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Investigation on the cycle performance and the combustion characteristic of two CO_2-based binary mixtures for the transcritical power cycle

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ABSTRACT

It is difficult to condense subcritical CO_2 in the CO_2 transcritical power cycle by the conventional cooling, because of CO_2's low critical temperature. With the aim to solve this problem, a new transcritical power cycle is proposed, using a CO_2-based binary mixture as working fluid. Two mixtures are considered, namely, n-butane/CO_2 and isobutane/CO_2. Because n-butane and isobutane are flammable, the flammability of the mixtures are worth of note as well as their cycle performance. A laminar flame combustion rate experimental platform is established to investigate the combustion characteristics of both mixtures under different mixing ratio. The results show that their critical temperature increases with increasing the organic fraction and their critical pressure shows a peak value in considered conditions. The critical temperature can reach 40 °C with the organic fraction of 0.0711 for n-butane/CO_2 and 0.0806 for isobutane/CO_2. Under these mixing ratios, the transcritical power cycle can run by the conventional water cooling. The thermal efficiency reaches the highest value of 12.78% under the mole ratio of 0.28/0.72 for n-butane/CO_2. Isobutane/CO_2 gives the best condition under the mole ratio of 0.32/0.68, with the thermal efficiency reaching 12.97%. The flammable critical mole ratios for n-butane/CO_2 and isobutane/CO_2 are 0.04/0.96 and 0.09/0.91, respectively.

1. Introduction

CO_2 is a natural working fluid which is widely known in refrigeration field. It is non-toxic, non-flammable and cheap. Recently, more and more researchers begin to investigate on the power cycle with CO_2 as working fluid. The supercritical CO_2 power cycle system has higher efficiency and smaller size than the steam Rankine cycle system.

Angelino et al. [1] added a regeneration process and a recompression process on the basis of the supercritical CO_2 (S-CO_2) Brayton cycle, which improved the cycle performance obviously. Moisseytsev et al. [2] proposed an intermediate cooling and reheating S-CO_2 Brayton cycle for sodium-cooled reactor under low core temperature. Al-sulaiman et al. [3] compared the thermal efficiency of several S-CO_2 Brayton cycles. Pan et al. [4] carried out an experimental research on a transcritical power cycle with CO_2 as working fluid. Some control laws of the system and a maximum power generation of 1.7 kW were obtained. In the CO_2 transcritical power cycle, because the critical temperature of pure CO_2 is as low as 31 °C, the subcritical CO_2 in the condenser is difficult to be condensed using conventional cooling water at 30 °C [5]. With the aim to solve this problem, a method is proposed recently to increase its critical temperature [6]. The critical temperature can be changed by mixing other fluids into CO_2, so a CO_2-based binary mixture with higher critical temperature can replace the pure CO_2 as working fluid of the transcritical cycle. This method can achieve the goal of condensing the working fluid by the conventional cooling water. Using this method, Pan et al. [7] analyzed the cycle performance with R290/CO_2 as working fluid. The glide of this mixture can improve the performance of the system, but the heat transfer was degraded respect to pure CO_2 [8]. Therefore, many researchers performed a lot experimental study to test the heat transfer of many zeotropic mixtures [9]. Also many computational

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Nomenclature

t	temperature (°C)
p	pressure (MPa)
$\dot{m}$	mass flow rate (kg·s^{-1})
η	efficiency
$\dot{p}$	output power (kW)
$\dot{Q}$	heat capacity (kW)
h	enthalpy (kJ·kg^{-1})
ρ	density (kg·m^{-3})
x	mole fraction (%)
d	thickness of the porous plate (m)
q	net heat flux (J·m^{-2}·s^{-1})
λ	thermal conductivity (W·m^{-1}·K^{-1})
ε	geometric coefficient of thermal conductivity
r	the distance from the measuring points to the center of the perforated plate (m)
R	radius of porous plate (m)
D	diameter of the premixed gas pipe (cm)
V	volume (L)
$\dot{V}$	volume flow (SLM)
S	flame combustion rate (cm·s^{-1})
ϕ	equivalence ratio
U	uncertainty
a, b, C	coefficient

subscript

br	brass
p	radial direction
L	laminar flow
c	circle center
cr	critical
isen	isentropic
pump	working fluid pump
tur	turbine
cond	condense
pp	pinch point
1, 2, 3, 4, 5, a, b	state points of working fluid

model were proposed based on experimental and theoretical results [10].

As a natural and environment friendly working fluid, butane is widely used in the refrigeration cycles [11,12]. Besides, it also can be used in the power cycle which is widely known as the organic Rankine cycle [13]. In this article, a little n-butane or isobutane is mixed into the pure CO_2 as the second component. N-butane and isobutane are flammable and explosive, which limit their application as working fluid. The combustion and explosion characteristic of these two pure organic fluids was studied by several researchers. However, the existence of CO_2 reduces the combustibility of the mixtures. The flame retardation of CO_2 for flammable fluids attracts many researchers' attention. Hu et al. [14] measured the premixed laminar burning velocity and the ignition delay time of n-butane under different pressure and temperature using a constant mole combustion bomb and a shock tube. The flame kinetics and the high temperature ignition kinetics were also conducted. Jiang et al. [15] measured the ignition delay times of the lean n-butane/hydrogen/argon mixtures using a shock tube at elevated pressure and temperature. Bosschaart et al. [16] reviewed the heat flux method for stabilizing the flat adiabatic flames and measuring the adiabatic burning velocities. The flame combustion rate of several mixtures had been measured. Luo et al. [17] studied the inhibitory mechanism of CO_2 in the methane-air chain explosion process using Gaussian 09 software and B3LYP/6-31G methods of DFT (Density Functional Theory). B3LYP is a very common function in DFT theory and 6-31G is the basis group for describing the atoms. Cao et al. [18] studied the effect of the CO_2 dilution ratio on methane-preheated air counter flow diffusion flames with GRI-Mech 3.0 mechanism which is an optimized detailed chemical reaction mechanism and capable to represent the natural gas flames and ignition best, including NO formation and containing 325 reactions and 55 species [19].

In this article, two natural and environment friendly organics, namely, n-butane and isobutane, having higher critical temperature, are selected as a component of the mixture, respectively. Both high cycle performance and sate operation are important factors for selecting working fluid. Therefore, a theoretical analysis on the cycle performance and an experimental study on the combustion characteristic which is represented by the flame combustion rate [20] are carried out for both CO_2-based binary mixtures with different mole ratio.

2. Methodology

The system for a transcritical power cycle using mixture working fluid is generally the same as that with pure working fluid. As shown in Fig. 1, it usually consists of a turbine, a heater, a regenerator, a condenser and a pump. Because the turbine outlet temperature is usually much higher than the cooling water, the regenerator is usually necessary for a CO_2 power cycle with the aim of enhancing the cycle performance. It is similar for a transcritical power cycle using a CO_2-based binary mixture. However, in some conditions with very high heated pressure, the regenerator isn't needed because the turbine outlet temperature decreases rapidly with increasing the heated pressure under constant temperature at the turbine entrance. The corresponding state points (a typical working condition) of the working fluid are shown in the T-s diagram (Fig. 2). It is worth noting that the outlet temperature of the regenerator in the low pressure side may be lower than the dew point temperature because of a large glide temperature difference of zeotropic mixture. That is to say, working fluid may begin to condense in the regenerator rather than the condenser.

