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Performance analysis of a zeotropic mixture (R290/CO_2) for trans-critical power cycle☆

Lisheng Pan [1,*], Xiaolin Wei [1], Weixiu Shi [2]

[1] State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China
[2] School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, Beijing 100044, China

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ABSTRACT

Low critical temperature limits the application of CO_2 trans-critical power cycle. The binary mixture of R290/CO_2 has higher critical temperature. Using mixture fluid may solve the problem that subcritical CO_2 is hardly condensed by conventional cooling water. In this article, theoretical analysis is executed to study the performance of the zeotropic mixture for trans-critical power cycle using low-grade liquid heat source with temperature of 200 °C. The results indicated that the problem that CO_2 can't be condensed in power cycle by conventional cooling water can be solved by mixing R290 to CO_2. Variation trend of outlet temperature of thermal oil in supercritical heater with heating pressure is determined by the composition of the mixture fluid. Gliding temperature causes the maximum outlet temperature of cooling water with the increase of mass fraction of R290. There are the maximum values for cycle thermal efficiency and net power output with the increase of supercritical heating pressure.

1. Introduction

It is helpful for improving energy utilization efficiency, relieving fossil energy shortage and promoting sustainable development of human society to exploit and recover low-grade heat energy. Power cycle with unconventional working fluid has good prospect in utilization of low-grade heat energy.

The Organic Rankine cycle (ORC) which has distinct advantage in using low-grade heat energy attracts interests of many researchers. Tchanche *et al.* [1] studied theoretical cycle performance of 20 fluids in ORC and pointed out that HFC134a is the most suitable fluid for small scale ORC system with solar energy as heat source. Madhawa Hettiarachchi *et al.* [2] proposed economic objective function for ORC with low temperature geothermal as heat source and executed theoretical analysis with ammonia, HCFC123, pentane and PF5050 as working fluids. Wang *et al.* [3] investigated the utilization of waste heat of engine and indicated that R11, R141b, R113 and R123 had slightly higher thermodynamic performance than other working fluids while R245fa and R245ca were the most environmentally friendly fluids for ORC system. Sauret and Rowlands [4] indicated that the selection of working fluid, design of radial-inflow turbine and the optimization of the operation conditions played major roles in determining the performance of ORC system. In order to maximize net power, five working fluids, namely R134a, R143a, R236ea, R245fa and *n*-pentane, were studied with geothermal heat sources temperature of 150 °C, and R134a had the best performance. Mikielewicz and Mikielewicz [5] proposed thermodynamic rules to screen working fluids for ORC and trans-critical power cycle and analyzed working fluids using these rules. Lakew *et al.* [6] screened working fluids for heat sources with different temperature. HFC227ea gave the highest net power with heat source temperature of 80–160 °C while HFC245fa gave the highest net power with heat source temperature of 160–200 °C. Lai *et al.* [7] analyzed the cycle performance of ORC with heat resource temperature of 300 °C and proposed that pentane had the best performance. Wang *et al.* [8] analyzed three zeotropic mixtures composed of R245fa and R152a and pointed out that a significant increase of thermal efficiency for zeotropic mixtures could be gained by using internal heat exchanger. Wang *et al.* [9] executed a comparative experimental study on pure and zeotropic mixture in low-temperature solar Rankine cycle. A pure fluid (R245fa) and two zeotropic mixtures (R245fa/R152a, 0.9/0.1; R245fa/R152a, 0.7/0.3) were selected as working fluid. It was concluded that the system using zeotropic mixture gave higher thermal efficiency compared with system using pure fluid R245fa.

Among unconventional fluids, HCFCs, HFCs, and HCs attract much attention. HCFCs and HFCs are not environmentally friendly fluids and HCs is flammable and explosive. CO_2 is environmentally friendly, safe and cheap fluid. CO_2 is a waste product in many industry processes. Many researchers studied on the carbon dioxide capture and storage (CCS) technology in order to mitigate greenhouse effect [10–12]. From this perspective, the cost of CO_2 is zero or even negative. Guo *et al.* [13] compared cycle performance between CO_2-based trans-critical power cycle and R245fa-based Rankine cycle using geothermal energy

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* Corresponding author.
E-mail address: panlisheng@imech.ac.cn (L. Pan).

