Experimental study on gasification of bituminous coal char with CO$_2$ catalysed by Fe (NO$_3$)$_3$

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Abstract. Effect of transition metal Fe (come from analytically pure Fe(NO$_3$)$_3$·9H$_2$O ) on Jin Jie coal char isothermal gasification by carbon dioxide in the condition of normal pressure is investigated in a self-built fixed bed reactor. Experimental results show that the gasification activity of Jin Jie coal char increases with the increment of Fe, and the loading saturation level of Fe is 3%. Adding 3% Fe can reduce the gasification temperature by 90°C, and shorten the coal char gasification time by 95 minutes. The higher the gasification temperature, the greater the increase in gasification activity factor $K$ and average gasification rate $R_m$. The parameter $K$ and $R_m$ reach the maximum at 3% catalyst addition at the same gasification temperature. Under a regime constant by chemical reaction, the reaction activation energy and the pre-exponential factor and reaction rate constant are calculated. The reaction rate constant of char loaded Fe increases around three times, and the activation energy constants with the raw char.

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. The addition of a catalyst in the coal gasification process can improve the gasification conditions, and the transition metal Fe is one of them. The acid waste contains a certain amount of Fe (NO$_3$)$_3$ in the steel industry and the titanium oxide manufacturing industry. Making full use of Fe (NO$_3$)$_3$, making it waste into treasure, and it not only eliminates the disposal cost of waste, but also Improves coal gasification conditions and promotes coal gasification. The results vary depending on the type of coal. Suzuki et al [4] used the impregnation method to uniformly mix the catalyst Fe (NO$_3$)$_3$ with the char sample, and studied the desorption properties of the coal char surface by TPD technique. The results show that the higher the Fe content in the coal char, the faster the gasification agent CO$_2$ in the coal char dissociation and adsorption speed of the surface, the faster the gasification reaction, and indirectly demonstrating that the presence of Fe can promote the oxygen exchange process during the catalytic gasification of coal char. When Yang and others [5] used the leaching method to study the vaporization of several metal-catalyzed brown coal char vapor, it was found that after adding the Fe Catalyst, the gasification activity of coal char was lower than that of raw coal char, but the gasification activity was higher than that of coal char after ash removal. It can be seen from this that the presence of Fe can promote coal gasification to a certain extent, but its catalytic effect is lower than that of the metal contained in coal ash. It is concluded that coal char added to the Fe series is more prone to
agglomeration and sintering inactivation than the original coal char during gasification process, and the catalytic action of metal elements in coal ash on coal gasification is weakened due to the inactivation of Fe catalyst [6].

Using bituminous coal from Jinjie in northern Shanxi Province as experimental coal sample, the catalytic effect of coal char-\(\text{CO}_2\) gasification is investigated by adding \(\text{Fe(NO}_3\}_3\) in different proportions. The relative kinetic parameters and the gasification rate constant are calculated by using homogeneous model as dynamic model. In addition, catalyst \(\text{Fe(NO}_3\}_3\) is added directly to raw coal without acid washing and ash treatment by immersion method to obtain coal char.

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 \(\text{N}_2\) and \(\text{CO}_2\) 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 \(\text{N}_2\) and \(\text{CO}_2\), respectively. \(\text{N}_2\) and \(\text{CO}_2\) are provided by \(\text{N}_2\) cylinders and \(\text{CO}_2\) 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 \(\text{N}_2\) 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 \(\text{warminutes}\), 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 \(\text{N}_2\) 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 \(\text{CO}_2\) atmosphere. After a certain period of constant temperature, the atmosphere is switched to a \(\text{N}_2\) 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.

In this study, pure \(\text{Fe(NO}_3\}_3\cdot9\text{H}_2\text{O}\) 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.

### Table 1. Coal quality analysis (%).

| Element Analysis, ad | Industry analysis, ad |
|---------------------|-----------------------|
| 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 figure 1, the char is made on the experimental device. The coking pressure is constant, and the gas N2 flow is 400 ml/min, and the average warming rate is 103°C/min. When the temperature is too low during the coking process, the remaining unreacted tar will block the coal char pores, hinder the transfer of the gasifier, and affect the gasification effect [7]. Higher coking temperature increases the order of carbon microstructure and decreases the ratio of carbon atoms in higher active edge layer to lower active graphite plane layer [8]. When the coking time is longer, it will increase the order of the coking structure, make the coking graphite, so that the micropores in the coking become narrower, and the area of coking surface that the gasifier can contact during the gasification process is reduced. The gasification activity of coking is reduced [9]. Therefore, in the study, the final temperature of coking is 800°C and the final temperature constant time is 8 minutes. For convenience, the raw coal char, impregnated char, and 1% Fe(Fe(NO3)3) char are respectively represented by raw-char, D-raw-char, and 1%-Fe-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. Eliminatesation of internal and external proliferation factors

The iron nitrate catalyst used in the experiment is decomposed into iron oxides during the process of coking [10]. Its catalytic mechanism is currently recognized as the mechanism of oxygen transfer:

\[ Fe_2O_3 + CO_2 \rightarrow Fe_2O_3(O) + CO \]  
\[ Fe_2O_3(O) + C_f \rightarrow Fe_2O_3(O) + C(O) \]  
\[ C(O) \rightarrow CO + C_f \]  

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 m0 is the initial coal char quality, mt is the coal char quality after t minutes of gasification, and m∞is the quality of the final ash.

