



Junlan Yang *, Linxiu Wang, Yifei Han, Xin Zhang and Yufan Du

School of Energy and Security Engineering, Tianjin Chengjian University, Tianjin 300384, China * Correspondence: yjlfg@163.com; Tel.: +86-13820491855

Abstract: In order to improve the efficiency of the system and promote its application in other industries, the performance of a thermoelectric subcooled CO₂ transcritical heat pump system was studied. A simulation model of the system was established using steady-state lumped parameter technology, and the experimental data were compared with the simulation results. The effects of cooling and chilled water flow rate and temperature, subcooling degree, compressor discharge pressure on the coefficient of performance (COP), and heating coefficient of performance (COPh) were analyzed. The results showed that COP/COPh increased with the increase in cooling and chilled water flow rate and chilled water temperature and decreased with the increase in cooling water temperature. The experimental COPh and COP of the system with a thermoelectric subcooler increased by 4.19% and 4.62%, respectively, compared to the system without it. The simulated data was in good agreement with the experimental data, and the error was within 10%, thus verifying the correctness of the model. When the subcooling degree increased to 11 °C, the system simulation results showed that COP/COPh increased by about 40% and 13.3%, respectively. The optimal high pressure was about 8.0 MPa, which corresponded to the maximum COP and COPh of the system of 3.25 and 4.25, respectively. The research results can provide a theoretical basis for future system optimization.

Keywords: thermoelectric subcooler; CO2 transcritical cycle; simulation; experimental measurement

1. Introduction

The world is paying more attention to environmental concerns due to fast economic expansion. At the 75th session of the United Nations General Assembly, China proposed the targets of "carbon peak" by 2030 and "carbon neutral" by 2060 to address the issue of global warming [1]. The main solution to the problem of carbon dioxide emission is to reduce the use of fossil fuels [2]. Heat pump technology has the potential to minimize the usage of fossil fuels while enhancing energy efficiency. The use of artificial (unnatural) working medium in heat pump units will cause environmental issues. For a long time, the widespread use of refrigerants, such as HFC, has intensified the global greenhouse effect [3,4]. To address this issue, China ratified the Kigali Amendment to the Montreal Protocol, which came into effect on 1 June 2022. The use of HFCs is also anticipated to be significantly reduced in the Chinese market [5,6]. The use of natural ingredients as refrigerants has gained widespread attention in recent years. Due to its advantages of large volume cooling capacity, good compatibility, low price, low viscosity, and low pressure ratio, carbon dioxide has begun to be used as a refrigerant worldwide [7]. However, CO_2 transcritical heat pump cycles also have several drawbacks, such as high operating pressure and large throttling losses, which result in low circulation efficiency [8,9].

In order to improve the system efficiency and reduce throttling loss, Dai et al. [10] proposed a new type of thermoelectric subcooler–expander coupled CO_2 transcritical refrigeration cycle and analyzed the energy losses and efficiencies in detail. Rigola et al. [11] used theoretical and experimental results to show that the CO_2 transcritical cycle with an internal heat exchanger could increase the cooling capacity and COP.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). A thermoelectric subooler (TESC) is composed of multiple thermoelectric elements in series or in parallel. Thermoelectric modules are able to pump heat from a cold surface to a hot surface through the Paltier effect. Its advantages include small size, light weight, reliable performance, and ease of use. It has been documented that the performance of a thermoelectric cooler in a heat exchanger is related to the influence of heat transfer area, thermal conductivity, and heat transfer mechanism [12,13]. In addition, the performance and operational reliability of TESC are significantly affected by the joule heat generated by the input current inside the module [14].

To improve the effectiveness of cooling facilities, many authors have proposed thermoelectric subcooling in transcritical CO_2 refrigeration systems. Koeln et al. [15] found that subcooling the outlet of the gas cooler of a CO₂ transcritical refrigeration system could significantly improve the efficiency of the system. In a heat pump experiment, Wang [16] discovered that including a subcooler might raise the product's energy efficiency ratio. Yang et al. [17] found that the application of a thermoelectric subcooler at the outlet of the air cooler in the transcritical CO₂ cycle could effectively improve the efficiency of the whole system. Li et al. [18] designed a subcooling device based on the principle of thermoelectricity and found that the cooling effect of the thermoelectric subcooling device was the best at 12 V working voltage. Astrain et al. [19] compared a CO₂ transcritical refrigeration system with a thermoelectric module, an air-cooled CO_2 transcritical system, and a system with internal heat exchange and found that the cooling efficiency of the system with a thermoelectric module was higher than the other two systems. Sánchez et al. [20] proposed a thermoelectric subcooling system and tested it in a CO₂ transcritical refrigeration unit. The results showed that under optimal operating conditions, the COP and cooling capacity of the refrigeration unit could be increased by 9.9% and 16.0%, respectively. Aranguren [21] conducted an experimental study on a transcritical CO₂ compression cycle with a thermoelectric subcooler, and the results showed that the experimental COP increased by 11.3% and the cooling capacity improved by 15.3%.

