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动力技术

采用 TG-FTIR 联用研究烟煤热解及热解动力学参数的确定

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摘 要 研究煤热解时的组分析出规律对进一步研究低 NO 燃烧或煤粉再燃时的均相 NO_x 还原反应来说都是非常重要的。采用 TG-FTIR 实验装置对两种中国烟煤在不同升温速率(10,20,50 和 80 ℃/min)下的失重及气体释放规律进行了研究,并将实验数据与 FG-DVC 软件的模拟结果进行了对比。通过对比发现,其中一种烟煤的模拟结果与实验数据比较相符,但另一种烟煤的模拟结果与实验数据偏差较大。偏差主要是由于 FG-DVC 模型中提供的有关动力学参数不准确所导致。基于FG-DVC 模型的假设,官能团热解形成的轻气体产物的释放过程可以用一系列平行独立的单方程模型描述,应用 FTIR 的实验结果对热解气体组分的动力学参数进行了修正。采用修正后的动力学参数,FG-DVC 能更准确的模拟该煤的热解过程。

关键词 煤热解 TG-FTIR 动力学参数 FG-DVC

中图法分类号 TK16; **文献标志码** A

The evolution of volatile species during pyrolysis has a significant effect on coal combustion and formation and reduction of pollutant emissions[1,2]. Since 1970, some kinetic models such as single equation model, two-equation model, and Solomon's general model etc have been presented in order to simulate the pyrolysis more reasonably. Solomon[3] researched the slow pyrolysis process for several American coals, obtained some kinetic parameters for gas evolution parameters for gas evolution and developed a general model called FG-DVC to simulate the pyrolysis process. This model takes account of the evolution of gases, tar, char and adsorbed molecular in detail. The FG-DVC model combines two models, one is the Functional Group (FG) model and the other one is the Depolymerization, Vaporization, Cross-linking (DVC) model. The FG model is used to simulate the gas evolution and the elemental and functional group compositions of the tar and char. The DVC model is employed to determine the amount and molecular weight of macromolecular fragments. The lightest of these fragments evolve as tar. Nine well-characterized coals were selected to form an FG-DVC data base. The minimum input to the FG-DVC model provided by the user is the ultimate analysis of coal on dry ash free basis. If the H/C and O/C atomic ratios for the interested coal fall into the grid of FG-DVC coal data base a pre-processor subroutine will generate the FG-DVC needed input files for the interested coal. Although the parameters used in FG-DVC code were determined by slow pyrolysis process, Solomon *et al* have compared the measured data with the FG-DVC model predictions and found the model can accurately simulate the process of rapid pyrolysis under the condition of American coal[4,5]. Because of the difference between the American coals and the Chinese coals, the kinetic parameters for many Chinese coals usually can't be derived directly from the interpolation scheme based on the data base. Instead, the kinetic parameters of the most closed coal to the Chinese coal in the van Krevelen

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diagram (a plot of H/C versus O/C atomic ratios) were used to simulate and error will be observed. However, there is seldom study on the quantitatively analysis of the gas evolution for domestic coals using TG-FTIR[6,7]. The aim of this work is to quantitatively analyze the pyrolysis process for two Chinese coals and to determine the kinetic parameters related to the main species for the coal which can't be simulate reasonably by FG-DVC code.

1 Experimental

1.1 Coal samples

Two bituminous coals, Zhunger coal and Shenhua coal, were dryinged at 50 ℃ for (4 ~ 5) h and then grinding with carnelian mortar before experiment. The coal analysis of samples was shown in table 1.

Tab. 1 The proximate and ultimate analysis of coal samples

	Proximate analysis /wt%				Ultimate analysis/wt%				
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}
Zhunger coal	2.75	21.82	28.28	47.15	77.41	5.04	15.50	1.50	0.55
Shenhua coal	5.71	10.53	27.75	56.01	80.64	4.85	12.50	1.43	0.58

1.2 TG-FTIR experiment

The pyrolysis of coal was performed at a thermogravimetric analyzer (TGA/SDTA851^e) coupling with FTIR (Nicolet 5 700). The pyrolysis conditions were as follows: coal sample weight, 50 mg; gas atmosphere, N_2; pressure, 0.1 MPa; total gas flow through the furnace, 150 mL/min. After purging, the sample was heated from room temperature to 105 ℃ (at 10 ℃/min) for 20 min to dry it and then to 900 ℃ for 20 min (at 10 ℃ /min, 20 ℃ /min, 50 ℃ /min and 80℃ /min respectively). At the same time, the volatile species were introduced to FTIR for qualitative or quantitative analysis. In order to make the quantitative analysis, the gas cell must be calibrated for interested gas species. A gas mixture of CH_4/CO/CO_2/N_2 with known concentration was mixed with N_2 and then entered into the gas cell. The species concentration in the gas cell was changed by changing the mixing ratio (gas mixture to N_2). A method was then established through polynomial fitting the known concentration.

