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# Thermal decomposition kinetics of carbide slag in air atmosphere

Jianyu Zhang<sup>1,2</sup>, Qi Cao<sup>1,2</sup>, Hongpan Liu<sup>3</sup>, Zhibiao Shang<sup>4</sup>, Xianhua Guo<sup>1,2</sup>, Yuan Li<sup>1,2</sup>, Jian Gu<sup>1,2</sup>, Dan Zhang<sup>1,2</sup>, Ming Jiang<sup>1,2,5</sup>, Fangdong Zhan<sup>1,2</sup>

<sup>1</sup> College of Resources and Environment, Yunnan Agricultural University, Kunming 650201, China;

<sup>2</sup> Yunnan Engineering Laboratory for Agro-environment Pollution Control and Eco-remediation, Kunming 650201, China;

<sup>3</sup> College of Materials and Chemical Engineering, Chongqing University of Arts and Sciences, Chongqing 402160, China;

<sup>4</sup> Guangdong Polytechnic College, School of Economics and Management, Zhaoqing 526100, China

<sup>5</sup> Email: mingjiang2010@163.com

**Abstract.** In this study, the thermal decomposition characteristics and kinetics of carbide slag were evaluated by simultaneous measurements of thermogravimetry (TG)/differential thermal (DTA) analyses under air atmosphere. The data revealed that mass thermal decomposition processes could be divided into three stages, in which the last two stages at 400- 490°C and 710-790°C underwent largest thermal decomposition weight loss. The thermal decomposition kinetic parameters were calculated by the Kissinger method and the corresponding apparent activation energies were estimated to 204.00 and 311.40 kJ·mol<sup>-1</sup>, respectively. The respective natural logarithms of pre-exponential factor (ln *A*) calculated by Kissinger method were 1.07×10<sup>11</sup> and 1.77×10<sup>12</sup>. For comparison, the thermal decomposition kinetic parameters were also calculated by FWO peak maximum evolution and FWO isoconversional methods. The apparent activation energies of the two last stages were recorded as 205.71 and 313.12 kJ·mol<sup>-1</sup>, respectively.

## 1. Introduction

Polyvinyl chloride (PVC) is one important plastic used worldwide in many applications. China is the world's largest producer and consumer country of PVC. The production of PVC is mainly performed from petroleum ethylene and calcium carbide acetylene. The "rich coal and little oil" principal in China[1] made the production of PVC mainly acetylene derived from hydrolysis of calcium carbide. The recent statistics suggested that PVC production by calcium carbide method accounted for 80% of total production capacity as of 2015[2].

Carbide slag is a hydrolysis waste residue issued during hydrolysis of calcium carbide to produce PVC. The chemical reaction could be summarized by:  $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Ca(OH)}_2$ [3], mainly composed of  $\text{Ca(OH)}_2$  with other metal oxides[4]. At present, many ways could be exploited to utilize carbide slag resources, including production of building materials[5] and preparation of chemical products[6] through environmental management[7]. Currently, only small portions of the enormous amounts of produced carbide slag each year in China are recycled by most enterprises. The open-air



dumping of waste carbide slag does not only occupy the land and prevent it from being used for useful purposes but also affect the environmental sanitation and pollute the surrounding water/soil sources[8-9]. At the long run, this will cause serious environmental pollution[10]. The high calcium content of carbide slag can be used as precursor of basic adsorbents. The preparation of high-efficiency and low-temperature calcium-based adsorbents for removal of acidic gases would achieve better waste treatment of these by-products.

In this study, the thermal decomposition kinetics and explored decomposition mechanism of carbide slag were studied by thermogravimetric analysis during temperature programming. The kinetic parameters of thermal decomposition reactions were obtained by means of the Flynn-Wall-Ozawa(FWO) and Kissinger methods.

## 2. Experimental

### 2.1. Materials

The carbide slag derived from a chemical plant in QuJing Yunnan (China) was crushed by a shredder then dried at 110°C for 48h. The obtained carbide slag was sieved at 200 $\mu$ m and used for further analysis.