Most scholars have established models to analyze the performance of CO_2 transcritical refrigeration cycles with thermoelectric subcoolers. In addition, some scholars have conducted research only through experiments. In this study, the performance of a transcritical CO_2 refrigeration cycle with a thermoelectric subcooler was investigated by experiments and simulation models. The system model was simulated by MATLAB software. In addition, the influence of chilled water flow rate and temperature, cooling water flow rate and temperature, cooling water flow rate and temperature, compressor discharge pressure, and subcooling degree on the performance of the system was also analyzed. The purpose of this study was to provide theoretical suggestions for further improving the performance and optimization of such systems.

2. Experiment Test

2.1. Refrigeration System

This section describes the configuration of a single-stage vapor compression system, including a thermoelectric subcooler (TESC). Figure 1 shows the schematic diagram of a refrigeration system and the system's P–H diagram.

The four main components of the experimental system were the CO_2 heat pump system, the water system, the data collecting system, and the control system. Figure 2 provides a flow chart of the system.

The main components and technical parameters of the heat pump system are shown in Table 1.



Figure 1. (a) Schematic diagram, (b) P–H diagram of the system.



Figure 2. CO₂ water–water heat pump system with a thermoelectric subcooler. 1—compressor, 2—oil separator, 3—gas cooler, 4—thermoelectric subcooler, 5—mass flow meter, 6—regenerator, 7—throttle valve, 8—evaporator, 9—gas–liquid separator, 10—water flow meter, 11—water pump, 12—electric heater, 13—water tank, 14—drain valve, 15—inlet valve, T—thermocouple, P—pressure transmitter.

Table 1. The main components and technical parameters of the heat pump system.

Equipment	Details
Compressor	The CO ₂ special compressor produced by Dorin (Torin) in Italy, model CD380H, speed 1450 rpm, rated input power 3.3 kW, oil injection capacity 1.3 kg, net weight 77 kg.
Gas cooler	Self-made casing heat exchanger, $\Phi 22.2$ seamless steel pipe as outer pipe, $\Phi 12$ nickel white copper threaded pipe as inner pipe, water pipe layer, CO_2 shell layer, pipe length 16 m, total heat exchange area of 1.2 m^2 , countercurrent form adopted to enhance heat transfer, maximum pressure 14 MPa.

Equipment	Details
Evaporator	Self-made casing heat exchanger, Φ 22.2 seamless steel pipe as outer pipe, Φ 12 nickel white copper threaded pipe as inner pipe, water pipe layer, CO ₂ shell layer, pipe length 16 m, total heat exchange area of 1.2 m ² , countercurrent form adopted to enhance heat transfer, maximum pressure 14 MPa.
Thermoelectric subcooler	Composed of thermoelectric refrigeration sheet, water cooler, and cold end fin of model TEC1-12710, with a size of $16 \times 1 \times 6$ cm.
Regenerator	Self-made casing-type internal heat exchanger, stainless steel material, copper tube with inner tube Φ 12, copper tube with outer tube Φ 19, heat exchange area 0.3 m ² , high temperature CO ₂ pipe from gas cooler, low temperature CO ₂ from evaporator flow outside the tube, countercurrent heat exchange.
CO ₂ expansion control valve	Inner diameter of the connecting pipe of 2.4 mm, cooling capacity of 8.6 kW, maximum pressure of 15 MPa, and working pressure difference of 0–10 MPa.
Gas-liquid separator	Self-made stainless steel gas–liquid separator, outer tube Φ 50, inner tube Φ 6, height of 0.5 m.
Oil separator	Homemade stainless steel oil separator, outer tube Φ 100, height 0.5 m, interface size 1–1/8 (28 mm).
CO ₂ high-pressure reservoir	Outer tube Φ 100, height 0.5 m.

Table 1. Cont.

2.2. Thermoelectric Subcooler (TESC)

The thermoelectric subcooler is composed of thermoelectric refrigerating sheets, a cold plate, and a radiator. The cold plate is mounted at the cold end of the stack. The thermoelectric subcooler uses the Peltier principle. Semiconductors are divided into N-type and P-type according to the different charge carriers. When the power is turned on, an electron transition occurs at the contact of these two semiconductor materials, which generates or absorbs energy, forming a cold and hot junction.