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with temperature of 80–120 °C. Chen *et al.* [14] studied on the performance of trans-critical power cycle with CO_2 and R32 as working fluids using low-grade heat energy. In order to reduce the flammability of HCs fluids, Garg *et al.* [15] investigated some mixtures composed of CO_2 and HCs. Zhang *et al.* [16,17] established a CO_2 trans-critical power cycle system driven by solar energy and obtain power generation efficiency of 8.78%–9.45%. Kim *et al.* [18] carried out research on CO_2 trans-critical cycle and CO_2 super-critical cycle with low-grade and high-grade heat energy.

CO_2 has a low critical temperature, which causes that CO_2 is difficult to condense in trans-critical power cycle system using conventional cooling water. This reason limits the application of CO_2 trans-critical power cycle in actual project. In order to solve the problem, this article studied on properties and cycle performance of a zeotropic mixture composed of R290 and CO_2.

2. Methodology

2.1. Working fluids

The mixture (R290/CO_2) considered is a binary mixture. Basic thermal properties and environment parameters of each component are listed in Table 1. Both materials are environmentally friendly, with zero ozone depression potential (ODP) and low global warming potential (GWP). GWP of CO_2 is 1 and GWP of R290 is about 20. The usage of environmentally friendly natural fluids is helpful for reducing ozone destruction and mitigating greenhouse effect. In addition, the cost of natural fluids is much lower than synthetic refrigerants like Freon. However, there are also some disadvantages for these two fluids. R290 is flammable, which limits its application. However, good sealing technology can ensure safety of the system and R290 is widely used in refrigeration industry today. High operating pressure and low critical temperature are disadvantages of CO_2 for power cycle. Therefore, excellent sealing technology is also needed for CO_2 trans-critical power cycle system. Low critical temperature results that subcritical CO_2 in condenser is difficult to be condensed by conventional cooling water. This problem is a main problem which limits the application of CO_2 trans-critical power cycle.

2.2. Trans-critical power cycle with R290/CO_2 as working fluid

In trans-critical power cycle, working fluid usually has a large superheat degree at the exit of turbine. If a regenerator is omitted in the cycle, much sensible heat of working fluid will be wasted in condenser. In order to improve thermal efficiency, a regenerator is needed to recover the sensible heat for trans-critical power cycle with the mixture as working fluid. In addition, regenerator may also recover some latent heat of the mixture fluid because of the existence of gliding temperature. This viewpoint is also proposed in reference [9]. In another word, for trans-critical power cycle with the mixture as working fluid, temperature of liquid mixture may be low enough to condense the gas mixture in regenerator. For mixture working fluid, fluid temperature decreases in condensing process, which reduces mean temperature difference between working fluid and cooling water. The good temperature matching between working fluid and cooling water which is caused by gliding temperature can lead to less exergy loss in condenser [20].

As shown in Fig. 1 [the *T*–*S* graph is for the zeotropic mixture of R290/CO_2 (mass fraction: 0.5:0.5) and is obtained in this article.]: Procedures 1–2 represent the expansion of working fluid in turbine; procedures 2–a show the cooling of low pressure gas fluid in regenerator; procedures a–4 indicate the cooling and condensing of working fluid in condenser; procedures 4–5 represent the pressure rise of working fluid in pump; procedures 5–b show the heating of high pressure fluid in regenerator; procedures b–1 indicate the heating of high pressure fluid in supercritical heater.

