Experimental study for the influence of Starch on Briquette Pyrolysis Characteristics

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Abstract. The influence of starch on the pyrolysis was studied from macro and micro angles. In this paper, briquette pyrolysis was operated with thermal analyzer. The experimental data showed that with the increase of starch content, the reaction rate was increased and the activation energy was decreased. The calorific value was improved in the briquette with starch. The starch does not change the oxygen-containing functional groups of the briquette, just increased the number of hydroxyl. And the specific surface area was increased, but the pore volume and the average pore size were decreased of briquette compared with the coal though the micropore morphology analysis.

Key words: binder; briquette gasification reaction; reaction activity; reaction rate.

1. Introduction
As people focus on improving energy efficiency and environmental protection, high efficiency and clean coal conversion and use more and more attention. Coal technology is an important clean coal technology, the state coal regarded as an effective way to promote energy conservation to be. The pulverized coal is processed into briquettes not only can reduce the use of lump coal resources insufficient contradiction, but also greatly reduce the use of the process of pulverized coal dust pollution. The lignite coal resources of lower coal rank coal is a high volatile, high moisture, high ash, low calorific value, low ash melting point of low-quality coal, is not conducive to transport and use. Lignite briquettes can be made to effectively improve its utilization. [1]

Present lignite coal technology mainly uses adhesive cold forming technology. Starch is often added to the composite binder as the main component of the binder to improve the mechanical strength of briquettes. Starch molecule contains a large number of alcoholic hydroxyl group, can promote the pyrolysis reaction briquette. Thermal processing of coal is one of the most important processes of coal processing. The research on the pyrolysis of briquettes is closely related to the thermal processing technology of briquettes. The research results obtained from the research on the pyrolysis of briquettes will directly guide the thermal processing of briquettes. Research results are the basis for coal gasification, coking and combustion applications. [2-3]

This paper will use the binder cold forming process to make the lignite into the briquette, with starch as the binder. Research the impact of starch on the processing of coal pyrolysis. And analysing the characteristics of coal pyrolysis reactor though the thermal gravimetric analysis, infrared analysis, pore analysis.
2. Experimental

2.1. Samples Collection and Preparation
The research selected lignite coal sample, using the national standard GB / T 212-2008 [4] way to test its industrial analysis and the results are shown in Table 1. Seen from the table, Maitreya lignite volatile, high moisture content, fixed carbon content is very low, as low-quality coal. Making lignite into the briquette, with the strach as the mainly binder. The mixture was made into the cylindrical briquette of diameter 35 mm, height 25 mm, at a pressure of 10 MPa. The weight of coal was about 30 g. All the briquette samples were preserved in sealed containers full of helium (He) to prevent undesired physical and chemical changes that were due to atmospheric oxidation. [5]

Table 1. Proximate analysis of Mile coal

| Proximate analysis/%(mass, adv) | M  | V  | A  | FC |
|--------------------------------|----|----|----|----|
| Proximate analysis/%(mass, adv) | 19.67 | 41.48 | 9.16 | 29.69 |

2.2. Pyrolysis experiment of briquette

Briquette pyrolysis were operated on a thermal analyzer (Model STA449F3, NETZSCH, German). Approximately 10 mg of dry coal sample was weighed and loaded into an open alumina crucible for each run. The sample was then heated to a final temperature of 900 °C at a fixed heating rate of 20 °C / min in a carbon dioxide atmosphere. Used the loading method in reference [1] to eliminate internal and external diffusion effects on briquette pyrolysis reactions. Got a coal pyrolysis DTG curve, as shown in Figure 1.

The pyrolysis temperature of peak corresponding shifts to the low temperature zone as the starch added seen from the figure. And the pyrolysis temperature of the peak corresponding with starch was less than the pyrolysis temperature without starch. The reason was that the gasification process is a complex process. Firstly, when the heat spread to the briquette surface, it occurred gasification reaction on briquette surface. The small molecules cleavaged and released, constantly. Since the pyrolysis rate of starch was faster than the coal, it had been occurred the coal pyrolysis reaction inside briquette. The weight loss rate of briquette with starch was faster. Therefore, the briquette pyrolysis of peak temperature was less than the coal pyrolysis peak temperature.
3. Results and discussion

3.1. Analysis of Pyrolysis Kinetic Parameters

It was assumed that the decomposition rate was equal to the precipitation rate of volatiles. According to the coal pyrolysis decomposition rate equation proposed by C.Y.W [6], the relationship between gas precipitation rate and concentration, which was shown in Equation (1).

\[ \frac{dx}{dt} = Ae^{-E/RT}(f - x) \]  

(1)

Where, \( f \) is the final conversion rate, %; \( x \) is the conversion rate at any time, %; \( A \) is the total coefficient of thermal decomposition rate, s\(^{-1}\); \( E \) is the total activation energy for thermal decomposition, KJ/mol.

