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Influence of binder component on kinetics of briquette gasification

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Influence of binder component on kinetics of briquette gasification

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Abstract. The influence of PVA on the gasification was studied from macro and micro angles. In this paper, briquette gasificaition was operated with thermal analyzer. The experimental data showed that with the increase of binder content, the reaction rate increased and the reaction time and activation energy reduced. Starch and PVA increased the linear molecular structure of briquette and improved the reaction rate. CaO inhibited graphite process of briquette. The shrinking core model can better describe the gasification reaction of briquette-CO_2.

1. Introdution

The global energy consumption increased sharply and is predicted to continuously boost for the next 50 years, caused by the industrialization growth both in developed and developing countries [1].With the promotion of mechanization of coal mining, the proportion of pulverized coal which mined in coalmine is rising. Making the pulverized coal into briquettes is not only slow down the contradiction of inadequate lump resources, but also greatly reduce the pollution of fly ash produced the using of pulverized coal dust. May 10, 2013, the National Development and Reform Commission newly revised the "Guiding Catalogue of Industrial Structure Adjustment (2013 version)". The directory will clearly make the development and application of molding coal, coal-water slurry, and comprehensive utilization of coal gangue, slime and other low calorific value fuel into the encouraged projects[2].

The briquette gasification is the most efficient, clean and effective way. By means of the introduction of catalyst, the catalytic gasification of coal can significantly increase the rate of gasification[3]. But now, the study of chemical reactivity of briquette is less. And few studies of briquette gasification are reported in the literature. In this study, using the method of non-isothermal thermogravimetry to invest the effect of binder components on briquette gasification reaction in cold forming technology and research the behavior of briquette gasification kinetics. To provide a theoretical basis for the gasification optimization, the gasification reactor selection and the amplification for design. It is practical significant to the promotion of industrial briquette cleanse and gasification.

2. Experimental

2.1. Samples collection and preparation

In the study, we selected Yunnan lignite as coal sample. Proximate analysis were performed according to the China's Nation Standard GB / T 212-2008. The analysis results were shown in Table 1. Seen from the table 1, Yunnan lignite was the low-quality coal which had a high volatile and moisture content and a low fixed carbon content. A measured amount of coal and PVA were mixed in a home-made mixing beater. 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.[4]

Table 1. Proximate analysis of Mile coal.

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

2.2. Briquette gasification

Briquette gasification 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 heated from ambient temperature to 105 °C. Maintained isothermally after 20 min, 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. The volume flow rates of nitrogen and argon, as a protective gas, were 50 mL / min, respectively. Use the non-heated assay to determine the gasification reaction rate constants and activation energy. Used the loading method in reference[5] to eliminate internal and external diffusion effects on briquette gasification reactions.

The C conversion and coal conversion formula are shown in Equation (1-2).

$$X_C = \frac{m - m_t}{m - m_a} \tag{1}$$

$$x = \frac{m - m_t}{m} \tag{2}$$

Using the RS reactivity index which Takarada[6-7] proposed to describe the size of briquette gasification reactivity. The smaller the RS value, the better the gasification reaction;

$$R_s = \frac{0.5}{t_{0.5}} \tag{3}$$

Where, m is the quality of experimental briquette (g); m_t is a moment quality during coal gasification proceeds(g); m_a is the quality of the end of the reaction(g); $t_{0.5}$ is the time at the carbonation conversion reached 50%(min).

3. Results and discussion

3.1. Gasification reaction rate

Gradually, with new pores informed and closed-pores opened , the contacted active site of the carbon, the activity of the specific surface area and the reaction rate is increased at the beginning of the briquette gasification reaction. With pores crushed and solid particles depleted, the reaction surface area is decreased and the active site of the carbon is reduced, then the reaction rate decreases at the post-reaction[8]. In order to research the effect of binder content of each component on the briquette gasification reactivity, compared the influence of different binder on C conversion rate during briquette gasification. The curve of conversion with different amounts of starch, CaO, PVA at 900 °C,

