Experimental study on gasification of bituminous coal char with CO₂ catalysed by CaO

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Abstract. The effects of CaO under normal pressure and CaO soaked in ammonia on the isothermal gasification of Jinjie bituminous coal char-CO₂ are studied on the self-built fixed-bed experimental bench with analytical pure CaO as the precursor. The experimental results show that the gasification activity of Jinjie coal char increases with the increase of Ca addition. The load saturation is 5% at 780°C gasification temperature, and the load saturation are 3% at 810°C, 850°C and 900°C. Adding 3% CaO coal char can reduce the gasification temperature by 120°C, and reduce the coal char conversion rate to 95% by 85 min at 900°C gasification temperature. After soaking in ammonia water, the gasification activity of coal char and the gasification activity of coal char added with CaO catalyst are increased to different degrees. At 850°C, the increase of K value and Rm reach the maximum when CaO catalyzes coal char gasification by ammonia immersion, which are 49.7% and 35.9%, respectively.

1. Introduction
The gasification temperature of the traditional coal gasification process is generally above 1000°C [1]. The energy consumption is large, the reaction temperature is high, and the equipment requirements are high [2,3], thus it promotes coal gasification reaction under medium and low temperature conditions. Yasuo O and other studies [4] have found that CaCO₃ can increase the reactivity of grade coal by 40 to 60 times at 700°C, and reduce the gasification temperature to below 1000°C. Zhu et al [5] conducted a series of studies on CaO as a catalyst for coal cracking. It was found that the coal cracking activation energy decreased by 34.5% and the cracking temperature decreased by about 60°C after adding CaO. Feng et al [6] studied the gasification of coal-steam by limestone. It was found that the catalysis was significantly higher than that of unsoaked limestone after soaking with sodium chloride solution or sodium carbonate solution before gasification. The reason may be that in addition to NaCl and Na₂CO₃ is a recognized coal gasification catalyst. The addition of additives promotes the distribution of CaO on the surface of coal char after limestone decomposition, which indirectly promotes the uniformity of CaO distribution on the surface of coal char [7].

In the past research on coal catalytic gasification, researchers mainly studied the effect of CaO on coal pyrolysis process, while the research on the impact of coal char gasification was relatively rare. At the same time, CaO has a wide range of sources, low prices and low cost. Coking plants, coal retorting, petroleum industry and chemical industry can produce ammonia with different concentrations as by-products, which are inexpensive. The reserves of bituminous coal in Jinjie are relatively large. It is of great significance to study the catalytic gasification process of Jinjie bituminous coal for its efficient and clean utilization in the later stage. This study analyzes pure CaO,
CaO immersed in ammonia water as a catalyst, and uses Shaanxi Jinjie coal as experimental coal sample. The effect of different proportions of catalyst on the gasification reaction of Jinjie coal char-CO$_2$ is investigated by adding different proportions of catalysts.

2. Experimental section

2.1. Experimental equipment and procedures

In order to simulate a large coal gasification plant, the experimental platform of figure 1 is constructed. During the experiment, the thermocouple is used to provide the temperature required for the reaction. The electric heating furnace and the temperature controller are used to jointly control the reaction temperature. After the N$_2$ and CO$_2$ pass through the pressure reducing valve, they respectively provide the gas source for the coal char preparation and gasification. The meters are used to control the flow of N$_2$ and CO$_2$, respectively. N$_2$ and CO$_2$ are provided by N$_2$ cylinders and CO$_2$ cylinders after decompression during coking and gasification respectively, and their purity are greater than 99.9%. During the experiment, the temperature is controlled by thermocouple and temperature controller. When coking, the coal sample is evenly spread out on the quartz boat. Under the protection of the N$_2$ atmosphere, the coal sample is slowly sent to the central constant temperature area of the fixed bed. After rising to a specified temperature at a certain rate of warming, the coal sample starts to time. At the time of gasification, the coal char was evenly spread out in the quartz boat. Under the protection of the N$_2$ atmosphere, the coal char is slowly sent to the central constant temperature zone of the fixed bed. After heating to gasification temperature, it was switched to a CO$_2$ atmosphere. After a certain period of constant temperature, the atmosphere is switched to a N$_2$ atmosphere again. And pulling the quartz boat out of the electric heating furnace and cooling it to room temperature to weigh, and cycling it back and forthing until the end of the experiment.

