Experimental Study on Thermal Decomposition and Kinetics of Carbonized materials in Nitrogen Atmosphere

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Abstract: Mine fires are the major disasters in process of coal production and mine timber fire is still a hazard resource that endangers the coal safety. In this paper, TGA is tested on carbonized materials at different heating rates. Physical changes, Chemical changes and thermal effect changes are analyzed according to the thermal decomposition process. The effects of heating rates on thermal decomposition process are studied. A thermal decomposition kinetic model advanced and parameters are obtained. Those researchers are beneficial to understand the ignition mechanism and flame spreading in coal mines.

Keywords: Cabonized materials; thermal decomposition; dynamic model

1. Introduction

Mine fires are the major disasters in process of coal production. With the improvement of mechanization and support conditions in coal production, the timbers(carbonized materials) employed as supporting declines. However, the absolute amount of timbers used in coal mines, especially in small scale mines, is still substantial. Therefore timber fire is still a hazard resource in coal mine. Lots of researches on the mine timber fire can be found in home and foreign documents[1-9]. For example, Chen Yuanping etc[1] compared PVC conveyor belt with timber on fire performance, heat release properties, smoke toxicity and reduction of light of CR by using cone calorimeter. Pan Dexiang etc[2] studied combustion characteristics of the fire-retardant conveyor belts, hairdryers and pine timber under the radiation of 35 Kilowatt per square meter and obtained the combustion characteristic parameters of these materials. For the mine timber fire, two processes should be analyzed. One is the process of thermal decomposition that provides the necessary fuels and another is the combustion in gas phase. The heat release rate of timber can be simulated by the product of produce fuel rate and heat of combustion, so the thermal decomposition rate determines the heat energy in the burning triangle. In a sense, the behavior of thermal decomposition of timber plays a key role both in ignition and fire spreading process. Inspection on the thermal decomposition behavior and rule of timber can promote the understanding of the mechanism of mine timber fire and establishing the timber fire model and the fire spread model require more works on the thermal decomposition process. So far, few researches are reported on the analysis of thermal decomposition kinetics of mine timber. In this paper, thermal decomposition characteristics of timber and its kinetics are studied, and the thermal decomposition kinetics model is advanced based on the experimental results.

2. Experimental apparatus and methods

TA-50 thermal analyzer made in Japan Shimadzu company is used. The relationship between thermal decomposition characteristics of timber and temperature is measured and the changes of calorific effect are recorded. Experimental temperature is program-controlled ranged from 25℃ to 800℃ at different heating rates of 5 ℃ min^{-1}, 10℃min^{-1}, 15℃min^{-1} and 20℃min^{-1}. The experimental samples of carbonized materials are homogenous dry timber. After fully grinded and filtered with a 30 meshes sieve, the small particles are kept as samples for which the physical effects such as heat transfer and mass transfer could be reduced. In order to reduce the impact of the second gas-solid reactions and ignore the mass diffusion factor, the quantity of sample must be controlled under 4mg.

3. Experimental results and analysis

3.1 Experimental results

Under nitrogen atmosphere, the weight loss of timber has experienced the following steps with temperature increasing. The first stage starts from room temperature to 130℃, while the moisture absorbed in the samples sublimate and the wax of timber is soften and melt. Within the temperature ranged from 130℃ to 220 ℃ weight loss occurs. It is a slow process of depolymerization and “glass” transformation. The third stage appears within the temperature from 220℃ to 380℃, and it is the main stage of thermal weight loss. In this

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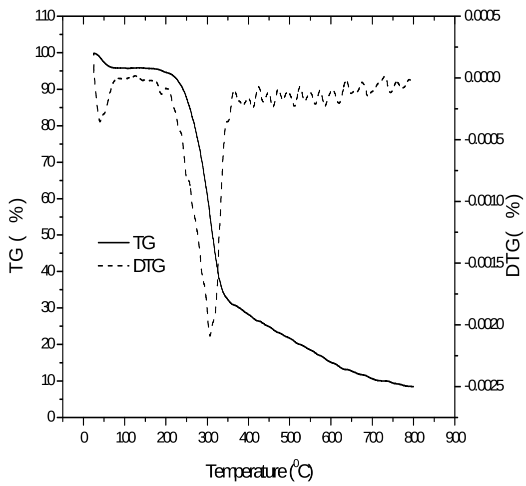
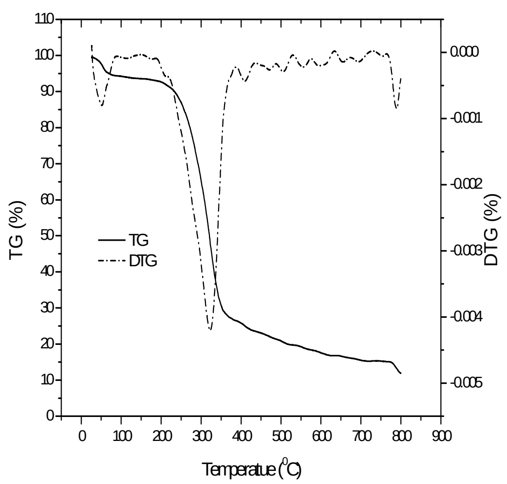
stage the lost weight of biomass generates small molecular gas and macromolecule condensable volatiles which lead to a significant weight loss phenomenon. At about 300℃ the rate of weight loss reaches crest value which shows a high peak in the DTG curves. Also, this stage is the main endothermic phase during the thermal weight loss process. The last stage corresponds to the slow decomposition of remnants which will generate carbon and ash in the end.