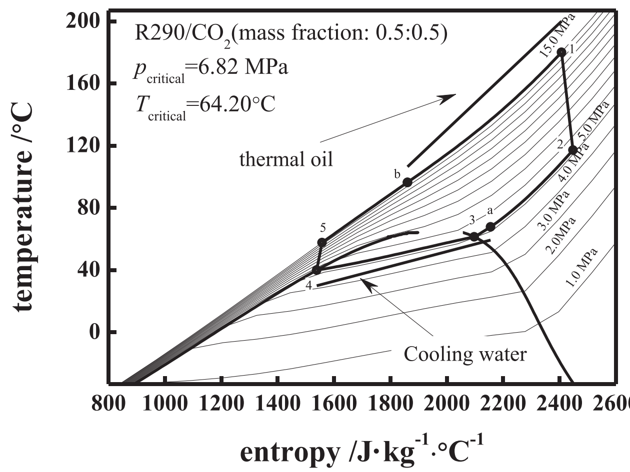


Fig. 1. *T*–*S* diagram for trans-critical power cycle using R290/CO_2.

2.3. Theoretical method

The cycle performance of trans-critical power cycle is analyzed using theoretical method. Heat energy is supplied by thermal oil with temperature and mass flow rate of 200 °C and 10 $kg\cdot s^{-1}$, respectively. Specific heat and density of thermal oil are 2.3 $kJ\cdot kg^{-1}\cdot °C^{-1}$ and 0.790 $kg\cdot m^{-3}$, respectively. The temperature of working fluid at turbine entrance is specified as 180 °C. Bubble point temperature in condenser is specified as 40 °C. This decision can ensure that subcritical fluid can be condensed in condenser by conventional cooling water. Pinch point temperature difference is specified as 10 °C for supercritical heater and regenerator and is specified as 5 °C for condenser. Turbine isentropic efficiency and pump isentropic efficiency are both specified as 0.75.

REFPROP 9.0 [21] is used in this article to obtain fluid thermal properties. When a few state properties are provided, such as temperature and pressure for single phase, REFPROP 9.0 can output other thermal properties, such as enthalpy, entropy, density and specific heat. In order to obtain thermal properties of a mixture fluid, mass fraction of each component fluid is also needed for the software. Great convenience is provided by the software and all thermal properties at each state point are obtained by it in this article.

Each state point of the cycle is specified by the following method. Parameters of state points 3 and 4 can be obtained by providing corresponding pressure (or temperature) and dryness to REFPROP 9.0. Parameters at turbine entrance (*e.g.* enthalpy and entropy) are calculated according to supercritical heating pressure and inlet temperature.

Table 1
Basic thermal properties and environment parameters of components [19]

Fluids	Molar mass /$g\cdot mol^{-1}$	t_b /°C	t_c /°C	p_c /MPa	LFL /%	ASHRAE 34 safety group	Atmospheric life /a	ODP	GWP $\times 10^{-2}$/a
CO_2	44.01	−78.4	31.0	7.38	–	A1	>50	0	1
R290	44.10	−42.1	96.7	4.25	2.1	A3	0.041	0	−20

When pressure and temperature at turbine entrance are provided to REFPROP 9.0, enthalpy and entropy at turbine entrance are outputted. Parameter of $h_{2,\text{isen}}$ can be obtained by inputting turbine inlet entropy and turbine outlet pressure. Then turbine outlet enthalpy can be computed according to Eq. (1). Finally, other parameters can be obtained by providing enthalpy and pressure at turbine exit to REFPROP 9.0. Using similar method, parameters at pump exit are calculated according to Eq. (2).

$$\eta_{\text{tur}} = \frac{h_1 - h_2}{h_1 - h_{2,\text{isen}}} \tag{1}$$

$$\eta_{\text{pum}} = \frac{h_{5,\text{isen}} - h_4}{h_5 - h_4}. \tag{2}$$

Net power output is defined as the difference between turbine power output and pump power consumption and can be expressed as Eq. (3). In trans-critical power cycle with regenerator, supercritical fluid absorbs heat energy not only in supercritical heater, but also in regenerator. Heat capacity absorbed by supercritical fluid in supercritical heater is from heat source while that in regenerator is from subcritical fluid. Therefore, thermal efficiency of the cycle is compressed as Eq. (4).

$$P_{\text{net}} = P_{\text{tur}} - P_{\text{pum}} \tag{3}$$

$$\eta_{\text{ther}} = \frac{P_{\text{net}}}{Q_{\text{heater}}} \tag{4}$$

Fig. 2 shows the block diagram of the performance analysis method used in the article. Pinch point analysis method is used in analyzing heat transfer in regenerator, heater and condenser. The block diagrams of each pinch point analysis method are shown in Fig. 2(b). Thermal oil outlet temperature, cooling water outlet temperature and parameters at state point a and state point b can be obtained by using iterative method.

