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Prediction of remnant volatile matter in the semicokes from coal partial gasification

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The semicokes from different coals were prepared under various temperatures by partial gasification method in a fixed bed. According to the analysis of the V_{daf} in the coals and semicokes, a new method is presented to predict the content of remnant volatile matter in the semicokes from coal partial gasification. The two fuel character indexes *FV* and *FC* were introduced to symbolize the second volatilized temperature and the fully volatilized temperature respectively. Then according to the proximate and ultimate analysis data of raw coal, the content of V_{daf} in the semicokes prepared under various temperatures can be predicted.

partial gasification, semicokes, content of volatile matter

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1 Introduction

As one of the advanced clean coal technologies, the integration technology of coal partial gasification and combustion has attracted many researchers [1–3]. According to the different characteristics of different constituents in raw coals during various thermal conversion processes, this technology utilizes the coals in another way. The volatile matter in coal is volatilized to generate gas under lower temperature and used as gaseous/liquid fuels or chemical materials. The solid residues called semicokes are mainly used as fuel in the combustion chamber to generate thermal energy. Therefore, it can improve the global energy utilization efficiency and protect the environment by reducing the pollution emissions. Many researchers have investigated the partial gasification properties of coals and the combustion characteristics of semicokes [4–7]. Some useful conclusions have been achieved.

When coals were heated, the moisture in the coals firstly vaporized. Then the volatile matter would be released. Many researchers have investigated the pyrolysis characteristics of volatile such as the release rate, the volatile constituents and general rules. Some useful models were introduced to describe the behavior of the volatile matter pyrolysis such as single equation model, double equation model, distributed activate energy model, Fu-Zhang general model and FG-DVC general model of Solomon [8, 9] and so on.

Some researchers used the following Gregory-Littlejohn relation [10] to describe the release behavior of volatile matter heated at the slow heating rate (1–10°C):

$$W_v = 3.162 \times \frac{10^9}{t^{3.914}},$$

where W_v was the released volatile of raw coal per mass on dry ash free basis and t was the final heating temperature.

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This formula was mainly adapted to the final heating temperature above 500°C. From the above expression, it can be seen that the release properties of volatile under slow heating rate were mainly related with the heating temperature. When the coals were heated at the fast heating rate, Fu [8] suggested that the empirical rule to calculate the maximum volatile production was still mainly related with the volatile content in raw coal and the final heating temperature although it had been affected by many factors such as coal types, heating conditions and particle diameters.

As the solid residues of coal partial gasification, the physical and chemical properties of semicokes were very different from the raw coals and cokes, especially the content of volatile matter in the semicokes. Some studies showed that the content of volatile matter in semicokes prepared from high volatile bituminous coal was as high as to 7%–8% or so. At present, the study on the content of remnant volatile matter in semicokes was not enough and the relating literature was not easily found. So it is very necessary to investigate the content of remnant volatile matter in semicokes from all kinds of coals.

In order to investigate the relation between the content of volatile matter in semicokes and the final heating temperature, firstly 16 semicokes from four raw coals were prepared in a small fixed bed under various final heating temperatures. Then the proximate analysis and ultimate analysis of semicokes were accurately made according to the national standards of China. At last, the relationship between V_{daf} in semicokes and the final heating temperature was carefully studied. Here what we considered was only slow and moderate heating rates, and the fast and flash heating rates were not considered. Because of the limitation of heating method and resource, the heating rate of coal partial gasification was usually slow and moderate.

2 Experiments

Three bituminous coals (Shenmu, Datong and Rizhao) and Beijing anthracite were selected to prepare semicokes. The mass of coals heated in the small fixed bed was 40 g or so and the average diameter was 0.9–5.0 mm. The small fixed bed was heated by electricity at a heating rate of 15 K min^{-1}. When the temperature of the particles measured by the thermocouples reached the preparation temperature, the heating stopped. The temperature of the particles was lowered to the ambient temperature after the constant temperature was kept for 30 min or so. Then the semicokes particles were collected and triturated to the average diameter of 0.18–0.30 mm used as the experimental samples. The proximate analysis and ultimate analysis of the samples were accurately made by the national standards of China (GB/T 212-2001). The proximate analysis data of raw coals and semicokes based on the air dry base were listed in Table 1.