In order to ensure that the gasification reaction is in the kinetic control stage of the intrinsic chemical reaction, the appropriate experimental conditions are first determined to eliminate the influence of internal and external diffusion factors during the gasification process. Therefore, preliminary tests are conducted at 850°C to determine the appropriate experimental conditions.

From figure 2, when maintaining a fixed bed with a CO2 flow of 400 ml/min and a particle size ≤62 μm, it is easy to know that with the reduction of coal char quality, the conversion rate of coal char increases at the same time. When the coal char mass is 0.2 g, the conversion rate curve of coal char no longer changes with the quality of coal char.
Figure 2. Change of the coal char conversion rate with coal coking quality.

From figure 3, maintaining the coal char mass 0.2 g, and a particle size ≤62 μm, and the coal char rate of different CO\textsubscript{2} flows coincides with the change of time.

From figure 4, when the coal char mass is 0.2 g and CO\textsubscript{2} flow is 400 ml/min, the particle size has little effect on coal Coke conversion rate.

In summary, the coal char mass of 0.2 g, the CO\textsubscript{2} flow of 400 ml/minutes, and the particle size≤62 μm are taken during the following gasification experiments. Under this condition, the conversion rate of coal char over time no longer depends on the coal char mass, CO\textsubscript{2} flow, and the particle size. This means that the effects of internal and external proliferation have been eliminated at this time.

3.2. Catalytic influence of catalyst on gasification of coal char

Figure 5 shows the gasification activity of catalyst Fe(NO\textsubscript{3})\textsubscript{3} at the gasification temperatures of 780°C, 810°C, 850°C and 900°C with the different added amounts of coal char. It can be seen that the gasification activity of coal char has been greatly improved after the addition of catalyst Fe(NO\textsubscript{3})\textsubscript{3},
and the gasification activity has gradually increased with the increase of catalyst addition. The catalyst load is saturated when the catalyst is added at 3%. After the catalyst is added above 3%, the gasification activity do not increase compared with 3%, and it is decreased at lower gasification temperatures (780°C, 810°C). At the same time, it can be seen from the figure that the gap of gasification activity of coal char under the different adding quantities is gradually narrowing with the increase of gasification temperature. This may be due to the fact that when the catalyst is added too much, it will block the transfer of the gasifier CO₂ to the coal char surface, and the degree of sintering of the catalyst will be increased accordingly when the gasification temperature rises, and the more the amount of addition, the more serious the sintering. At the same, element Fe is prone to S poisoning when catalyzing coal gasification as a catalyst, and the lower the gasification temperature, the more severe the poisoning. Increasing the gasification temperature will have a significant inhibitory effect on the poisoning of Fe element [7].

![Figure 5](image_url)

**Figure 5.** Effect of Fe(NO₃)₃ addition on the gasification characteristics of coal char at different gasification temperature.

Table 2 and figure 6 show the trends of gasification activity factor K and mean gasification rate Rm under the different gasification temperatures and catalyst addition. It can be seen that both K and Rm gradually increase in the amount of catalyst added and obtain a maximum value at 3%. At the same time, the K and Rm increase at the different gasification temperatures: at the gasification temperature of 780°C, compare to the K value of the non-catalyst, the largest increase in K after adding a catalyst are 1.53 times, and 2.24 times, 2.61 times, and 3.48 times at the other gasification temperatures.
Respectively, the increasing range increases gradually with the increase of gasification temperature. It is indicated that the higher gasification temperature is beneficial to the increase of maximum gasification activity of the coal char. At the gasification temperature of 780°C, the maximum value of the Rm is 0.68 times than that of the non-catalyst, and are 0.72 times, 1.07 times, and 2.06 times at the other gasification temperatures respectively. The higher the gasification temperature, the greater the increase, and it is indicated that the gasification temperature increase is also conducive to the entire process of gasification. At the same time, it is easy to know that the gasification activity of less catalyst addition is comparable to that of coal gasification at the optimal addition with the increase of the gasification temperature. It is indirectly indicated that the catalyst Fe(NO$_3$)$_3$ is prone to S poisoning at lower gasification temperature, and the increase of gasification temperature will inhibit the poisoning of catalyst.

| addition | gasification temperature | 0     | 1%    | 2%    | 3%    | 5%    |
|----------|--------------------------|-------|-------|-------|-------|-------|
| 780°C    | K×100                    | 1.33  | 2.45  | 2.65  | 3.37  | 2.65  |
|          | Rm                       | 0.37  | 0.54  | 0.52  | 0.62  | 0.56  |
| 810°C    | K×100                    | 1.87  | 3.82  | 4.50  | 6.07  | 4.22  |
|          | Rm                       | 0.46  | 0.65  | 0.70  | 0.79  | 0.69  |
| 850°C    | K×100                    | 2.77  | 8.19  | 9.32  | 9.98  | 9.66  |
|          | Rm                       | 0.60  | 1.06  | 1.18  | 1.24  | 1.23  |
| 900°C    | K×100                    | 6.02  | 18.63 | 25.78 | 26.96 | 27.8  |
|          | Rm                       | 1.08  | 2.49  | 3.19  | 3.31  | 3.42  |

Figure 6. Relationship curves of Fe(NO$_3$)$_3$ addition to K and Rm at different gasification temperatures.

