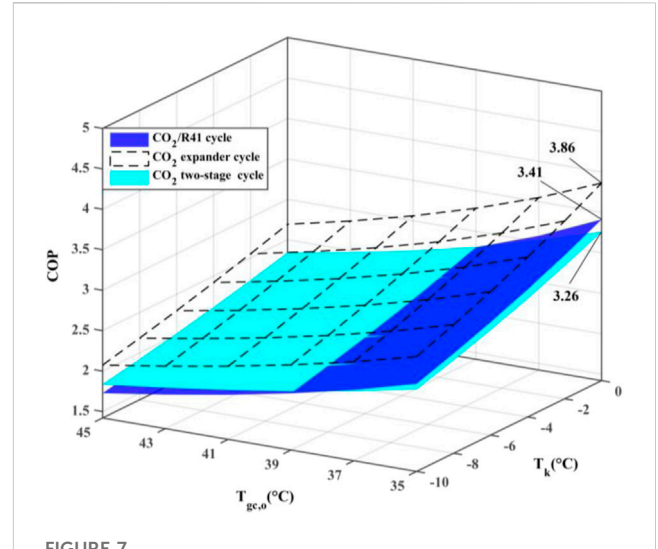

FIGURE 7
The maximum COP *versus* T_k and $T_{gc,o}$ in three cycles.
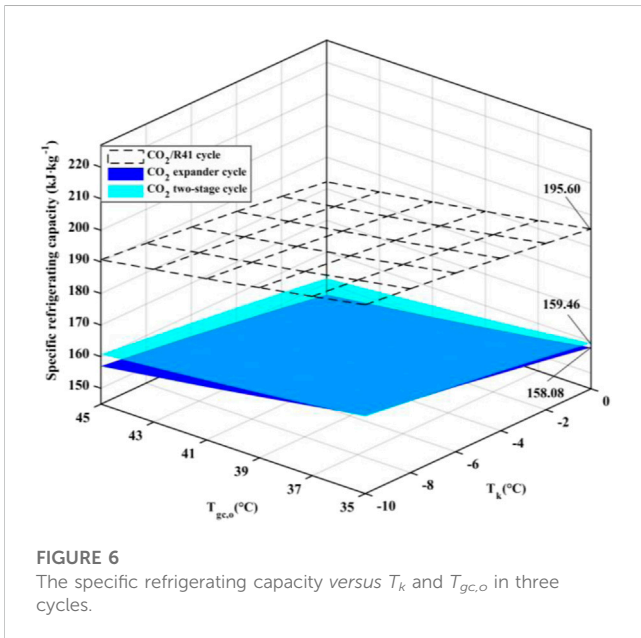

FIGURE 6
The specific refrigerating capacity *versus* T_k and $T_{gc,o}$ in three cycles.
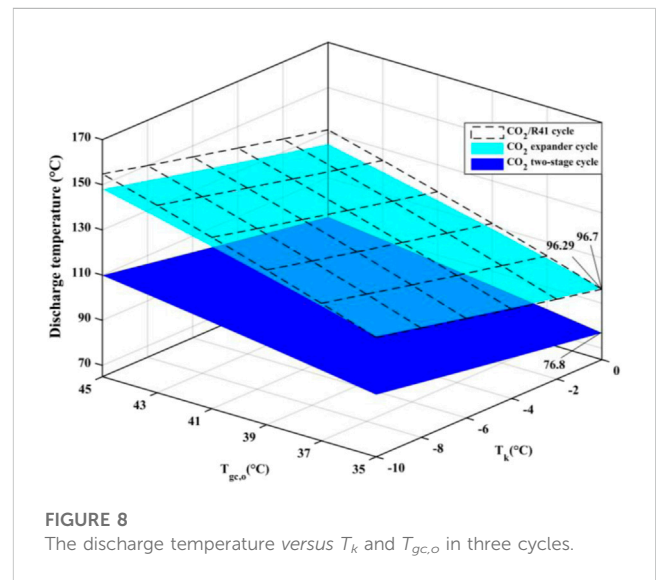

FIGURE 8
The discharge temperature *versus* T_k and $T_{gc,o}$ in three cycles.

refrigerating capacity than the other two cycles. Take the specific condition (T_k = 0°C and $T_{gc,o}$ = 35°C) as an example: the difference of specific refrigerating capacity between CO_2/R41 cycle and CO_2 expander cycle can reach 23.73%, while it can reach 22.66% for the specific refrigerating capacity between CO_2/R41 cycle and CO_2 two-stage cycle.