3 Results and discussion

The pyrolysis process of coals under slow and moderate heating rates can be classified into two stages [12]. The main constituents such as tar and high molecule species were volatilized in the first stage under 600°C or so. During the second stage, the small molecule such as H_2 was volatilized and kept a longer time than the first stage. So the pyrolysis process was deeply related with the constituents in the raw coals and the final heating temperature. In order to describe the new method to predict the content of remnant volatile matter in semicokes from coal partial gasification, the proximate analysis and ultimate analysis data were investigated carefully. Then two fuel character indexes were introduced: the fuel volatile character index *FV* and the fuel coke character index *FC*. They can be defined as follows:

$$FV = [C_{0\mathrm{daf}} + 0.3S_{0\mathrm{daf}} + 4\times(H_{0\mathrm{daf}} - O_{0\mathrm{daf}}/8)]\times\frac{V_{0\mathrm{daf}}}{100}, \quad (1)$$

$$FC = [C_{0\mathrm{daf}} + 4\times(H_{0\mathrm{daf}} - O_{0\mathrm{daf}}/8)]\times\frac{100 - V_{0\mathrm{daf}}}{100}, \quad (2)$$

Table 1 Proximate analysis of coal and semicokes (%)

Fuel	Rizhao	500°C	600°C	700°C	800°C	Beijing	500°C	600°C	700°C	800°C
M (%)	0.42	0.24	0.38	0.17	0.27	1.04	0.24	0.17	0.35	0.54
A (%)	20.31	21.14	22.08	22.81	23.62	24.74	25.87	26.15	26.24	26.58
V (%)	18.19	10.42	9.05	7.09	4.53	7.81	5.97	5.19	4.33	2.97
FC (%)	61.08	68.2	68.49	69.93	71.58	66.41	67.92	68.49	69.08	69.91
Fuel	Shenmu	500°C	600°C	700°C	800°C	Datong	500°C	600°C	700°C	800°C
M (%)	6.88	0.48	0.46	0.36	0.37	3.62	0.85	0.41	0.32	0.53
A (%)	8.53	10.96	11.72	12.36	13.05	16.09	19.88	20.58	21.58	21.78
V (%)	27.6	15.18	12.47	9.76	5.68	26.48	10.27	9.45	6.21	5.22
FC (%)	56.99	73.38	75.35	77.52	80.9	53.81	69.00	69.56	71.89	72.47

where C_{0daf}, H_{0daf}, S_{0daf}, O_{0daf} and V_{0daf} are the contents of the elements C, H, S, O and volatile matter in raw coal on the dry ash free basis. The fuel volatile character index *FV* can be used to symbolize the character temperature that presents the beginning temperature of the second volatilization stage. The higher value of *FV* symbolized the lower second volatilization temperature. The fuel coke character index *FC* can be used to symbolize the character temperature for the ending of the full volatilization. The higher value of *FC* symbolized the higher full volatilization temperature.

Then t_s was defined as the second volatilized temperature to symbolize the character temperature for the beginning of the second volatilization stage. Here we assume the temperature corresponding to V_{daf} =1/3V_{0daf} was the second volatilized temperature. The relation curve between t_s and *FV* was shown in Figure 1 based on the experimental data and accordingly, the following expression can be drawn:

$$t_s = 1008.31 - 14.74 \times FV. \tag{3}$$

It showed that the relationship between t_s and *FV* was linear.

At the same time t_m was used to symbolize the character temperature for the ending of the full volatilization. Here we assume the temperature corresponding to V_{daf}=0 was the fully volatilized temperature. The relation curve between t_m and *FC* was shown in Figure 2 and the following relational expression can be obtained:

$$t_m = 657.4403 + 5.2563 \times FC. \tag{4}$$

It showed that the relationship between t_m and *FC* was also linear.

Thus substituting the proximate and ultimate analysis data of raw coals into eqs. (1) and (2), we can get the values of the two fuel indexes *FV* and *FC*. Then substituting the values of *FV* and *FC* into eqs. (3) and (4), the values of t_s and t_m can be calculated.

