ORIGINAL ARTICLE

Experimental study on supercritical carbon dioxide gasification of biomass

Chenchen Zhou, Zhiwei Ge[*], Yu Wang, Fei Shang and Liejin Guo

Abstract

With the excessive use of fossil energy and concern for environmental protection, biomass gasification as an effective means of biomass energy utilization has received widespread attention worldwide. Supercritical carbon dioxide (SCCO$_2$) (T $\geq$ 31.26 °C, $P \geq$ 72.9 atm) has the advantages of near liquid density and high solubility, and the supercritical carbon dioxide gasification of biomass will be a promising technology. However, there has been no research on the technology at present. In this work, experimental study on supercritical carbon dioxide gasification of biomass were carried out in a batch reactor. The influences of temperature, residence time, the amount of carbon dioxide and catalyst on gas yield and fraction were investigated. Experimental results showed that the gas yield and carbon gasification efficiency (CE) of biomass gasification increased with increasing temperature, reaction time or the amount of carbon dioxide. As the gasification temperature increased from 700 °C to 900 °C, the gas yield increased from 23.53 to 50.24 mol/kg biomass and CE increased from 47.26% to 94.53% in CO$_2$ atmosphere at 30 min. The gasification efficiency of biomass was greatly improved with catalyst, and the effect of impregnated catalyst was better than that of mechanical mixing. The gas yield increased from 23.72 to 50.24 mol/kg biomass with the increasing of the equivalent ratio from 0 to 1 at 900 °C and 30 min. Finally, a detailed supercritical carbon dioxide gasification mechanism of biomass was proposed.

Keywords: Biomass, Supercritical carbon dioxide, Catalyst, Gasification

1 Introduction

With the rapid development of the economy, the demand for energy will continue to grow, large amounts of fossil energy are consumed. At the same time, large quantities of greenhouse gases are emitted into the atmosphere, causing environmental pollution and rising temperatures [1, 2]. Fossil fuels have collectively been the single largest source of CO$_2$ emissions, responsible for nearly 65% of the global greenhouse gas emissions [3–5]. It is estimated that by 2035, the total consumption of primary energy sources is equivalent to consumption of 2.8×10^8 tons of standard coal [6–8]. The massive consumption of traditional fossil energy, on the one hand, will bring serious pollution to the natural environment, on the other

hand, it also faces the threat of resource exhaustion [9, 10]. Renewable energy is cleaner and more efficient than traditional fossil fuels, biomass energy has the advantages of wide source, renewable and environmentally friendly, and is one of the effective energy sources to replace traditional fossil fuels. Biomass energy is now used in a wide range of applications and researchers have conducted profound research in the manufacture of syngas, synthetic ethanol gasoline and bioelectricity generation [11–13].

Biomass gasification is considered be an efficient means of biomass energy utilization. There have been a lot of studies on gasification converts biomass into gaseous products (H$_2$, CO, CH$_4$, and CO$_2$) at high temperatures with air, steam, carbon dioxide or with the mixture of air-steam, air-carbon dioxide, steam-carbon dioxide, etc. [14–16]. The gasification behavior was affected by various parameters. Tavasoli et al. [17] carried out a series of

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experiments in a continuous downflow fixed bed microreactor. They found that, to obtain a gas product richer in H_2 and CO, the operating conditions should be optimized at a gasification temperature around 900 °C, an oxygen-to-nitrogen ratio of 0.08 and a reaction time of 30 min. Lv et al. [18] studied the air-steam gasification of pine sawdust in a fluidized bed reactor. They reported that as the gasification temperature increases, the H_2 content in the gaseous product increases and the CO content decreases. They obtained a syngas with the yield of $1.43 - 2.57 \, \text{Nm}^3$ per kg biomass and the LHV of $6.74 - 9.14 \, \text{MJ/Nm}^3$ in the selected ranges of experimental conditions.

In addition to air and steam gasification of biomass, carbon dioxide gasification of biomass is currently the most widely concerned. The gasification of biomass carbon dioxide can further reduce the carbon dioxide in the environment, and can effectively reuse the carbon dioxide, again into carbon monoxide, for various ways of use. Mani et al. [19] in their study of carbon dioxide gasification of wheat straw coke, pointed out that increasing the reaction temperature could effectively increase the conversion rate of the reaction. When the reaction temperature was 750 °C and the reaction time was 45 minutes, the conversion of straw coke could only reach 50%, while when the temperature was increased to 900 °C, the conversion of straw coke could reach 100% in the same reaction time. Seo et al. [20] studied the carbon dioxide gasification of red pine coke at different temperatures and showed that an increase in reaction temperature increased the carbon monoxide content of the product, indicating that an increase in temperature facilitated the progress of the reaction. Huang et al. [21] investigated the effect of metal catalysts on the rate of carbon dioxide gasification reaction of biomass coke, and the results showed that the rate of carbon dioxide gasification reaction increases with the increase of alkali metals, and different metal elements have different effects on the reaction. The catalytic efficiency of metal elements on the reaction was K > Na > Ca > Fe > Mg. Guizani et al. [22] studied the effect of CO_2 introduction in a biomass fast gasification process at 850 °C. Because of reactions of CO_2 with gases, tars and char, the CO_2 and biochar yields decreased. Kwon et al. [23] observed a substantial reduction in tar collection during the gasification of macroalgae in a 30% CO_2/70% N_2 atmosphere at 550 °C in the presence of CO_2. CO_2 enhances the gasification process by accelerating the thermal cracking of the volatile chemicals produced during the thermal degradation of the macroalgae. The gas yield is improved while the oil yield decreases. Gao et al. [24] investigated the effect of CO_2 on the gasification process of lignite to varying degrees. They found that CO_2 promoted the

gasification process of coal by enhancing the cleavage of benzene rings and the breakage of hydroxyl, methyl and methylene groups. The gas yield and surface area of the char were enhanced by further gasification with CO_2. When carbon dioxide and biomass are co-gasified, more carbon monoxide is produced to reduce carbon dioxide, effectively reducing carbon emissions and greenhouse gases, making more efficient use of biomass energy and meeting the needs of the current carbon neutral era [25–27]. From the viewpoint of CO_2 consumption and CO yield enhancement, the utilization of CO_2 is preferable as a gasifying agent.

Although carbon dioxide gasification of biomass has been a lot of research, but there are still many problems to be solved [28–30]. In actual biomass gasification reactions, the use of carbon dioxide as a gasification agent often does not allow for complete gasification and with most experimental temperatures above 1000 °C, safety issues need constant attention. The properties of carbon dioxide change when the temperature is higher than the critical temperature Tc = 31.26 °C and the pressure is higher than the critical pressure Pc = 72.9 atm, which is supercritical carbon dioxide [31–33]. Its density is close to that of a liquid, its viscosity is close to that of a gas and its diffusion coefficient is 100 times that of a liquid, making it surprisingly soluble. It can be used to dissolve a variety of substances and then extract the active ingredients from them. Many applications of supercritical CO_2 are now well established and in use, particularly, supercritical CO_2 fluids are used as a good extractant to extract oily substances [34–36]. Considering the large amount of high oil produced during the pyrolysis of biomass and the special properties of supercritical carbon dioxide, the oil produced during the biomass gasification process can be dissolved by supercritical carbon dioxide and the two mixed well to promote the decomposition and gasification of this material and increase the carbon conversion rate of biomass [37, 38], supercritical carbon dioxide gasification of biomass has a better reaction process and gasification results compared to normal carbon dioxide gasification of biomass.