![Figure 1. Experimental device diagram.](image)

2.2. Catalyst addition and coking

The sifted bituminous coal is used as the original coal in the experiment. The coal quality analysis data are shown in table 1.

| Table 1. Coal quality analysis (%) |
|-----------------------------------|
| **Industrial analysis, ad** | **Element Analysis, daf** |
| M | A | V | FC* | C | H | N | O* | S |
| 4.92 | 5.78 | 33.19 | 56.11 | 78.18 | 4.47 | 0.84 | 16.10 | 0.41 |

Analytical pure CaO and CaO after immersion of pure ammonia water (mass concentration 25% ~ 28%) are analyzed as additives in this study respectively. In this study, pure CaO is analyzed as the precursor of Catalyst, which is added according to the ratio of metal atomic mass to original coal mass. The catalyst precursor is placed in deionized water by immersion method, stirred for a moment, so that the catalyst precursor is dissolved in deionized water as much as possible, and then the weighed raw coal is added to the deionized water and stirred evenly with a glass rod. After stirring for a
moment, place the sample in a thermostat and dry the sample at 108°C for 3 hours. Another catalyst is to replace the original deionized water with a certain amount of analytical pure ammonia water. The other steps are the same, which are sealed and allowed to stand for 24 hours before being placed in the incubator, and then the coal sample is dried at 108°C for 3 h in an incubator.

In figure 1, the char is made on the experimental device. The coking pressure is constant pressure, and the gas N₂ flow is 400 ml/min, and the average warminutesg rate is 103°C/min. The final temperature of coking is 800°C, and the final temperature is maintained for 8 min. For convenience, the raw coal char, coal char soaked in ammonia water, and 1% Cao char are respectively represented by raw-char, A-raw-char, and 1%-CaO-char, and other proportional catalyst addition and so on.

Gasification is carried out at the normal pressure. At least 2 repetitive experiments are performed in each group of conditions to reduce the experimental error and ensure the reliability of experimental data.

3. Outcomes and discussions

3.1. Catalytic mechanism

At present, the catalytic mechanism of alkaline earth metal oxide CaO is generally recognized as the oxygen transfer mechanism [8].

\[
\begin{align*}
\text{CaO} + \text{CO}_2 & \rightarrow \text{CaO} \cdot O + \text{CO} \\
\text{CaO} \cdot O + C_f & \rightarrow \text{CaO} + C(O) \\
C(O) & \rightarrow \text{CO} + C_f
\end{align*}
\]

3.2. Eliminatesation of internal and external proliferation factors

To indicate the degree of gasification of coal char, the fixed carbon conversion rate \(x\) of coal char is defined as:

\[
x = \frac{m_0 - m_t}{m_0 - m_\infty}
\]

The \(m_0\) is the initial coal char quality; \(m_t\) is the coal char quality after \(t\) minutesutes of gasification; and \(m_\infty\) is the quality of the final ash.

Active Factor \(K\) can quantitatively and accurately describe the gasification activity of coal char [9]:

\[
K = \frac{2}{\tau_{0.5}}
\]

In the formula, \(\tau_{0.5}\) indicates the gasification reaction time corresponding to the coal coke conversion rate reaching 50%.

Literature [10] pointed out that when the coal char mass is 0.2 g, the CO₂ flow rate is 400 ml/min, and the particle size is ≤62 μm, the carbon conversion rate reaction process is no longer affected by coal char mass, CO₂ flow rate and particle size, indicating that this time It is no longer affected by the internal and external diffusion of particles, thus ensuring that the experimental reaction is in the chemical reaction kinetics control stage.

3.3. Catalytic influence of catalyst on gasification of coal char

Figure 2 and table 2 show the gasification characteristics of coal char with different CaO addition amounts.
Figure 2. Effect of CaO addition on the gasification characteristics of coal char at different gasification temperature.