3.2 Thermal decomposition process of mine timber

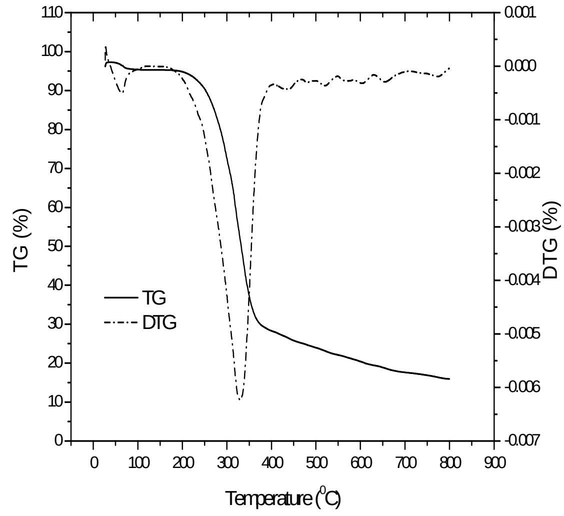
The features of thermal decomposition includes such thermal behaviors as endothermic or exothermic, the mass loss, the release of volatiles, carbon layer collected and the other related properties respectively. The thermal decomposition occurring in an inert or vacuum atmosphere comprise of two processes. One is chemical thermal degradation and another is chemical decomposition under higher temperature.



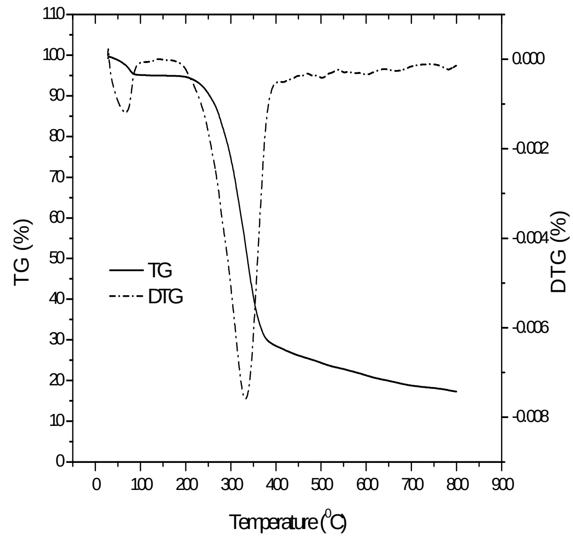
(a) 5℃/min



(b) 10℃/min



(c) 15℃/min



（d）20℃/min

Figure 1 Weight loss curves of thermal decomposition at different heating rates in Nitrogen atmosphere.

In the process of thermal degradation a few chemical bonds in material structure are broken while few changes happen in the structure and property after heated. At a higher temperature thermal decomposition occurs. In the process of thermal decomposition the chemical bonds broken and large scale volatile gases generate, and then liquids (tar) and carbonized residue are left. So physical phases and chemical properties of the mine timber change basically. For timber, the thermal degradation occurs under both high temperature (>300 ℃) and lower temperature (<300℃), figure 2 shows the thermal decomposition processes.

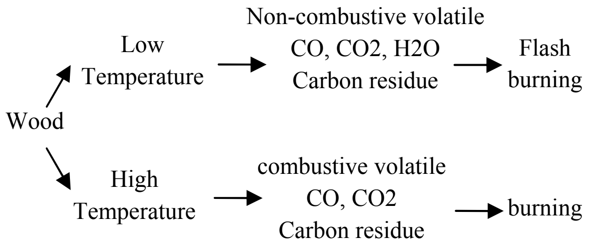


Figure 2 Schematic diagram of timber thermal decomposition

Under nitrogen atmosphere, timber has only one major thermal decomposition process which corresponds to the peak in DTG curve shown in figure 1. When temperature reaches to 380℃, the percentage of weight of solid residue under nitrogen atmosphere is nearly 15% to 30% compared with the initial weight. Finally, with temperature increasing samples continue to lose weight gradually and until the final residues remain constantly.