In this paper, previous research on biomass gasification is studied to understand the main products of biomass gasification process and the difficult point of gasification - tar. Combining the properties of supercritical carbon dioxide and the gasification process of biomass in carbon dioxide atmosphere, a model for gasification of biomass in supercritical carbon dioxide is proposed. In this reaction, the nature of supercritical carbon dioxide is used to facilitate the gasification of biomass, which is a new and effective use of carbon dioxide. It is also an innovative attempt to improve the utilization of biomass energy to reduce carbon emissions.

2 Experimental

2.1 Raw biomass material and catalyst

The original material used as the feedstock for biomass gasification is rice husk. It was obtained from a farm in Xi'an, China. The sample was sieved with its particle size ranging from 200 to 300 mesh. The results of proximate and ultimate analysis of biomass material used for the experiment are presented in Table 1. K_2CO_3 was used in this work as catalyst, it was anhydrous reagents and was supplied by the Tianli Chemical Regents Co. Ltd.

2.2 Apparatus and procedure

The schematic diagram of biomass gasification system is shown in Fig. 1. The system includes a gas cylinder, temperature controller, pressure sensor, and gas measurement and analysis systems. The batch reactor was made of a Inconel 625 tube with an inside diameter of 8 mm and a heating-length of 200 mm. The gasifier was placed inside electrical furnaces, which provided the heat for gasification reactions. Rice husk was fed into the gasifier before added CO_2 from gas cylinder which can be controlled by needle valve. One K-type thermocouples were inserted inside the gasifier, respectively, in order to control and keep the desired temperature in each experiment. The system pressure is measured by the pressure sensor (PA23/8465, Keller). All instrumentation signals

are monitored and collected with a computer-based IMP-2333 distributed data acquisition system.
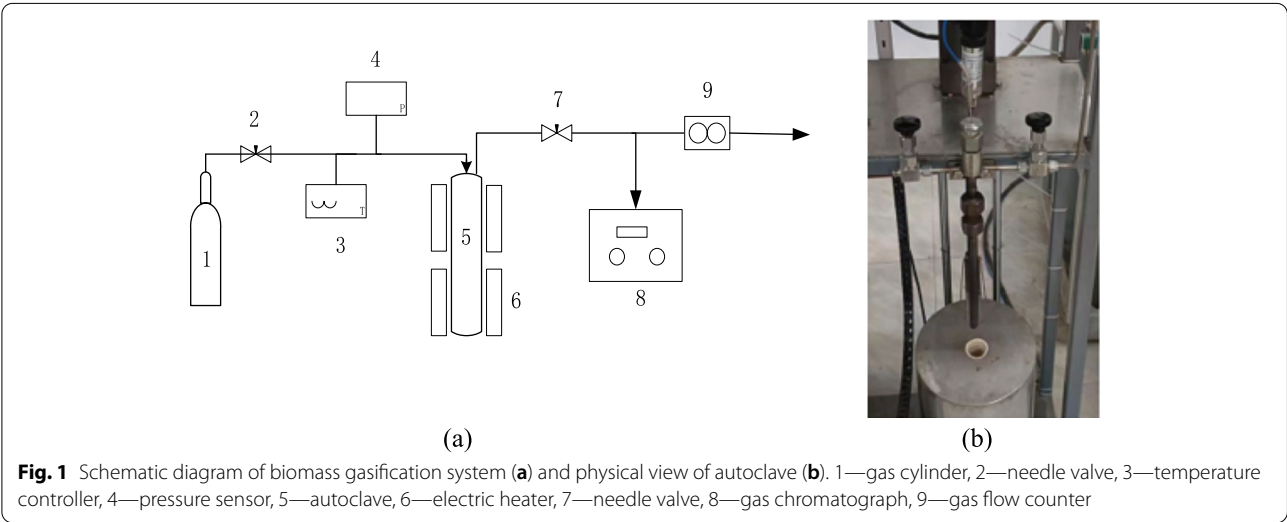
Rice husk was gasification under supercritical carbon dioxide (T $\geq$ 31.5 °C, P $\geq$ 7.38 MPa). Therefore, the reactor should be kept in a supercritical carbon dioxide environment. Prior to each test, a certain amount of rice husk powder was added to the autoclave, tighten and secure the autoclave to ensure a good gas tightness of the reaction system and carbon dioxide was repeatedly pumped into the reactor through a high-pressure gas cylinder to exhaust the air in the reactor, which was filled with high-pressure carbon dioxide. The pressure in the autoclave is kept at a defined value by valve regulation and measurement by a pressure sensor. Gasifier were heated with 100 °C/min to the desired reaction temperature. The gasification temperature was controlled from 700 to 900 °C with 50 °C increments. The gasifier was heated to the desired temperature and pressure through the external electrical furnaces. When the experiment is finished, the autoclave is brought down to room temperature by water cooling and all the gas in the reaction system is collected using a gas bag and the total amount of gas is tested by a gas flow meter.

The gas product containing H_2, CO, CH_4 and CO_2 was collected periodically through a gas syringe and then measured by a gas chromatograph (GC Agilent 7890A) with a

Table 1 the elemental analysis and the proximate analysis of biomass used in the experiment

Elemental analysis (wt%)					Proximate analysis (wt%)				Qb,ad (MJ/kg)
C	H	S	N	O^a	M	A	V	FC	
40.66	5.61	0.51	1.11	32.11	4.1	15.9	64.45	15.55	17.54

^{a} By difference

Fig. 1 Schematic diagram of biomass gasification system (**a**) and physical view of autoclave (**b**). 1—gas cylinder, 2—needle valve, 3—temperature controller, 4—pressure sensor, 5—autoclave, 6—electric heater, 7—needle valve, 8—gas chromatograph, 9—gas flow counter

thermal conductivity detector and capillary column C-2000 with argon as the carrier gas purchased from Institute of Chemical Physics, Lanzhou.