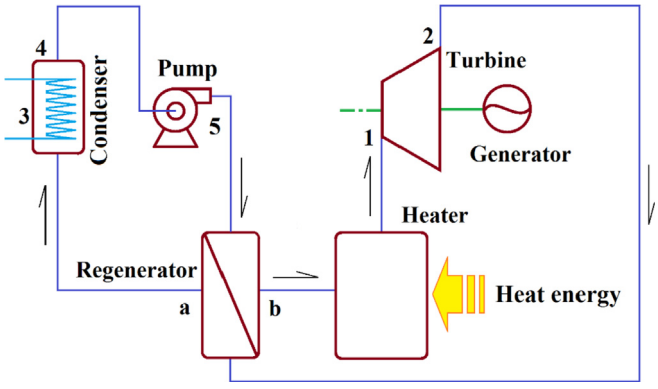

Fig. 1. System diagram for the transcritical power cycle using mixture working fluid.

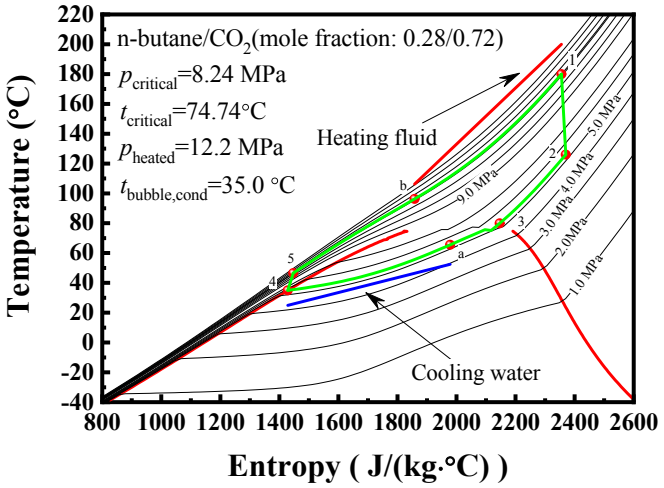

Fig. 2. T-s diagram for the transcritical power cycle using n-butane/CO_2 (0.28/0.72).

2.1. The theoretical method for the cycle performance

With the aim to analyze the cycle performance, a theoretical model is established for the transcritical power cycle with CO_2-based binary mixture as working fluid. Their critical parameters are also achieved besides their cycle performance.

In the theoretical analysis, many parameters should be specified. The density of the heating fluid, the thermal oil, is specified as 790 kg m^{-3} and its initial temperature is 200 °C. The specific heat capacity is another important factor which is specified as 2.30 kJ kg^{-1}.°C^{-1}. The cold water with temperature of 25 °C is used to cooling the working fluid in the condenser. Its density and specific heat capacity are specified as 1000 kg m^{-3} and 4.19 kJ kg^{-1} °C^{-1}, respectively. At the entrance of the turbine, the temperature of the working fluid keep constant as 180 °C. A temperature glide usually appears as the mixture evaporates. Only the azeotropic mixture has constant evaporating temperature besides the pure fluid. Therefore, the bubble point temperature in the condenser is specified as 35 °C rather than the evaporating temperature. The temperature differences at the pinch points in the heater and the regenerator are specified as 10 °C and the minimum temperature difference in the condenser is specified as 7 °C. The regenerator isn't used if the temperature at the turbine exit isn't higher than that at the pump exit under the specified pinch point temperature difference in the regenerator, which is judged and controlled by the theoretical model. The isentropic efficiency of the turbine is specified as 0.88 and the isentropic efficiency of the pump is specified as 0.65.

In the theoretical analysis, the properties and the state parameters of the considered working fluids are obtained by REFPROP [21]. All the state parameters can be calculated by inputting two independent state parameters, e.g. temperature and pressure, to the software in the superheated gas zone, the supercooled liquid zone, and the supercritical zone. One the saturated line, these data can be obtained by a saturated temperature or a saturated pressure. For the mixed fluid, the properties and the state parameters are obtained according to the mole ratio of the mixture, also based on REFPROP.

In the turbine, the temperature and pressure of the working fluid decreases during the expansion process, as well as the enthalpy. The inlet state of the turbine can be specified by the heated pressure and the final heated temperature. Then, with the inlet parameters and the isentropic efficiency, the enthalpy at the exit of the turbine can be calculated according to equation (1).

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

In the regenerator, the hot working fluid from the turbine heat the cold working fluid from the pump. The heat balance equation can be expressed as,

$$h_2 - h_a = h_b - h_5 \tag{2}$$

In the condenser, the heat capacity is expressed as equation (3a) and the state of the working fluid at the exit of the condenser is determined by the condensing temperature for pure fluid or the bubble point temperature for mixture. After specifying the cycle, outlet temperature of the cooling fluid is determined by the pinch point temperature difference in the condenser. Then, mass flow rate of the cooling fluid can be calculated by equation (3b).

$$\dot{Q}_{\text{cond}} = \dot{m}_{\text{fluid}}(h_a - h_4) \tag{3a}$$

$$\dot{Q}_{\text{cond}} = \dot{m}_{\text{cooling}}\left(t''_{\text{cooling}} - t'_{\text{cooling}}\right) \tag{3b}$$

With the inlet parameters and the isentropic efficiency, the outlet parameters in the pump can be calculated according to equation (4).

$$\eta_{\text{isen,pump}} = \frac{h_{4,\text{isen}} - h_3}{h_4 - h_3} \tag{4}$$

The heat capacity in the supercritical heater can be expressed as equation (5). Mass flow rate and outlet temperature of the working fluid are used to ensure that the pinch point temperature difference in the supercritical heater is equal to the specified value.

$$\dot{Q}_{\text{heater}} = \dot{m}_{\text{fluid}}(h_1 - h_b) \tag{5a}$$

$$\dot{Q}_{\text{heater}} = \dot{m}_{\text{heating}}\left(t'_{\text{heating}} - t''_{\text{heating}}\right) \tag{5b}$$

Fig. 3 shows the flow chart of the calculation process.

In the purpose of recovering waste heat or using geothermal energy, a higher net power gotten is usually more valuable than a higher thermal efficiency [22]. Therefore, a parameter, named specific power, is proposed. It stands for the ratio of the net output power to the mass flow rate of the heating fluid. It is expressed as,

$$\dot{P}_{\text{specific}} = \frac{\dot{P}_{\text{net}}}{\dot{m}_{\text{heating fluid}}} \tag{6}$$

The theoretical analysis focuses on the cycle performance, including the thermal efficiency and the specific output power.