3. Results and Discussion

3.1. Thermal properties

Critical temperature of CO_2 is 31.0 °C, while conventional cooling water temperature is usually about 30 °C. Therefore, it is difficult to condense fluid using conventional cooling water in trans-critical power cycle system with pure CO_2 as working fluid, especially in summer conditions. Critical temperature of R290 is 96.7 °C. For the mixture (R290/CO_2), critical temperature varies in the range of 31.0–96.7 °C and increases with the increase of mass fraction of R290. Mass fraction of R290 should be high enough to make the mixture be condensed by conventional cooling water in condenser. This section analyzes thermal properties of the mixture and discussed the minimum mass fraction of R290 to ensure that the mixture can be condensed by conventional cooling water in condenser.

If critical temperature of the mixture is 10 °C higher than cooling water temperature, subcritical fluid may be condensed by cooling water temperature. Therefore, mass fraction of R290 with critical temperature of 40 °C may be the minimum mass fraction of R290. As shown in Fig. 3, when mixture temperature is 40 °C, both pressures of saturated liquid and saturated gas decrease with the increase of mass fraction of R290. The saturated liquid pressure is higher than saturated gas one. When the mass fraction of R290 is lower than 0.24, the critical temperature of the mixture is lower than 40 °C. When the mass fraction of R290 is higher than 0.24, the critical temperature of mixture is higher than 40 °C, as also shown in Fig. 4. In order to ensure that the mixture can be condensed by conventional cooling water in condenser, mass fraction of R290 should be higher than 0.24. In analysis of cycle performance, the range of R290 mass fraction is specified from 0.35 to 1.0.

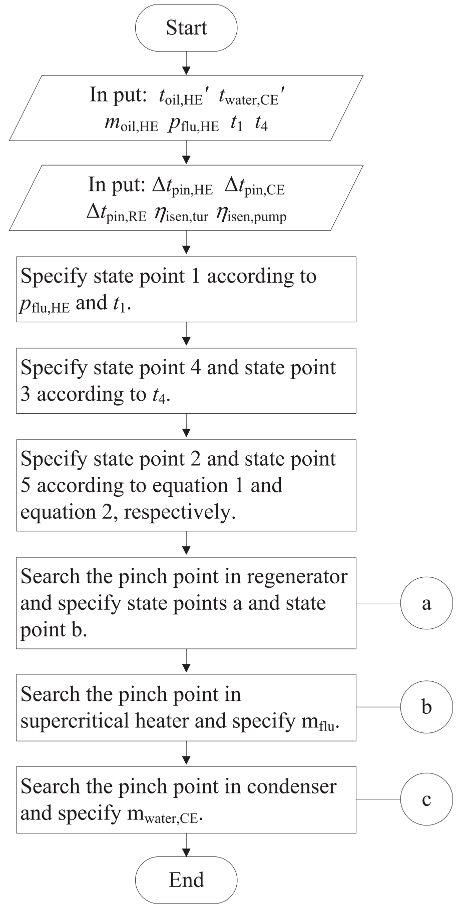
Fig. 4 shows the phase diagram of the mixture (R290/CO2) at 5.242 MPa. When the mixture pressure is 5.242 MPa, both temperatures of saturated liquid and saturated gas increase with the increase of mass fraction of R290. The saturated gas temperature is higher than saturated liquid one. The difference between saturated gas temperature and saturated liquid temperature is defined as gliding temperature of the mixture. Gliding temperature increases firstly and then decreases with the increase of mass fraction of R290 and the maximum value appears when mass fraction of R290 is 0.56. When mass fraction of R290 is lower than 0.85, critical pressure is higher than 5.242 MPa, while the critical pressure is lower than 5.242 MPa when mass fraction of R290 is higher than 0.85. From Fig. 3, it can be found out that the critical pressure is 5.242 MPa when mass fraction of R290 is 0.85.