N_2 atmosphere, and with CO_2 as gasification agent are shown in the figure 1. And the time are listed in Table 2 when the C conversion was 90%.
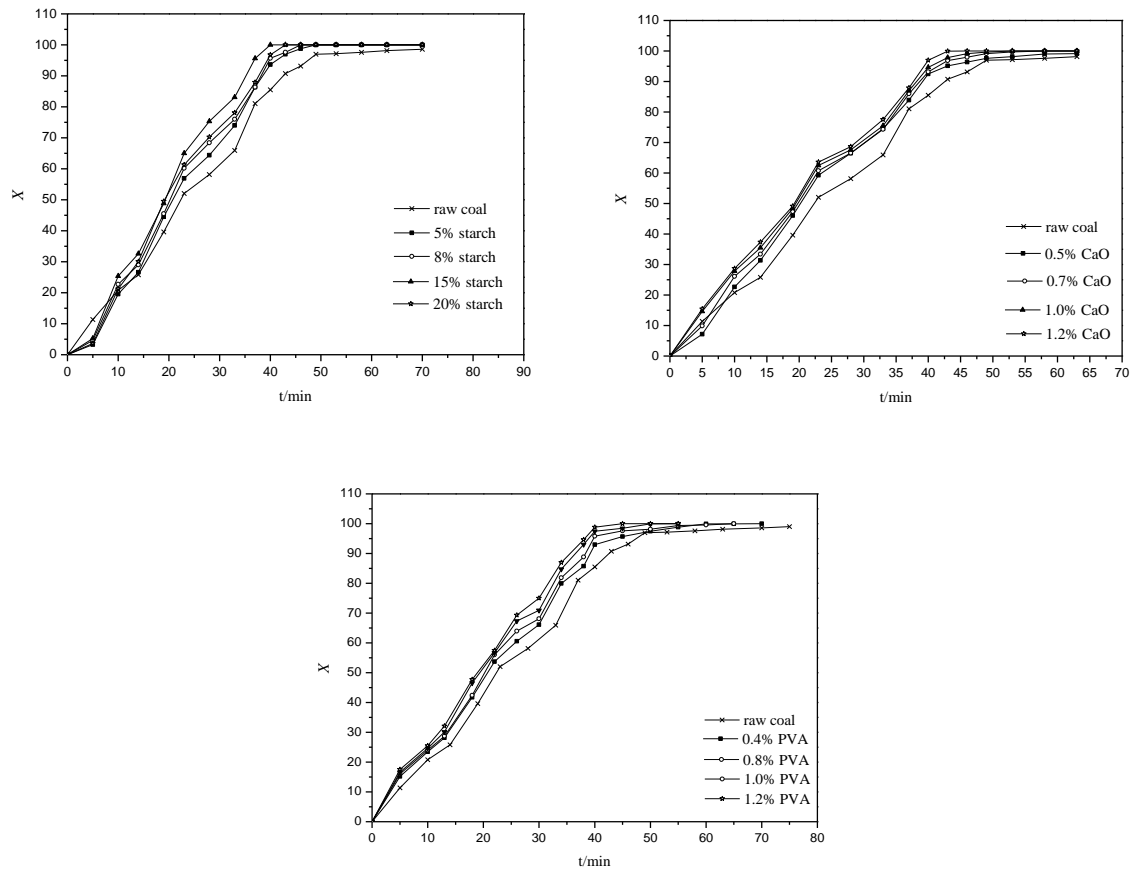

Figure 1. Conversion rate over time at 900°C.

Table 2. The reaction time at X_C=90%.

Sample	Time/min
Raw coal	42.58
5% starch	38.51
8% starch	38.17
15% starch	35.21
20% starch	37.63
0.5% CaO	39.42
0.7% CaO	38.68
1.0% CaO	38.19
1.2% CaO	37.70
0.4% PVA	39.17
0.8% PVA	38.33
1.0% PVA	36.55
1.2% PVA	35.59