For a thermoelectric refrigerating sheet, the theoretical cold end cooling capacity (Q_c) and power consumption (W_e) can be calculated using Equations (1) and (2), respectively [10].

$$Q_{\rm c} = (\alpha_p - \alpha_n) A T_c - 0.5 A^2 R - K (T_H - T_C)$$
(1)

$$W_e = (\alpha_v - \alpha_n)AT_c + A^2R \tag{2}$$

where α refers to the Seebeck coefficient, V/K; P and N refer to the subscripts; A refers to the current; T_C refers to the cold end temperature in K; R refers to the resistance in Ω ; K refers to the thermocouple thermal conductivity, W/K; and T_h refers to the hot end temperature in K.

In order to better measure the pros and cons of the thermoelectric subcooler, the ratio of the cooling capacity to the power consumption of the thermoelectric subcooler, namely, the efficiency *COPsc*, can be calculated as follows:

$$COP_{sc} = \frac{Q_c}{W_e} \tag{3}$$

Due to the hot end of the thermoelectric subcooler constantly emitting heat during operation, the water cooled method is utilized to quickly disperse heat and prevent overheating damage.

Fins are added to the thermoelectric subcooler's cold end in order to expand the heat exchange area to cool the refrigerant in the pipeline. Here, the thermal contact resistance between the thermoelectric tube and the pipe is reduced by the thermal paste. The size of the thermoelectric subcooler is marked in Figure 3. Figure 4 is a physical diagram of the thermoelectric subcooler.



Figure 3. Structure of the thermoelectric subcooler.



Figure 4. Physical diagram of the thermoelectric subcooler.

In order to achieve the subcooling degree of 5 °C, the cooling capacity of the thermoelectric subcooler should be 1.5 kW according to calculation using Equation (4) assuming the evaporation temperature is 0 °C, the discharge pressure of compressor is 8.5 MPa, the outlet temperature of the gas cooler is 35 °C, and the mass flow of the CO₂ is 180 kg/h.

Thus, 22 thermoelectric refrigerating sheets of the model TEC1-12710 were chosen with the size of $40 \times 40 \times 3.4$ mm. The specific parameters are shown in Table 2.

$$Q = Gr(h_3 - h'_3) \tag{4}$$

where h_3 refers to the enthalpy value of the gas cooler outlet; h'_3 refers to the enthalpy value of the thermoelectric subcooler outlet; *Gr* refers to the refrigerant mass flow; and *Q* refers to the refrigerant capacity of the thermoelectric subcooler.

Table 2. Performance parameters of thermoelectric refrigerating sheet.

Model	Maximum Operating Temperature/ °C	Maximum Cooling Capacity/ W	Maximum Temperature Difference/ °C	Input Voltage/ V	Maximum Current/ A
TEC1-12710	80	89	65	12	10

2.3. Experimental Condition

The performance of the CO_2 transcritical water–water heat pump system was evaluated under various operating conditions, including with and without a thermoelectric subcooler.

The experiment's rated working conditions were as follows: CO_2 mass flow rate of 180 kg/h, cooling water flow rate of 0.5 m³/h, chilled water flow rate of 1.2 m³/h, inlet temperature of cooling water of 20 °C, and inlet temperature of chilled water of 12 °C.

The variable working conditions of the experiment were as follows: (1) variation of the mass flow rate of CO₂ from 160 to 200 kg/h, (2) variation of cooling water flow rate from 0.8 to 2 m³/h and cooling water temperature from 20 to 30 °C, (3) variation of chilled water flow rate from 0.4 to 1 m³/h and chilled water temperature from 10 to 20 °C.

2.4. Experimental Data Processing

2.4.1. System Cooling Capacity

Calculations were made based on the exothermic heat dissipation on the chilled water side of the evaporator:

$$Q_1 = c_{p1} \frac{g_{w1} \cdot \rho_{w1}}{3600} (t_{win} - t_{wout})$$
(5)

where Q_1 refers to the refrigeration capacity; c_{p1} refers to the constant pressure specific heat of the chilled water; g_{w1} refers to the volume flow of the chilled water; ρ_{w1} refers to the density of the chilled water; and t_{win} and t_{wout} refer to the inlet and outlet water temperature of the chilled water, respectively.

2.4.2. The Heat Dissipation of the Gas Cooler

The heat absorption on the cooling water side of the gas cooler was calculated as follows:

$$Q_2 = c_{p2} \frac{g_{w2} \cdot \rho_{w2}}{3600} (t_{w,out} - t_{w,in})$$
(6)

where Q_2 refers to the heat absorption; c_{p2} refers to the specific heat of the cooling water; g_{w2} refers to the volume flow of the cooling water; ρ_{w2} refers to the density of the cooling water; and $t_{w,in}$ and $t_{w,out}$ refer to the inlet and outlet water temperature of the cooling water, respectively.