2 Kinetic Model

According to the FG-DVC model, the evolution of each species is assumed to be independent from the other species and the evolution rate can be represented by a first-order rate with a Gaussian distribution of activation energies[8]. The assumed first-order reaction rate for release of the ith functional group (X_i, also called precursor pool in the FG-DVC input files) can be expressed as following equation shown:

$$\frac{dX_i}{dt} = -k_i X_i \tag{1}$$

And the rate constant k_i in eq. (1) is given by an Arrhenius expression with a Gaussian distribution of activation energies:

$$k_i = A_i \exp((-E_i \pm \sigma_i)/RT)) \tag{2}$$

Where A_i is the pre – exponential factor, E_i is the average active energy, σ_i is the width of the Gaussian distribution and R is the gas constant. A non – isothermal method is used to obtain the kinetic parameters[9—13]. As the coal sample is heated at a constant heating rate H:

$$H = \frac{dT}{dt} \tag{3}$$

then the eq. (1) can be transformed to:

$$\frac{dX_i}{dT} = -\frac{k_i X_i}{H} \tag{4}$$

At the temperature (T_{max}) at which the rate of species evolution reaches a maximum, the temperature derivative of evolution rate should equal to zero, *i. e.*

$$\frac{\mathrm{d}\left(\frac{\mathrm{d}X_i}{\mathrm{d}t}\right)}{\mathrm{d}T}=0,\ \text{at}\ T=T_{\max} \tag{5}$$

Eq. (5) can be rewritten to the following form by substituting eq. (1) and eq. (2) into eq. (5):

$$\frac{\mathrm{d}\left(\frac{\mathrm{d}X_i}{\mathrm{d}t}\right)}{\mathrm{d}T} = -k_i\frac{\mathrm{d}X_i}{\mathrm{d}T}-X_i\frac{\mathrm{d}k_i}{\mathrm{d}T} = -k_iX_i\left[\frac{E_i}{RT_{\max}^2}-A_i\exp\left(-\frac{E_i}{RT_{\max}}\right)/H\right] = 0\ at\ T=T_{max} \tag{6}$$

The equality holds if and only if the term in the square brackets equals to zero, *i. e.*

$$\ln\left(\frac{H}{T_{\max}^2}\right)=\ln\left(\frac{A_iR}{E_i}\right)-\frac{E_i}{RT_{\max}} \tag{7}$$

It can be found from eq. (7) that the $\ln\left(\frac{H}{T_{\max}^2}\right)$ is liner variation with $\frac{1}{T_{\max}}$. After the evolution rates for each species at different heating rates are measured through experiment, the kinetic parameters then can be determined from the slope and the intercept in eq. (7). After A_i and E_i are determined, σ_i and Y_i can be fitted to experimental data using a trial-and-error approach.

3 Results and Discussion

3.1 Thermogravimetric characteristic

The TG/DTG curves and simulated weight loss by FG – DVC code of Zhunger coal and Shenhua coal during pyrolysis were presented in figure 1 and figure 2.

The weight loss was increased as temperature goes up. After pyrolysis finished, Zhunger coal had higher WL_{ex} than Shenhua coal, as shown in table 2. This may be caused by higher V_{daf} in Zhunger coal. Meanwhile, from the DTG curves, the $R_{\max}$ and $T_{\max}$ could be obtained, as shown in table 2.