### 2.2. Methods

The thermogravimetry experiments were carried out on a thermogravimetric-differential thermal analyzer (TGA, model, Beijing Everlasting Scientific Instrument Factory). The experimental conditions were based on Al<sub>2</sub>O<sub>3</sub> powder as reference material and sample amount of 15 $\pm$ 5mg. After heating, air was purged into the reaction tube at gas flow rate of 10mL/min and temperature from room temperature (22°C) to 1000°C. The heating rates varied as follows: 10 K/min, 15 K/min, 20 K/min, and 25 K/min.

## 3. Results and discussion

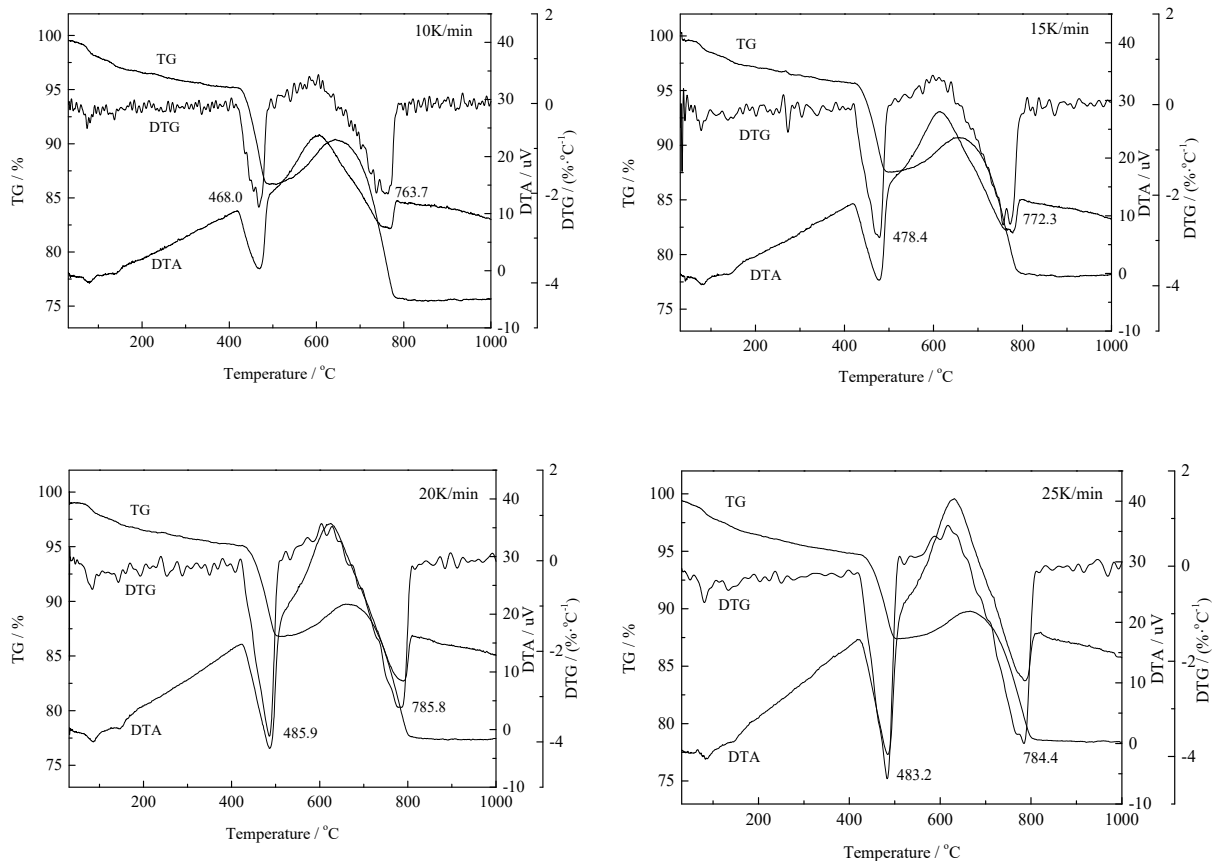
### 3.1. Thermal decomposition characteristics of carbide slag