2.4.3. Coefficient of Performance

The COP and COPh of the entire refrigeration system were calculated using the following formulas. The system's total power consumption included the power consumed by the compressor and the TESC (Equation (9)).

$$COP = \frac{Q_1}{W_{com} + W_{TESC}} \tag{7}$$

$$COPh = \frac{Q_2}{W_{com} + W_{TESC}}$$
(8)

$$W_{TESC} = V_{TEM} I_{TEM} \tag{9}$$

2.5. Experimental Error Analysis

This section analyzes the possible errors in the experiment resulting from many uncertain factors in the operational process.

2.5.1. Data Acquisition System

The data acquisition equipment included a platinum resistance temperature sensor, pressure sensor, electric power transmitter, turbine water flow meter, and electromagnetic CO_2 mass flow meter. The parameters of each data acquisition device are shown in Table 3 below.

Table 3. Technical parameters of each data acquisition equipment.

	Equipment	Measuring Range	Precision or Grade of Precision	Conditions of Use	Instructions
Temperature	Platinum resistance temperature sensor	-50 to 400 $^\circ\mathrm{C}$	A grade 0.1%	_	Siemens 7MC1006-1DA16-Z T10
Pressure	Pressure transducer	1 kPa to 40 MPa	$\pm 0.25\%$	—	Siemens 7MF1567-3DE00-3AA1
Power	Electric power transmitter	0–866 W	0.2%	Operating temperature: 0–45 °C	Suzhou honow FPW-201

	Equipment	Measuring Range	Precision or Grade of Precision	Conditions of Use	Instructions
Water flow	Turbine flow meter	0.2–1.2 m ³ /h	Level 0.5 (water calibration)	Temperature of measured medium: −20 to 120 °C; pressure: ≤25 Mpa	Dayt and LWGAYA-15 The connection mode is threaded connection
CO ₂ mass flow rate	Coriolis mass flow meter	0–250 kg/h	0.5 grade	Standard temperature: -50 to 150 °C, fluid Pressure measurement tube: 23 MPa	Siemens 7ME4100-1CL10-1DA1

Table 3. Cont.

2.5.2. Uncertainty of Chilled Water Flow

The flowmeter used to measure the flow rate of chilled water was 1.6 m³/h, the measurement accuracy of the flowmeter was 0.5 level, and the uncertainty was $\delta v_w = 0.008 \text{ m}^3/\text{h}$. The smallest chilled water flow in the measurable range was 0.8 m³/h, and the maximum relative uncertainty of chilled water flow was 1%.

2.5.3. Uncertainty of Refrigerant Mass Flow Rate

The mass flow meter used to measure the mass flow of the refrigerant had a range of 0-250 kg/h, and the uncertainty of the mass flowmeter was $\delta q = 0.1 \text{ kg/h}$. The maximum relative uncertainty of mass flow was 0.063%.

2.5.4. The Uncertainty of Cooling Capacity and COP

Because the cooling capacity and COP were calculated indirectly from other data collected, their errors can be analyzed using the power of second method, that is, if Y is a function of n independent variables, x_{ζ} is the independent variable affecting the function Y, and the error of Y can be determined by Equation (10):

$$\frac{\delta Y}{Y} = \sum_{\zeta=1}^{n} \left[\left(\frac{\delta x_{\zeta}}{x_{\zeta}} \right)^2 \right]^{\frac{1}{2}}$$
(10)

Due to $Q = f(m_w, t_{wi}, t_{wo})$, the uncertainty of the cooling capacity Q can be calculated as follows:

$$\frac{\delta Q}{Q} = \left[\left(\frac{\delta m_w}{m_w} \right)^2 + \left(\frac{\delta t_{win}}{t_{win}} \right)^2 + \left(\frac{\delta t_{wout}}{t_{wout}} \right)^2 \right]^{\frac{1}{2}} = \left[(0.5\%)^2 + (0.1\%)^2 + (0.1\%)^2 \right]^{\frac{1}{2}} = 0.52\%$$
(11)

Due to $W = f(Gr, t_{in,com}, t_{out,com}, P_{in,com}, P_{out,com})$, the uncertainly of the compressor power consumption W can be calculated as follows:

$$\frac{\delta W}{W} = \left[\left(\frac{\delta Gr}{Gr} \right)^2 + \left(\frac{\delta t_{in,com}}{t_{in,com}} \right)^2 + \left(\frac{\delta t_{out,com}}{t_{out,com}} \right)^2 + \left(\frac{\delta P_{in,com}}{P_{in,com}} \right)^2 + \left(\frac{\delta P_{out,com}}{P_{out,com}} \right)^2 \right]^{\frac{1}{2}} \\ = \left[(0.5\%)^2 + (0.1\%)^2 + (0.1\%)^2 + (0.25\%)^2 + (0.25\%)^2 \right] \\ = 0.62\%$$

Due to COP = f(Q, W), the uncertainty of COP can be calculated as follows:

$$\frac{\delta COP}{COP} = \left[\left(\frac{\delta Q}{Q} \right)^2 + \left(\frac{\delta W}{W} \right)^2 \right]^{\frac{1}{2}}$$
$$= \left[(0.52\%)^2 + (0.62\%)^2 \right]^{\frac{1}{2}}$$
$$= 0.81\%$$
(12)

where m_{w1} refers to the flow rate of chilled water in kg/s; t_{win} and t_{wout} refer to the inlet and outlet water temperatures of the chilled water of the evaporator, respectively, respectively, in °C; *P* refers to the measured pressure in MPa; and *W* refers to the compressor consumption power in kW.