In this study, gas molar fraction, carbon gasification efficiency (CE) and gas yield were used to evaluate the biomass gasification in SCCO$_2$. The expressions are defined as follow Equations:
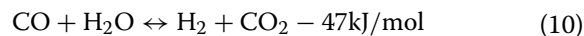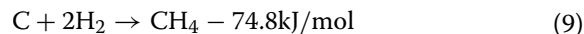
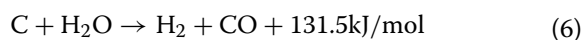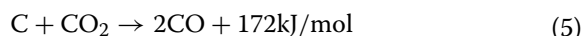$$\text{Gas molar fraction} = \frac{\text{Molar number of each gas}}{\text{Total molar of all gas product}} \times 100, /\% \tag{1}$$

$$CE = \frac{\text{Carbon mass in gas product} - \text{Carbon mass in gas added}}{\text{Carbon mass in rice husk}} \times 100, /\% \tag{2}$$

$$\text{Gas Yield} = \frac{\text{Molar number of gas product}}{\text{Mass of bimass in the feedstock}}, \text{mol/kg} \tag{3}$$

3 Results and discussion

The reaction steps and mechanisms of biomass in SCCO$_2$ are crucial when studying the properties of gasification. Based on the results of previous studies [39, 40], the complex series of reactions involved in biomass gasification Eqs. (4)–(10) show that the main reactions of biomass gasification with SCCO$_2$ are as follows:

$$\text{Biomass} \xrightarrow{\text{Pyrolysis}} \text{Gas} + \text{Char} + \text{Tars} \tag{4}$$

$$C + CO_2 \rightarrow 2CO + 172\text{kJ/mol} \tag{5}$$

$$C + H_2O \rightarrow H_2 + CO + 131.5\text{kJ/mol} \tag{6}$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO + 247\text{kJ/mol} \tag{7}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO + 206\text{kJ/mol} \tag{8}$$

$$C + 2H_2 \rightarrow CH_4 - 74.8\text{kJ/mol} \tag{9}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 - 47\text{kJ/mol} \tag{10}$$

3.1 Effect of temperature on biomass gasification

The effect of temperature on biomass gasification was investigated. Reactions were performed at five temperatures from 700 to 900 °C with 50 °C increments. The pressure of gasifier was maintained at 8-10 MPa. Gasification tests were carried out in argon and carbon dioxide atmosphere respectively. The effect of temperature on gas yield and CE is shown in Fig. 2. The composition of the gas product in different temperature are shown in Fig. 3.

From Fig. 2, it can be seen that the higher the gasification temperature, the greater the gas yield and the CE. The gas yield increased from 22.12 to 39.85 mol/kg biomass in the atmosphere of argon and increased from 23.53 to 50.24 mol/kg biomass in the atmosphere of carbon dioxide, and the CE increased from 44.26% to 80.8% in the atmosphere of argon and increased from 47.26% to 94.53% in the atmosphere of carbon dioxide with the increase of the gasification temperature from 700 to 900 °C. The increase in gas yield was mainly attributed to the char gasification. The endothermic char gasification rate was enhanced greatly, and char gasification is more likely to occur in CO$_2$ atmosphere than in argon
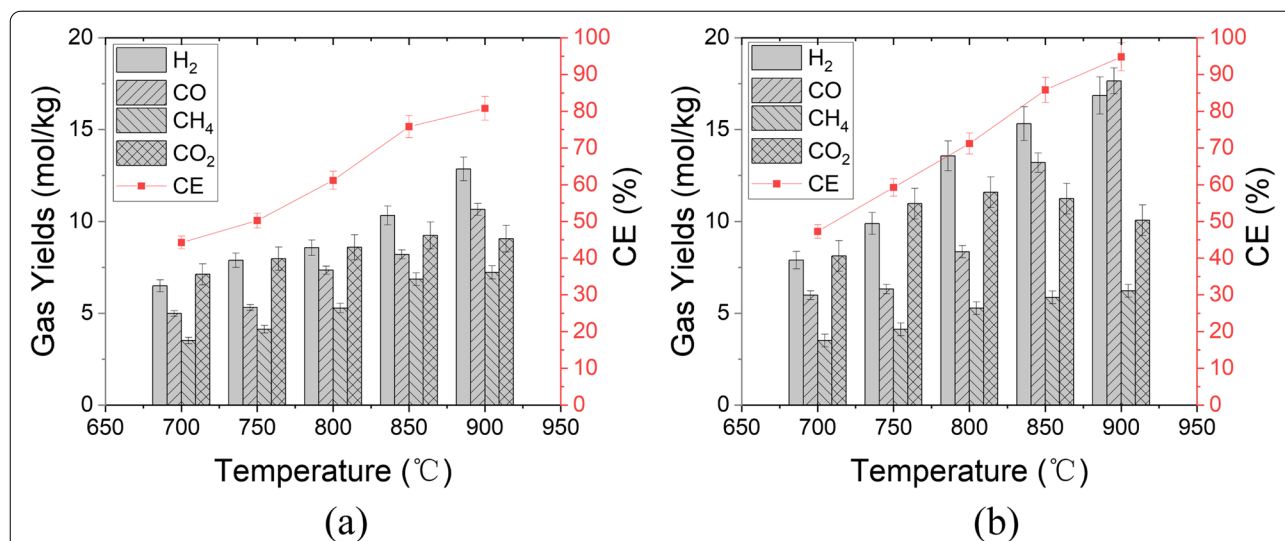
Fig. 2 Effect of gasification temperature on the yields of the gas product and CE. (Reaction Time = 30 min; K$_2$CO$_3$: Biomass = 1) **a** argon atmosphere; **b** supercritical carbon dioxide atmosphere

Fig. 3 Effect of gasification temperature on the composition of the gas product. (Reaction Time = 30 min; K_2CO_3: Biomass = 1) **a** argon atmosphere; **b** supercritical carbon dioxide atmosphere
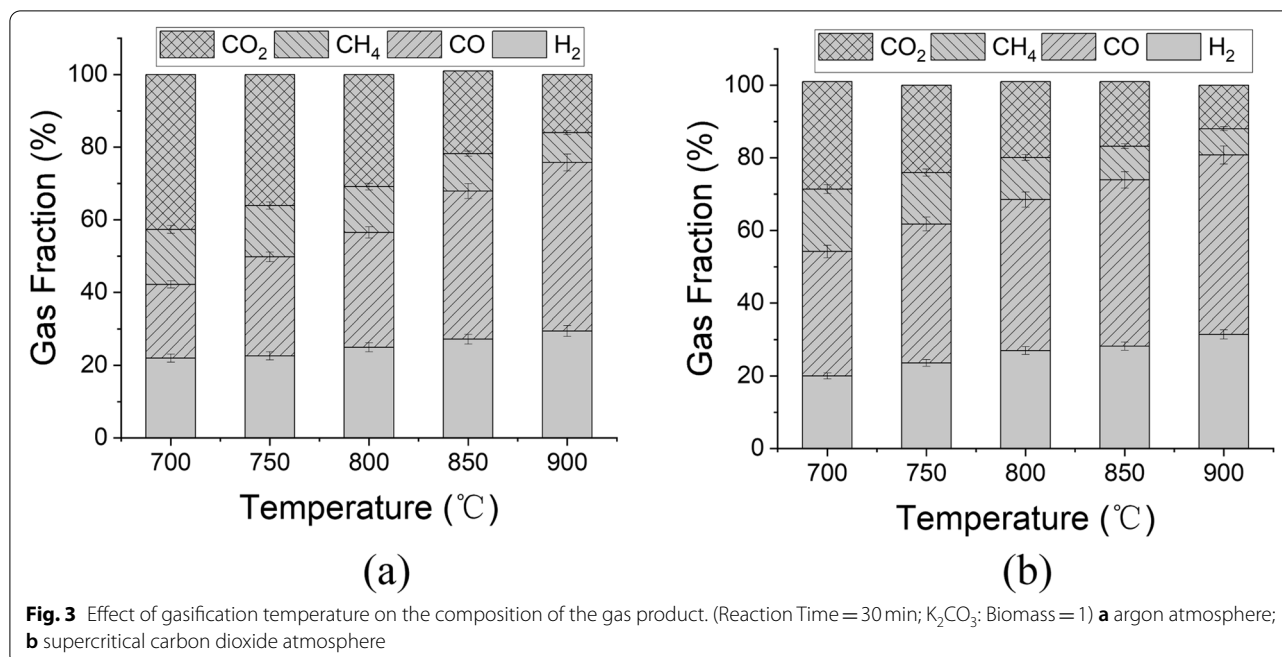
atmosphere. Consequently, compared with the reaction in argon, the gas yield of biomass gasification reaction increased by 10.39 mol/kg, and the CE increased by 14.73% in CO_2 atmosphere.