2.2. The experimental method for the flammability

The flame combustion rate can be measured by a new method named heat flux method. The temperature distribution of the perforated plate is detected by some thermocouples to determine whether the flat flame is in an adiabatic state. If the temperatures of the test points on the perforated plate tend to be consistent, the flat flame is recognized as adiabatic. At this adiabatic state, the flame combustion rate is equal to the mixed gas flow rate. The interpolation method is also used to calculate the flame combustion rate. The established experimental system using the heat flux method is shown in Fig. 4 [23]. It consists of a heat flux burner, a water bath system, a gas supply system, a temperature measurement system and some other components.

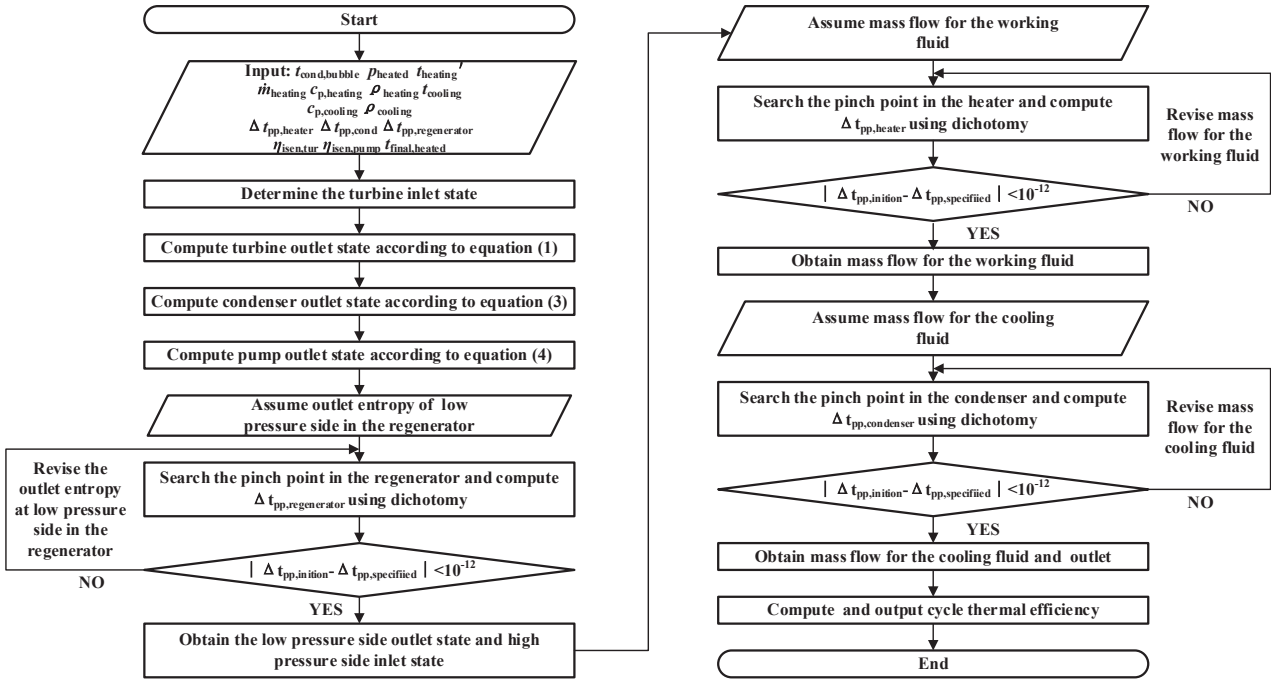

Fig. 3. Flow chart of the calculation process for one condition.

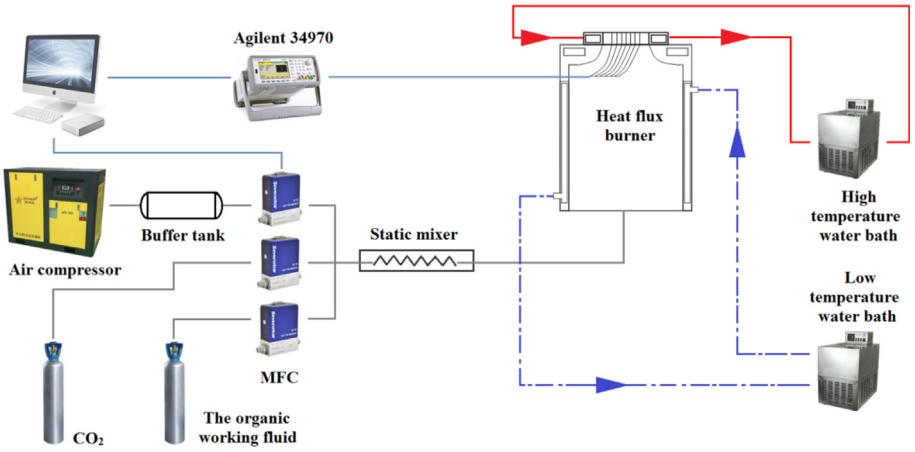

Fig. 4. Schematic diagram of the experimental system using heat flux method.

The low temperature water bath provides constant temperature water of 25 °C which flows in a water jacket of the burner to ensure that the initial mixed gas is maintained at a constant temperature in the static mixer. The high temperature water bath provides constant temperature water of 85 °C which flows in a jacket near the perforated plate of the burner to ensure good thermal insulation of the flat flame to meet the technical requirements of the heat flux method. The air is supplied by an air compressor and its pressure can be stabilized by a buffer tank. A static mixer is used to fully premix the mixed gas. The temperature distribution of the perforated plate is measured by 8 E-type thermocouples. The temperature data and the pressure data is collected by an Agilent data acquisition. The data of the mass flow rate is treated by the special software of the flow meter.

The temperature of the perforated plate distributes radially, which can be expressed as,

$$\bar{t}_p(r) = -\frac{a}{b} + \left[\frac{q(R^2-r^2)}{2db\varepsilon} + \left(\frac{a}{b}+t_R\right)^2\right]^{\frac{1}{2}} \tag{7}$$

The radial thermal conductivity of the perforated plate is,

$$\lambda_p = \varepsilon\lambda br(t) = \varepsilon(a+b\cdot t) \tag{8}$$

Then, the temperature distribution of the perforated plate can be simplified,

$$\bar{t}_p(r) = t_c - \frac{q}{4\lambda_p d}r^2 = t_c + Cr^2 \tag{9}$$

According to equation (9), the flame insulation coefficient C can be obtained by fitting temperature distribution of the perforated plate and the square of the radius. By the way of the interpolation method, the flame combustion rate is equal to the mixed gas flow

rate at corresponding equivalence ratio ϕ when C is equal to 0.

2.3. Uncertainty of the measurement

On this experimental system, three flow controllers are used to control and measure the flow rate of air, CO_2 and the organic fluid. Their accuracy is ±0.35% full span. The span range of the flow meters for air, CO_2 and the organic fluid is 30 SLM (standard litre per minute), 15 SLM and 6 SLM, respectively. Eight E-type thermocouples with the accuracy of ±0.5 °C are used to measure the temperature distribution of perforated plate. Therefore, the standard uncertainty of the air flow rate, the CO_2 flow rate and the organic fluid flow rate is $0.105/\sqrt{3}$ SLM, $0.0525/\sqrt{3}$ SLM and $0.021/\sqrt{3}$ SLM, respectively. The standard uncertainty of temperature values is $0.5/\sqrt{3}$°C.

