Influence of Different Catalysts on Coal Char-CO₂ Gasification

G Zhang¹,², X L Suo¹, J G Sheng¹ and X Tan¹

¹Huadian electric power research institute Co., LTD. Hohhot 010020, Inner Mongolia, China

E-mail: 532213847@qq.com

Abstract. The influence of catalyst Fe(NO₃)₃, CaO and composite catalysts on the thermostatic gasification process of char-CO₂ at atmospheric pressure were studied in this paper. The experimental conclusions indicate that the catalytic effect of CaO is stronger than that of Fe(NO₃)₃ at relatively low gasification temperatures. As the gasification temperature increases, the catalytic gap between the two catalysts decreases. The catalytic effect of the composite catalyst at lower gasification temperatures is between the single component catalysts CaO and Fe(NO₃)₃. When the gasification temperature exceeds 850℃, the promoting effect of the composite catalyst is better than that of the two single-component catalysts. After adding composite catalyst, the time of the coal char is shorter by 103 minutes than the original char, which is shortened by 18 minutes compared with the two single-component catalysts, and the gasification temperature is lowered by 100℃, lower than 120℃ of one-component CaO, and higher than 90℃ of Fe(NO₃)₃.

1. Introduction
China's CO₂ emissions rank first in the world all the year round. In order to accelerate green development, it is imperative to reduce CO₂ emissions [1]. China's coal is the main source of CO₂ production. How to improve coal utilization efficiency, reduce CO₂ emissions, and reduce pollutant emissions has become the research direction of many scholars, and coal gasification is one of its research directions. Normal coal char gasification temperature generally exceeds 1000℃ [2]. It needs high reaction temperature, high energy consumption and high equipment requirements during gasification [3,4]. In this context, the research on catalytic coal gasification technology at low and medium temperatures has been promoted. Fe(NO₃)₃ is one of the components of acid waste in the iron and steel industry and titanium oxide manufacturing industry. If Fe(NO₃)₃ can be fully utilized to make it waste, it will have a good effect on its treatment. Suzuki et al. [5] mixed the chemical components Fe(NO₃)₃ and coke sample by dipping method, and then analyzed the desorption state of the surface of coal char by using TPD technology. The study found that the more iron content in coal char, the faster the dissociation and adsorption of carbon dioxide in the outermost layer of coal char, which can accelerate the gasification process of coal char, and also indirectly shows that Fe ions can promote coal char oxygen exchange process during gasification[5]. Yasuo Ohtsuka et al. [6] found that CaCO₃ can accelerate the activity of low-grade coal by 50 times at 700℃ approximately. Zhu Tingyu et al. [7] found that under nitrogen environment, adding CaO can reduce the cracking activation
energy of coal by about 34.5%, and reduce the initial cracking temperature by about 60℃. Zhu, Z. et al. [8] found that the catalyst with Fe(NO$_3$)$_3$ as the precursor showed the highest activity, and that with FeC$_6$H$_5$O$_7$ showed medium activity, and that with FeCl$_3$ showed the least activity. Asami. et al. [9] found that comparison of the initial rates of uncatalyzed and catalyzed gasification reveals that iron addition can lower the reaction temperature by 120 K.

In this study, the Jinjie bituminous coal was used as the experimental coal sample. By adding Fe(NO$_3$)$_3$, CaO and the two catalysts in different proportions. the catalytic effect on the CO$_2$ gasification of Jinjie coal char was explored and the most Good addition amount and degree of gasification activity at the optimum addition amount were got.

2. Experimental section

2.1. Experimental instruments and methods

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

The preparation of coal char and CO$_2$ gasification experiments are shown on the devices in chart 1. Throughout the process, the purity of the N$_2$ and CO$_2$ atmospheres is greater than 99.9%. During the experiment, a thermocouple and a temperature controller jointly control the experimental temperature. When the coal char is gasified, the coal char is evenly tiled on a quartz boat, and in the N$_2$ environment, slowly place the coal sample in the middle constant temperature area of the experimental device. After the temperature reaches the reaction temperature, it changes to the CO$_2$ atmosphere. After maintaining the constant temperature environment for a certain period of time, it is necessary to switch the environment to nitrogen again, at the same time, remove the experimental sample from the experimental device, then cool it to room temperature, and finally weigh it.

2.2. Addition of catalyst and preparation of coal char

The source of the raw coal sample in the experiment was the screened bituminous coal from the northern border of Shanxi. The coal test results see list 1.

| List 1. Experimental coal sample test results (%) |
|-----------------------------------------------|
| Industrial composition assay, ad | Element assay, 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 |
In this study, the pure Fe(NO\(_3\))\(_3\) \cdot 9H\(_2\)O, the analytical pure CaO and the different mixing ratios of the two catalysts were used as precursors of the catalyst. The catalyst is added according to the rate of the weight of the metal atom to the weight of the raw coal. The catalyst was placed in deionized water according to the immersion method, and then the experimental coal sample was put into it, and finally it was stirred uniformly by an instrument. After mixing well, put the experimental coal sample in a constant temperature instrument and dry it at a constant temperature of 108\(^\circ\)C for 3 hours.