Figure 7 depicts the maximum COP of the three studied cycles with various evaporation temperatures (T_k) and the outlet temperature of the gas cooler ($T_{gc,o}$). The expander can recover a portion of the expansion work for driving the compressor, which leads to a significantly higher COP of a CO_2 expander cycle. Moreover, the CO_2/R41 cycle is observed to have a higher COP compared with the CO_2 two-stage cycle when the outlet temperature of the gas cooler is less than 39°C. For instance, when T_k = 0°C and

$T_{gc,o}$ = 35°C, the maximum COP of the CO_2/R41 cycle is about 4.6% higher than that of CO_2 two-stage cycle.

Excess discharge temperature is a serious problem in CO_2 compressors, because the superheated refrigerant vapor may reduce the viscosity of lubricating oil, which affects the reliability and safety of the compressor. It is universally acknowledged that the most significant advantage of a two-stage cycle is its ability to reduce the discharge temperature of a compressor, as shown in Figure 8. It can be found that the difference in discharge temperature between the CO_2/R41 cycle and CO_2 expander cycle is negligible and is reduced with the decrease of $T_{gc,o}$. Under the specific condition of T_k = 0°C and $T_{gc,o}$ = 35°C, the discharge temperature of CO_2/R41 cycle is even lower than that of CO_2 expander cycle, by about 0.4°C. Therefore, the CO_2/R41 cycle is competitive with the
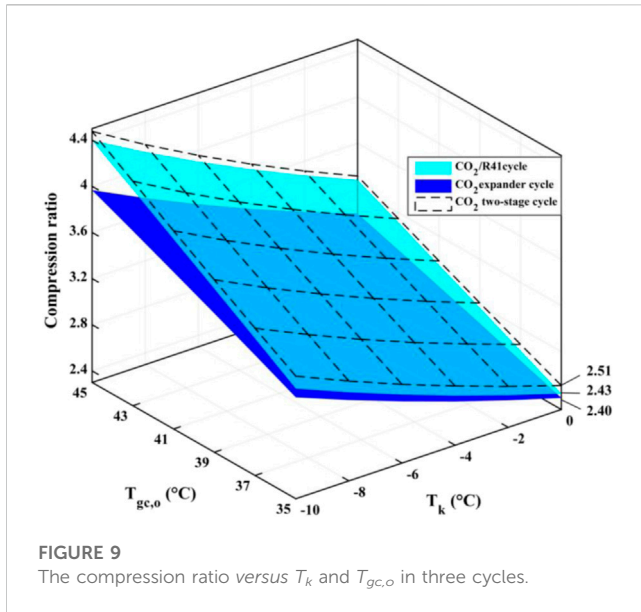
FIGURE 9
The compression ratio *versus* T_k and $T_{gc,o}$ in three cycles.
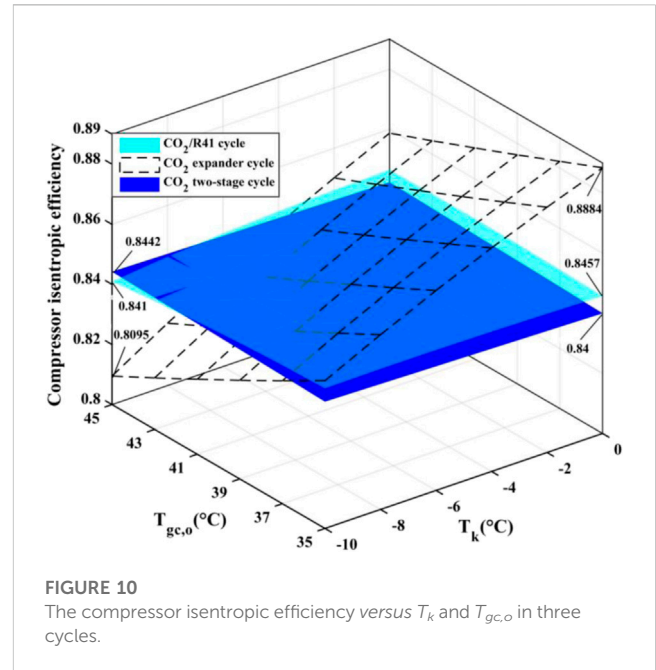

FIGURE 10
The compressor isentropic efficiency *versus* T_k and $T_{gc,o}$ in three cycles.

CO_2 expander cycle in terms of exhaust temperature, especially at a lower $T_{gc,o}$.