Table 2. Coal char gasification activity factors K×100 (minutes⁻¹) and mean gasification rate Rm (%/minutes) with different CaO additions and at different gasification temperatures.

| Gasification Temperature | 0% | 1% | 3% | 5% | 10% |
|--------------------------|----|----|----|----|-----|
| 780°C                    | K×100 | 1.33 | 3.86 | 6.33 | 7.96 | 5.66 |
|                          | Rm   | 0.37 | 0.61 | 0.68 | 0.74 | 0.68 |
| 810°C                    | K×100 | 1.87 | 7.34 | 11.30 | 12.61 | 8.87 |
|                          | Rm   | 0.46 | 0.73 | 1.05 | 1.08 | 0.88 |
| 850°C                    | K×100 | 2.77 | 17.11 | 23.45 | 24.71 | 18.98 |
|                          | Rm   | 0.60 | 1.64 | 2.06 | 2.06 | 1.64 |
| 900°C                    | K×100 | 6.02 | 23.27 | 43.13 | 43.76 | 27.95 |
|                          | Rm   | 1.08 | 2.83 | 4.44 | 4.31 | 2.98 |
It can be seen from figure 2 that the gasification activity of coal char has been greatly improved after the addition of catalyst CaO. When the gasification temperature is above 810°C, the gasification activity of coal char is gradually increased with the addition of catalyst, and the catalytic loading is saturated when the addition amount is 3%. After the addition amount exceeds 3%, the coal char gasification activity is relatively reduced, indicating that excessive catalyst loading can also cause blockage of coal char pores and affect the transfer of gasification agent while catalyzing the gasification of coal char [11]. When the gasification temperature is 780°C, the catalyst load saturation is 5%, the coal char gasification activity is higher than the catalyst loading of 3% and 10%, and the activity difference is lower than other gasification temperatures. When the gasification temperature is above 810°C, the catalyst loading is 3%, and the coal char gasification activity which the loading is 5% is equivalent to 3% of the load. With the increase of gasification temperature, the gasification activity of coal char with 10% catalyst loading gradually increases gap with the gasification activity of coal char of 3% catalyst loading. It indicates that when the catalyst addition amount is too large, it will increase the blockage of coal coke pores. At the same time, as the gasification temperature increases, the degree of sintering of the catalyst will increase, and the degree of blockage of coal char pores will increase correspondingly.

![Graph](image)

**Figure 3.** Relationship curves of CaO addition to K and Rm at different gasification temperatures.

It can be seen from figure 2 that the effect of the catalyst addition amount on K at 780°C gasification temperature is saturated at 5%, and the catalyst saturation at other gasification
temperatures is 3% as the gasification temperature increases. The effect of catalyst addition on \( R_m \) is saturated at 3%.

3.4. Effect of catalyst on gasification temperature and time

It can be seen from figure 4 that the time for the coal char added 3% CaO to reach 50% conversion at 780\(^\circ\)C is equal to the time for the original coal char to reach 50% conversion at 900\(^\circ\)C, indicating that CaO can reduce the gasification temperature by 120\(^\circ\)C. At the same time, it can be seen that the coal char conversion rate of adding 3% CaO at a temperature of 900\(^\circ\)C to 95% requires 45 minutes, while the original coal char needs more than 130 minutes to achieve the same conversion rate.

![Figure 4](image-url)

**Figure 4.** Degree to which catalyst reduces gasification temperature and time.

3.5. Effect of additives on CaO catalytic coal gasification

Figure 5 and table 3 show the effect of additives on CaO-catalyzed coal char gasification at different gasification temperatures.
It can be seen from figure 5 and table 3 that the gasification activity of coal char is increased to different degrees compared with the original coal char after immersion in ammonia water. The higher the gasification temperature, the more obvious the increase of coal char gasification activity. The gasification activity is equivalent at 780°C gasification temperature. The K value is 2.01 after adding ammonia water at 810°C gasification temperature, which is 7.5% higher than the original coal char, and the K values are 3.54 and 7.24 at 850°C and 900°C gasification temperature respectively. Which increased by 13.5% and 20.3% respectively compared with raw coal char. The variation of Rm is relatively small. Rm is basically equal at 780°C, and is 0.48, 0.67, and 1.18 at 810°C, 850°C, and 900°C respectively, which are 4.4%, 5.7%, and 9.3% respectively. It can be seen that the maximum gasification activity and the whole gasification process of coal char have been improved to different degrees after immersion in ammonia water, and the higher the gasification temperature, the greater the increase, and the maximum gasification activity is better than the whole gas process. The increase of coal char gasification activity after adding ammonia water may be due to the fact that some alkaline metal oxides or alkaline earth metal oxides in raw coal may be separated by free radicals in an alkaline environment during the process of stirring and stirring after adding ammonia water [12]. And these oxides are typical catalysts for catalytic coal char gasification, so that ammonia water indirectly plays a catalytic role in the gasification of coal char.