As shown in Fig. 3, saturated gas line and saturated liquid line should intersect at the point of $x_{290} = 0.24$ and $x_{290} = 1.0$. The intersection at $x_{290} = 1.0$ (fluid is pure R290) represents that saturated gas pressure is equal to saturated liquid pressure at 40 °C. The intersection at about $x_{290} = 0.24$ (critical temperature of the mixture is 40 °C) also represents that saturated gas pressure is equal to saturated liquid pressure at 40 °C. It is known that data at critical condition isn't easy to be obtained and is unstable. Therefore, REFPROP can't give enough accurate data near critical point. This is the reason why two saturated pressure lines seem not intersect at $x_{290} = 0.24$. This also is the reason why saturated lines are missed at critical point in Fig. 1. The lack of accurate data near critical point also leads that two saturated temperature lines seem not intersect at $x_{290} = 0.85$ in Fig. 4.

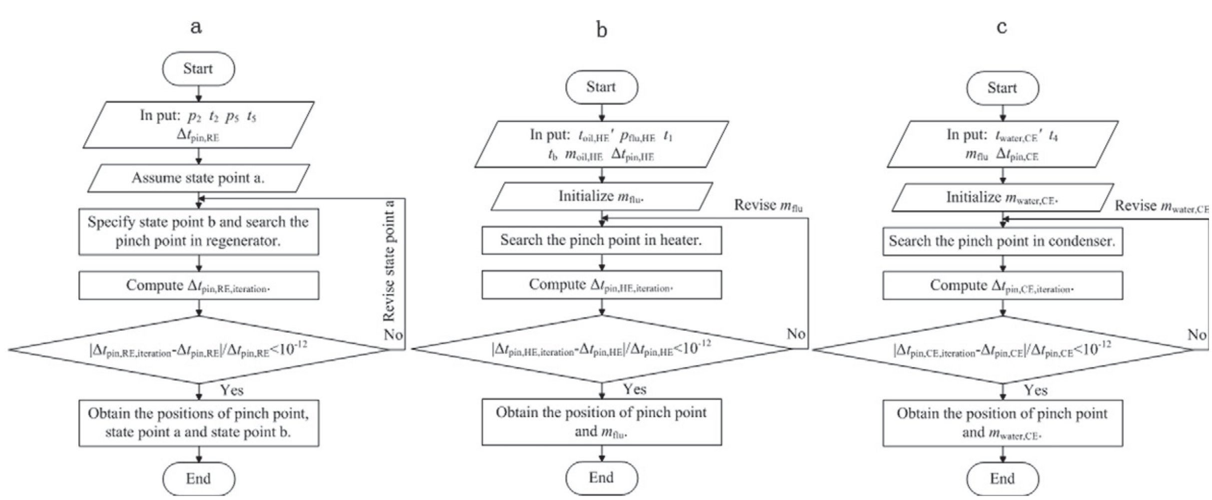
3.2. Cycle performance

As shown in Fig. 5, in considered conditions, there are three variation trends of thermal oil outlet temperature: when mass fraction of R290 is low, there are two inflection points of thermal oil outlet temperature (a minimum value and a maximum value); when mass fraction of R290 is 0.6, 0.7 or 0.8, thermal oil outlet temperature increases firstly and then decreases with the increase of heating pressure (a maximum value); when mass fraction of R290 is 0.9 or 1.0 (pure R290), thermal oil outlet temperature decreases firstly and then increases with the increase of heating pressure (a minimum value). Thermal oil outlet temperature is determined by several factors, namely, the corresponding position of thermal oil inlet state and fluid outlet state in *T–S* graph (thermal oil outlet temperature generally decreases with the left moving of the position of thermal oil inlet state in *T–S* graph), position of pinch point in heater (thermal oil outlet temperature generally decreases with the downwards moving of the position in *T–S* graph) and inlet temperature of low pressure fluid in regenerator (thermal oil outlet temperature generally decreases with inlet temperature of low pressure fluid in regenerator). Different factors may dominate in different conditions. For example, when mass fraction of R290 is 0.4 or 0.5, the first decrease trend is mainly caused by left moving of the corresponding position of thermal oil inlet state and fluid outlet state in *T–S* graph; the first increase trend is mainly resulted from upwards moving of the pinch point position in heater in *T–S* graph; and the second decrease trend is mainly due to the decrease of inlet temperature of low pressure fluid in regenerator.