As shown in Fig. 3, the content of H_2 and CO increased, while that of CO_2 and CH_4 decreased with the gasification temperature increased. In Fig. 3a, the gas composition produced by biomass gasification in an argon environment can be seen. Raising the gasification temperature from 700 to 900 °C, it was found that the H_2 content increased from 21.98 to 29.45 vol% and the CO content from 20.22 to 46.32 vol%, whilst the CO_2 content decreased from 42.65 to 15.98 vol% and CH_4 decreased from 15.15 to 8.25 vol% respectively. Similarly, in Fig. 3b, it can see that the gas composition of biomass gasification in supercritical carbon dioxide atmosphere has a similar trend to that in Fig. 3a with the gasification temperature increased.

With gasification temperature increasing, all the endothermic reactions from (4) to (10) were strengthened and caused the increment of H_2 and CO. Higher temperature favored the products in reactions of (4), (5), (6) and (7) as well as the reactants in reactions (8), and so caused the decreases in the contents of the CO_2 and CH_4. Therefore, as far as rice husk decomposition is concerned, to carry out the reaction at elevated temperatures is favorable since the content of H_2 and CO in the gas product is increased with the gasification temperature. By comparing Fig. 3a and b, it can be seen that at the same temperature, the content of hydrogen and carbon monoxide in the gas composition increases significantly compared with that in the argon atmosphere. At 900 °C, the content of hydrogen and carbon monoxide increases by 2.02 vol% and 3.21 vol% respectively. This is because in the atmosphere of carbon dioxide, the concentration of carbon dioxide is higher, reaction (5) and (7) are easier to carry out, and the content of hydrogen and carbon monoxide is higher than that of argon. Table 2 shows the comparison with other studies of carbon dioxide gasification of biomass, which could be found that the gas yield and CE both have the obvious advantages when supercritical carbon dioxide gasification of biomass. A similar property to supercritical carbon dioxide is supercritical

Table 2 Comparison with other studies of carbon dioxide gasification of biomass

|	Conditions	H_2 (mol/kg)	CO (mol/kg)	CE (%)
Hurley et al. [42]	700 °C, 30 min	0.5	4.6	36.8
	800 °C, 30 min	0.5	5.4	57.9
Garcia et al. [43]	700 °C, 74 min	2.5	3.68	/
Seo et al. [20]	850 °C, 30 min	/	2	21
	950 °C, 30 min	/	5.4	73.4
	1050 °C, 30 min	/	11.7	96.5
This study	700 °C, 30 min	7.89	5.98	47.26
	750 °C, 30 min	9.37	7.05	60.32
	800 °C, 30 min	13.56	8.34	71.18
	850 °C, 30 min	5.13	12.45	86.57
	900 °C, 30 min	16.85	17.65	94.53

water, and there have been many studies on supercritical water gasification of biomass. Yan [41] studied the energy conversion of household kitchen waste via integrated hydrothermal carbonization and supercritical water gasification. The integrated H_2 yield of SCWG from hydrothermal carbonization-derived liquids (3.94 mol/kg) was lower than that of direct SCWG (4.59 mol/kg). However, higher H_2 fractions and lower CO_2 were found during the SCWG of the derivatized liquids, indicating that CO_2 production during gasification could be effectively reduced by integrated hydrothermal carbonization.

3.2 Effect of reaction time on biomass gasification

The reaction residence time of biomass in the reactor is an important factor in exploring the law of biomass gasification with supercritical carbon dioxide. Reactions were performed at six reaction-times from 5 to 30 min with 5 min increments. The impact of various reaction times on the supercritical carbon dioxide gasification of biomass is shown in Fig. 4.