Since the compression ratio has a significant influence on wear and how leakproof the equipment is during the operation, it can affect the reliability and safety of the equipment. Therefore, it is an important performance index for a compressor. Figure 9 depicts the compression ratio of the compressor in the three studied cycles under various conditions. It is observed that for a low $T_{gc,o}$, the differences of the compression ratio among the three studied cycles are very small, while the compression ratio of the CO_2 expander cycle is obviously lower than that of both CO_2/R41 cycle and CO_2 two-stage cycle for a high $T_{gc,o}$. For example, the differences in the compression ratio between CO_2/R41 cycle and CO_2 expander cycle is less than 1.24% when $T_{gc,o}$ is 35°C and is about 10% when $T_{gc,o}$ is 45°C.

For a compressor, isentropic efficiency is an important parameter affecting the comprehensive performance of a vapor compression refrigeration/heat pump cycle. It expresses the power consumption ratio between the isentropic compression process and the actual compression process. Figure 10 shows the isentropic efficiencies of the compressor in the three studied cycles under various conditions. In the CO_2 two-stage cycle, the inter-stage pressure can be given from the geometric mean value of low and high pressures. According to Eqs 2, 6, it can be seen that the isentropic efficiency of the high-pressure compressor (HP) is equal to that of the low-pressure compressor (LP). It is noted that the value of compressor isentropic efficiency in the CO_2 two-stage cycle represents that of a single compressor (i.e., HP or LP) in Figure 10. In CO_2 two-stage cycle and CO_2/R41 cycle, the isentropic efficiency of the compressor varies little with the change of T_k and $T_{gc,o}$, especially for CO_2 two-stage cycle. Meanwhile, it can be seen that the differences in the compressor isentropic efficiency between the CO_2/R41 cycle and CO_2 two-stage cycle are very small (i.e., less than 0.0057) under the studied conditions. In contrast, the operation condition has an obvious effect on the isentropic efficiencies of a compressor in the CO_2 expander cycle.
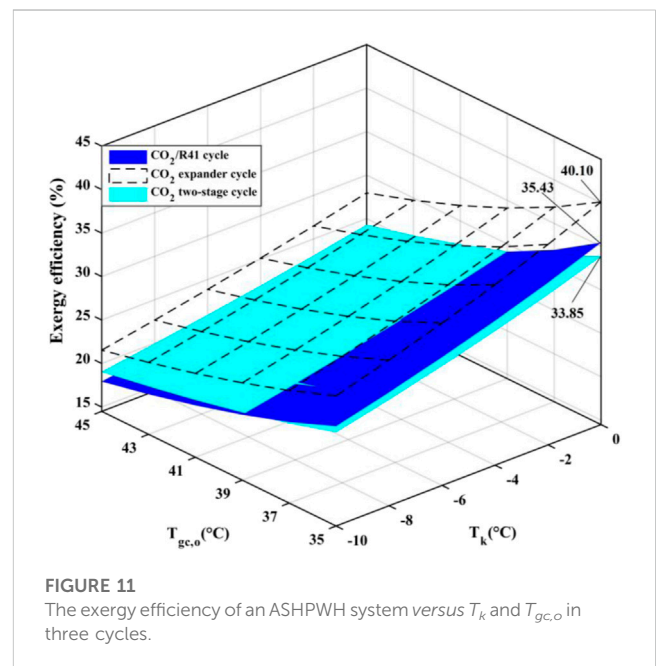

FIGURE 11
The exergy efficiency of an ASHPWH system *versus* T_k and $T_{gc,o}$ in three cycles.

It is well known that the transcritical cycle is suitable for application in heat pump water heater systems. Since the temperature glide of the refrigerant in gas coolers can be perfectly coupled to that of the heated water, the three studied transcritical cycles are used in an ASHPWH system in the present work. In order to identify and quantify the thermodynamic losses, the exergy efficiency of an ASHPWH system under three transcritical cycles are analyzed in detail on the basis of the second law of thermodynamics. Figure 11 delineates the variation of exergy efficiency of the ASHPWH system under three transcritical cycles for various parameters of $T_{gc,o}$ and T_k. It can be seen that the system exergy efficiency under the CO_2/R41 cycle is higher than that

TABLE 5 The irreversible loss of every component in the studied systems.

	CO$_2$/R41 cycle	CO$_2$ two-stage cycle	CO$_2$ expander cycle
I_{com}	0.1284	—	0.1563
$I_{HP\ com}$	—	0.0758	—
$I_{LP\ com}$	—	0.0681	—
I_{gc}	0.2307	0.1739	0.2972
I_{IHE}	0.0483	0.0511	0.0635
I_{TV}	0.1838	0.2163	—
I_{EXP}	—	—	0.0305
I_{IC}	—	0.0328	—
I_E	0.0545	0.0435	0.0515

under CO$_2$ two-stage cycle when the outlet temperature of the gas cooler is less than 39°C (i.e., $T_{gc,o} \leq 39$°C).

