

Article

Two-Stage Dry Reforming Process for Biomass Gasification: Product Characteristics and Energy Analysis

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Abstract: The utilization of biomass can not only alleviate the energy crisis but also reduce the pollution of fossil fuels to the environment. Biomass gasification is one of the main utilization methods, which can effectively convert biomass into high-value and wide-use gasification gas. However, this process inevitably produces the by-product tar, which affects the yield of syngas. In order to solve this problem, a two-stage process combining biomass pyrolysis and CO₂ catalytic reforming is proposed in this paper, which is used to prepare high calorific value syngas rich in H₂ and CO and reduce the by-product tar of biomass gasification while realizing the resource utilization of CO₂. The effects of the reforming temperature and CO₂/C ratio on the gas yield and calorific value of biomass were investigated by catalytic gasification reforming device, and the system energy consumption was analyzed. With the increase of reforming temperature, the yield of CO increased, and the yield of H₂ and the calorific value of gas increased first and then decreased. Increasing the CO₂/C ratio within a proper range is beneficial to the formation of syngas. When the reforming temperature is 900 °C and the CO₂/C ratio is 1, syngas with a high gas calorific value is obtained, which is 2.75 MJ/kg is obtained. At this time, the yield of H₂ and CO reached the maximums, which were 0.46 Nm³/kg and 0.28 Nm³/kg, respectively. Under these conditions, the total energy consumption of the system is 0.68 MJ/kg, slightly more than 0, and does not require too much external heat.

Keywords: biomass; pyrolysis; gasification; tar reforming; syngas



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1. Introduction

Nowadays, fossil fuels remain the primary source of global energy consumption, accounting for 83.1% in 2021 [1]. However, overdependence on finite fossil fuel reserves can lead to an energy crisis [2]. In addition, burning fossil fuels produces harmful sulfur and nitrogen pollutants and significant amounts of carbon dioxide, which impedes progress toward achieving carbon reduction goals. Biomass is regarded as the ideal alternative to fossil energy, due to its renewable, low S and N content and zero-carbon nature [3,4]. Unfortunately, some drawbacks of utilizing biomass, including variability in chemical composition and physicochemical properties, low bulk density, and low energy density, have restricted its widespread application [5,6].

To improve the quality of biomass energy and expand the application scenarios of biomass energy, biomass is converted by liquid-phase catalytic [7], thermochemical [8,9], and biochemical methods [10]. Biomass particles, biochar, bio-oil, and biogas were used as target products [11]. Among them, the preparation of syngas by different reforming technologies has received extensive attention. According to the type of gasification agent [12],

it can be divided into oxidation reforming [13,14], steam reforming [15,16], and dry reforming [17,18]. Dry reforming is the reforming of biomass using CO₂ as the gasification agent. Dry reforming not only realizes the resource utilization of biomass and CO₂ but also provides technical support for carbon neutrality [19]. However, research on dry reforming mainly focuses on fuels such as natural gas and methane, with less research on biomass [18]. Pohoely M et al. [20] found that the use of carbon dioxide as a gasification agent had a significant positive impact on the conversion of biomass fuels into gaseous heating compounds and the reduction of tar compounds. X Hu et al. [21] explored the experimental effect of biomass dry reforming. The results showed that dry reforming dominated at higher temperatures, bio-oil was completely converted at 700 °C, and H₂ and CO were the main products at 800 °C. Encinar et al. [22] studied the effect of temperature on the yield and composition of gas products from biomass CO₂ gasification. The results show that with the increase of in temperature, the yield of gasification products increaseds and the calorific value decreaseds. With the increase of in H₂ concentration, the concentration of CO and C_mH_n decreased, the carbon conversion rate increased, and the concentration of CH₄ and CO decreased. Sadhwani et al. [23] studied the effects of temperature and CO₂/C ratio on biomass CO₂ gasification. The experimental results show that the changes of in temperature and CO₂/C ratio affect the production of CO and H₂, and the peak value of CO₂ gasification is slightly higher than that of air gasification. However, the inevitable by-product tar in the reforming process will condense at low temperatures. Condensing tar can cause downstream pipeline blockage and energy waste [24]. Tar cracking by increasing the temperature is energy-intensive, so the catalytic method has been employed for further improving the yield and quality of syngas with lower energy consumption [25].