It can be seen from Fig. 4a that the carbon gasification efficiency of the biomass increases with the increase of the reaction residence time at all temperatures. At 700 °C, the carbon gasification efficiency increased from 38.25% to 67.28%, while at 900 °C, the CE increased from 49.85% to 94.53% with the increase of residence time. As can be seen from the Fig. 4a, there is little difference in CE at different temperatures at 5 minutes. This is because in the early stage of the reaction, biomass pyrolysis reaction (Eq. 4) is mainly carried out to release carbon-containing gases, and the difference in carbon gasification efficiency is small. As the reaction time increases, other reactions (Eqs. (5)–(10)) also intensify. The reaction becomes more and more complex. The CE increases rapidly in the early stage (before 15 min), and more slowly in the late stage. At high temperatures, endothermic reactions, especially Eqs. (5) and (6)), occur at a faster rate than at low temperatures. As a result, under the same reaction residence time, the higher the temperature, the higher the carbon gasification efficiency.
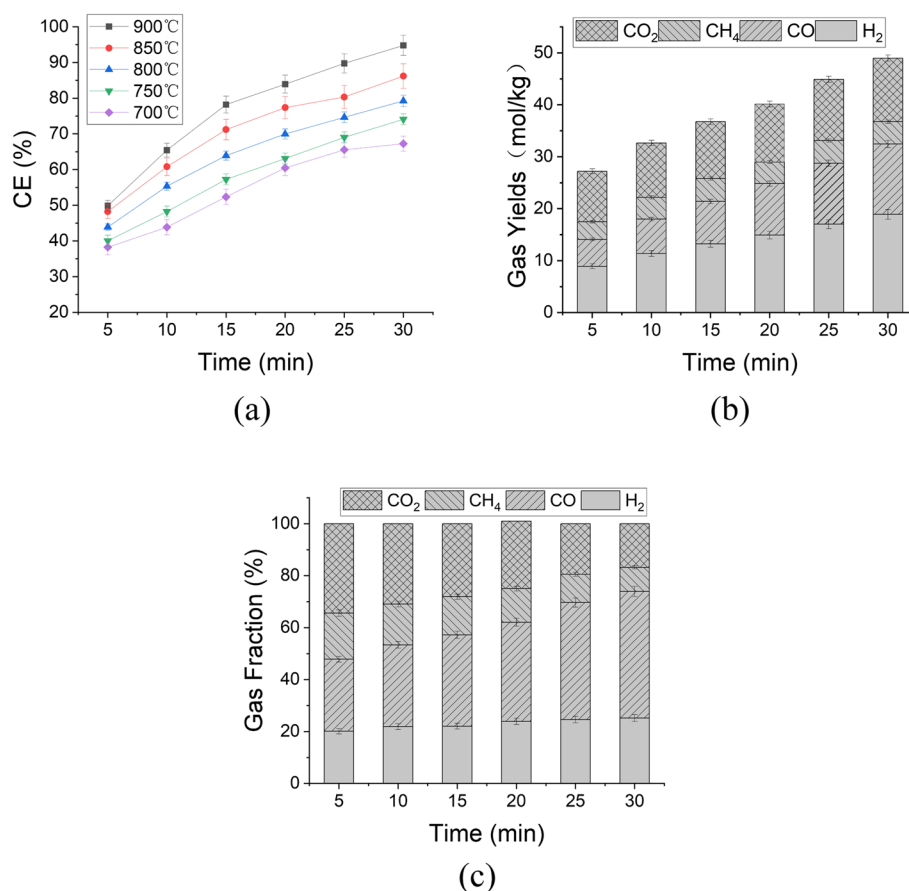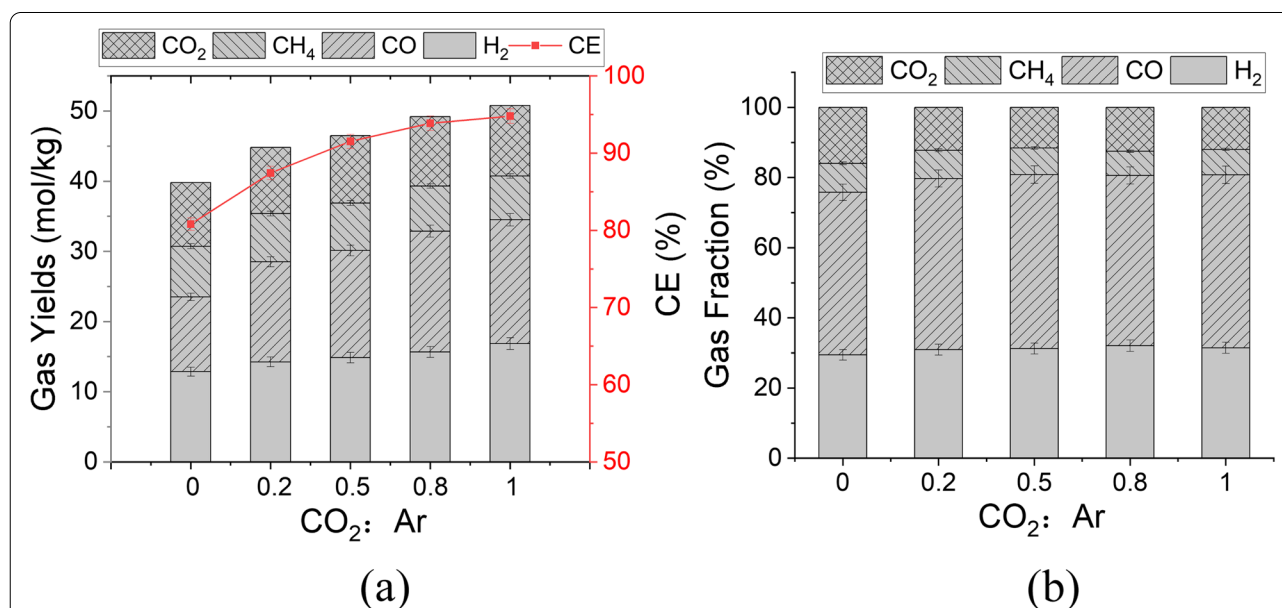

Fig. 4 Effect of reaction time on the supercritical carbon dioxide gasification of biomass (900 °C; K_2CO_3: Biomass = 1): **a** CE; **b** gas yields of biomass gasification; **c** composition of the gas product

From Fig. 4b, the gas yield increased from 23.72 to 50.24 mol/kg biomass with the increase of the reaction stay time from 5 to 30 min. What's more, it was found that the gas yield of H_2 increased from 6.55 to 16.32 mol/kg biomass and the gas yield of CO increased from 6.30 to 17.20 mol/kg biomass. With the increase of reaction residence time, the yields of hydrogen and carbon monoxide increase more, while those of carbon dioxide and methane increase less. There is even a slight drop in CO_2 production from 25 to 30 minutes. This is mainly because the main reaction that occurs during this time is Eq. (5). The char-coke gasification reaction consumes part of the carbon dioxide, leading to the gas yield of carbon dioxide decreased, thus generating more carbon monoxide, so that the carbon monoxide yield is greatly improved. As shown in Fig. 4c, the content of H_2 and CO increased, while that of CO_2 and CH_4 decreased and the gas yields is increased with the reaction stay time increased. Raising the reaction stay time from 5 to 30 min, it was found that the H_2 content increased from 20.08 to 25.18 vol% and the CO content from 27.76 to 48.72 vol%, whilst the CO_2 content decreased from 34.39 to 16.78 vol% and CH_4 decreased from 17.76 to 9.29 vol% respectively. The reason for the above results is that as the reaction time increases, at 900 °C, Eqs. (5)-(8) are all taking place. These reactions consume carbon dioxide and methane, which is conducive to the production of more carbon monoxide and hydrogen, and high temperature inhibits the endothermic reaction (Eqs. (9) and (10)), which is conducive to the production of syngas.

3.3 Effect of the amount of carbon dioxide

The amount of CO_2 is also an important factor in supercritical CO_2 gasification of biomass. In this paper the amount of carbon dioxide in the reactor is controlled by adjusting the ratio of carbon dioxide to argon. The ratios of carbon dioxide to argon in the experiments were 0, 0.2, 0.5, 0.8 and 1. The results of supercritical carbon dioxide gasification of biomass with the amount of carbon dioxide are shown in Fig. 5.