As shown in Fig. 6, the outlet temperature of cooling water in condenser increases with the increase of supercritical heating pressure and increases firstly and then decreases with mass fraction of R290. There is a gliding temperature in condenser and the gliding temperature increases firstly and then decreases with increase of mass fraction of R290. When the inlet temperature of cooling water and pinch point temperature difference in condenser keep constant, the variation of gliding temperature causes that outlet temperature of cooling water increases firstly and then decreases. Outlet temperature of cooling water is also influenced by inlet temperature of fluid in condenser, while



(a) Block diagram of performance analysis method for the zeotropic mixture.



(b) Block diagrams of pinch point temperature difference

Fig. 2. The block diagram of the performance analysis method used in the article. (a) Block diagram of performance analysis method for the zeotropic mixture. (b) Block diagrams of pinch point temperature difference.

inlet temperature of fluid in condenser (outlet temperature of low pressure fluid in regenerator) is influenced by inlet temperature of high pressure fluid in regenerator (outlet temperature of fluid in pump). The inlet temperature of high pressure fluid in regenerator and that of low pressure fluid in condenser increase with the increase of supercritical heating pressure, as well as the outlet temperature of cooling water. The farther away the outlet temperature of fluid in pump from the critical temperature, the weaker the impact of outlet pressure in pump on outlet temperature. Critical temperature increases with the increase of R290 mass fraction, so the impact of outlet pressure

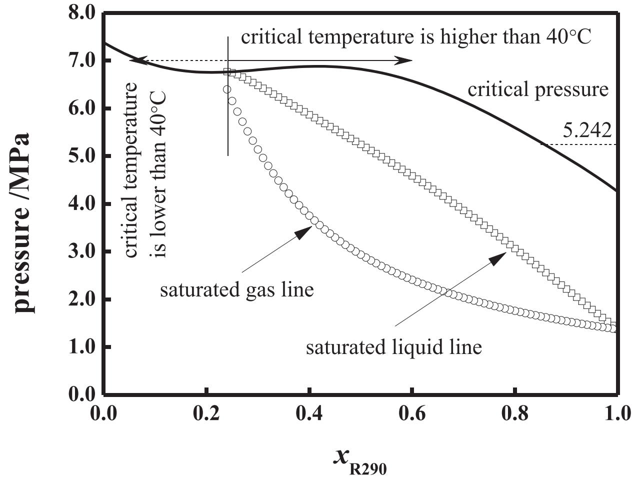


Fig. 3. Phase diagram of binary mixture (R290/CO_2) at 40 °C.

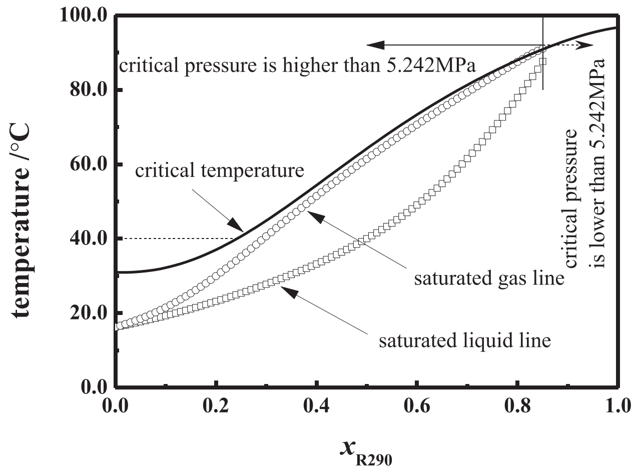


Fig. 4. Phase diagram of binary mixture (R290/CO_2) at 5.242 MPa.

in pump on outlet temperature becomes weak with the increase of R290 mass fraction. When working fluid is pure R290, the impact of heating pressure on outlet temperature of cooling water is little.