3.3 Kinetic analysis of timber thermal decomposition

Thermal decomposition of solid carbonized materials can be expressed as the following reaction process [3, 4, and 5]:

A (Solid) →B(Solid) + C(Gas)

Carbonized material A produces a solid phase B and combustible gas C in condition of being heated. The reaction is usually assumed to be irreversible because the airflow used in the experiment will take away the volatile gases that produced in the reaction.

The dynamic equations of differential form and integral form in non-uniform, non-constant temperature conditions can be advanced according to the characteristic equations of weight loss of solid carbide fuel and the Arrhenius equation. The integral method is used to proceed dynamic analysis in this article. Combined with the differential form of dynamic equations, the timber kinetic equation can be given as follows:

$$g(a) = \frac{A}{\beta}\int_{T_0}^{T} \exp(-E/RT)dT \qquad (1)$$

Here α can be expressed as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \qquad (2)$$

Coats and Redfern [10] have solved the integral equation of equation 1 as follows:

$$\ln\left[\frac{g(a)}{T^2}\right] = \ln\left\{\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right\} - \frac{E}{RT} \qquad (3)$$

The parameters used in the equation 1, 2 and 3 are indexed in table 1.

For 2RT/E<<1, if the form of $g(a)$ is correct, the curve of $\ln\left[g(a)/T^2\right]$ plots with 1/T should be a straight line, whose rate of slope is -E/R. The intercept of this straight line includes the frequency factor A. when $g(a)$ is determined, the activation energy E and the frequency factor A can be obtained from the rate of slope and intercept described above. The usual forms of $g(a)$ used in solid reaction kinetics are shown in table 2.

Table 1 parameters list

parameter	Represent
a	Weight loss percentage
A	Pre-exponential factor (min^{-1})
R	Gas constant
β	Heating rate (℃/min)
E	Activation energy (KJ/mol)
T	Initial temperature (K)
$g(a)$	Reaction model function

Table 2 common forms of $g(a)$

Models	Forms of $g(a)$
Zero-order reaction model O_0	a
First-order reaction model O_1	$-\ln(1-a)$
Second-order reaction model O_2	$(1-a)^{-1}$
Third-order reaction model O_3	$(1-a)^{-2}$
cylindrical symmetry model of Phase boundary reaction R_2	$1-(1-a)^{1/2}$
spherical symmetry model of Phase boundary reaction R_3	$1-(1-a)^{1/3}$
One-dimensional diffusion model D_1	a^2
Two-dimensional diffusion model D_2	$(1-a)\ln(1-a)+a$
Three-dimensional diffusion model D_3	$[1-(1-a)^{1/3}]^2$
Four-dimensional diffusion model D_4	$(1-2a/3)-(1-a)^{2/3}$

According to experimental results in nitrogen atmosphere, the thermal weight loss of timber is a continuous process which occurs in the range of temperature from 220℃ to 380℃. So the parameter T in equation 3 is belong to this temperature interval and the dynamic models of apparent reaction in the thermal weight loss process can be constructed.

By calculating 10 kinds of common forms $g(\alpha)$ shown in Table 2, it can be concluded that the first-order model has the best linear as shown in figure 3. Compared with the thermal kinetic under air atmosphere[3], timber thermal decomposition process under nitrogen atmosphere is simplified, it can be described as "single-stage dynamic model of the first-order thermal decomposition reaction". This model is different to the "two-component stages dynamic model of the first-order thermal decomposition reaction" under air atmosphere.

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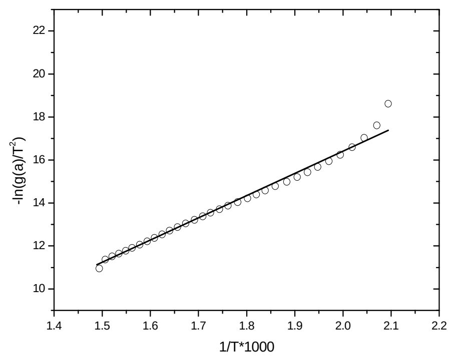

Figure 3 -ln(g(a)/T^2)~1/T＊1000 in Nitrogen atmosphere

According to figure 3, it can be calculated that the activation energy E of timber thermal decomposition is 89.9 KJ/mol and the frequency factor A equals 1.24E+04s-1 under nitrogen atmosphere.

4. Conclusions

Thermal decomposition under nitrogen atmosphere under nitrogen atmosphere has been investigated. It helps us to understand details of the ignition and flame spread to evaluate more accurately the mechanism of mine timber fire. The following conclusions are obtained:

(1) Under nitrogen atmosphere, the timber thermal weight loss mainly goes through three stages with temperature increasing.

(2) The thermal decomposition process is simpler under nitrogen atmosphere than that in air atmosphere. The kinetic model can be described as the single-stage and first-order thermal decomposition reaction.

(3) The calculated activation energy E of timber thermal decomposition is 89.9 KJ/mol and the frequency factor A equals 1.24E+04s-1 under nitrogen atmosphere.

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