Because equivalence ratio can be calculated by equation (10), the uncertainty of equivalence ratio can be expressed as equation (11). The internal diameter of the pipe for the premixed gas is 3 cm. The relation between the premixed gas flow rate and the flame combustion rate can be expressed as equation (12), so the uncertainty of the flame combustion rate can be calculated as equation (13). When the pure organic fluid is measured, the CO_2 flow rate and its uncertainty are both zero. Therefore, the uncertainty of the laminar flame combustion rate is 0.159 cm s^{-1} for a pure organic and 0.177 cm s^{-1} for the mixture working fluid. Its uncertainty is much lower than its value, so the uncertainty is not shown in the following figures for the laminar flame combustion rate.

$$\varphi = \frac{\dot{V}_{\text{air,need}}}{\dot{V}_{\text{air,real}}} = \frac{6.5 \times 4.76 \times \dot{V}_{\text{orgnic}}}{\dot{V}_{\text{air,real}}} \tag{10}$$

$$U_{\varphi} = \sqrt{\left(U_{\dot{V},\text{orgnic}}\frac{\partial\varphi}{\partial\dot{V}_{\text{orgnic}}}\right)^2 + \left(U_{\dot{V},\text{air}}\frac{\partial\varphi}{\partial\dot{V}_{\text{orgnic}}}\right)^2} \tag{11}$$

$$\begin{aligned} S_L &= \frac{298.15 \times 1000 \cdot \left(\dot{V}_{\text{organic}} + \dot{V}_{CO2} + \dot{V}_{\text{air}}\right)}{0.25 \cdot \pi \cdot D^2 \times 273.15 \times 60} \\ &= 2.574 \cdot \left(\dot{V}_{\text{organic}} + \dot{V}_{CO2} + \dot{V}_{\text{air}}\right) \end{aligned} \tag{12}$$

$$U_{S,L} = \sqrt{\left(U_{\dot{V},\text{orgnic}}\frac{\partial S_L}{\partial\dot{V}_{\text{orgnic}}}\right)^2 + \left(U_{\dot{V},CO2}\frac{\partial S_L}{\partial\dot{V}_{CO2}}\right)^2 + \left(U_{\dot{V},\text{air}}\frac{\partial S_L}{\partial\dot{V}_{\text{air}}}\right)^2} \tag{13}$$

However, it worth noting that the above uncertainty of the laminar flame combustion rate only takes the measurement of the gases flow rate into account. In fact, there are two other factors impact uncertainty, such as the accuracy of the E-type thermocouples and the two fitting processes. Meanwhile, the temperature uncertainty is also transmitted by the fitting processes. In this analysis, only uncertainty of the flow rate meter is taken into account rather than the thermocouples and the fitting processes.

3. Results and discussion

3.1. The cycle performance of the CO_2-based binary mixtures

The cycle performance is impacted by the fluid's critical parameters, such as the critical temperature and the critical pressure [24]. The critical parameters of the mixture are determined by the components and the mixing ratio which also influence the cycle performance [25].

The theoretical method is used to calculate the critical temperature and the critical pressure of the mixtures, namely, n-butane/CO_2 and isobutane/CO_2. As shown in Fig. 5, the critical temperature of both mixed fluids increases with increasing the fraction of the organic fluid in the considered conditions. The critical pressure of isobutane/CO_2 reaches the peak of 7.91 MPa when the mole fraction of the organic fluid is 0.3. When the mole fraction of the organic fluid is 0.32, the critical pressure of n-butane/CO_2 reaches the highest value of 8.27 MPa. The organic fluids, n-butane and isobutane, play a significant role in increasing the critical temperature of the mixed fluids. If the critical temperature of the mixture is higher than 40 °C, the subcritical working fluid can be condensed by the conventional cooling water in the condenser. That is to say the transcritical power cycle using that mixture can operate with conventional cooling water. In order to ensure that the critical temperature of the mixtures is higher than 40 °C, the mole fraction of the organic fluid should be higher than 0.0711 and 0.0806, for n-butane/CO_2 and isobutane/CO_2, respectively. Differently from the pure CO_2, the zeotropic mixture also gives a temperature glide in subcritical conditions. Therefore, dew temperature is higher than bubble temperature in the condenser for the transcritical power cycle with CO_2-based binary mixture. Fig. 5 also shows the temperature glide of the two mixtures with bubble temperature of 35 °C. When the mole fraction of the organic fluid is less than 0.06, the critical temperature is lower than 35 °C, so there isn't a temperature glide with bubble temperature of 35 °C. In the other considered conditions, the temperature glide for both the mixtures increases with increasing the mole fraction of the organic fluid.

In order to compare the cycle performance using pure CO_2 to that using CO_2-based binary mixture, the thermal efficiency and the specific power of the supercritical CO_2 Brayton cycle are provided firstly, as shown in Fig. 6. Pure CO_2 can hardly be condensed by 25 °C cooling water with the pinch point temperature difference of 7 °C, so in this analysis pure CO_2 releases heat under supercritical pressure which is specified as 7.5 MPa. The other parameters have been specified in the methodology.

A peak appears on both the thermal efficiency line and the specific power line. The highest thermal efficiency is 7.57% at an optimal heated pressure of 11.1 MPa. The peak value on the specific power line is 14.67 kJ kg^{-1} under 12.0 MPa. The thermal efficiency is generally determined by the average temperature when CO_2 absorbs and releases heat. The absorbing heat temperature increases firstly and then decreases with rising the heated pressure, which causes the peak of the thermal efficiency line. The specific power is dominated by not only the thermal efficiency, but also the heat capacity of the supercritical heater. Under constant turbine inlet temperature, the turbine outlet temperature decreases with the increase of the heated pressure. Under the effect of the regenerator, CO_2's temperature at the entrance of the supercritical heater decreases while the heat capacity of the supercritical heater increases with increasing the heated pressure. Therefore, the specific power shows a peak under higher optimal heated pressure.