3. Simulation Model Establishment

In this section, the CO₂ transcritical water–water heat pump model is discussed in detail by establishing a mathematical model and using MATLAB to call physical parameters in Refprop software. The system is mainly composed of a compressor, gas cooler, thermoelectric subcooler, throttle valve, and evaporator. The use of energy conservation and related principles to establish the model can effectively supplement the problem of incomplete data caused by the limitation of test conditions. The model can be used to comprehensively analyze the impact of different parameters on the performance of the system and provide theoretical guidance to further understand the performance of and investment required for a heat pump system.

3.1. Compressor Model

Mass flow rate of CO₂ refrigerant

$$G_r = \frac{V_{th}\eta_v}{3600v_s} \tag{13}$$

Volume efficiency [22]:

$$\eta_v = 0.976728 - 0.0921418 \left(\frac{P_2}{P_1}\right)^{0.714} \tag{14}$$

where V_{th} refers to the calculated exhaust volume in m³/h; v_s refers to the compressor refrigerant specific capacity; P_2 refers to the compressor exhaust pressure in MPa; and P_1 refers to the compressor suction pressure in MPa.

The compressor power consumption can be calculated by Equation (15):

$$W_{com} = \frac{G_{\rm r}(h_2' - h_1)}{\eta_{is}\eta_m} \tag{15}$$

where η_{is} and η_m are calculated using empirical formula [22,23]:

$$\eta_m = 0.26 + 0.7952 \left(\frac{P_2}{P_1}\right) - 0.2803 \left(\frac{P_2}{P_1}\right)^2 + 0.414 \left(\frac{P_2}{P_1}\right)^3 - 0.0022 \left(\frac{P_2}{P_1}\right)^4 \tag{16}$$

$$\eta_{is} = 0.995541 - 0.107987 \left(\frac{P_2}{P_1}\right)^{0.714} \tag{17}$$

In Equations (16) and (17), h'_2 refers to the isentropic enthalpy value of compressor outlet state point; h_1 refers to the enthalpy value when the machinery is inhaled; η_m refers to the mechanical efficiency; and η_{is} refers to the isentropic efficiency.

3.2. Gas Cooler

The model of the gas cooler was constructed by the centralized parameter method, and the following assumptions were made:

- 1. When the refrigerant and water are exchanged heat, it is a one-dimensional steadystate model, and the temperature and flow rate of the refrigerant and the water are evenly distributed in the corresponding cross section.
- 2. All the heat losses of the gas cooler are ignored, and the outer pipe wall is considered to be adiabatic.
- 3. The pressure drop of the water in the tube is ignored.

- 4. The thermal conduction process only occurs in the horizontal direction of fluid flow.
- 5. The system operation state is steady.
- 6. The refrigerant flows along the tube and is evenly distributed.

According to the energy conservation law, the heat released by the refrigerant is the same as that absorbed by cooling water. Thus, the following equation can be obtained:

$$Q_{CO_2} = G_r(h_2 - h_3) \tag{18}$$

Cooling water side heat absorption equation:

$$Q_w = m_{w2}cp_2(t_{w,out} - t_{w,in})$$
(19)

Total heat transfer equation:

$$Q_{CO_2} = Q_w = KA_2 \bigtriangleup t \tag{20}$$

where m_{w2} refers to the cooling water flow in kg/s; c_{pw} refers to the specific heat capacity of the cooling water at constant pressure in kJ/(kg·°C); A₂ refers to the heat exchange area of the gas cooler in m²; and Δt refers to the logarithmic average temperature difference in °C.

The parameters involved can be calculated as follows:

(1) Using the outer surface of the inner tube as a reference, the total heat transfer coefficient solution equation is established.

$$K = \frac{1}{\left(\frac{1}{h_{CO_2} + r_1}\right) + \frac{\delta}{\lambda} \ln \frac{d_{w,o}}{d_m} + \left(\frac{1}{h_w} + r_2\right) \frac{d_{w,o}}{d_{w,i}}}$$
(21)

where r_1 and r_2 refer to the fouling coefficient of the inner and outer tubes, respectively; $d_{w,o}$ refers to the inner tube outside diameter in mm; and $d_{w,i}$ refers to the inner diameter of the inner tube in mm.