At last two dimensionless parameters y_v and θ were introduced to predict the remnant volatile in semicokes. They can be defined as

$$y_v = \frac{V_{daf}}{V_{0daf}},$$

$$\theta = \frac{t_m - t}{t_m - t_s},$$

where V_{daf} and V_{0daf} were the contents of volatile in the semicokes and raw coals respectively, t was the final heating temperature and t_s and t_m were the second volatilized temperature and the fully volatilized temperature respectively, θ was the dimensionless temperature.

By analyzing the experimental data, the relation between y_v and θ can be expressed as

$$y_v = 0.0091 + 33.3177\theta. \tag{5}$$

The relation curve between y_v and θ was shown in Figure 3.

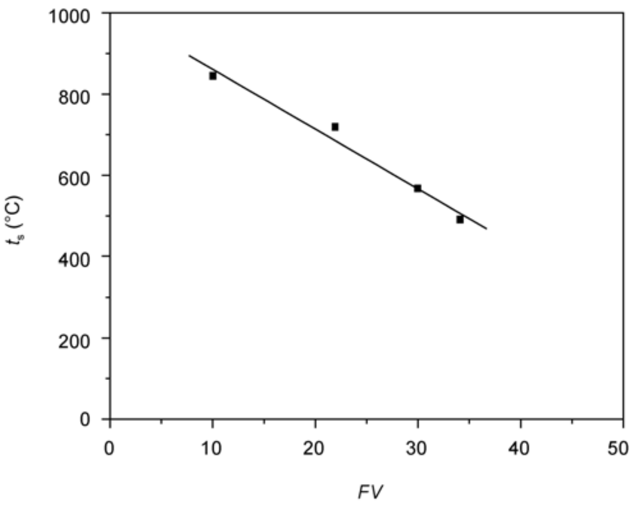

Figure 1 Relation between t_s and *FV*.

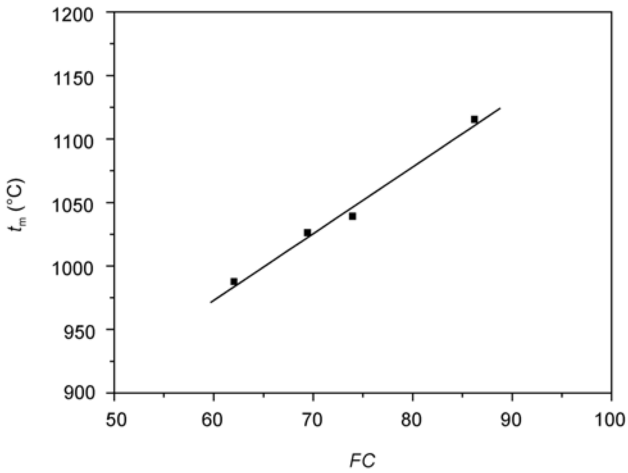

Figure 2 Relation between t_m and *FC*.

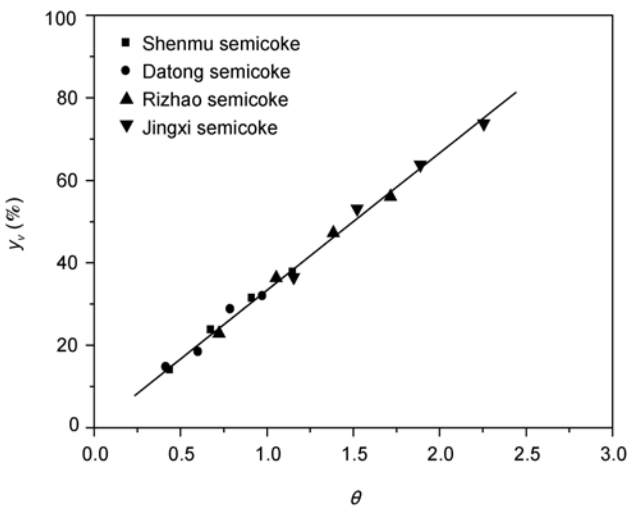

Figure 3 Relation between y_v and θ of semicokes from experiment.

It can be seen that the relation between y_v and θ was well linear.

Above all, the content of remnant volatile matter V_{daf} in the semicokes prepared under temperature t can be predicted by eq. (5). This formula was adapted to the slow and moderate heating rate and the final heating temperature higher than 500°C. Usually the heating rates of coal partial gasification was slow and moderate and the final heating temperature was above 500°C, so eq. (5) was very well adapted to predicting the content of remnant volatile matter V_{daf} in the semicokes prepared under various temperatures from partial gasification of different types of coals.