Coking device as shown in figure 1. The coal char is produced under normal pressure, the flow rate of nitrogen is 300 ml/min to 500 ml/min, and the heating speed is 100\(^\circ\)/min to 105\(^\circ\)/min[10,11]. For easy identification, coal char without catalyst, char made with 3% Ca and 3% Fe are expressed as raw-char, D-raw-char, 3Ca-char, 3Fe-char respectively, and the coar prepared by adding 2% Ca and 1% Fe composite catalyst is represented by 2Ca1Fe-char, and addition of other proportions of the catalyst and so on.

3. Methods
The carbon conversion rate of coal coke \(x\) can reflect the degree of gasification of coal char, its formula is:

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

Where \(m_0\) is the weight of coal coke before the experiment; \(m_t\) is the weight of coal char after \(t\) minutes of experiment; \(m_{\infty}\) is the weight of ash after the experiment.

In this paper, the activity factor \(K\) is used to reflect the gasification activity of coal char [10], and its calculation formula is:

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

In the formula, \(\tau_{0.5}\) reflects the corresponding time when the coal char gasification reaction conversion rate is 50%.

Reference[12,13] stated that the char weight is about 0.2g, the flow rate of CO\(_2\) is 300ml/min to 500ml/min, and the coal diameter achieves 62 \(\mu\)m or less, the reaction process of carbon conversion no longer changes with coal particle size, CO\(_2\) flow rate, and char mass. It is suggested that the coal char gasification process is not related to the internal and external particle diffusion factors, which can ultimately ensure that the test course is not affected by external factors.

4. Results and discussion

4.1. Effect of different catalysts on coal char gasification results
It has been found that for two catalysts of one component, saturation is obtained when the addition amount is 3% respectively. The catalysts mixed in two different ratios maximized the catalytic effect when added in an amount of 2% Fe and 1% Ca.

Chart 2, chart 3 and list 2 shows the effect of different catalysts at the gasification temperatures of 780\(^\circ\)C, 810\(^\circ\)C, 850\(^\circ\)C and 900\(^\circ\)C with the coal char. As known from figure 2 and figure 3, the catalyst can greatly promote coal char gasification, and the rate is increased a lot. The catalytic effect of CaO is stronger than that of Fe (NO\(_3\))\(_3\), and as the temperature rises, the gap between the two narrows, showing that the higher temperature, Fe (NO\(_3\))\(_3\) becomes more obvious than that of CaO in catalytic advantage. For a composite catalyst in which two single-component catalysts are mixed in a certain ratio. When gasified at 780\(^\circ\)C, the catalytic result is lower than that of single-component CaO, and as the gasification temperature increases, its catalytic effect is equivalent to one-component CaO at 810\(^\circ\)C gasification temperature. At 850\(^\circ\)C and 900\(^\circ\)C gasification temperature, the catalytic strength of the composite catalyst is stronger than that of the single-component catalyst CaO, and the gap becomes larger as the gasification temperature increases. It is showed that the catalytic activity of the
composite catalyst is analogous to that of the one-component Fe(NO$_3$)$_3$. The composite catalytic effect is stronger than that of the single component. The advantage of the composite catalysis is not manifested in the gasification process due to the S poisoning of the Fe element at low temperature. The higher temperature, the higher gasification temperature inhibits the poisoning of the catalyst S, and the Fe element in the composite catalyst begins to transform into $\alpha$-Fe, FeO and Fe$_3$O$_4$ in a reducing atmosphere. The Ca element in the added CaO promotes the reduction of Fe species, resulting in relatively more $\alpha$-Fe, while the reduced Fe species has fluidity and is the main active component of catalytic coal-CO$_2$ gasification[14]. It is known from the above analysis that Ca element promotes coal char-CO$_2$ gasification and promotes Fe-catalyzed coal-CO$_2$ gasification reaction, which results in higher catalytic activity than single-component catalyst.

It can be seen from chart 2 that under 900℃, the coal char conversion of 3% Fe, 3% Ca, 2% Fe+1% Ca is reached at 45 min, 45 min, and 30 min, respectively. 95% yet the raw coal char gasification takes 130 min to reach the same conversion rate. The catalyst improves the gasification reaction rate of coal char, and the increase rate of composite catalyst is higher than that of single-component catalyst.