(2) Logarithmic mean temperature difference:

$$\Delta t = \frac{\left(t_{w,in} - t_{CO_2,out}\right) - \left(t_{w,out} - t_{CO_2,in}\right)}{\ln\left(\frac{t_{w,in} - t_{CO_2,out}}{t_{w,out} - t_{CO_2,in}}\right)}$$
(22)

(3) Heat transfer area:

$$=\pi d_{w,o}l\tag{23}$$

where *l* refers to the tube length in m.

In the cycle process, the gas cooler exothermic heat in the transcritical and the conventional cycle in the subcritical exothermic heat release are very different, which is caused by the special thermal properties of CO_2 . At present, more and more researchers have started studying the heat exchange correlation type of the air cooler in depth. According to the literature, the heat exchange working conditions of the heat exchange correlation type established by Yoon et al. were similar to this paper; thus, we selected the heat exchange correlation type of Yoon [24]:

$$Nu_{CO2} = a \operatorname{Re}_{CO_2}{}^{b} \operatorname{Pr}_{CO_2}{}^{c} \left(\frac{\rho_{PC}}{\rho_f}\right)^{n}$$
(24)

where ρ_{pc} refers to the critical density of fluids, and ρ_f refers to the fluid density.

А

Heat transfer coefficient on the cooling water side:

$$h_w = \frac{Nu_w \cdot \lambda_w}{l} \tag{25}$$

3.3. Thermoelectric Subcooler

When the model was established, the input parameters included the cooling capacity and the number of thermoelectric refrigerating sheets. The output parameter was the degree of subcooling.

By calculation, 22 refrigerants sheets with a cooling capacity of 70 W and type TEC1-12710 constituted a thermoelectric subcooler, and the total cooling capacity of the thermoelectric subcooler was 1.5 kW.

1. The CO₂ side cooling capacity:

$$Q = Gr(h_3 - h'_3) \tag{26}$$

2. The cooling capacity of the thermoelectric subcooler [10]:

$$Q_{\rm c} = n \left[\left(\alpha_p - \alpha_n \right) A T_c - 0.5 A^2 R - K (T_H - T_C) \right] \tag{27}$$

3. Equation for conservation of energy:

$$Q = Q_c \tag{28}$$

3.4. Throttle Valve

The throttle process in the throttle valve assumes that the enthalpy values before and after the throttling are equal:

$$h_{3'} = h_{4'} \tag{29}$$

3.5. Evaporator

The simulation model using a centralized parametric method was built on a lab jacketed evaporator based on the following assumptions:

- 1. The casing used is uniform and regularly round.
- 2. The chilled water and refrigerant both flow in a certain dimensional direction.
- 3. The chilled water and refrigerant are evenly distributed in the tube.
- 4. The heat transfer loss of the evaporator is not considered.
- 5. The interference caused by the lubricating oil and other similar factors on the heat exchange is ignored.

Heat absorption of refrigerant:

$$Q_{\rm r} = Gr(h_1 - h_{4'}) \tag{30}$$

Heat release on the side of chilled water:

$$Q_{\rm ld} = c p_1 \mathbf{m}_{w1} (t_{win} - t_{wout}) \tag{31}$$

Total heat exchange:

$$Q_{\rm r} = Q_{ld} = KA_1 \bigtriangleup t_1 \tag{32}$$

where m_{w1} refers to the flow rate per second of chilled water in kg/s; t_{win} refers to the temperature of the chilled water inlet in °C; t_{wout} refers to the outlet temperature of chilled water in °C; A_1 refers to the heat transfer area of chilled water in m^2 ; K refers to the heat transfer area of chilled water in m^2 ; K refers to the heat transfer rate of the evaporator, $W/(m^2 \cdot K)$; and Δt_1 refers to the logarithmic average temperature difference in °C.

The parameters involved can be calculated as follows:

1. Using the outer surface of the inner tube as a reference, the total heat transfer coefficient solution equation is established as shown in Equation (33):

$$K = \frac{1}{\left(\frac{1}{h_r} + r_1\right) + \frac{\delta}{\lambda} \ln \frac{d_{ld,\rho}}{d_m} + \left(\frac{1}{h_{ld}} + r_2\right) \frac{d_{ld,\rho}}{d_{ld,i}}}$$
(33)

where r_1 and r_2 refer to the fouling coefficient on the CO₂ side and the chilled water side, respectively, and d_m refers to the average diameter of the tube.

2. The heat transfer coefficient on the chilled water side is calculated using the Dittus– Boelter correlation [25]:

$$Nu_{ld} = 0.023 \text{Re}^{0.8} \text{Pr}^n \tag{34}$$

where n = 0.4 when the fluid is heated, and n = 0.3 when the fluid is cooled.