Table 3. Char gasification activity factor K * 100 (min⁻¹) and the average rate of gasification Rm (%/min) under the different temperature of gasification.

| Temperature | raw-char | A-raw-char | 3Ca-char | A-3Ca-char |
|-------------|----------|------------|----------|------------|
| 780°C       | 1.33     | 1.35       | 6.33     | 7.18       |
|             | 0.37     | 0.37       | 0.68     | 0.69       |
| 810°C       | 1.87     | 2.01       | 11.30    | 13.93      |
|             | 0.46     | 0.48       | 1.05     | 1.11       |
| 850°C       | 2.77     | 3.54       | 23.45    | 35.10      |
|             | 0.60     | 0.67       | 2.06     | 2.80       |
| 900°C       | 6.02     | 7.24       | 43.13    | 47.75      |
|             | 0.93     | 1.18       | 4.44     | 6.02       |

After immersion in ammonia water, the catalytic effect of CaO at different gasification temperatures increased to varying degrees. Compared with CaO-catalyzed coal char gas immersion without ammonia immersion, the K value after ammonia immersion increased by 13.4%, 23.3%, 49.7%, 10.7%, respectively. The maximum value of K increased at 850°C gasification temperature.
After immersion in ammonia water, Rm increased by 1.47%, 5.71%, 35.9%, and 36.6%, respectively, and the increase was basically reached at the gasification temperature of 850°C. The ability of CaO to catalyze the gasification of coal char after immersion in ammonia water may be due to the fact that on the one hand, the addition of ammonia water can cause a part of the catalytic metal oxide in the coal to exist as a free radical, thereby indirectly increasing the gasification of coal char active. On the other hand, during the impregnation and mixing process, some CaO chemically reacts into a saturated solution of Ca(OH)₂. During the coking process, Ca(OH)₂ decomposes into CaO with smaller particle size, which makes CaO in coal char. The distribution in the medium is more uniform, and the more uniform the distribution of CaO in the coal char, the more obvious the catalytic effect. During the impregnation and mixing process, according to the same ion effect, the added ammonia water will decompose part of the hydroxide ions, and the hydroxide ions will inhibit the dissolution of Ca(OH)₂, thereby promoting the precipitation of Ca(OH)₂. Furthermore, the conversion of CaO to Ca(OH)₂ is promoted, and finally the CaO distribution is more uniform during the coking process, and the effect of CaO catalyzing the gasification of coal char is improved.

4. Conclusion

- The CaO has a load saturation of 5% at a gasification temperature of 780°C, and a load saturation of 3% at a gasification temperature of 810°C, 850°C, and 900°C. At the same gasification temperature, as the amount of catalyst added increases, the K value and the average gasification rate Rm gradually increase, and reach the maximum at the optimum addition amount. Under the same catalyst addition amount, with the increase of gasification temperature, the increase of K value first increases and then decreases, and the average gasification rate Rm increases gradually, and with the increase of gasification temperature, the increase in Rm has a slowing trend.
- Compared to the raw coal char gasification, adding 3% CaO coal char can reduce the gasification temperature by 120°C. The time to achieve a coal char conversion rate of 95% can be shortened by 85 minutes at a gasification temperature of 900°C.
- Compared with coal char and CaO catalyst, the coal char gasification activity of coal char and CaO catalyst increased after being soaked in ammonia water. The maximum gasification activity of coal char immersed in ammonia water and the whole gasification process increase with the increase of gasification temperature, and the maximum gasification activity is improved better than the whole gasification process. At the gasification temperature of 850°C, the increase of K value and Rm reach the maximum when CaO catalyzes coal char gasification by ammonia immersion, which is 49.7% and 35.9%, respectively.

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