The mole fraction is another important parameter that impacts the mixture's cycle performance. Therefore, the mixing ratio of the mixtures is also optimized with the process as shown in Fig. 7. Firstly, the optimal thermal efficiency and specific power are obtained by optimized the heated pressure at each mixing ratio and the maximums are obtained. Then, the maximum values of the thermal efficiency and the specific power for different mixing ratios are compared together. Finally, the maximum thermal efficiency and the maximum specific power for different all the heated pressure and the mixing ratio are obtained. The above theoretical method for cycle performance is used for the computation of every condition. The trend of the thermal efficiency and the specific

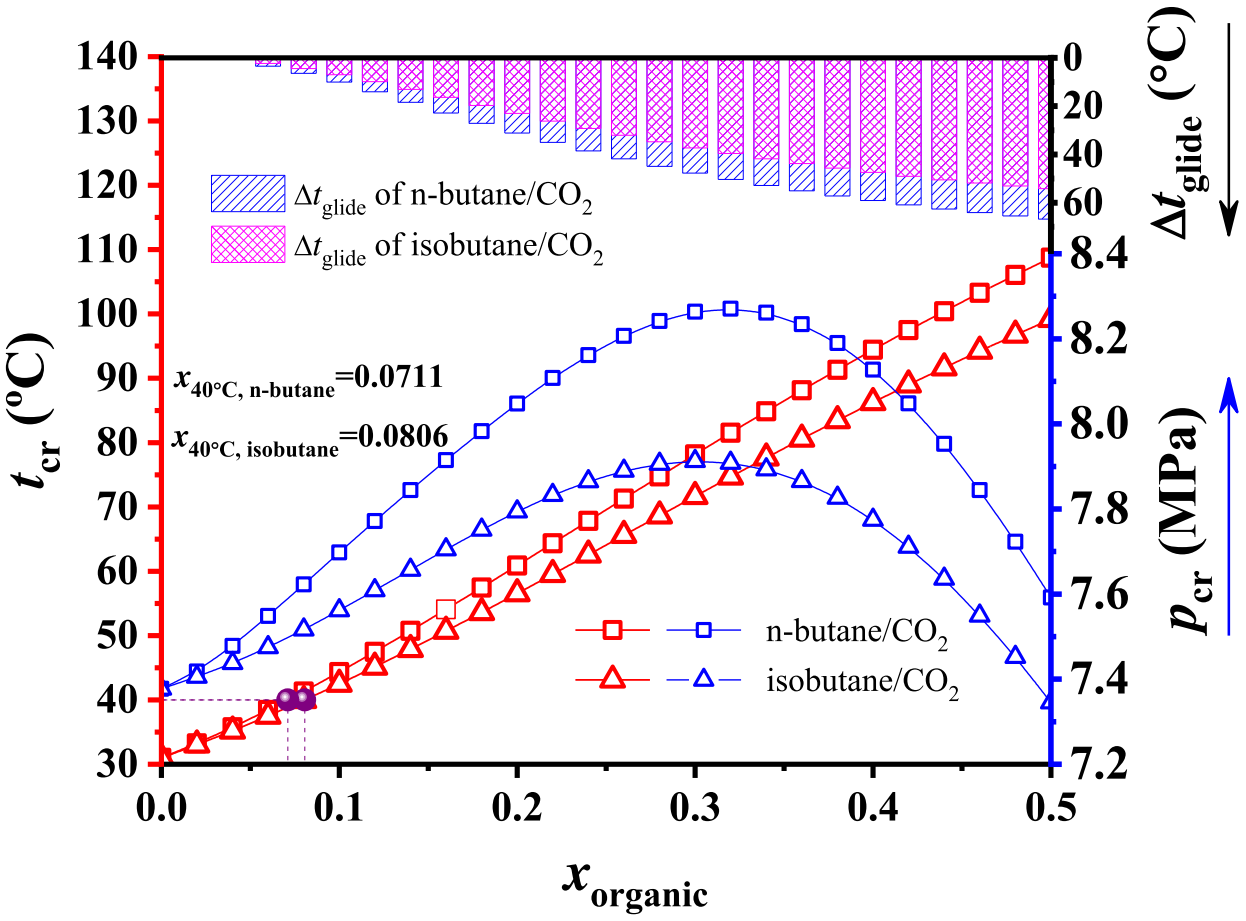

Fig. 5. Variation of the critical parameters and the temperature glide of n-butane/CO_2 and isobutane/CO_2 with the mole fraction of the organic fluid.

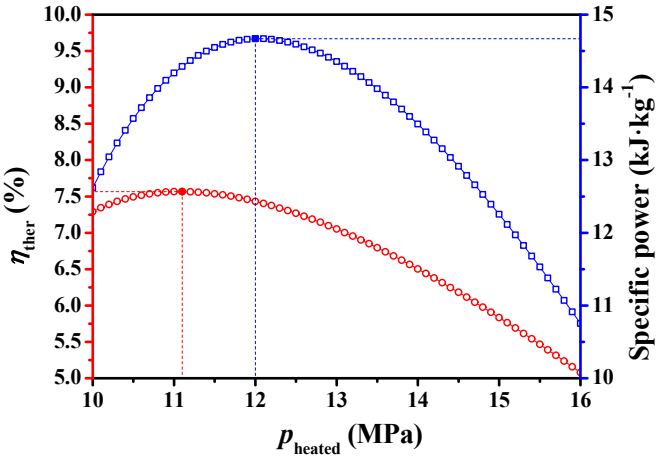

Fig. 6. Variation of the thermal efficiency and the specific power of the supercritical CO_2 Brayton cycle.

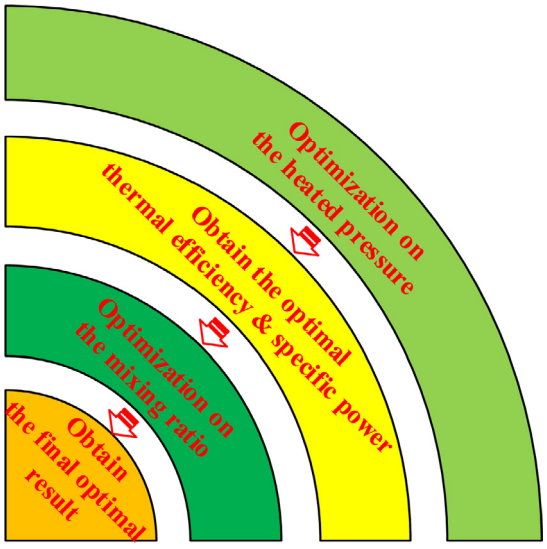

Fig. 7. Optimization process for the thermal efficiency and the specific power.

power for the CO_2-based binary mixtures is similar as that for pure CO_2. Therefore, only the maximum values and the optimal heated pressures are shown in the following two figures, paying more attention to the influence of the mixing ratio.

Fig. 8 shows the variation of the optimal thermal efficiency of both the mixed fluids with the mole fraction of the organic fluid. For each mixing ratio, the thermal efficiency is optimized, so each point in Fig. 8 indicates the maximum thermal efficiency under the optimal heated pressure. There is a maximum value for the thermal efficiency of both mixtures with increasing the mole fraction of the organics. The thermal efficiency of n-butane/CO_2 reaches the maximum of 12.78% with the optimal heated pressure of 12.2 MPa

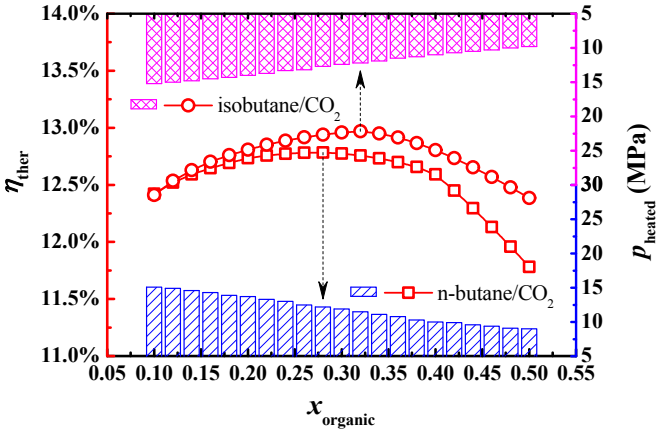

Fig. 8. Variation of the optimal cycle thermal efficiency and the corresponding heated pressure of n-butane/CO_2 and isobutane/CO_2 with the mole fraction of the organic fluid.

and the mole fraction of 0.28. For isobutane/CO_2, the maximum thermal efficiency of 12.97% appears in the condition with the optimal heated pressure of 12.2 MPa and the mole fraction of 0.32. Isobutane/CO_2 has higher thermal efficiency in the considered mixing ratios.