Compared to [26,27], Kew and Cornwell [28] heat transfer related formulas were selected as the correlation relationship of CO_2 boiling heat transfer coefficient in the evaporator due to the similar dimensions and other relevant parameters with the laboratory evaporator model. The details are as follows [28]:

$$h_r = 30 \cdot \text{Re}_r^{0.857} \cdot Bo^{0.714} \cdot (1-x)^{-0.143} \cdot \frac{\lambda_r}{n \times d_r}$$
(35)

where h_r refers to the heat transfer coefficient on the refrigerant side, $W/(m^2 \cdot K)$; λ_r refers to the thermal conductivity coefficient for the refrigerant side, $W/(m \cdot K)$; x refers to dryness; Re_r refers to Reynolds number; and *Bo* refers to boiling number.

3.6. Solving the System Model

The matching module was developed in MATLAB and solved in accordance with the mathematical model of each component. Characteristics such as cooling/heating capacity and COP/COPh were determined by inputting the compressor discharge pressure, the tube diameter of the evaporator and gas cooler, and the temperature and flow rate of the chilled water and the cooling water. A compressor module, gas cooler module, thermoelectric subcooler module, throttle valve module, and evaporator module made up the overall system. Each component was meticulously simulated using the defined model, and data on endothermic and exothermic heat were calculated. The absolute value of the relative error of cooling capacity and heat absorption was taken as the convergence condition. If the error was less than 5%, the program continued calculation; otherwise, the parameters were reassumed. Figure 5 is the flow chart of system model calculation.



Figure 5. The flow chart of system model calculation.

4. Results and Discussion

4.1. Analysis of Experimental Results

4.1.1. The Variation of the Cooling Water Flow Rate

Figure 6 shows the relationship between COPh and cooling water flow. With continuous increase in the cooling water flow, the heating coefficient of performance and the variation trend were similar for the systems with and without a subcooler. At the same time, the heating coefficient of the system with a subcooler increased by 3.14% compared to that without it under the same conditions.



Figure 6. Influence of cooling water flow rate on COPh.

4.1.2. Variation of Cooling Water Temperature

As can be seen from Figure 7, regardless of whether the system was equipped with a subcooler, the COPh decreased as the cooling water temperature increased, which was similar to the trend of heating coefficient of performance of the system without a subcooler.

Under the same conditions, the COPh efficiency of the system with a subcooler increased by 2.63% compared to the system without a subcooler.



Figure 7. Influence of cooling water temperature on COPh.

4.1.3. Variation of Chilled Water Flow

Figure 8 shows the variation trend of coefficient of performance with increasing chilled water flow rate with and without a subcooler. From Figure 8, it can be seen that the COP of the system increased with the increase in chilled water flow rate with or without a subcooler, and the coefficient of performance of the system with a subcooler was 1.62% higher than that of the system without a subcooler.



Figure 8. Influence of chilled water flow on COP.

4.1.4. Variation of Chilled Water Temperature

Figure 9 shows the trend of coefficient of performance with and without a subcooler. As can be seen from Figure 9, the system cooling efficiency COP increased with the increase in chilled water temperature regardless of whether the system was equipped with a thermoelectric subcooler. The COP of the system with a subcooler was significantly higher than that of the system without a subcooler by 3.14%.

4.2. System Model Validation

When the experimental and simulated working conditions of the transcritical CO_2 heat pump system with a thermoelectric subcooler were the same, the results obtained by the two methods were compared and analyzed, and the relative error was used in the analysis process:

relative error =
$$\frac{\text{simulation value} - \text{experimental value}}{\text{experimental value}} \times 100\%$$
 (36)



Figure 9. Influence of chilled water temperature on COP.

Figures 10 and 11 show the experimental and simulated values of COPh when the flow rate and temperature of cooling water were changed. It can be seen that when the cooling water flow rate increased, the experimental data and simulation data showed an upward trend, and the consistency was higher at 0.4–0.55 m³/h. When the cooling water temperature gradually increased, COPh continued to decrease, and the analog value was generally slightly higher than the experimental results with an error margin of about 8.6%.



Figure 10. Influence of cooling water temperature on COPh.



Figure 11. Influence of cooling water flow rate on COPh.

Figure 12 compares the refrigeration coefficient of performance of the experimental data and simulated data for different chilled water temperatures. As the temperature of chilled water gradually increased, the experimental value and the simulated value of COP gradually increased. The trend of the two was similar, and the simulation results were slightly higher than the experimental results.



Figure 12. Influence of chilled water temperature on COP.

4.3. Simulation Result Analysis

4.3.1. Influence of the Subcooling Degree

With the increase in thermoelectric subcooling sheets, the degree of subcooling increases. As can be seen from Figures 13 and 14, the cooling capacity/heating capacity was positively correlated with COP/COPh and the degree of subcooling. When the subcooling increased from 1 to 11 °C, the cooling capacity increased from 1 to 7 kW, the heating capacity increased from 5.75 to 11.75 kW, COP increased by 40%, and COPh increased by 13.3%. This was due to the increase in thermoelectric cooling sheets, which led to an increase in the degree of subcooling.