The catalysts suitable for the reforming process include transition metals [26,27], noble metals [28], alkali/alkaline earth metals [29], carbon [30,31], and naturale minerals [32,33]. A Ni-based catalyst, with its economic feasibility and remarkable performance in C-H, C-C, and OH bonds breakage, is more practical for the reforming process [34]. Therefore, the effect of Ni-based catalysts in reforming reactions has been investigated extensively. Hu et al. [35] investigated a Ni catalyst for the catalytic reforming of tar from the pyrolysis gasification process of pine wood chips. The results showed that Ni contributed to tar cracking and the syngas yield increasing. However, in the complex reforming environment, the catalytic effect of single metals is often unsatisfactory. And due to the severe conditions of the reforming process, Ni-based catalysts are prone to sintering and carbon deposition, resulting in catalyst deactivation and a decrease in syngas yield [36]. Xu et al. [37] researched on the Ni/Al₂O₃ catalyst deactivation and regeneration in the dry reforming of bio-oil. It has been obtained observed that the H₂ yield dramatically decreased owing to catalyst deactivation and Ni sintering. One of the effective methods to improve carbon deposition resistance and reaction stability is the development of high-performance catalysts. Li et al. [38] investigated the effect of γ -Al₂O₃ as a Ni-based catalyst support on the high-temperature steam reforming of rice husks for syngas production. The results showed that the gasification of rice husks at 800 °C significantly reduced tar production and increased gas production by 30%. Carlo et al. [39] developed a Ni-based catalyst with Ca₁₂Al₁₄O₃₃ as a support for the steam reforming of biomass, and it was found that the tar conversion was more than 90%, and the cycle stability of the Ca₁₂Al₁₄O₃₃-supported catalyst was prominent. Ca₁₂Al₁₄O₃₃ (calcium alumina) is chemically stable, with a cage-like structure and large surface area, which can provide more attachment sites for active components and reduce carbon deposition. In our previous work, a high-performance catalyst, with Ni as an active component, CeO₂ as a promoter, and Ca₁₂Al₁₄O₃₃ as a support, was proven to be effective in promoting the conversion of tar and hydrogen yield in the steam reforming process [40].

In addition to the construction of catalysts, the two-stage process of biochar pre-removal is also a promising technology. The two-stage process of biochar pre-removal can reduce carbon deposition and increase syngas yield. Hakan et al. [41] proposed a two-stage steam gasification process, including gasification and volatile reforming steps, and more hydrogen is generated through a two-stage process. In the simulation study

from Li et al. [42], it was demonstrated that the hydrogen yield significantly increased from 73.7 g/kg to 102.9 g/kg when using a two-step process instead of a one-step process due to the higher carbon conversion. Yang et al. [43] proposed a novel process consisting of pyrolysis and in-line cascaded catalytic reforming. The biochar formation on the NiAl_2O_4 catalyst was negligible because of the removal of the biochar, and the yield and quality of syngas were improved due to the catalytic effect of biochar on pre-reforming.

In this paper, a two-stage process integrating biomass pyrolysis and catalytic dry reforming to produce syngas is proposed, which uses CO_2 as a gasification agent to realize the capture and utilization of greenhouse gases. Through the separation of pyrolysis and reforming reactors, biochar is left in the pyrolysis reactor, and pyrolysis gas and gaseous tar enter the reforming reactor for catalytic dry reforming. Compared with the general biomass dry reforming, the two-stage process reduces the carbon deposition of the catalyst and improves the catalyst performance, thereby increasing the gas yield. The products of the process were analyzed to verify the feasibility of pyrolysis gas and tar as raw materials for catalytic reforming reactions. The factors affecting the catalytic reforming reaction were investigated. According to the relevant research, the reforming temperature and CO_2/C ratio affect the yield and calorific value of H_2 , CO , etc. This experiment explores the law of gas yield and calorific value of gas production with temperature and CO_2/C ratio under the two-stage process and determines the optimal reforming temperature and CO_2/C ratio. Because the pyrolysis and reforming reactions are endothermic reactions, the energy consumption of the whole process is high. Therefore, the energy relationship of the whole process is studied to provide a theoretical feasibility analysis for the practical application of two-stage dry reforming for bioenergy upgrading.

2. Methodology

2.1. Materials

2.1.1. Biomass

Corn cobs, one of the most common biomasses in Northeast China, were selected as the experimental raw material. The ultimate and proximate analysis of corn cob was shown in Table 1. The biomass components (lignin, cellulose, hemicellulose) were tested by paradigm fraction analysis [39], and the results are shown in Table 2.

Table 1. Ultimate and proximate analysis of biomass.

Raw Materials		Ultimate Analysis(%)					Proximate Analysis (%)			
	C	H	O	N	S	Moisture	Ash	Volatile	Fixed Carbon	
Corn cob	46.78	5.96	46.76	0.48	0.03	1.39	3.76	79.00	15.85	

Table 2. Biomass component analysis.

Groups	Hemicellulose	Cellulose	Lignin	NDS	Ash
Content/%	25.40	62.11	9.90	1.56	2.40