The TG - DTG - DTA curves of carbide slag in air at different heating rates are gathered in Figure 1. Note that the carbide slag final weight loss rate was always maintained between 20~30%. These findings were similar to thermal decomposition process of carbide slag under nitrogen atmosphere[11]. The thermal decomposition characteristics of carbide slag at different heating rates are listed in Table 1. The mass thermal decomposition process could be divided into three stages. The weight loss during the first stage was the smallest, and ascribed to evaporation of adsorbed water molecules from surface of carbide slag. The maximum mass loss rate temperatures ( $T_{max}$ ) of carbide slag during the second stage were recorded as 468.0°C, 478.4°C, 485.9°C, and 483.2°C. In the third stage, these values increased to 763.7°C, 772.3°C, 785.8°C and 784.4°C, respectively.

**Table 1.** Pyrolysis characteristics of carbide slag.

Heating rate $\beta / (K \cdot min^{-1})$	Weight loss / (%)			Temperature range of weight loss / (°C)		
	1	2	3	1	2	3
10	4.75	8.15	10.05	31~468	468~489	710~764
15	3.75	7.65	10.15	31~410	410~478	715~772
20	3.81	7.55	9.73	31~415	415~486	750~786
25	4.75	7.05	7.15	31~400	400~483	723~784

At peak of DTG curves of carbide slag, the DTA curves in the second stage showed downward endothermic peak (Figure 1).  $\text{Ca(OH)}_2$  was identified as the main component of thermal decomposition reaction of carbide slag under air atmosphere. The DTA curves of carbide slag during the third stage contained upward exothermic peak, indicating that the temperature stage was composed of combustion heat release of residual carbon in carbide slag under air. The heating rate depicted great influence on thermal mass loss. As heating rate increased, TG curve moved to high temperatures.



**Figure 1.** TG-DTG-DTA curves of carbide slag.

### 3.2. Decomposition kinetics of carbide slag

**3.2.1. Kinetic theory of thermal decomposition.** According to the Arrhenius equation and non-isothermal (usually linear heating) kinetic theory, the thermal decomposition reaction of solids could be expressed by Eqs. (1) to (2) [12].

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

where  $\alpha$  is the conversion rate at any time  $t$  or temperature  $T$  during thermal decomposition in % .  $\alpha$  can be obtained using Eq. (3) [13], where  $m_0$  is the starting mass,  $m_t$  is mass at any time  $t$  or temperature  $T$  of thermal decomposition process,  $m_f$  is final residual mass at the end of thermal decomposition reaction,  $t$  represents time of thermal decomposition in s,  $A$  is a pre-exponential factor

of thermal decomposition in  $s^{-1}$ ,  $E$  is the activation energy of thermal decomposition reaction in  $kJ/mol$ ,  $R$  is the universal gas constant ( $8.314 J/mol \cdot K$ ),  $T$  is the thermal decomposition temperature in  $K$ ,  $\beta$  is the heating rate in  $K/min$  or  $^{\circ}C/min$ , and  $f(\alpha)$  is a function of differential kinetic mechanism determined by the type of reaction.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (3)$$

Here, the kinetic parameters (activation energy  $E$ , pre-exponential factor  $A$ ) of carbide slag thermal decomposition reaction were obtained by the FWO and Kissinger methods. Meanwhile, the activation energy  $E$  was solved by Flynn-Wall-Ozawa (FWO) method and the results of both methods were compared.

**3.2.2. Kissinger method results.** The Kissinger method [14] is a perfect non-nuclear kinetic equation, which does not require any mechanism model to solve the activation energy of the reaction. This would prevent blindness of model selection as shown in Eq. (4):

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{max}} \quad (4)$$

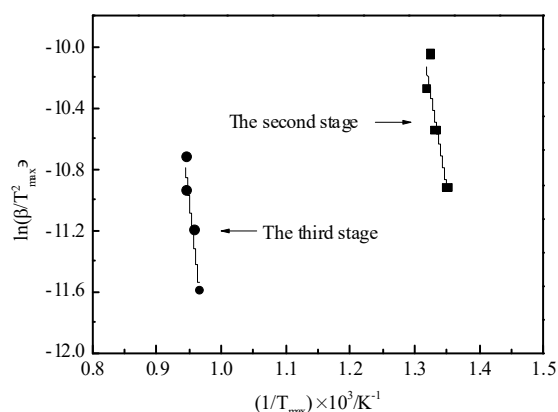
where  $T_{max}$  is peak decomposition temperature in  $K$ . The physical meanings of the remaining parameters are the same as in Section 3.2.1.