As shown in Fig. 9, the specific power under each mixing ratio is optimized, so each point in Fig. 9 indicates the maximum specific power under the optimal heated pressure. There is a maximum specific power for both mixtures with increasing the mole fraction of the organics. The specific power of n-butane/CO_2 reaches the maximum of 30.49 kJ kg^{-1} with the optimal heated pressure of 15.5 MPa and the mole fraction of 0.12. For isobutane/CO_2, the maximum specific power of 30.60 kJ kg^{-1} appears in the condition with the optimal heated pressure of 15.5 MPa and the mole fraction of 0.14. Generally speaking, isobutane/CO_2 shows higher specific power in the considered mixing ratios. The higher the mole fraction of the organic fluid is, the more obvious the advantage of isobutane/CO_2 is.

From the above analysis, it is also indicated that the CO_2-based binary mixtures have much better performance than pure CO_2. However, it must be noted that the cooling condition is impossible to set consistent for the supercritical CO_2 Brayton cycle and the transcritical power cycle using CO_2-based binary mixture.

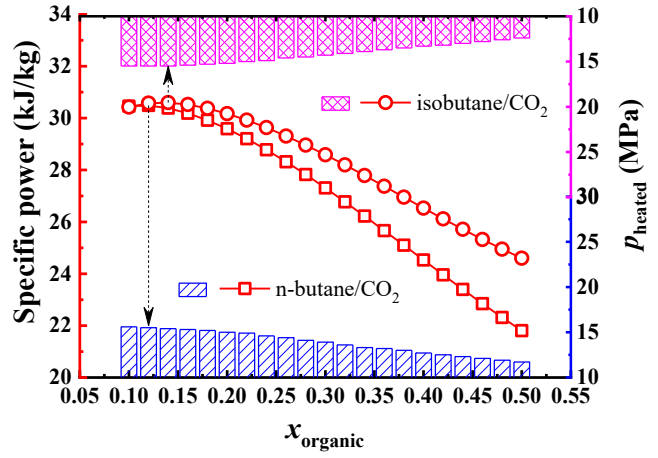

Fig. 9. Variation of the optimal specific power and the corresponding heated pressure of n-butane/CO_2 and isobutane/CO_2 with the mole fraction of the organic fluid.

The optimal mole fraction can be specified for the maximum thermal efficiency or the maximum specific power. However, a lower mole fraction of the organic fluid is also be recommended in consideration of the flammability.

3.2. Verification of the experimental system

In this section, the experimental system is verified by comparing some experimental results of the two pure organics with that obtained by some other researchers. Prince et al. [26] mainly studied the flame combustion rate and the ignition delay time of n-butane at different pressure and compared their results with San Diego's. Bosschaart et al. [16] measured the flame combustion rate of several hydrocarbons including isobutane and compared the experimental data with Davis's. Together with the new experimental data, these references' results are summarized in Fig. 10a. The red symbol that stands for the result obtained by the above experimental system is in good agreement with the other researchers' results. As shown in Fig. 10b, lines of the flame combustion rate of isobutane are similar to that of n-butane. The result is also in good agreement with that obtained by the other researchers'.

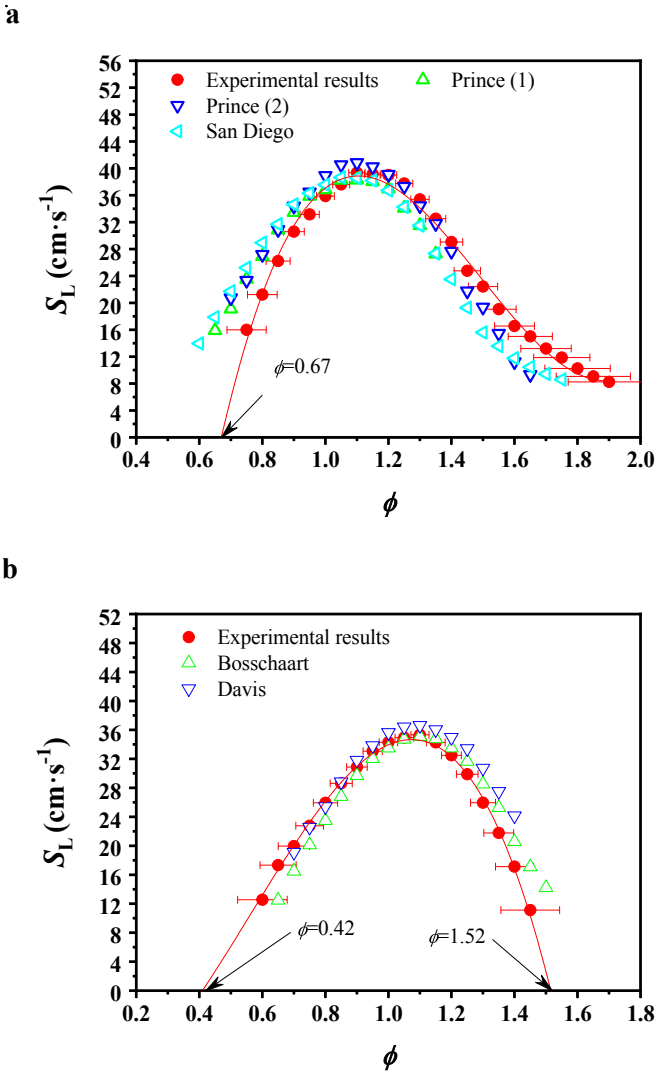

Fig. 10. Results of the flame combustion rate for both the pure organics (a. n-butane; b. isobutane).

The two curves are obtained by fitting the experimental results. They shows the variation trend of the laminar flame combustion rate with the equivalent ratio. The extrapolation method is used to find the intersection point between the cure of the laminar flame combustion rate and the horizontal axis. It is indicated that the flame combustion rate tends to be 0 cm s^{-1}, when $\phi_{\text{n-butane}}$ is 0.67 and $\phi_{\text{isobutane}}$ is 0.42, respectively. That means the organic fluids can't combustion when the equivalence ratio is lower than 0.67 and 0.42, respectively. When isobutane is rich, a higher equivalence ratio than 1.52 leads to no burning. From the above figures, it can also be illustrated that the uncertainty of the equivalence ratio increases with the decreases of the flame combustion rate. This phenomenon also exist in the following figures.