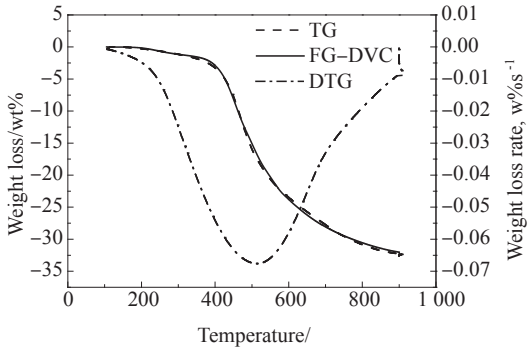

Fig. 1 TG/DTG and simulated weight loss curves of Zhunger coal at 50 ℃/min

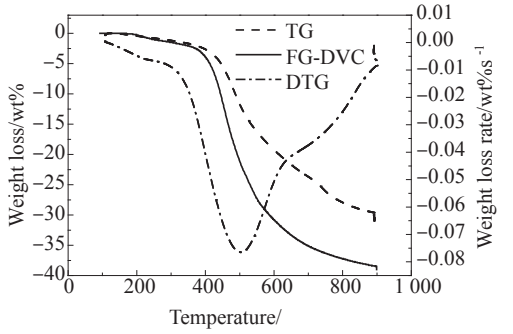

Fig. 2 TG/DTG and simulated weight loss curves of Shenhua coal at 50 ℃/min

Tab. 2 The characteristic parameters of coal samples

Sample	$R_{\max}$/(10^{-2}w% s^{-1})	$T_{\max}$/(℃)	WL_{ex}/(wt%)	WL_{ca}/(wt%)
Zhunger	-6.76	513	-32.62	-32.54
Shenhua	-7.65	503	-31.11	-39

Shenhua coal had higher $R_{\max}$ and lower $T_{\max}$. This meant that the active energy for Shenhua coal was small and the weak aliphatic chains were more than Zhunger. The final weight loss calculated by FG-DVC (WL_{ca}) also contained in table 2. From figure1, figure 2 and table 2, it was found that the calculation error for Zhunger coal was very small, but the difference between TG curve and FG-DVC curve for Shenhua was obvious and the error was around 10%. The coordinates of the two coals in the van Krevelen diagram were shown in figure 3. It can be seen from the figure 3 that

the Zhunger coal coordinates in the van Krevelen diagram fall into the grid of library-coal data, while the Shenhua coal coordinates are far from the grid. So the FG-DVC input files for the Zhunger coal can be generated by means of an interpolation scheme which is based on the three surrounding coals database. And the input files for Shenhua coal are generated based on the library coal most closely located in the van Krevelen diagram. As the parameters in the input files are not accuracy, the calculation error for Shenhua coal was bigger. The following section will focus on the evolution of gases for Shenhua coal in order to modify the kinetic parameters in the input files and improve the simulation results eventually.

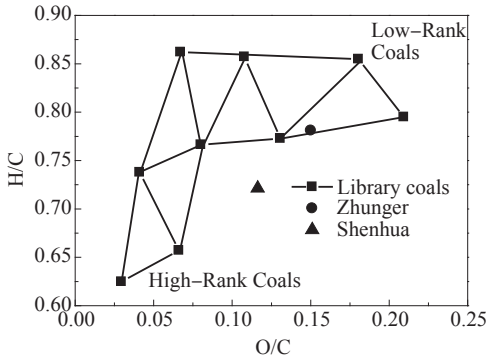

Fig. 3　The van Krevelen diagram for two bituminious coals and the library coals of the FG-DVC code

3.2　Evolution characteristic of gases

The variation of gas evolution with temperature at different heating rates could be seen from figure 4 to figure 6. For 10 ℃/min, evolution of CO_2 started at about 180℃, and reached the first maximum at about 457℃ and then reached the second maximum around 716℃. The first peak appeared due to the decomposition of carboxyl functional group. The second peak at higher temperature was caused by more stable function group such as ether. It was also found that the second peak was more important than the first peak except 80℃/min curve. The T_{max} for both peaks at different heating rate were shown in table 3. The T_{max} was higher with higher heating rates. This was caused by the more difference between coal sample and thermocouple with higher heating rate. The width of temperature related to CO_2 evolution also became bigger with the heating rate increased. This was caused by deeper overlapping degree with higher heating rate.

The evolution curves of CH_4 at different heating rate were shown in figure 5. Formation of CH_4 started at about 340 ℃ and reached the maximum evolution at about 525 ℃, 556 ℃ and 577 ℃ for 20 ℃ /min, 50 ℃/min and 80 ℃/min respectively. The formation of CH_4 finished at the end of the liner heating step and no obvious formation of CH_4 was found during temperature