Linear fitting was performed according to Eq. (4) with  $\ln(\beta/T_{max}^2)$  as ordinate and  $T_{max}^1/10^{-3}K^{-1}$  as abscissa. The slope of the fitted straight line was identified as  $-E/R$  and intercept as  $\ln(AR/E)$ . These two plots allowed obtaining  $E$  and  $A$ . The second and third stages carbide slag thermal decomposition showed maximum peaks, which can be obtained from TG-DTG curve (Figure 1). The obtained data can be processed according to Figure 1 ( $\beta$ ,  $\lg\beta$ ,  $T_{max}/K$ ,  $\ln(\beta/T_{max}^2)$ ,  $(T_{max}^1/10^{-3}K^{-1})$ ). The analyses of DTG curves are presented in Table 2.

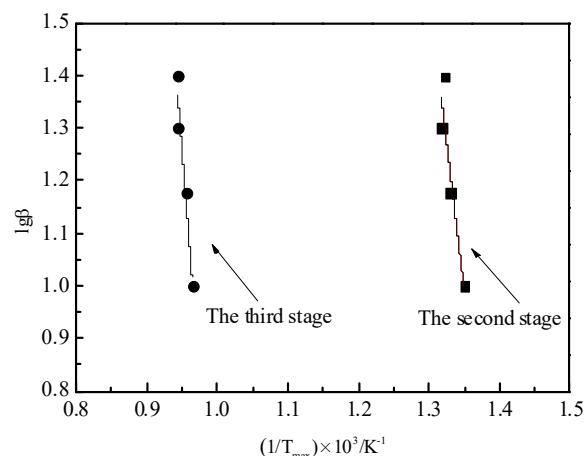
The results of fitting are shown in Figure 2. The linear equation of the second stage can be obtained from the plot of  $Y = -24.53715X + 22.19173$ . The thermal decomposition activation energy  $E$  was estimated to  $204.00 kJ \cdot mol^{-1}$  with pre-exponential factor  $A$  of  $1.07 \times 10^{11}$ . The linear equation of the third stage was identified as:  $Y = -37.4552X + 24.57829$ , with thermal decomposition activation energy  $E$  of  $311.40 kJ \cdot mol^{-1}$  and  $A$  of  $1.77 \times 10^{12}$ .

**Table 2.** Analyzing date of DTG curves.

Stage number	$\beta/K \cdot min^{-1}$	$T_{max}/^{\circ}C$	$T_{max}/K$	$\ln(\beta/T_{max}^2)$	$(1/T_{max}) \times 10^3 / K^{-1}$
The second stage	10	468	741.15	-10.9138	1.34926
	15	478.4	751.55	-10.5362	1.33058
	20	485.9	759.05	-10.2684	1.31744
	25	483.2	756.35	-10.0381	1.32214
The third stage	10	763.7	1036.85	-11.5853	0.96446
	15	772.3	1045.45	-11.1964	0.95652
	20	785.8	1058.95	-10.9343	0.94433
	25	784.4	1057.55	-10.7085	0.94558



**Figure 2.** Fitting curves of  $\ln(\beta/T_{\max}^2) - 1/T_{\max}$  by Kissinger method.



**Figure 3.** Fitting curves of  $\lg\beta - 1/T_{\max}$ .

**3.2.3. Flynn-Wall-Ozawa method.** The activation energies were also calculated using the FWO [15] peak maxima and FWO isoconversional methods, and the results were compared with those of Kissinger method (Eq. (5) for FWO):

$$\lg \beta = \lg \left[ \frac{AE}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E}{RT_a} \quad (5)$$

where  $G(\alpha)$  is the integral kinetic mechanism function determined by the reaction type,  $T_a$  is temperature at the same conversion rate at different heating rates in K, and the physical meanings of the remaining parameters are the same as in Section 3.2.1.