2.1.2. Catalyst

In this paper, CO_2 is used as a gasification agent. If the catalyst contains an adsorbent, it will adsorb CO_2 in situ to generate CaCO_3 , resulting in catalyst agglomeration and poor catalytic effect. Therefore, nickel-based catalysts without adsorbents are used. The nickel-based catalyst was prepared by co-precipitation method using Ni as the active component, CeO_2 as the promoter, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as the carrier, and the mass ratio of 15:6:85. Firstly, $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ was calcined in a muffle furnace at 900 °C for 2 h to obtain pure CaO . According to the mass ratio, CaO , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added to a beaker containing deionized water to prepare a suspension. When the

suspension was prepared, it was noted that CaO would react violently with water to cause droplets or CaO powder splashing. CaO should be slowly added to the water while stirring. After the suspension was prepared, it was placed on a magnetic stirrer and stirred at room temperature for 3 h. The stirred suspension was dried in a 120 °C drying oven for 12 h to a hard solid. The dried solid was taken out and calcined at 500 °C for 3 h in a muffle furnace. After calcination and cooling, deionized water was added to make a suspension, and it was stirred on a magnetic stirrer for 3 h. The suspension was dried in a drying oven at 120 °C for 12 h to a hard solid, and then the dried solid was calcined at 1000 °C for 4 h in a muffle furnace. After the calcined solid was cooled, it was ground into powder to obtain an unactivated catalyst. The unactivated catalyst was reduced at 800 °C in H₂ atmosphere for 3 h to obtain the activated catalyst required for the experiment. The X-ray diffraction (XRD) patterns of the catalysts are shown in Figure 1. The main components of the catalyst before activation are NiO, CeO₂, and Ca₁₂Al₁₄O₃₃, while NiO becomes the active component Ni after activation.

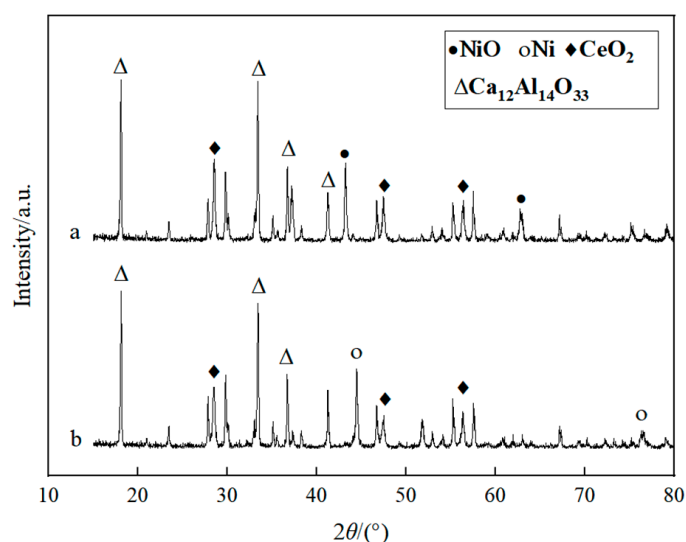


Figure 1. XRD pattern of nickel-based catalysts: (a) for unactivated sample and (b) for activated sample.

2.2. Biomass Pyrolysis Experiments

The experiments in this paper mainly include biomass pyrolysis experiment and catalytic dry reforming experiment. Biomass pyrolysis occurs under high temperatures to produce pyrolysis gas, tar, and biochar. Temperature is an important factor in biomass pyrolysis, and the liquid product reaches a peak between 450 °C and 550 °C [44]. Therefore, this biomass pyrolysis experiment was carried out at 500 °C.

The experimental system and apparatus are shown in Figure 2. The pyrolysis reactor is a 1.5 kW electrically heated furnace. In the experiment, 1 L/min N₂ was introduced into the reaction system as an inert carrier, and then the biomass with $m_0 = 5$ g was put into the pyrolysis reactor through the sample barrel. The biomass was pyrolyzed at 500 °C to produce pyrolysis gas, tar, and char. The pyrolysis gas and gaseous tar left the reactor under the promotion of N₂ and entered the tar collection part. The tar collection part is composed of four gas bottles and a drying tower in series. The first three gas bottles are filled with isopropanol solution, the fourth gas bottle is filled with deionized water, and the drying tower is filled with water-absorbing discoloration silica gel. When the gaseous tar and pyrolysis gas pass through the series device, the isopropanol solution cools and absorbs the tar, the deionized water is used to wash the gas, the drying tower is used to dry the pyrolysis gas, and finally, the pyrolysis gas is passed into the portable infrared gas analyzer for component detection and collection. The masses of coke, tar, and pyrolysis gas were measured to be m_1 , m_2 , and m_3 , respectively, and the mass of water was $m_0 - m_1 - m_2 - m_3$. The concept of gas yields (H₂, CO, CH₄, C_mH_n, CO₂) was introduced to react more accurately to the pyrolysis products.

Chromatographic conditions: chromatographic column HP-5MS (30.0 m × 250 µm, 0.25 µm), chromatographic column starting temperature 40 °C, constant temperature 5 min; after that, the temperature was raised to 280 °C at a rate of 10 °C/min and kept constant for 10 min. Carrier gas He, carrier gas flow 1.0 mL/min, split ratio 10:1, injection volume 1 µL.

Mass spectrometry conditions: EI source, electron energy 70 eV, ion source temperature 230 °C, quadrupole 150 °C, scanning mode scan, scanning mass range 35–500 µ, solvent delay 2 min.

Tar is mainly composed of compounds with molecular weights of less than 200, occupying 93.2%. As detected by gas chromatography, tar consists of up to several hundred species of molecules, mainly aromatic compounds, and the compounds with a high proportion are shown in Table 6.