Figure 13. Influence of subcooling degree on heating/cooling capacity.



Figure 14. Influence of subcooling degree on COP/COPh.

4.3.2. Influence of Cooling Water Flow Rate and Temperature

At rated conditions, COP/COPh is shown against cooling water flow rate in Figure 15. The chart shows a considerable positive correlation between COP/COPh and cooling water flow. According to the calculation results, increasing the cooling water flow would cause a heat exchange between the refrigerant and the cooling water.



Figure 15. Influence of cooling water flow rate on COP/COPh.

As can be seen in Figure 16, there was a slight inverse relationship between cooling water temperature and COP/COPh. The COPh was around 2.5 and the COP was approximately 1.5 when the cooling water temperature was 30 $^{\circ}$ C.



Figure 16. Influence of cooling water temperature on COP/COPh.

4.3.3. Influence of Chilled Water Flow Rate and Temperature

From Figures 17 and 18, it can be seen that COP/COPh had a positive correlation with chilled water flow rate and temperature. As the chilled water flow increased, COP increased from 1.2 to 3.2 and COPh increased from 2 to 4.5. It can be seen that the heat exchange between the chilled water and refrigerant in the evaporator was strengthened due to increased chilled water flow rate. The evaporation process was endothermic. With the increase in chilled water temperature, the heat exchange between the refrigerant and chilled water in the evaporator was strengthened, so the system efficiency increased.



Figure 17. Influence of chilled water flow rate on COP/COPh.



Figure 18. Influence of chilled water temperature on COP/COPh.

4.3.4. Influence of Compressor Discharge Pressure

As can be seen from Figure 19, the system's COP and COPh increased as the discharge pressure increased, and the variation trend gradually decreased, with the optimal high pressure existing. The highest values of COP and COPh of the system were 3.25 and 4.25, respectively, when the compressor discharge pressure was about 8.0 MPa.



Figure 19. Influence of compressor discharge pressure on COP/COPh.

5. Conclusions

Based on the existing experimental bench, the corresponding model of a CO_2 transcritical water–water heat pump system with a thermoelectric subcooler was established by MATLAB. The compressor, gas cooler, subcooler, throttle valve, and evaporator were simulated and tested, and the simulation results were compared with the experimental results. The results are as follows:

- 1. Through calculation, it was found that the uncertainty of the experiment was less than 1%, indicating that the accuracy of the experiment was high. When the cooling water flow increased, COPh continued to rise, regardless of whether the system was equipped with a thermoelectric subcooler. COP increased with increased chilled water flow and temperature.
- 2. The simulation results of the system were compared with the experimental results, and the error was generally less than 10%, thus verifying the high accuracy of the established simulation model.
- 3. Through simulation calculation, it was found that with the increase in chilled water flow and temperature, COP and COP showed a gradual upward trend.
- 4. When the discharge pressure of the compressor changed, COP and COPh corresponded to an optimal high pressure of about 8 MPa.

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Nomenclature

А	current, A
Во	boiling number
COP	coefficient of performance
COP _h	heating coefficient of performance
cp	specific heat at constant pressure, kJ/(kg·K)
$d_{w,o}$	Outside diameter of the inner tube, mm
$d_{w,i}$	inner diameter of the inner tube, mm
Gr	refrigerant mass flow, kg/s
8w1	volume flow of the chilled water, m ³ /h
<i>8w</i> 2	volume flow of the cooling water, m ³ /h
h	specific enthalpy, kJ/kg
Κ	thermocouple thermal conductivity, W/K
1	tube length, m
m_{w1}	cooling water mass flow rate, kg/s
m_{w2}	chilled water mass flow rate, kg/s
Р	pressure, MPa
Q	refrigeration capacity of thermoelectric subcooler, kW
Q_1	refrigeration capacity, kW
Q_2	heating capacity, kW
R	resistance, Ω ;
Rer	Reynolds number
r	fouling coefficient, m ² ·°C/W
t	temperature, °C

Т	thermoelectric subcooler temperature, K
v_s	compressor refrigerant specific capacity
W	power consumption, kW
x	dryness
Greek symbols	
α	Seebeck coefficient, V/K
$\eta_{ m m}$	mechanical efficiency
η_{is}	isentropic efficiency
η_v	volumetric efficiency
ρ	density, kg/m ³
Subscript	
С	cold end
сот	compressor
h	hot end
п	N-type
р	P-type
TESC	thermoelectric subcooler
w_1	chilled water
w_2	cooling water
w, in	inlet water of the cooling water
w, out	outlet water of the cooling water
win	inlet of the chilled water
wout	outlet of the chilled water

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