As can be seen in Fig. 5a, both the CE and gas yields increased as the amount of CO_2 increased. The CE and gas yields increased from 80.8% and 39.79 mol/kg to 94.53% and 50.79 mol/kg respectively when the ratio of CO_2 to argon increased from 0 to 1. The greatest increase in CE and CO yield was seen when the ratio of carbon dioxide to argon was increased from 0 to 0.2, with a 3.6 mol/kg increase in CO yield, which had less and less effect on CE and gas yield as the amount of carbon dioxide increased. The main reasons for this are the increased amount of carbon dioxide, the greater ease with which reaction (5) can proceed, the increased consumption of fixed carbon in the biomass and the consequent increase in the rate of carbon gasification. And when there is an excess of CO_2, the effect of the amount of CO_2 on the gas yield and CE is reduced, mainly because there is a range of contact surfaces between CO_2 and the solid, and the excess CO_2 are not in contact to have a reduced effect on the gasification. As can be seen from the changes in the gas fraction in Fig. 5b, the gas fraction only changes when carbon dioxide is added, with the carbon monoxide

Fig. 5 Effect of the amount of CO_2 on the supercritical carbon dioxide gasification of biomass (900 °C; 30 min; K_2CO_3: Biomass = 1): **a** CE and gas yields of biomass gasification; **b** composition of the gas product

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content increasing and the carbon dioxide content decreasing, with less significant changes in the gas fraction as the amount of carbon dioxide increases.

3.4 Effect of catalyst on biomass decomposition

Alkaline catalysts have good catalytic effect in biomass gasification process. In this experiment, potassium carbonate was selected as catalyst to be added into the reaction. Both catalyst and biomass are solid particles, which are not easy to mix uniformly. Therefore, two mixing methods are considered. The first is to add the two to the reactor, and then mix them evenly in the ultrasonic shock. The second method is to mix potassium carbonate into a solution, soak the biomass in the solution, mix thoroughly, and then put the soaked solution into a drying furnace to dry, and finally obtain a dry biomass material impregnated with catalyst.

3.4.1 Mechanical mixing

In the reaction of biomass gasification, the amount of catalyst added is an important factor. As can be seen from Fig. 6a, the carbon gasification efficiency of biomass increases with the increase of the equivalent ratio. It is worth noting that when the catalyst equivalent is changed from 0 to 0.2, the gasification efficiency of biomass has a significant increase, but it is obvious that with the increase of temperature, this effect is significantly enhanced, especially at 900 ℃, the gasification efficiency suddenly increased, increased by 27.1%. The main reason for this is that they are particles with less surface contact and less catalytic effect due to lower temperature. When the temperature gradually increases, potassium carbonate gradually reaches the melting point (891 ℃) [44] and begins to melt, which can wrap the biomass particles, and the catalytic effect is significantly enhanced. Especially when the catalyst melts completely when the
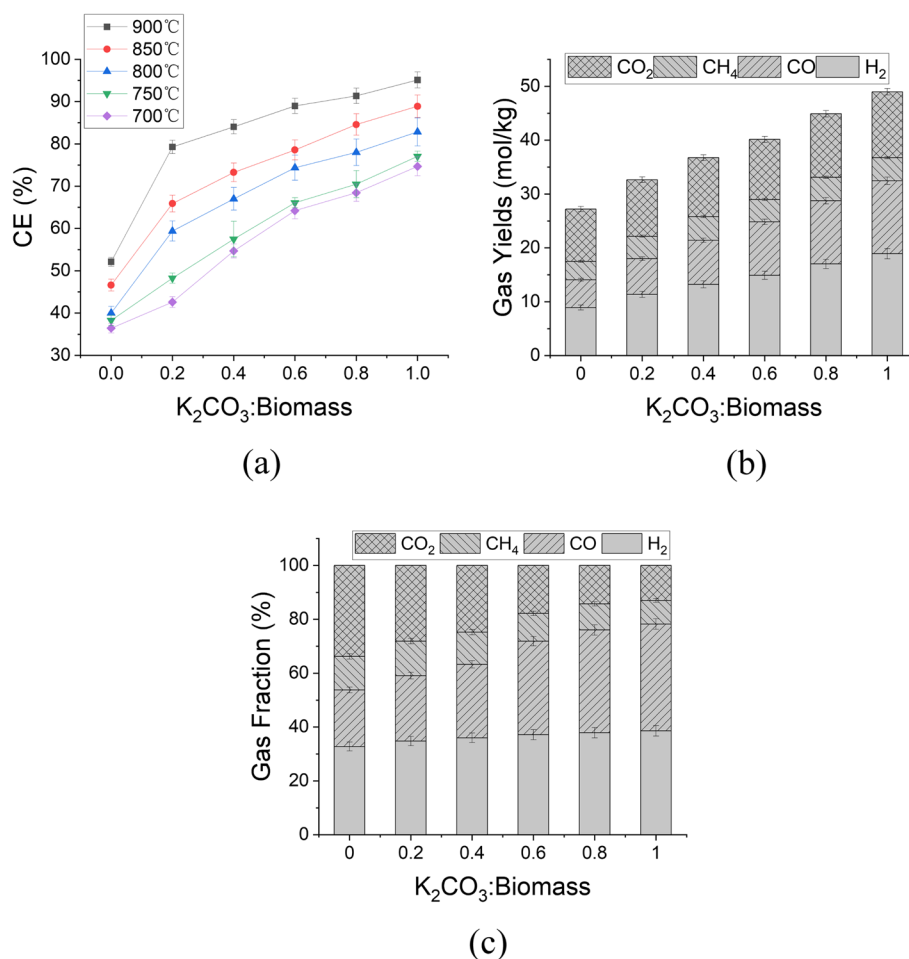
Fig. 6 Effect of K_2CO_3 (mechanical mixing) on the supercritical carbon dioxide gasification of biomass (900 ℃; 30 min): **a** CE; **b** gas yields of biomass gasification; **c** composition of the gas product

temperature reaches 900 °C, the carbon gasification efficiency increases sharply.

As shown in Fig. 6b and c, the content of H_2 and CO increased, while that of CO_2 and CH_4 decreased and the gas yields is increased with the equivalent of catalyst increased. From Fig. 6b, the gas yield increased from 23.72 to 50.24 mol/kg biomass with the increase of the equivalent ratio from 0 to 1. What's more, it was found that the gas yield of H_2 increased from 6.55 to 16.32 mol/kg biomass and the gas yield of CO increased from 6.30 to 17.20 mol/kg biomass. With the increase of the equivalent of catalyst, the yields of hydrogen and carbon monoxide increase more, while those of carbon dioxide and methane increase less. In Fig. 6c. Raising the equivalent ratio of K_2CO_3: biomass from 0 to 1, it was found that the H_2 content increased from 32.77 to 38.61 vol% and the CO content from 20.98 to 39.65 vol%, whilst the CO_2 content decreased from 33.78 to 12.98 vol% and CH_4 decreased from 12.47 to 8.77 vol% respectively. At high temperatures, heat absorption reactions (Eqs. (5)-(8)) are more likely to occur, carbon dioxide and methane are more readily converted to hydrogen and carbon monoxide, and the addition of potassium carbonate as a catalyst reduces the activation energy of the reaction, these reactions are more likely to occur, and the content and yield of hydrogen and carbon monoxide are increased.