Table 6. The main components of biomass tar.

Serial Number	Name	Molecular Formula	Relative Molecular Mass	Relative Content (%)
1	N-Methyl-1,3-propanediamine	C ₄ H ₁₂ N ₂	88.15	3.20
2	p-Methyl phenol	C ₇ H ₈ O	108.14	0.53
3	1,4-Benzenediol	C ₆ H ₆ O ₂	110.11	4.15
4	2,3-Dihydrobenzofuran	C ₈ H ₈ O	120.15	10.32
5	4-Hydroxybenzaldehyde	C ₇ H ₆ O ₂	122.12	1.17
6	p-Ethyl phenol	C ₈ H ₁₀ O	122.16	4.15
7	2,5-Dihydroxytoluene	C ₇ H ₈ O ₂	124.14	5.35
8	Glycerol monoacetate	C ₅ H ₁₀ O ₄	134.13	1.17
9	3,4,5-Trimethylphenol	C ₉ H ₁₂ O	136.19	1.70
10	3-Methoxy-4-methylaniline	C ₈ H ₁₁ NO	137.18	1.12
11	4-Methylguaiacol	C ₈ H ₁₀ O ₂	138.16	3.24
12	3-Methoxycatechol	C ₇ H ₈ O ₃	140.14	0.99
13	P-Vinyl Guaiacol	C ₉ H ₁₀ O ₂	150.17	6.83
14	Vanillin	C ₈ H ₈ O ₃	152.15	4.17
15	Lilac Alcohol	C ₈ H ₁₀ O ₃	154.16	3.92
16	1,6-Anhydroglucopyranose	C ₆ H ₁₀ O ₅	162.14	2.68
17	Isoeugenol	C ₁₀ H ₁₂ O ₂	164.20	2.83
18	Diglycerin	C ₆ H ₁₄ O ₅	166.17	1.28
19	Acetosyringone	C ₁₀ H ₁₂ O ₄	196.20	3.30
20	Supramolecular	—	>200	6.80

2.3. Experimental Process of Biomass Catalytic Dry Reforming

A two-stage experimental setup was used in this experiment, in which the catalyst and biomass were placed separately, and the system and setup are shown in Figure 2. Besides the biomass pyrolysis reactor, another electrically heated furnace is equipped as catalytic reforming reactor filled by the catalyst in the two-stage process. The pyrolysis products, tar, and pyrolysis gas undergo catalytic gasification reforming reaction under the action of nickel-based catalyst and reforming agent CO₂, and the large molecules of organic matter tar and methane break down into small-molecule synthesis gas, such as H₂ and CO. The effect of CO₂/C ratio on the CO₂ catalytic gasification reforming process was explored by varying the CO₂ flow rate. The main chemical reactions involved in the CO₂ gasification reforming of biomass are shown in Table 7.

Table 7. The main chemical reactions involved in biomass CO₂ reforming gasification process.

Reaction	Equation	Numbering
Pyrolytic reaction	$\text{CH}_{1.591}\text{O}_{0.821} \rightarrow \text{C} + \text{CO} + \text{H}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{CH}_4 + \text{Tar}$	(1)
Tar CO ₂ reforming reaction	$\text{CH}_x\text{O}_y + a\text{CO}_2 \rightarrow b\text{CO} + c\text{H}_2 + d\text{CH}_4 + e\text{H}_2\text{O}$	(2)
Methane CO ₂ reforming reaction	$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$	(3)
Water gas reaction	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	(4)
Boudouard reaction	$\text{C} + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2\text{H}_2$	(5)
Water gas shift reaction	$\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$	(6)
Methanation of carbon	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$	(7)
	$\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4$	(7)

In this experiment, the gas yield, H_2/CO ratio, H_2 and CO yield and calorific value of reformed gas, and CO_2 utilization were investigated, and the relevant definitions are as follows.

1. H_2/CO ratio, X . The ratio of the volume of H_2 to CO produced by biomass gasification reforming:

$$X = \frac{V_{H_2}}{V_{CO}} \quad (2)$$

where V_{H_2} is the volume of H_2 produced by gasification reforming, Nm^3 ; V_{CO} is the volume of CO produced by gasification reforming, Nm^3 .

2. H_2 and CO yield, Y_{Q-H_2} . The total volume of H_2 and CO gas produced by gasification reforming of biomass per unit mass:

$$Y_{Q-H_2} = \frac{V_{H_2} + V_{CO}}{m} \quad (3)$$

where Y_{Q-H_2} is the H_2 and CO yield, Nm^3/kg ; V_{CO} is the volume of H_2 and CO produced by biomass gasification reforming, Nm^3 , respectively; and m is the mass of input biomass, kg.

3. Calorific value of reformed gas, HHV . High level calorific value of syngas produced by gasification reforming of biomass per unit mass:

$$HHV = \frac{4.178 \times Q_g \times V_g}{m} \quad (4)$$

where HHV is the calorific value of reformed gas MJ/kg ; and Q_g is the calorific value of gas. V_g is the volume of gas produced by biomass gasification reforming, Nm^3 ; and m is the mass of input biomass, kg.