Figure 4 shows the relation between y_v and θ of semicokes from other experiments prepared under different final heating temperatures. From this figure it can be seen that the calculating values of the content volatile matter in semicokes were well agreed with the results measured by experiments. The semicokes of ref. [13] were prepared by Shenmu Binxian and Wangfeng raw coals in a small fixed bed with N_2 atmosphere at a heating rate of 10 K min^{-1}. The content of remnant volatile matter in semicokes was very low because the final heating temperature was so high as to 900°C. The semicokes of ref. [14] were heated in a crucible with a lid by electric furnace and the final heating temperature was 550°C, 600°C, 650°C, and 700°C. The content of volatile was also very low because of the fast heating rate. The semicokes of ref. [15] came from Shenmu, Datong, Dongshan and Yangcheng raw coals heated in a high-pressure reactor with Ar atmosphere and the final heating temperature was 500°C and 550°C. It can be seen that the y_v of semicokes from Yangcheng anthracite was higher than other semicokes because the content of volatile in Yangcheng anthracite was very low. During the heating process little volatile matter could be released. The semicokes of ref. [16] were prepared by Spanish Sovilla semi-anthracite with N_2 atmosphere at the heating rate of 60 K min^{-1}. The semi- cokes of refs. [17, 18] came from Spanish ML, TU, American Q1, and Australian Q2 bituminous coals heated to 850°C with N_2 atmosphere at the heating rate of 60 K min^{-1}. From Figure 4 it can be found that the relation between y_v and θ of different semicokes prepared by different researchers with similar methods was well linear and agreed with the calculating results. Therefore, eq. (5) was very well adapted to predicting the content remnant volatile in semicokes from different coals and it was adapted to not only Chinese coals but also foreign coals.

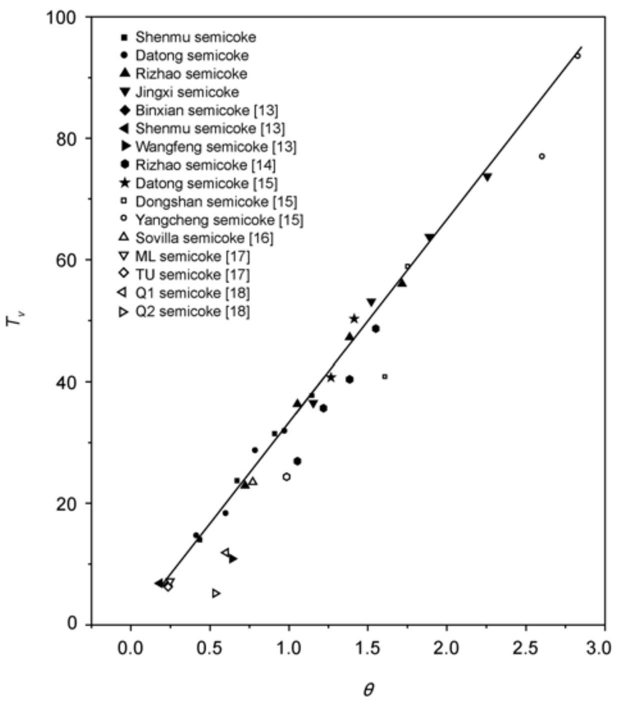

Figure 4 Relation between y_v and θ of semicokes from literatures.

4 Conclusion

In this paper, a new prediction method of the V_{daf} content in the semicokes prepared under various temperatures was described according to the analysis of the V_{daf} in raw coals and semicokes from different preparation temperatures. Two fuel character indexes FV and FC were introduced to symbolize the second volatilized temperature t_s and the fully volatilized temperature t_m respectively. Then the t_s and t_m can be calculated by the proximate analysis and ultimate analysis data of raw coals according to eqs. (3) and (4). Thus, the content of V_{daf} in semicokes can be predicted by eq. (5). The calculating results agree well with the experimental results from the other literatures. It is proved that eq. (5) was very adapted to the prediction of the content of remnant volatile matter V_{daf} in semicokes from coal partial gasification.

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