3.4.2 Impregnation method

Under the same reaction temperature and residence time conditions, different operating methods have a great influence on the gasification of rice husk. As can be seen from Fig. 7a, at 700 °C, there is little difference in the efficiency of rice husk gasification between the carbon dioxide atmosphere and the argon atmosphere, mainly because carbon dioxide and carbon react slowly at lower temperatures, which has little effect on the gasification effect. The addition of the catalyst reduces the activation energy of the reaction, so the reaction rate can also be increased at lower temperatures and the gasification efficiency is significantly higher. At lower temperatures, the effect of impregnation through the catalyst is much stronger than that of mechanical agitation, and as the
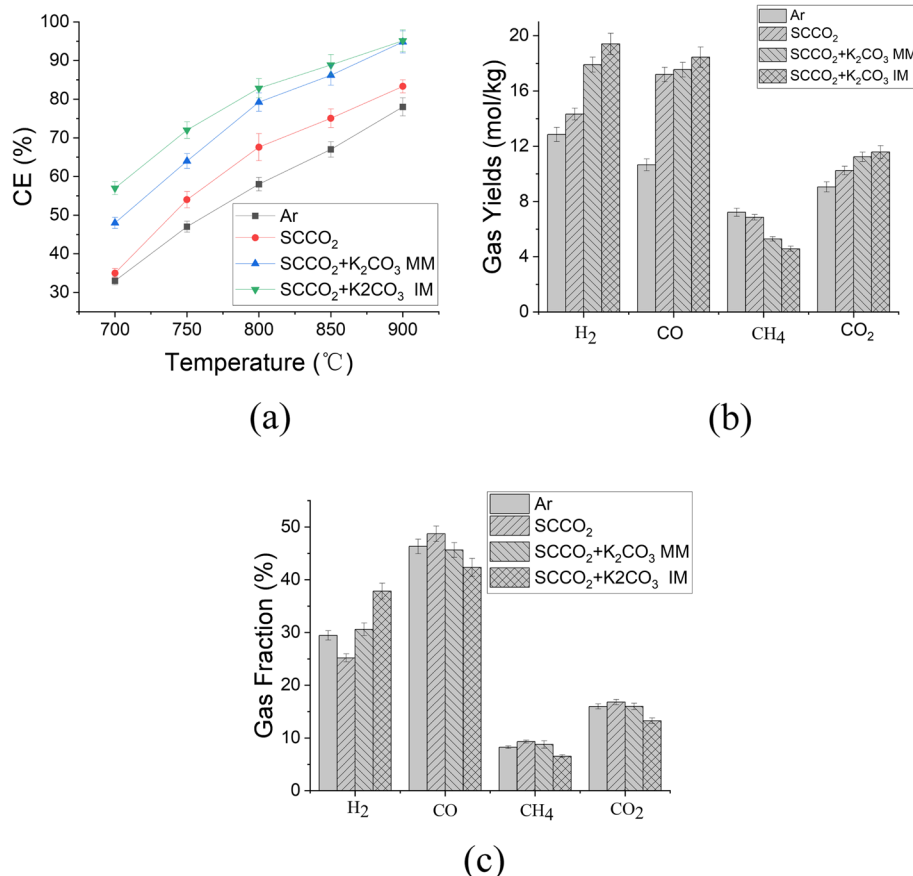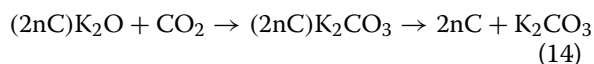

Fig. 7 Effect of different conditions on the supercritical carbon dioxide gasification of biomass (900 °C; 30 min): **a** CE; **b** gas yields of biomass gasification; **c** composition of the gas product

temperature increases, the catalytic effect between them reaches agreement, and at 900 °C, the gasification effect under both treatment conditions becomes consistent, this is because at 900 °C, the melting point of the potash has been exceeded and is in a molten state, and the effect is significantly enhanced, with the same effect as that achieved by prior impregnation treatment.

As can be seen in Fig. 7b, the addition of the catalyst significantly increased the hydrogen production by a large amount. In the supercritical carbon dioxide atmosphere, the addition of the catalyst increased the hydrogen yield from 12.32 mol/kg to 19.41 mol/kg, an increase of 26.79%. Compared to argon, the carbon monoxide yield in supercritical carbon dioxide increased from 10.65 mol/kg to 17.2 mol/kg. This was due to the presence of large amounts of carbon dioxide in the atmosphere reacting with the coke (Eq. (5)), so the carbon monoxide yield increased considerably, suggesting that the addition of carbon dioxide to the production of syngas from biomass gasification is a way to increase the syngas yield.

As shown in Fig. 7c, it can see that in a supercritical carbon dioxide atmosphere, the gas produced has the lowest hydrogen content and less reaction than in argon. This is mainly because the atmosphere contains a lot of carbon dioxide, which will produce more carbon monoxide with the carbon in the biomass, thereby inhibiting the production of hydrogen. Adding a catalyst accelerates the conversion of methane to hydrogen (Eqs. (7) and (8)), resulting in more hydrogen and less methane. Compared with the pure supercritical CO_2 atmosphere, the hydrogen content increased by 12.7% after impregnation of the catalyst, while the methane and carbon dioxide content decreased by 3.2% and 3.5%, respectively.

After the addition of catalyst, the gasification reaction effect of rice husk is significantly enhanced and more syngas can be obtained. This possible explanation is that Wen [44] proposed the reaction mechanism of C-CO_2 catalyzed by K_2CO_3:

$$K_2CO_3 + C \rightarrow 2K + 3CO \tag{11}$$

$$2K + 2nC \rightarrow 2CnK \tag{12}$$

$$2CnK + CO_2 \rightarrow (2CnK)OCO \rightarrow (2nC)K_2O + CO \tag{13}$$

$$(2nC)K_2O + CO_2 \rightarrow (2nC)K_2CO_3 \rightarrow 2nC + K_2CO_3 \tag{14}$$

The mechanism of C-CO_2 reaction catalyzed by alkali metal is suitable to be explained by oxygen transfer theory [45]. That is, alkali metal salts are first reduced with carbon, and then oxidized by an oxidizing atmosphere, so that the catalytic gasification of biomass is realized by a cyclic redox reaction. According to the experimental results of catalyst impregnation and mechanical mixing, under the same conditions, the reaction rate of rice husk after impregnation is significantly faster than that of mechanical mixing, which indicates that there is more potassium attached to biomass particles through impregnation, and there are more active sites, and the reaction effect is better.