4. CO_2 utilization, L_{CO_2} . The volume of initial CO_2 input minus the volume of CO_2 produced by gasification reforming of unit mass of biomass:

$$L_{CO_2} = \frac{V_O - V_{CO_2}}{m} \quad (5)$$

where L_{CO_2} is the CO_2 utilization rate, Nm^3/kg ; V_O is the initial input CO_2 volume, Nm^3 ; V_{CO_2} is the volume of CO_2 produced by gasification reforming, Nm^3 ; and m is the mass of the input biomass, kg.

3. Results and Discussions

3.1. Effect of Reforming Temperature

Figure 3 shows the effect of temperature on the reforming process, and the experimental results are similar to those of Encinar et al. [22]. With the increase of reforming temperature, the yield of CO increased, but the yield of H_2 , CH_4 , and $CmHn$ increased first and then decreased, reaching the maximums at $900^\circ C$, which were $0.28 Nm^3/kg$, $0.14 Nm^3/kg$, and $0.15 Nm^3/kg$, respectively. Notably, the yield of CO was always higher than that of H_2 . The H_2/CO ratio decreases with the increase of reforming temperature since the addition of CO_2 promotes the reverse reaction of water-gas shift (Equation (6)). From Figure 3c, the H_2 and CO yields and calorific value of gas increase first and then decrease when the reforming temperature increases and reach the maximums at $900^\circ C$, which are $0.74 Nm^3/kg$ and $2.75 MJ/kg$, respectively.

Compared with biomass steam gasification [45], CO_2 is involved in the reaction. As a gasification agent, the whole process realizes the resource utilization of CO_2 . Figure 3d shows the effect of reforming temperature on CO_2 utilization rate. The increase in reforming temperature can promote the endothermic CO_2 reforming reactions of tar and methane, to improve CO_2 utilization. Therefore, when the reforming temperature exceeds $900^\circ C$, the reforming gas calorific value and H_2 and CO production are the largest, and the CO_2 capture rate is higher.