Simplify Equation (1),

\[ \ln \frac{dx}{dt} = \ln[A(f - x)] - \frac{E}{RT} \]  

(2)

Fitting the straight lines of A and B. Pyrolysis kinetic parameters were shown in figure 2 and table 2.

| Samples     | \( T_{max}/^\circ C \) | \( A/\text{min}^{-1} \) | \( E_a/\text{KJ} \cdot \text{mol}^{-1} \) |
|-------------|-------------------------|--------------------------|---------------------------------|
| Raw coal    | 462                     | \( 1.880 \times 10^{-3} \) | 22.084                          |
| starch-5%   | 462                     | \( 1.463 \times 10^{-3} \) | 17.712                          |
| starch-8%   | 462                     | \( 1.109 \times 10^{-3} \) | 16.708                          |
| starch-15%  | 462                     | \( 1.082 \times 10^{-3} \) | 15.494                          |
| starch-18%  | 462                     | \( 1.506 \times 10^{-3} \) | 16.941                          |
| starch-20%  | 462                     | \( 1.776 \times 10^{-3} \) | 18.471                          |

With the addition of starch, the pyrolysis activation energy of the samples were decreased firstly and then increased, seen from the figure 2, which was shown that the addition of starch components has an...
impact on the pyrolysis process. As the amount of addition increased, the pyrolysis activation energy was lower and the promoting effect on the pyrolysis process was stronger, when the amount was less than 18%. However, when the starch content exceeds 18%, the pyrolysis activation energy was increased and the promotion effect was decreased. The excessive addition of starch was changed the pore structure of coal samples, in some extent. The small pores made the product less volatile and hindered the heating of the coal particles. Therefore, the addition of starch had an effect on the heat and mass transfer during the pyrolysis process and weakened the promotion effect.

3.2. Testing of briquette moisture, ash and low calorific value

Table 3. Moisture, ash and net calorific power of lignite after drying.

| Sample     | $M_{ad}$ | $A_{ad}$ | $Q_{net, ad}$ |
|------------|----------|----------|---------------|
| Raw coal   | 12.57    | 11.38    | 18.145        |
| starch-5%  | 11.33    | 10.78    | 20.483        |
| starch-8%  | 10.89    | 11.03    | 20.488        |
| starch-15% | 9.59     | 11.99    | 20.536        |

We must ensure the coal ash can not be increased, when choosing the type of binder, firstly, during the production process of the briquette. The heat of the briquette would be reduced by the excessive ash. And it would hinder the effluence of volatiles, reduce the briquette pyrolysis rate and thermal efficiency. Analysis the ash and calorific value of the samples based on the national testing standards. The results were shown in the table 3. The ash content was reduced and the calorific value was improved in the briquette with starch. The reason was that starch as an organic polymer increased the volatile content of the briquette and calorific value.

3.3. FTIR Analysis

Fig. 3 FTIR spectra of samples

The reason of increasing the briquette pyrolysis reaction rate was related to the briquette surface activity. Therefore, making a FTIR test of raw coal and briquette to measure the containing composition of oxygen-containing functional groups. The test was detected by TENSOR Model 37 Fourier Transform Infrared Spectrometer (FTIR) from BRUKER Spectroscopy, Germany. The measurement results shown in Figure 3. From the test results, Starch molecule contains a large number of hydroxyl groups (3400cm$^{-1}$). The briquette molecule has not the new functional group structure compared with the coal, which shown that the starch does not change the oxygen-containing functional groups of the briquette, just increased the number of hydroxyl.
3.4. Micropore Morphology Analysis

Table 4. Micropore Parameters of Samples

| Sample    | Specific Surface area(m²g⁻¹) | Pore Volume(cm³g⁻¹) | Average Pore Diameter(nm) |
|-----------|-------------------------------|--------------------|---------------------------|
| Raw coal  | 2.73                          | 0.0804             | 123.60                    |
| starch-5% | 9.214                         | 0.0774             | 104.33                    |
| starch-8% | 18.62                         | 0.0543             | 95.26                     |
| starch-15%| 23.35                         | 0.0511             | 79.97                     |

The ASAP 2020 system was also used for micropore morphology analysis. The micropore morphology of the coal sample was determined by CO₂ adsorption at 0 °C. The micropore surface area and volume were estimated using a Dubinin–Rudushkevich (D-R) model. The pore size distribution (PSD) was calculated using a nonlocal density functional theory (NLDFT) model. The results were shown in Table 4. The specific surface area was increased, but the pore volume and the average pore size were decreased of briquette compared with the coal.

The rich microporous structure was beneficial to the evenly distribution of the pyrolysis uniform temperature and improved the heat and mass transfer conditions in the fuel level. The pyrolysis volatilization rate was improved, thereby the rate of pyrolysis reactions was increased.

4. Conclusion

During the gasification reaction, the briquette has a better reactivity adding the starch. Starch increased the linear molecular structure of briquette and improve the react rate. Adding the binder made the DTG curve moved to the low temperature area during the gasification reaction. And the pyrolysis temperature of the peak corresponding in the briquette was lower than the coal. The starch does not change the oxygen-containing functional groups of the briquette, just increased the number of hydroxyl. And the specific surface area was increased, but the pore volume and the average pore size were decreased of briquette compared with the coal though the micropore morphology analysis.

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