It is reported that the gasification reactivity of samples adding a binder has a certain improvement, compared with raw coal seen from the figure 1. And the chemical reactivity is increased with the binder content increased. The raw coal reaction time required for 42.58 min when the C conversion rate is 90%. The reaction time is decreased with the binder content increased as can be seen from Table 2. The reason is that adding starch and PVA makes the linear molecular structure increased in briquette. Constantly, these straight-chain molecules which unstable thermally are cracking. Thereby it increases the rate and shorts the time of briquette gasification, effectively. CaO may be has a influence on carbon crystal structure during the pyrolysis stage. It increases the active site of the reaction interface and the activity surface area. The more the added binder content, the more favorable the pyrolysis reaction is, which is beneficial to the subsequent gasification reaction.
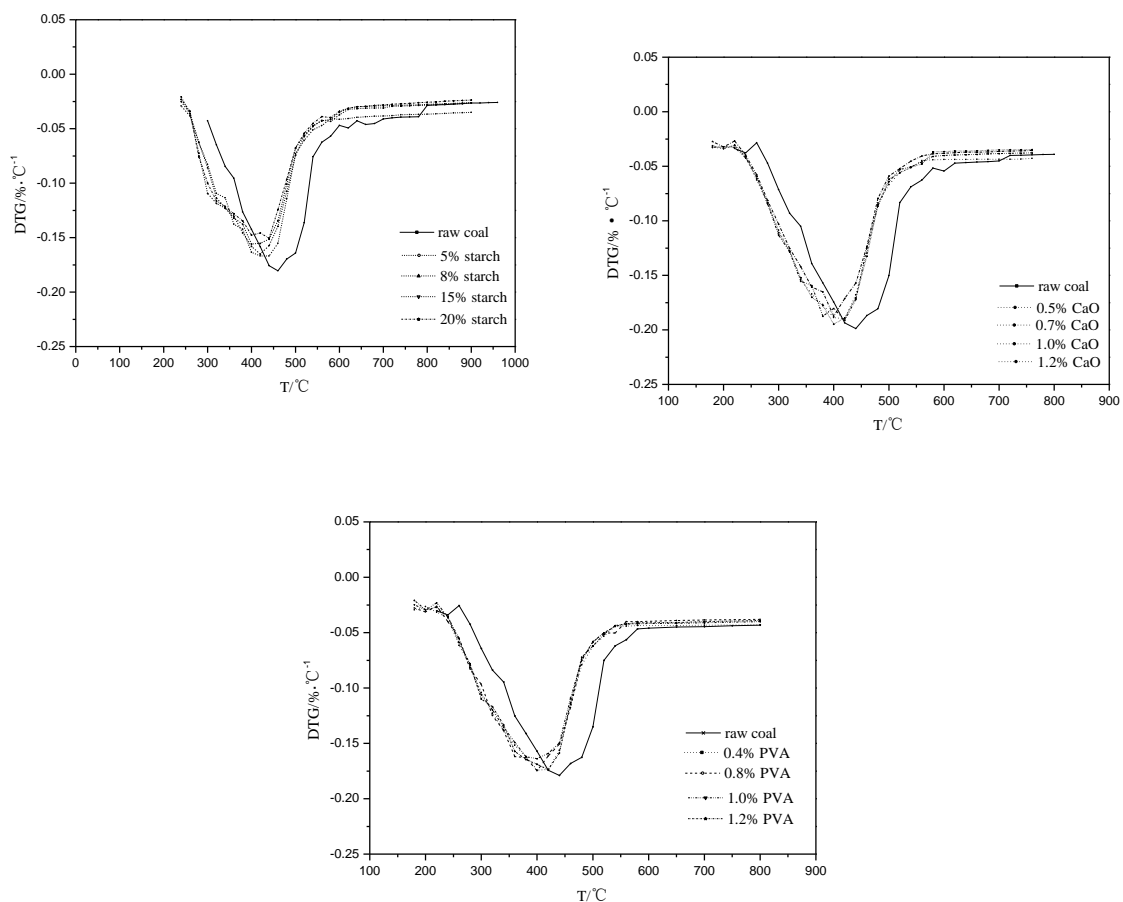
3.2. Gasification reactivity

Figure 2. DTG curves of gasification at 20°C·min^{-1}.

The gasification DTG under N_2 atmosphere and with CO_2 as gasifying agent is shown in figure 2. The gasification temperature of peak corresponding shifts to the low temperature zone as the binder added seen from the figure. And the gasification temperature of the peak corresponding is less than the pyrolysis temperature as the same content binder. The reason is that the gasification process is a complex process that gasification and pyrolysis reaction react at the same time. Firstly, when the heat and gasification agent spread to the briquette surface, it occurred gasification reaction on briquette surface. The small molecules cleavaged and released, constantly. Since the transfer rate of gasifying agent was less than the heat, primarily, it has been occurred the pyrolysis reaction inside briquette. As

the superposition reaction rate of gasification and pyrolysis was faster than the pyrolysis reaction rate alone, its weight loss rate is faster. Therefore, the gasification peak temperature was less than the pyrolysis peak temperature.