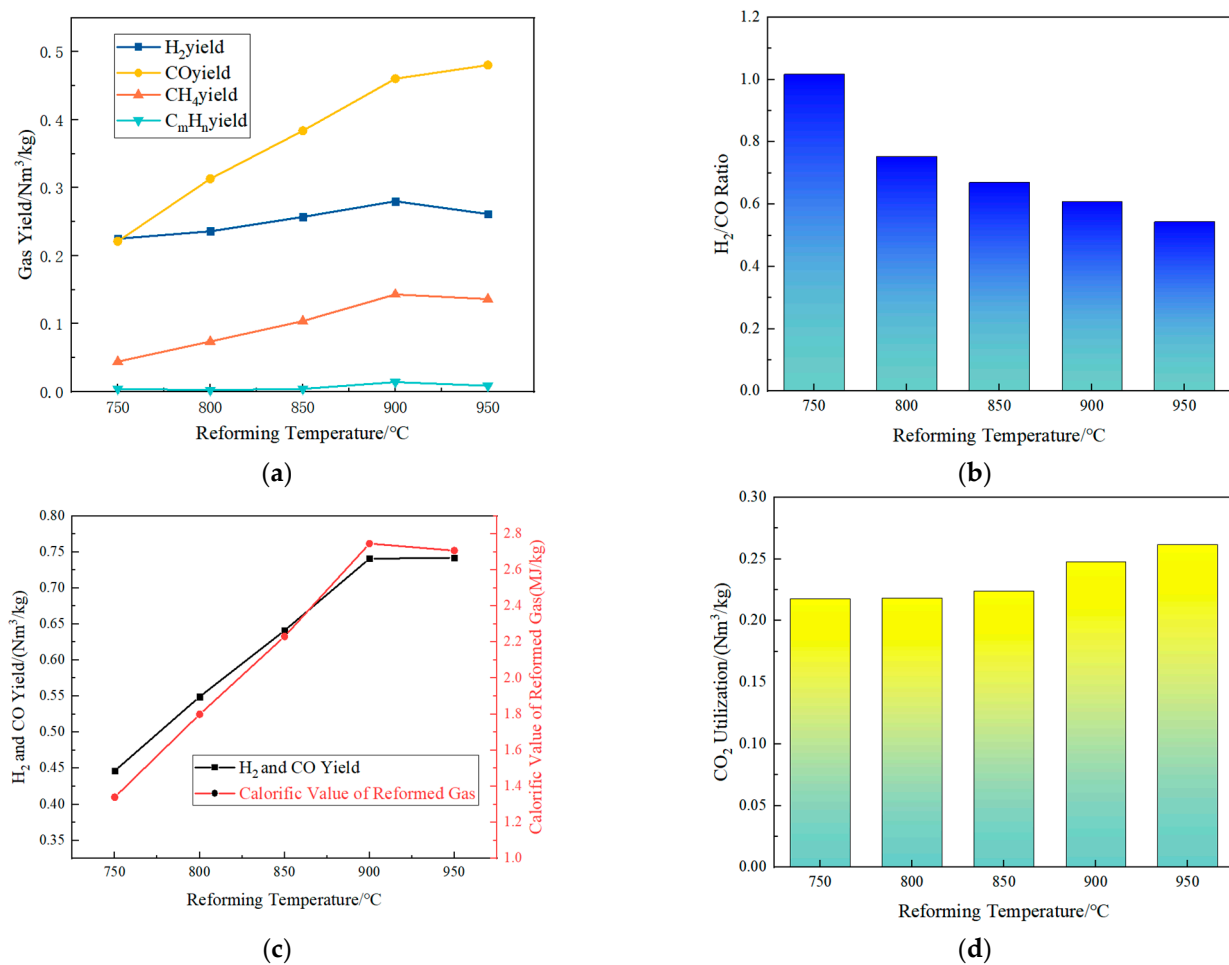


Figure 3. Influence of reforming temperature on (a) Gas yield (b) H₂/CO ratio (c) Potential H₂ yield and calorific value of reformed gas (d) CO₂ utilization (CO₂/C ratio = 1.0).

3.2. Effect of CO₂/C Ratio

The influence of CO₂/C ratio on the reforming process is shown in Figure 4. The CO₂/C ratio is the ratio of the introduced CO₂ to the reaction C. The CO₂/C ratio is introduced to determine the amount of CO₂ introduced to facilitate the conversion of C in the pyrolysis gas and tar. Similar to the results of Y Cheng et al. [46], With the increase of CO₂/C ratio, the yield of CO increased, the yield of H₂ and CH₄ increased first and then decreased, and the yield of C_mH_n did not change much. When the CO₂/C ratio is 0, the biomass pyrolysis process is carried out, the yield of CO and H₂ is low, and more tar is produced. When the CO₂/C ratio increases, the CO₂ reforming of tar (Equation (1)) is promoted, and the yields of CO, H₂ and CH₄ are increased. When the CO₂/C ratio continues to increase, the tar reaction tends to be complete, which promotes the CO₂ reforming reaction of CH₄ (Equation (2)) and the water-gas shift reverse reaction (Equation (6)), reduces the H₂ yield and CH₄ yield, and increases the CO yield. Affected by the change of H₂ and CO yields, the H₂ and CO ratio, H₂ and CO yields, and gas calorific value all increase first and then decrease with the increase of CO₂/C ratio, as shown in Figure 4b,c. It can be seen from Figure 4c that when CO₂/C = 0.5, the yields of H₂ and CO are greater than the calorific value of gas production. This is because the CO₂ reforming of tar is mainly carried out at this time, the yield of H₂ in syngas reaches the maximum, and the yield of CO is relatively large, so the yield of H₂ and CO reaches the maximum. When the CO₂/C ratio continues to increase to 1, the H₂ and CO yields decrease due to the promotion of the reverse reaction of water-gas shift, but at this time, the CO₂ reforming of tar is still ongoing, CH₄ and C_mH_n reach the maximum value, and the CO yield is high, so

the calorific value of the gas reaches the maximum value, which is greater than the H_2 and CO yields.