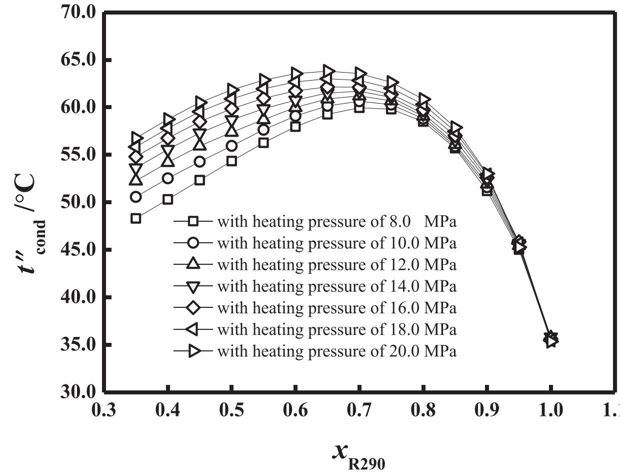


Fig. 6. Variation of cooling water outlet temperature with mass fraction of R290.

When zeotropic mixture is used in the cycle, heat transfer fluid temperature matches well because of gliding temperature and outlet temperature of cooling water is higher than that using pure fluid. Therefore, less cooling water is needed. Gliding temperature in condenser is harmful to enhancing thermal efficiency and bubble temperature in condenser is specified as constant in the analysis. When flow rate of cooling water keeps constant, the use of mixture fluid can decrease the average condensing temperature, which can enhance thermal efficiency.

As shown in Fig. 7, thermal efficiency increases firstly and then decreases with the increase of supercritical heating pressure and the maximum thermal efficiency increases with the increase of R290 mass fraction. The maximum of thermal efficiency with pure R290 does not appear in considered conditions. Thermal efficiency is determined by the average absorbing heat temperature and average releasing heat temperature. For mixture fluid, when heating pressure is low, average absorbing heat temperature increases with increasing of heating pressure, causing that thermal efficiency increases with the increase of heating pressure; when heating pressure is high, the inlet temperature of low pressure fluid in regenerator decreases and the outlet temperature of high pressure fluid in regenerator decreases, which causes that average absorbing heat temperature and thermal efficiency decrease with the increase of heating pressure. Thermal efficiency with pure R290 as working fluid is higher than that with mixture as working fluid. The reason is that there is no gliding temperature for the pure fluid and the average releasing heat temperature is lower.

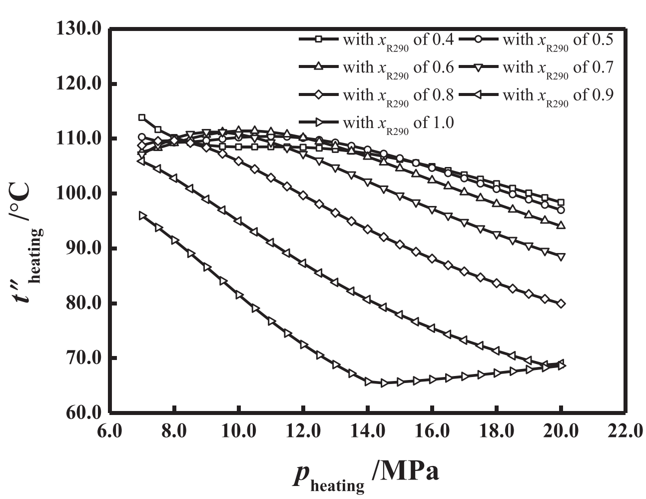


Fig. 5. Variation of thermal oil outlet temperature with heating pressure.