As shown in Fig. 11, there are four typical flame forms. The best form for fuel combustion is the normal flame which usually occurs when the equivalence ratio is about 1.0, as shown in Fig. 11a. In this condition, the fuel is fully used by combustion. When the air is in rich, the flame is usually lifted by the excess air, as shown in Fig. 11b. The lifted flame is easily blown out by increasing air supply continually. On the other hand, if the fuel is in rich, a small bubble will appear in the center of the flame, as shown in Fig. 11c. The bubble grows with rising the fuel supply. Finally, the bubble flame turns into a double-layer flame which has two obvious flame layer in the whole flame, as shown in Fig. 11d.

3.3. Combustion characteristics of the mixed working fluids

In this section, the flame combustion rate of the mixtures with different mixing ratio is measured. As shown in Fig. 12, the peak flame combustion rate of n-butane/CO_2 (0.15/0.85) is 16.11 cm s^{-1} with the equivalence ratio of 0.8. When the equivalence ratio is higher than 0.8, the laminar flame combustion rate of the mixture decreases with the increase of the equivalence ratio. With lower equivalence ratio, it increases with increasing the equivalence ratio. The maximum flame combustion rate of the mixture is much lower than that of pure n-butane. Moreover, the peak position shifts significantly from $\phi = 1.05$ (pure n-butane) to $\phi = 0.80$ (n-butane/CO_2). The flame combustion rate of isobutane/CO_2 also decreases toward both sides with the peak position ($\phi = 0.85$, $S_L = 13.6$ cm s^{-1}) as the center. There is a large change for the peak position compared with that ($\phi = 1.1$, $S_L = 35.33$ cm s^{-1}) of pure isobutane. By mixing organic fluid into CO_2, the mixture becomes flammable. However, it has much lower flame combustion rate compared with the pure organic.

Compared with the fuel gases, CO_2 has high specific heat capacity and low diffusivity. Therefore, the capacity in absorbing environmental heat increases with increasing the concentration of CO_2 in the mixtures, which leads the decrease of the flame temperature [27]. Furthermore, CO_2 in the fuel can prevent full diffusion combustion. Eventually, the flame combustion rate shows a sharp decline as the fuel contains so much CO_2.

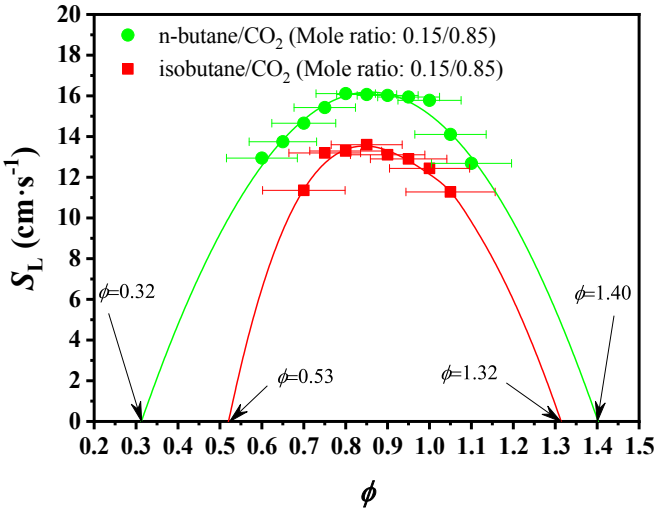

Fig. 12. Variation of the flame combustion rate with the equivalence ratio.

In the microscopic combustion reaction processes, CO_2 consumes a large amount of H radicals to produce OH. The reaction equation (7) goes in the opposite direction, inhibiting the heat release during the reaction. Moreover, the consumption of the free radical in the combustion reaction prolongs the cleavage of the chemical bonds. These are the microscopic mechanisms for the decrease of the flame combustion rate.

$$CO + OH \rightarrow CO_2 + H \quad (14)$$

The minimum equivalence ratio specified in the experiment is 0.6 for n-butane/CO_2 (0.15/0.85), the reason of which is that the flame begins to tremble and is blown out soon with the equivalence ratio of 0.35. Before it is blown out, a lifted flame is observed under some oxygen-rich combustion conditions. The maximum equivalence ratio in the experiment goes up to 1.1. When the equivalence ratio is higher than 1.1, the flame form becomes unstable. Under the condition with the equivalence ratio of 1.5, the flame form becomes a double-layer flame. For isobutane/CO_2 (0.15/0.85), the considered range of the equivalence ratio is from 0.7 to 1.05.

Two lines are obtained by fitting the experimental points. They are extended to the horizontal axis. The intersection points of the extrapolation line and the horizontal axis locate at $\phi = 0.32$ and $\phi = 1.40$, which indicates that the combustion limits are 0.32 and 1.40, respectively, for n-butane/CO_2 (0.15/0.85). The same method is used to find the combustion limits of isobutane/CO_2 (0.15/0.85). The results are 0.53 and 1.32, respectively.

As shown in Fig. 13, the peak point locates at ($\phi = 0.95$ and $S_L = 20.34$ cm s^{-1}) for n-butane/CO_2 (0.20/0.80). This peak flame combustion rate is much higher than that of n-butane/CO_2 (0.15/

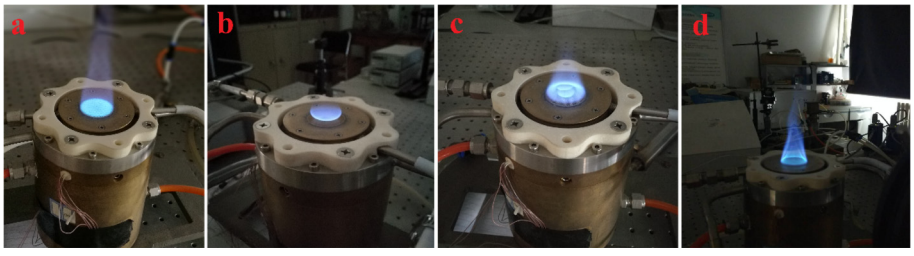

Fig. 11. Flame forms of n-butane in the experimental study (a. normal flame with ϕ of 1.0; b. lifted flame with oxygen-rich combustion; c. bubble flame with fuel-rich combustion; d. double-layer flame with fuel-rich combustion).