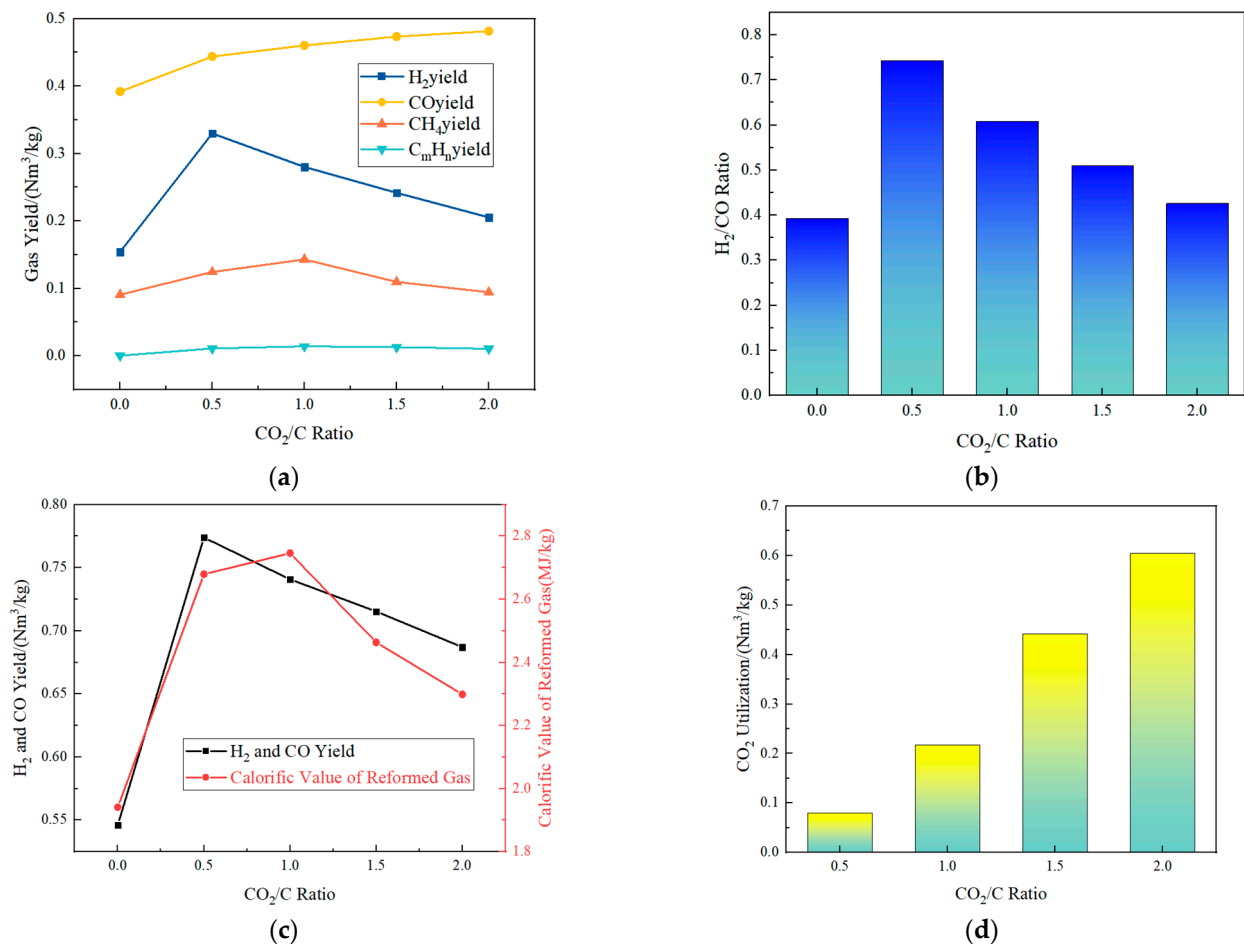


Figure 4. Effect of CO_2/C ratio on (a) Gas yield (b) H_2/CO ratio (c) Potential H_2 yield and calorific value of reformed gas (d) CO_2 utilization each investigated index (reforming temperature = $900\text{ }^\circ\text{C}$).

Figure 4d shows the effect of CO_2/C ratio on CO_2 utilization rate. With the increase of CO_2/C ratio, the CO_2 reforming reaction of tar and methane is promoted, and the CO_2 utilization rate is improved. However, when too much CO_2 is injected, the CO_2 concentration in the gas will also increase; therefore, the calorific value of gas production is dropped. Therefore, based on comprehensive analysis, with the calorific value of gas production as the main index and a comprehensive analysis of other indicators, it can be concluded that the CO_2/C ratio is the best at 1.

4. Energy Analysis of Biomass Catalytic Dry Reforming System

From the above experimental study, the best reforming parameters were obtained: reforming temperature is $900\text{ }^\circ\text{C}$ and CO_2/C ratio is 1. Since both pyrolysis and reforming reactions are endothermic reactions and require a lot of energy, the total energy consumption of the system was explored to verify the feasibility of the two-stage biomass CO_2 catalytic reforming process.

Figure 5 shows the energy balance for the catalytic dry reforming of biomass. Biomass pyrolysis produces pyrolysis gas, tar, and biochar, in which pyrolysis gas and tar enter the catalytic gasification reforming reactor. Under the action of gasification agent (CO_2), the pyrolysis gas and tar undergo catalytic gasification reforming reaction, and the tar is cracked into small molecules, and finally reformed into syngas. During the whole process, the input energy is the pyrolysis reaction and gasification reforming reaction function, and the raw material (biomass, CO_2) is heated. The raw material temperature is set at $25\text{ }^\circ\text{C}$

and the pyrolysis temperature is set at 500 °C, without considering any heat loss. In order to reduce the energy input, the biochar produced by the pyrolysis reaction is burned to provide energy for the whole system, and the high-temperature syngas is cooled to 200 °C for waste heat recovery. The total energy consumption of the system (Q_{Total}) consists of four main components: pyrolysis reactor energy consumption (Q_P), biochar combustion heat release from the pyrolysis reaction (Q_C), syngas waste heat recovery (Q_{RE}), and reforming reactor energy consumption (Q_R). The calculation formula is shown below:

$$Q_{Total} = Q_P + Q_R - Q_C - Q_{RE} \quad (6)$$

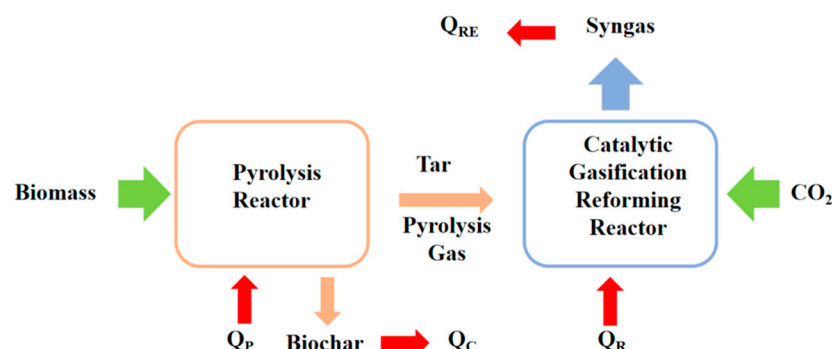


Figure 5. Material and energy balance of biomass CO₂ catalytic gasification reforming system.