![Chart 2: Effect of different catalysts on coal char gasification process](image-url)
List 2. Catalyst for $K \times 100 \text{ min}^{-1}$ and $R_m$ (%/min)

| Gasification Temperature | 0       | 3%Fe | 3%Ca | 2%Fe+1%Ca |
|--------------------------|---------|------|------|-----------|
| 780°C                    | K 1.33  | 3.37 | 6.33 | 4.84      |
|                          | $R_m$ 0.37 | 0.62 | 0.68 | 0.71      |
| 810°C                    | K 1.87  | 6.07 | 11.30| 10.43     |
|                          | $R_m$ 0.46 | 0.79 | 1.05 | 1.07      |
| 850°C                    | K 2.77  | 9.98 | 23.45| 30.29     |
|                          | $R_m$ 0.60 | 1.24 | 2.06 | 2.72      |
| 900°C                    | K 6.02  | 26.96| 43.13| 49.45     |
|                          | $R_m$ 1.08 | 3.31 | 4.44 | 6.67      |

Chart 3. Relationship between catalyst and $K$ and $R_m$

4.2. The extent of gasification temperature reduction
From chart 4, it can be seen that the time for the raw coal char to reach 50% conversion rate at 900°C is equal to the time for the coal char with 3% Fe and 3% Ca to reach 50% coal char conversion at 810°C and 780°C. The time when the composite catalyst with 1% Ca and 2% Fe reached 50% conversion at 800°C was identical to that the original char reached 50%. The effect of the composite catalyst is between the one-component Ca and Fe.
5. Conclusions

- On the self-built small fixed bed test bench, after the addition of a single-component catalyst or a composite catalyst, the coal gasification process has accelerated significantly. The catalytic effect of CaO on coal char gasification is stronger than that of Fe(NO$_3$)$_3$. And as the temperature increases, the catalytic gap between two single-component catalysts is shrinking. At 780°C gasification temperature, the vitality of the composite is lower than that of the one-component CaO. And the catalytic effect at 810°C gasification temperature is equivalent to that of one-component CaO. At 850°C and 900°C temperature, the one-component catalyst CaO has weaker catalytic strength than the composite catalyst, and as the gasification temperature rises, the gap becomes wider. It is showed that the catalytic performance of the composite catalyst is similar to that of the one-component Fe(NO$_3$)$_3$. Catalytic effect increases with increasing gasification temperature.

- After adding Fe(NO$_3$)$_3$, CaO and composite catalyst respectively, the gasification time of coal char is shortened by 85 min, 85 min and 103 min respectively, and the gasification temperature is reduced by 90°C, 120°C and 100°C respectively. The gasification temperature of the composite catalyst decreases is less than that of single-component CaO and is higher than that of Fe(NO$_3$)$_3$.

- The experimental data of the thesis is based on small experimental equipment. In the future, if large-scale industrial production can be achieved, the optimal actual blending ratio of catalyst and coal char and the gasification temperature and production efficiency that industrial equipment can withstand must be considered Improvement.

References

[1] Chen J W 2011 Proposal on medium/long term goal of carbon emission reduction strategy in china Science & Technology Review 29(15) 3

[2] Hao X W, Wang L and Wu J Z 2008 Progress of research on coal mild gasification Coal conversion 31(2) 83-89

[3] Zhu T Y, Zhang S Y, Huang J J and Wang Y 2000 Effect of calcium oxide on pyrolysis of coal in a fluidized bed Fuel 64 271-284

[4] Li X, Grace J R and Watkinson A P 2001 Equilibrium modeling of gasification: a free energy minimization approach and its application to a circulating fluidized bed coal gasifier Fuel 80 195-207

[5] Suzuki T, Inoue K and Watanabe Y 1989 Steam pulsed gasification of Na$_2$CO$_3$ or Fe(NO$_3$)$_3$ loaded yallourn coal char Fuel 68(5) 626-30
[6] Yasuo O and Kenji A 1997 A Highly active catalysts from inexpensive raw materials for coal gasification Catalysis Today 39 111-125
[7] Zhu T Y, Tang Z, Huang J J, Zhang J M and Wang Y 1999 Thermo-gravimetric study of coal mild gasification Journal of fuel chemistry and technology 27(5) 420-423
[8] Zhu Z 2002 Iron catalysts for CO$_2$ pulsed gasification of xianfeng brown coal char Journal of Fuel Chemistry and Technology 25(3) 222
[9] Asami K, Sears P, Furimsky E and Ohtsuka Y 1997 Gasification of brown coal and char with carbon dioxide in the presence of finely dispersed iron catalysts Fuel Processing Technology 47(2) 139-151
[10] Xie K C 2002 Coal structure and its reactivity Bei Jing: Science Press, 38(1) 289-359
[11] Zhang S Y, Lv J F and Wang W X 2004 Effect of heat treatment on the reactivity and microstructure of coal-char Journal of fuel chemistry and technology 32(6) 673-678
[12] Wang M M, Zhang J S Zhang S Y, Wu J H and Yue G X 2007 Effect of pyrolysis conditions on the structure and gasification reactivity of char Coal Conversion 30(3) 21-24
[13] Chen H W, Suo X L, Chen L, Yu W F and Huang X L 2012 Experimental Study on gasification of Jin Jie coal char with CO$_2$ catalysed by CaO and Fe(NO$_3$)$_3$ Journal of Chinese Society of Power Engineering 32(11) 885-890
[14] Xu X F, Cui H and Gu Y D 1996 The effect of demineralization on CO$_2$ gasification reactivity of iron, nickel-loaded chars Clean Coal Technology 2(4) 28-31