3.5 Supercritical carbon dioxide gasification mechanism of biomass

By studying the effects of different influencing factors on the supercritical carbon dioxide gasification of biomass under a wide range of parameters, a detailed mechanism was summarized as shown in Fig. 8. At the beginning of the reaction, a large amount of gas is produced during the initial pyrolysis at high temperatures. At the same time, large amounts of tar and coke-char are produced in the reactor. Secondly, the high temperature facilitates the tar cracking reaction, producing more light hydrocarbons and other gas phase products (CO, CO_2 and H_2). Supercritical CO_2 dissolves the tar and facilitates the tar dispersion and cracking reactions. In addition, carbon dioxide acts as a gasification agent and coke gasification is enhanced by the Boudouard reaction [46]. The experimental results show that temperature and residence time play a crucial role in promoting pyrolysis and tar cracking reactions. Also, the Boudouard reaction of the coke is an important way to promote complete gasification due to the addition of carbon dioxide as a gasifier agent.

The conversion of gas products was the crucial part of the supercritical carbon dioxide gasification mechanism of biomass. Water-gas shift (Eq. (10)), methanation (Eq. (8)), dry reforming of methane (Eq. (10)) and their reverse reactions were critical reaction pathways that would occur in this reaction system containing H_2, CO, CH_4 and CO_2. The low temperature facilitated the balance of the water–gas shift reaction to H_2 generation but limited the reaction rate (Eq. (10)). The high temperature was conducive to moving to the direction of steam reforming of CH_4 (Eqs. (7) and (8)), which could increase H_2 and CO yield. At the same time, it can be seen that extending the reaction time would affect the final gas composition. The longer the reaction time, the more hydrogen and carbon monoxide production. Therefore, it is feasible to select an appropriate reaction temperature and suitable catalysts to enhance hydrogen and carbo monoxide yield from this part of the reaction mechanism. At the same time, the addition of a catalyst can greatly reduce the activation energy required for the reaction and the reaction can proceed more easily. Adding the right amount of catalyst can help us to obtain higher syngas yields.

Fig. 8 Supercritical carbon dioxide gasification mechanism of biomass
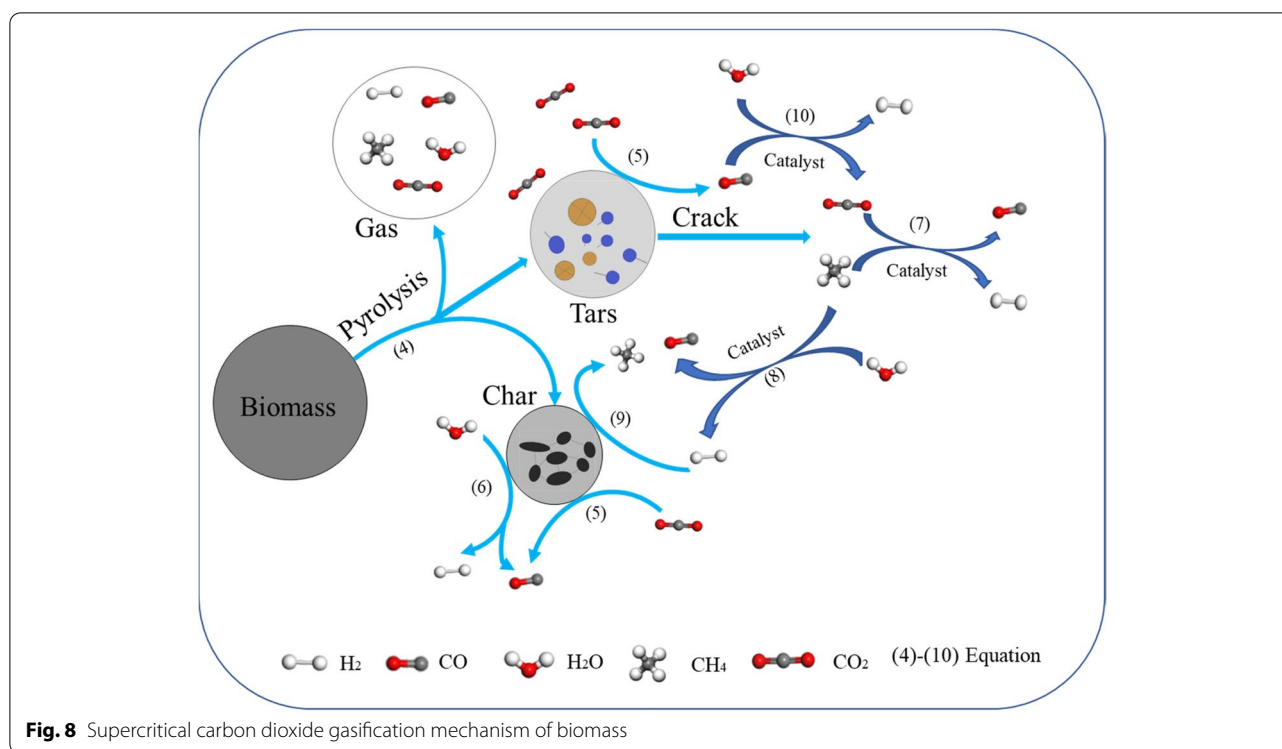
4 Conclusions

The supercritical carbon dioxide gasification of rice husk for gas production carried out in a fixed gasifier with the use of K_2CO_3 as catalyst has shown encouraging results. The main conclusions of this paper are as follows:

1. Compared with argon atmosphere, the gas yield and carbon gasification rate of rice husk gasification is higher in a supercritical CO_2 atmosphere. The gas yield and CE were 50.24 mol/kg biomass and 94.53% in CO_2 atmosphere compared to 39.85 mol/kg biomass and 80.8% in argon atmosphere when the reaction is at 900 °C and 30 min.
2. The temperature and stay time are important factors to the rice husk gasification. With the temperature and reaction time increasing, the content of H_2 and CO increased, while CO_2, CH_4 decreased rapidly. The gas yield and carbon gasification efficiency of biomass gasification increases with the amount of carbon dioxide. When there is an excess of carbon dioxide, the effect of increasing the amount of carbon dioxide on gasification will be reduced.
3. Potassium carbonate is a good catalyst for enhancing gas production from rice husk gasification and the effect of impregnated catalyst is better than that of mechanical mixing. The gas yield increased from

23.72 to 50.24 mol/kg biomass and the CE increased from 53.21% to 94.53% with the increase of the equivalent ratio from 0 to 1 at 900 °C and 30 min.
4. The mechanism of supercritical carbon dioxide gasification of rice husk is summarized, providing a theoretical basis for supercritical carbon dioxide gasification of biomass.

Authors' contributions
GZW developed the concept of supercritical CO$_2$ gasification, which guided the conduct of the experiments and the revision of the manuscript. ZCC was responsible for much of the preliminary research, experimental work and writing of the manuscript. WY and SF provides guidance and assistance during the experiment. GLJ provided the assistance in the writing of the manuscript as well as in its revision. The author(s) read and approved the final manuscript.

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Availability of data and materials
All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate
There are no ethical issues in this paper.

Consent for publication
The author consents to the publication of this article.

Competing interests
Liejin Guo is an editorial advisory board member for Carbon Neutrality and was not involved in the editorial review, or the decision to publish this article. All authors declare that there are no competing interests.

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