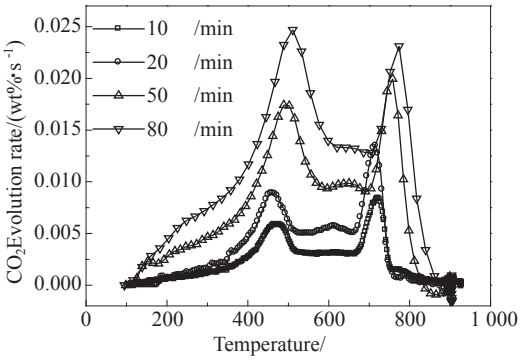

Fig. 4 Evolution rate curves of CO_2 during pyrolysis for Shenhua coal sample at different heating rates

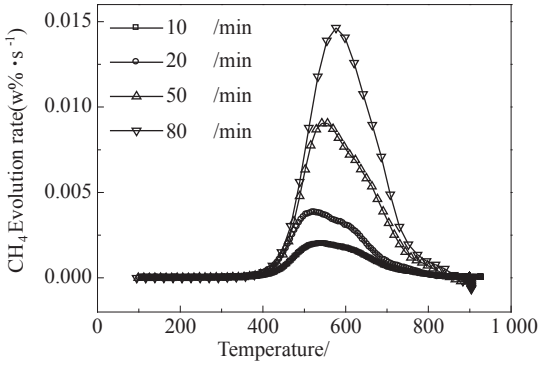

Fig. 5 Evolution rate curves of CH_4 during pyrolysis for Shenhua coal sample at different heating rates

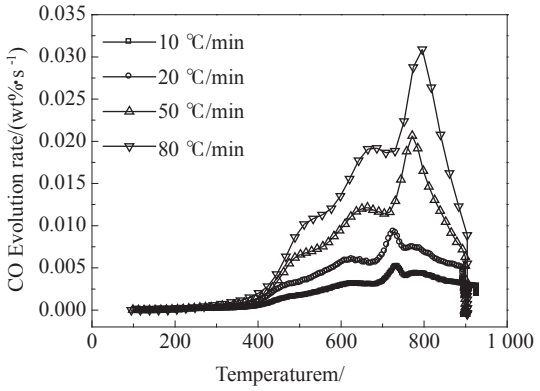

Fig. 6 Evolution rate curves of CO during pyrolysis for Shenhua coal sample at different heating rates

holding step. As shown in table 3, the T_{max} also shifted to higher value for higher heating rate. The CH_4 was mainly formed by the reaction in which the methyl chain and aliphatic bridges of a larger molecule were broken.

The evolution curves of CO during pyrolysis were shown in figure 6. Evolution of CO started at about 280℃. For 20℃/min, evolution curves reached the first peak at about 626℃ and then decreased a little. CO also had two shoulder peaks. The second and maximum peak was around 727℃. The CO was released form the ether O group in the original coal. As shown in table 3, the T_{max} also shifted to higher value for higher heating rate.

Tab. 3 The T_{max} for gas at different heating rates

Gas	20 ℃/min	50 ℃/min	80 ℃/min
CO_2	456.68 ℃	488.00 ℃	510.94 ℃
	716.05 ℃	757.90 ℃	773.76 ℃
CH_4	525.49 ℃	556.06 ℃	576.64 ℃
CO	626.06 ℃	663.71 ℃	686.15 ℃
	726.64 ℃	771.36 ℃	795.66 ℃

3.3 Modified FG-DVC Model

The kinetic parameters for gas, as shown in table 4, were determined by employed the value in table 3 to formula (7). The data in table 4 were in the input format of the FG-DVC model. Y_i is the initial fraction of a particular function group with the modified kinetic parameters in the input files, the weight loss and the yield of gases during pyrolysis were recalculated at 80 ℃/min.

Tab. 4 The kinetic parameters for gases

Precursor pool	$A/s^{-1}\times10^9$	(E_0/R)K	(σ/R)/K	Y_i
1 – CO_2 – loose	0.38	13 230	2 000	0.077 790
3 – CO_2 – tight	0.1	22 295	2 000	0.530 000
32 – CH_3	0.81	16 878	1 800	0.025 215
13 – CO – loose	0.025	18 117	1 000	0.002 989
10 – CO – tight	0.10	19 388	3 000	0.031 924