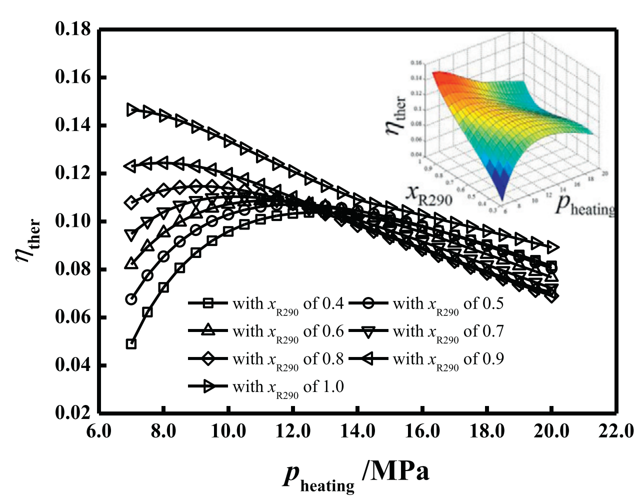


Fig. 7. Variation of thermal efficiency with heating pressure.

As shown in Fig. 8, the net power output increases firstly and then decreases with the increase of heating pressure and increases with the increase of R290 mass fraction. The net power output is mainly determined by heat capacity in supercritical heater and thermal efficiency. The lower the outlet temperature of thermal oil, the higher the heat capacity in supercritical heater and net power output. The higher the thermal efficiency, the higher the net power output. Influenced by these two factors, there is the maximum net power output with the variation of heating pressure.

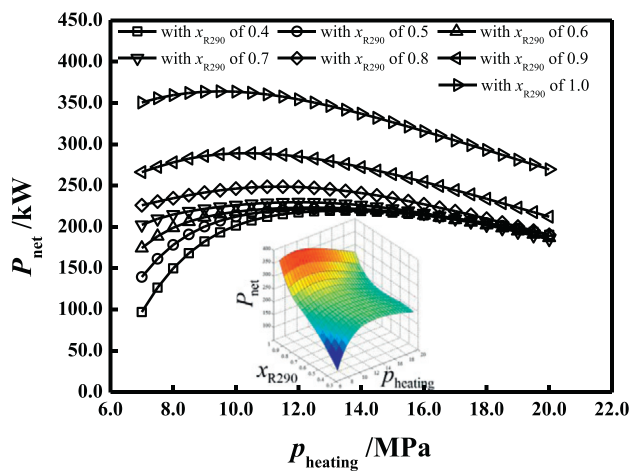


Fig. 8. Variation of net power output with heating pressure.

4. Conclusions

In this article, theoretical method is used to investigate a zeotropic mixture working fluid (R290/CO_2) for trans-critical power cycle driven by 200 °C thermal oil. Some thermal properties and cycle performance of the mixture are obtained.

(1) When the mass fraction of R290 is 0.24, critical temperature of the mixture is equal to 40 °C. In order to make sure that fluid can be condensed in condenser by conventional cooling water, the fraction of R290 should be higher than 0.24.

(2) Variation trends of thermal oil outlet temperature with heating pressure are complex because of the particularity of mixture fluid and the existence of regenerator. Outlet temperature of cooling water increases with the increase of heating pressure and increases firstly and then decreases with the increase of mass fraction of R290.

(3) There are maximum values of thermal efficiency and net power output with the variation of heating pressure. The maximum thermal efficiency and the maximum net power output increase with the increase of mass fraction of R290.

Nomenclature

h	enthalpy, kJ·kg^{-1}
LFL	low flame limit, %
M	molar mass, g·mol^{-1}
m	mass flow rate, kg·s^{-1}
P	power output, kW
p	pressure, MPa
Q	heat capacity, kW
t	temperature, °C
x	mass fraction
η	efficiency
1, 2, 3, 4, 5, a, b	state points of trans-critical power cycle

Subscripts

b	boiling
CE	condenser
c	critical
flu	working fluid
HE	supercritical heater
isen	isentropic
pin	pinch point
pum	pump
RE	regenerator
ther	thermal
tur	turbine

Superscripts

′	inlet
″	outlet

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