Table 5 shows the irreversible loss of each component in the studied systems under a specific condition (i.e., $T_k = 0$°C and $T_{gc,o} = 35$°C). It can be found that the gas cooler and throttling valve are the two main components in terms of irreversible loss in the studied systems. Due to the large pressure drop, the throttle valve produces a large irreversible loss in a refrigeration/heat pump system, which leads to low exergy efficiency for the system, as shown in Figure 11. However, the throttling valve is still usually used as a component in a CO$_2$ refrigeration/heat pump system, because it has been difficult to design and manufacture an expander which can be satisfactorily used in a high-pressure CO$_2$ refrigeration/heat pump system.

6 Conclusion

In this paper, the optimum mass ratio of CO$_2$/R41 azeotropy mixture was defined and calculated based on the comprehensive consideration of thermodynamic properties and safety. A thermodynamic model was proposed to evaluate and compare the performance of three developed cycles. The main conclusions are listed as follows:

(1) The optimum mass ratio of CO$_2$/R41 azeotropy mixture is 0.583/0.417 (i.e., volume ratio is 0.52/0.48).
(2) The CO$_2$/R41 azeotropy refrigerant with optimum mass ratio is eco-friendly and particularly strong for the transcritical cycles because of its low critical temperature (37.67°C).
(3) It may be feasible to use a simple CO$_2$/R41 cycle to replace the complex CO$_2$ two-stage cycle and CO$_2$ expander cycle because of the following reasons:
   • The optimum high pressure of the CO$_2$/R41 cycle is more than 26.9% lower than that of CO$_2$ expander cycle and is more than 32.6% lower than that of CO$_2$ two-stage cycle under the same conditions, which can help to improve the tightness and safety of the system.

   • The CO$_2$/R41 cycle has a higher specific refrigerating capacity than the other two cycles.
   • Under a low outlet temperature of the gas cooler, CO$_2$/R41 cycle is highly competitive with CO$_2$ two-stage cycle in terms of COP and exergy efficiency.
   • The compression ratio and discharge temperature of the compressor in CO$_2$/R41 cycle are similar to those of CO$_2$ expander cycle.
(4) For a refrigeration/heat pump system with CO$_2$/R41 transcritical cycle, the outlet temperature of the gas cooler is required to be less than 39°C to obtain a more competitive performance for the system.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

DW: Data curation, Writing- original draft preparation. ML: writing- reviewing and editing. ZG: conceptualization, methodology, Software. SM: conceptualization, methodology, Software. SD: conceptualization, writing- reviewing and editing. All authors contributed to the article and approved the submitted version.

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Conflict of interest

Author FY was employed by the company Anhui MBO Intelligent Technology Co. Ltd.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Nomenclature

B	volume fraction of component in the mixture
C	the flammability limit (%)
H	specific enthalpy of state point (kJ kg^{-1})
I	specific irreversible loss (kJ kg^{-1})
P	pressure (MPa)
Q	the specific refrigerating capacity (kJ kg^{-1})
R	compression ratio
s	specific entropy (kJ kg^{-1}K^{-1})
T	temperature (K)
w	specific work input (kJ kg^{-1})

Greek symbols

β	efficiency of heat exchanger
Δ	difference
ε	isentropic efficiency
η	exergy efficiency
ρ	density

Subscripts

1,2,2s,3,4,4s,5,5s,6,7,8	state point
C	cold side
CO$_2$	pure CO$_2$
CO$_2$/R41	mixture of CO$_2$ and R41
com	compressor
cri	critical
E	evaporator
ef	external fluid
en	environment
equ	equation
EXP	expander
gc	gas cooler
H	heat side
i	inlet
IC	intercooler
IHE	internal heat exchanger
is	isentropic
ite	iterative
k	evaporation
o	outlet
opt	optimum
r	refrigerant

TV	throttling valve
tot	total

Acronyms

ASHPWH	air-source heat pump water heater
COP	coefficient of performance
GWP	global warming potential
HFCs	hydrofluorocarbons
HP	high-pressure compressor
LFL$_V$	lower flammability limit (volume fraction)
LP	low-pressure compressor
ODP	ozone depleting potential
UFL$_V$	upper flammability limit (volume fraction)