3.3. Gasification kinetic parameters

Coal will generate coke or semi-coke after pyrolysis and part of pyrolysis, at a certain temperature. It has occurred heterogeneous gas-solid reactions with the gasification agent (CO_2): $C + CO_2 = 2CO + Q$. Taking into the effect of briquette volume, simulate the type gasification kinetics using the shrinking core model[9]. It is assumed that the reaction gas cannot diffuse into the interior of the particle or it is consumed when it is not diffused into the particle. The reaction occurred only on the particle surface and push in one layer and layer.

Model expression is:

$$x = (1 - Kt)^3 \tag{4}$$

$$\frac{dx}{dt} = K(1-x)^{\frac{2}{3}} \tag{5}$$

As K and gasification agent concentration are related, the model can be rewritten as

$$\frac{dx}{dt} = k_0 y_{CO_2}^n \exp(-\frac{E_a}{RT})(1-x)^{2/3} \tag{6}$$

Where, K: reaction rate constant, min-1; k_0: pre-exponential factor, min-1; Ea: activation energy; n: gas partial pressure index; y_{CO_2}: CO_2 volume fraction. Gasification kinetics parameters can be obtained by fitting type gasification rate using the shrinking core model equation (6) as shown in Table 3.

Table 3. Kinetic parameters of samples at 900°C.

Sample	K/kJ·min^{-1}	E_a/kJ·mol^{-1}	K_0/min^{-1}	n
5% starch	0.121	62.75	4.775×10^{-4}	0.570
8% starch	0.129	58.18	3.095×10^{-3}	0.890
15% starch	0.166	49.74	2.954×10^{-3}	1.064
20% starch	0.142	75.48	2.88×10^{-4}	0.566
0.5% CaO	0.097	70.95	2.905×10^{-4}	0.731
0.7% CaO	0.114	66.21	3.850×10^{-4}	0.440
1.0% CaO	0.127	59.14	3.003×10^{-3}	0.871
1.2% CaO	0.129	58.69	3.777×10^{-3}	0.884
0.4% PVA	0.122	65.35	5.11×10^{-4}	0.59
0.8% PVA	0.127	61.58	1.178×10^{-3}	0.715
1.0% PVA	0.148	56.86	2.922×10^{-3}	0.82
1.2% PVA	0.151	44.78	0.03	1.168

With the content of the binder is added, the reaction rate constant is increased, but the activation energy is reduced at the same gasification temperature, as can be seen from Table 3. It is indicating that the binder has a catalytic effect on the gasification reaction. The reaction constant of the 20% starch coal is less than the 18% starch sample, but its activation energy is large. To research the reason, I analysis briquette pore and pore specific surface area between the 15% starch sample and 20% starch sample. The results are shown in Table 4.

Derived from Table 4, the pore volume and average pore diameter of 20% starch sample is smaller than 15% starch sample. It proved that too much binder content will cover the surface of briquette, blockage the briquette pore, and obstruct type gasification.

Table 4. Properties of the 15% starch sample and 20% starch sample.

Sample	Pore Volume /cc·g^{-1}	Surface area /m^2·g^{-1}	Average Pore Diameter/nm
15% starch sample	0.0614	23.02	103.6
20% starch sample	0.0501	25.35	84.97

4. Conclusions

(1) During the gasification reaction, the briquette has a better reactivity adding the binder. Starch and PVA increase the linear molecular structure of briquette and improve the react rate. CaO inhibits graphite process of briquette, which slows down the more orderly trend of carbon crystal structure in briquette. And it increases the active site and the activity of the specific surface area of the reaction interface. So that the briquette has a better reactivity.

(2) The binder makes DTG curve move to the low temperature area during the gasification reaction. And the gasification temperature of the peak corresponding was less than the pyrolysis temperature as the same binder content. This is because that the briquette gasification reaction is the result of the combination of pyrolysis and gasification. It has a faster weight loss rate than the individual pyrolysis.

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