The total energy consumption per unit mass of biomass in the whole process (Q_{Total}) and its sub energy consumptions are shown in Table 8. The total energy consumption of the system with optimal process parameters is used as an example. Among them, the pyrolyzer energy consumption (Q_P) is measured by the TGA-DSC simultaneous thermal analyzer, 2.37 MJ/kg. 0.23 kg/kg of biochar can be produced from the pyrolysis of biomass, and its combustion exotherm (Q_C) is 7.55 MJ/kg (assuming that the biochar consists of carbon completely). Using the HSC software, it can be calculated that the heat recovery (Q_{RE}) of high-temperature syngas to be cooled to 200 °C is 2.17 MJ/kg, and this energy can be used to preheat the agent and biomass. Similarly, the reforming energy consumption (Q_R) is 8.03 MJ/kg, as shown in Table 9, which mainly includes the energy consumption for heating pyrolysis gas and tar to the reforming temperature (Q_{PG}), the energy consumption for heating agent CO₂ to the reforming temperature (Q_{CO_2}), and the energy consumption for various heat-absorbing gasification reforming reactions (Q_{GR}). It can be seen that the Q_{Total} is 0.68 MJ/kg under the best process parameters, which is just slightly more than 0. The system is basically auto-thermal and does not need much heat from outside.

Table 8. Total system energy consumption of biomass CO₂ catalytic gasification reforming process.

Reaction Condition		Q_P (MJ/kg)	Q_C (MJ/kg)	Q_R (MJ/kg)	Q_{RE} (MJ/kg)	Q_{Total} (MJ/kg)
Name	Number					
Reforming Temperature/°C (CO ₂ /C ratio = 1.0)	750	2.37	7.55	0.83	1.92	−6.27
	800			3.12	2.01	−4.07
	850			5.49	2.09	−1.78
	900			8.03	2.17	0.68
	950			8.34	2.30	0.86
CO ₂ /C Ratio (reforming temperature = 900 °C)	0			0.98	1.38	−7.53
	0.5			5.19	1.67	−1.66
	1.0			8.03	2.17	0.68
	1.5			9.72	2.71	1.83
	2.0			10.99	3.31	2.49

Table 9. Q_R of biomass CO_2 catalytic gasification reforming process.

Reaction Condition		Q_{pG} (MJ/kg)	Q_{CO_2} (MJ/kg)	Q_{GR} (MJ/kg)	Q_R (MJ/kg)
Name	Number				
Reforming Temperature/ $^{\circ}\text{C}$ (CO_2/C ratio = 1.0)	750	0.41	1.26	−0.84	0.83
	800	0.49	1.36	1.27	3.12
	850	0.58	1.46	3.45	5.49
	900	0.67	1.57	5.80	8.03
	950	0.76	1.67	5.92	8.34
CO_2/C Ratio (reforming temperature = $900\text{ }^{\circ}\text{C}$)	0	0.67	0.00	−1.64	−0.98
	0.5	0.67	0.73	3.80	5.19
	1.0	0.67	1.57	5.80	8.03
	1.5	0.67	2.40	6.65	9.72
	2.0	0.67	3.24	7.08	10.99

5. Conclusions

Aiming at the new two-stage CO_2 catalytic gasification reforming process proposed in this paper to prepare high-yield gas calorific value syngas rich in H_2 and CO , the pyrolysis characteristics of corncob as a biomass sample were first studied, and then CO_2 reforming of pyrolysis gas and tar was carried out. It can be seen that when the temperature is $900\text{ }^{\circ}\text{C}$ and the CO_2/C ratio is 1, the calorific value of the syngas reaches a maximum of 2.75 MJ/kg , and the CO yield and H_2 yield reach larger values of 0.24 kg/kg and 0.44 kg/kg , respectively. At this time, the H_2/CO ratio is less than 1. Under this condition, the analysis of the total energy consumption of the system shows that the total system energy consumption is only slightly greater than 0, and the system is basically in a self-heating state. However, it is worth noting that the total energy consumption in the calculation system is based on the theoretical calculation of material and energy conservation. Moreover, the current industrial use of H_2 and CO to synthesize methanol is at a higher H_2/CO ratio. However, the H_2/CO ratio obtained in this experiment is relatively low, so the next step will use H_2O and CO_2 as gasification agents to obtain high H_2/CO ratio syngas more suitable for industrial synthesis.

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