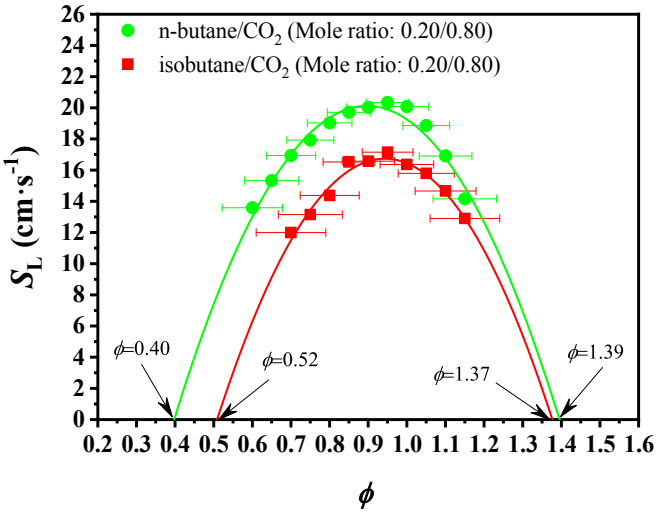

Fig. 13. Variation of the flame combustion rate with the equivalence ratio.

0.85) which is only 16.11 cm s^{-1}. Due to the increase of the organic fraction, the peak flame combustion rate of isobutane/CO_2 (0.20/0.80) also rises rapidly to 17.16 cm s^{-1} and the corresponding equivalence ratio is 0.95.

The experimental range of the equivalence ratio is from 0.60 to 1.15. The flame begins to tremble with lower equivalence ratio and is blown out soon with the equivalence ratio of 0.40. By the extrapolation method, the combustion limits of n-butane/CO_2 (0.20/0.80) can be obtained with the values of 0.40 and 1.39. For isobutane/CO_2 (0.20/0.80), the experimental range of the equivalence ratio is from 0.70 to 1.15. The flame is blown out with the equivalence ratio of 0.50. The combustion limits of isobutane/CO_2 (0.20/0.80) are 0.52 and 1.37.

As shown in Fig. 14, the peak flame combustion rate increases up to 23.73 cm s^{-1} for n-butane/CO_2 and 19.63 cm s^{-1} for isobutane/CO_2, with the organic fraction of 0.25. The according equivalence ratio is 1.0 for both mixtures. There is also a significant rise for the peak flame combustion rate, compared with the above mixting ratios.

For n-butane/CO_2 (0.25/0.75), the experimental range of the equivalence ratio is from 0.60 to 1.20 and the flame is blown out

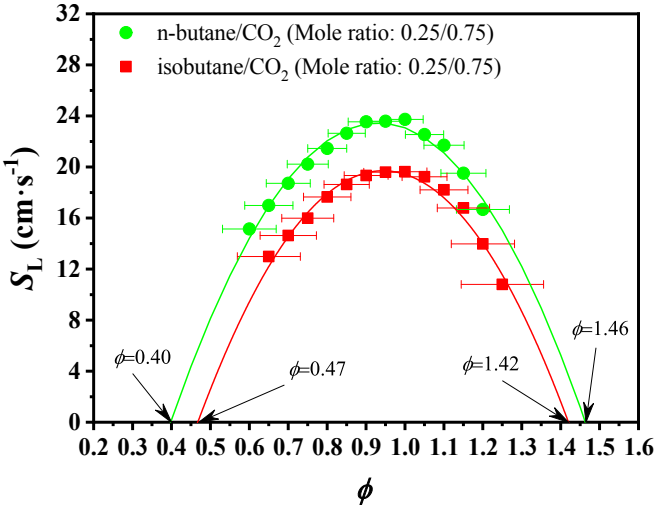

Fig. 14. Variation of the flame combustion rate with the equivalence ratio.

with the equivalence ratio of 0.40. The combustion limits obtained by the extrapolation method are 0.40 and 1.46. For isobutane/CO_2 (0.25/0.75), the experimental range of the equivalence ratio is from 0.65 to 1.25. The flame is blown out with the equivalence ratio of 0.50. The combustion limits of isobutane/CO_2 (0.25/0.75) are 0.47 and 1.42.

Two additional series of experiment were carried out, in order to obtain the flammable critical mole ratio for n-butane/CO_2 and isobutane/CO_2. In the experiment, the fraction of the organic fluid decreases from 0.15 until the flame goes out, with the equivalence ratio changed to maintain the flame. According to the observation, the flame of n-butane/CO_2 died out when the organic fraction reached 0.04. In another word, the flammable critical mixing ratio for n-butane/CO_2 is 0.04/0.96 (mole ratio). Using the same method, the flammable critical mixing ratio for isobutane/CO_2 is 0.09/0.91 (mole ratio). That is to say, the mixture can't burn if n-butane fraction is lower than 0.04 or isobutane fraction is lower than 0.09. If the organic fraction is lower than the flammable critical fraction, the mixture is safe considering the flammability.

As indicated in the above analysis, the flammability of each mixture increases with increasing the mole fraction of the organics. The thermal efficiency and the specific power show peak values with changing the mole fraction of the organics. That is to say, the optimal mole fraction for the maximum thermal efficiency or the maximum specific power should be found out, as well as the mole fraction of the organics should be decreased for lower flammability. However, the above perfect aim is hardly to achieve. The maximum thermal efficiency or specific power means a certain flammability, while non-flammability means sub-optimal cycle performance. According to the regularities and the data about the cycle performance and the flammability presented above, the suitable mixing ratio should be specified by the ventilation condition, the explosion protection, the object function, and so on for the actual application. For example, the optimal mixing ratio should be selected with good ventilation condition and low explosion-proof demand for as high efficiency or specific power as possible. In the other hand, low mixing ratio should be preferred with the purpose of non-flammable.

4. Conclusions

In order to solve the condensing problem in the CO_2 transcritical power cycle, a new transcritical power cycle using CO_2-based binary mixture as working fluid is proposed. Two CO_2-based binary mixtures, n-butane/CO_2 and isobutane/CO_2, are investigated by the theoretical method and the experimental method. The aim is to provide the applicability of the two mixture working fluids for the practical project.

(1) With rising the organic fraction, the critical temperature of the mixtures increases obviously, while the critical pressure shows a peak in the considered conditions. The critical temperature of n-butane/CO_2 can rise to 40 °C with n-butane fraction of 0.0711. If isobutane is used, an organic fraction higher than 0.0806 is needed to ensure that the critical temperature isn't lower than 40 °C. With a slightly high critical temperature, the transcritical power cycle with CO_2-based binary mixture as working fluid can run using conventional cooling water. It is also helpful for reducing the cycle pressure and enhancing the cycle performance to mix n-butane or isobutane into CO_2. The maximum cycle thermal efficiency of n-butane/CO_2 is 12.78% when n-butane fraction is 0.28. When the isobutane fraction is 0.32, the cycle thermal efficiency reaches the maximum of 12.97%.

(2) With mixing a certain amount of n-butane or isobutane into CO_2, the mixture becomes flammable. The flammable critical mole ratios for n-butane/CO_2 and isobutane/CO_2 are 0.04/0.96 and 0.09/

0.91 (mole ratio), respectively. Its combustibility increases with rising the organic fraction, which indicates that the flammability of the mixtures (n-butane/CO_2 and isobutane/CO_2) is greatly inhibited by CO_2. The results obtained by the theoretical method and the experimental method provide some basis data for studying on the transcritical power cycle with CO_2-based binary mixture as working fluid. The component of the mixture and its mixing ratio should be specified according to the actual condition.

Acknowledgments

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