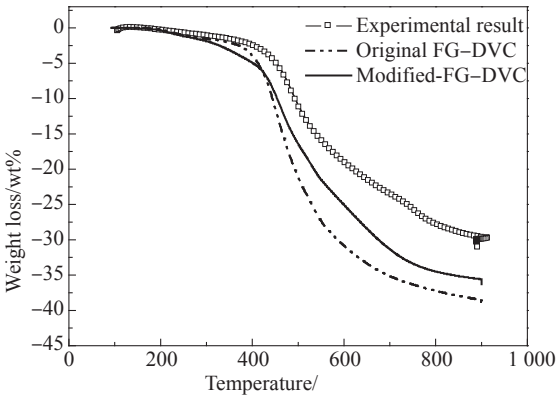

Fig. 7 Comparison of modified FG-DVC simulation on weight loss with experimental result and original FG-DVC simulation on weight loss at 80 ℃/min

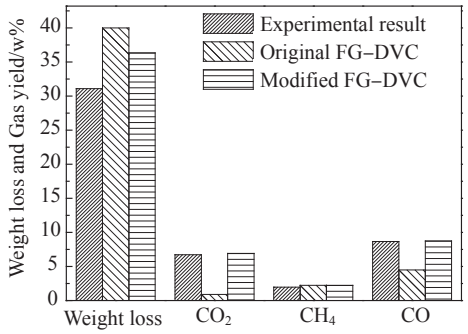

Fig. 8 Comparison of modified FG-DVC simulation with perimental result and original FG-DVC simulation at 80 ℃/min

As shown in figure 7 and figure 8, the simulation had a great improvement. Especially, the simulation yield of CO_2 and CO fitted the experimental data very well. It also can be found the simulated weight loss was still a little more was still a little more TG results. It was because that the kinetic parameters were determined only for CO_2, CH_4 and CO and the kinetic parameters for other species such as Tar, H_2 and H_2O were not available. This may be improved in later work.

4 Conclusions

The pyrolysis experiment and numerical simulation of two types of Chinese bituminous coal at different heating rates were performed using TG – FTIR analysis and FG – DVC model separately. The weight loss and the evolution rate of CH_4, CO and CO_2 during pyrolysis were measured. The thermogravimetric characteristic and the evolution characteristic of gases were obtained from the experiment data.

(1) Shenhua coal had smaller active energy and more weak aliphatic chains than Zhunger coal.

(2) CO_2 and CO had two shoulder peaks during evolution process while CH_4 had only one peak around 550℃. The T_{max} shifted to higher value for higher heating rate. The width of temperature related to gas evolution also became bigger with higher heating rate.

(3) FG-DVC model can simulate the pyrolysis very well for for Zhunger coal, but the difference between experimental data and FG-DVC curve for Shenhua was obvious.

(4) The kinetic parameters for CH_4, CO and CO_2 were obtained from experiment data. The FG-DVC model was modified with the calculated kinetic parameters of Shenhua coal. Using the modified model, the numerical simulation fitted the experimental results more reasonably for Shenhua coal.

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The Simulation Research of Buck-Boost Converter

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[**Abstract**] PSpice is a powerful simulation software, simulation results are very close to the true state of the circuit. The overall working stages of Buck-Boost converter is simulated and analyzed by PSpice. The working process of the Buck-Boost circuit includes the transient process of start-up circuit and the steady working process. All the stages of stored energy elements of Buck-Boost converter are also introduced. The large number of visual simulation waveforms are given. Thus the understanding of Buck-Boost converter is deepened.

[**Key words**] Buck-Boost converter Pspice transient analysis steady-state

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Experiment Research on Bituminous Coal Pyrolysis by TG-FTIR and Determination of Pyrolysis Kinetic Parameters

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[**Abstract**] It is significant to study the components and the relevant concentration of volatile matters released during pulverized coal pyrolysis, which is fundamental for the further study of low NO_x combustion and NO_x reduction during coal reburning process. The devolatilisation experiments of two types of Chinese bituminous coal were performed using TG-FTIR (Thermogravimetry combined with Fourier Transform Infrared Spectroscopy) analysis. Four heating rates (10, 20, 50 and 80 ℃/min) were adopted to research the weight loss and gases evolution. The numerical simulations were performed by using FG-DVC (Functional Group and Depolymerization, Vaporization, Cross-linking) model on the experimental coals. It was indicated that the simulation results were well fitted for one of the two types of coal but not very well for another. The error was caused by the inaccuracy of the kinetic parameters of the main species provided by FG-DVC model. The kinetic parameters are then corrected by introducing FTIR results to a series of first-order formulation by assuming that the light gases evolution are parallel and independent in FG-DVC model. By adopting the corrected kinetic parameters the simulation results are agreed with experiments data much better.

[**Key words**] coal pyrolysis TG-FTIR kinetic parameters FG-DVC