3.3. Effect of catalyst on gasification temperature and time

It can be seen from figure 7 that the time for the coal char added 3% Fe to reach 50% conversion at 810°C is equal to the time for the original coal char to reach 50% conversion at 900°C, indicating that Fe can reduce the gasification temperature by 90°C. At the same time, it can be seen that the coal char conversion rate of adding 3% Fe at a temperature of 900°C to 95% requires 45 minutes, while the original coal char needs more than 130 minutes to achieve the same conversion rate.
3.4. Dynamic parameter calculation
The gasification reaction of coal char with CO\(_2\) is irreversible gas-solid reaction. The rate equation for gas-solid reactions in chemically dynamic controlled areas is generally expressed as [5]:

\[
\frac{dx}{dt} = k(1-x)^n
\]  \(\text{(5)}\)

When n equals 1, the gasification reaction is a primary homogeneous model. At the same time, the coal char particles are considered to be composed of evenly distributed small particles. The gasification reaction occurs simultaneously on the inner and outer surfaces of the particles [11]. Its integral expression is:

\[-\ln(1-x) = kt\]  \(\text{(6)}\)

The natural logarithm form of the Arrhenius formula is:

\[\ln k = \ln A - \frac{E}{RT}\]  \(\text{(7)}\)

In the study, when the homogeneous model is used as the kinetic model, the k-value of the reaction
rate constant and the correlation coefficient are calculated at the gasification temperatures of 780°C, 810°C, 850°C and 900°C, as shown in table 2. According to the k value calculated at different temperatures, the straight line shown in figure 8 is obtained by regression of formula 7, and the activation energy E (slope) and the pre-factor \( A(\text{truncation}) \) are calculated as shown in table 3.

Table 3. Gasification rate constant and correlation coefficient of coal char at the different gasification temperatures.

| Gasification temperature | Raw coal char k \( \times 10^3 \) | Correlation coefficient | Raw coal char added 3% Fe k \( \times 10^3 \) | Correlation coefficient |
|-------------------------|--------------------------|--------|--------------------------|--------|
| 780°C                   | 3.78                     | 0.9992 | 9.19                     | 0.9983 |
| 810°C                   | 5.43                     | 0.9995 | 14.09                    | 0.9989 |
| 850°C                   | 9.03                     | 0.9990 | 23.26                    | 0.9974 |
| 900°C                   | 21.6                     | 0.9979 | 56.88                    | 0.9995 |

Table 4. Kinetic parameters of the different coal chars.

| Kinetic parameters | Raw coal char E (kJ·mol\(^{-1}\)) | lnA | Coal char added 3% Fe E (kJ·mol\(^{-1}\)) | lnA |
|--------------------|-----------------------------------|-----|------------------------------------------|-----|
|                    | 155.6                             | 12.06 | 156.4                                    | 12.87 |

It can be seen from tables 3 and 4 that the correlation coefficients of the different coal chars under the homogeneous model are all greater than 0.99, indicating that the homogeneous model can describe the gasification process well. At the same time, it is easy to know that the same coal char gasification rate constant increases with the increase of gasification temperature. At the same gasification temperature, the gasification rate constant is greatly improved compared with the original coal char after adding the catalyst. After the addition of the catalyst, there is almost no change in the activation energy of gasification, indicating that the catalyst does not reduce the activation energy of gasification [12].

4. Conclusions
- The transition metal Fe has a load saturation of 3%. The time for coal char added 3% Fe to reach 50% conversion at 810°C is equal to the time for raw coal char to reach 50% conversion at 900°C. At the same time, the coal char conversion rate of adding 3% Fe at a temperature of 900°C to 95% needs 45 minutes, while the original coal char needs more than 130 minutes to achieve the same conversion rate. At 900°C gasification temperature, the gasification temperature plays a major role. At lower gasification temperatures, the influence of the catalyst gradually becomes the main factor.
- After adding the catalysts, the gasification activity factor K and the average gasification rate Rm of the coal char are different at the different gasification temperatures. The higher the gasification temperature, the greater the increase. And at the same gasification temperature, the gasification active factor K and the average gasification rate Rm reach a maximum at 3% of the catalyst addition amount.
- In the chemical reaction control area, the homogeneous model is used as the kinetic model to calculate the kinetic parameters. After adding the catalyst, the gasification reaction rate is nearly three times higher than that of the original coal char, and the gasification activation energy is basically unchanged.

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