Under different heating rates ( $\beta$ ), the conversion rates  $\alpha_{\max}$  at peak decomposition temperatures  $T_{\max}$  looked approximately equal. Meanwhile,  $T_a$  in Eq. (5) was replaced by  $T_{\max}$ , and  $\ln(\beta)$  was plotted as ordinate and  $1/T_{\max}$  as abscissa. After fitting, the slope of the straight line obtained after fitting was identified as  $-0.4567E/R$ , and allowed determination of  $E$ . The relevant data and processing ( $\beta$ ,  $T_{\max}$ ,  $\ln(\beta)$ ,  $(1/T_{\max}) \times 10^3$ ) obtained by combining with Figure 1 are listed in Table 3, and the linear fittings are depicted in Figure 3.

**Table 3.** The basic data of the kinetics and the conversion rate of maximum peak by TG/DTG curves.

Stage number	$\beta/K \cdot \min^{-1}$	$T_{\max}/^{\circ}\text{C}$	$T_{\max}/\text{K}$	$\lg\beta$	$(1/T_{\max}) \times 10^3 / \text{K}^{-1}$	$m_0/\text{mg}$	$m_t/\text{mg}$	$m_f/\text{mg}$	$\alpha_{\max}/\%$
The second stage	10	468	741.15	1	1.34926	14.5	12.908	10.975	45.2
	15	478.4	751.55	1.176	1.33058	15.1	13.493	11.802	48.7
	20	485.9	759.05	1.301	1.31744	16.2	14.391	12.547	49.5
	25	483.2	756.35	1.398	1.32214	15.5	13.856	12.153	49.1
The third stage	10	763.7	1036.85	1	0.96446	14.5	11.351	10.975	89.3
	15	772.3	1045.45	1.176	0.95652	15.1	12.188	11.802	88.3
	20	785.8	1058.95	1.301	0.94433	16.2	12.921	12.547	89.8
	25	784.4	1057.55	1.398	0.94558	15.5	12.493	12.153	89.8

A linear variation of the second stage was obtained by fitting the curve in Figure 3. The formula:  $Y = -17.2X + 17.6$  was obtained with correlation coefficient  $R = 0.9313$ . The corresponding thermal

decomposition activation energy was  $E = 313.12 \text{ kJ/mol}$ . For the third thermal decomposition stage, the linear equation was identified as:  $Y = -11.3X + 16.3$ , with  $R = 0.8827$  and  $E = 205.71 \text{ kJ/mol}$ .

Compared to Kissinger method,  $E$  values calculated by both methods were relatively close. To verify that conversion rate  $\alpha_{\max}$  at peak decomposition temperature  $T_{\max}$  was approximately equal under different heating rates  $\beta$ , mass  $m_t$  in TG curve was obtained from  $T_{\max}$  of DTG curve for all four graphs in Figure 1. Note that  $m_0$  and  $m_f$  were known parameters. From Eq. (1), the peak conversion rate  $\alpha_{\max}$  at thermal decomposition of carbide slag can be calculated at peak decomposition temperature. The relevant data processing ( $m_0$ ,  $m_b$ ,  $m_f$ ,  $\alpha_{\max}$ ) are gathered in Table 3. The  $\alpha_{\max}$  values at different heating rates  $\beta$  looked similar, with average of 48.1% and 89.3%, respectively. Therefore,  $\alpha_{\max}$  can be approximated as a fixed value, consistent with literature reports [16] and indicating the applicability and effectiveness of the proposed method.

#### 4. Conclusions

The thermal decomposition process of carbide slag under air could be divided into three stages. The first stage was characterized by evaporation of adsorbed water molecules on the surface of carbide slag. The second stage produced  $\text{Ca(OH)}_2$  as main component of carbide slag thermal decomposition reaction. The third stage was characterized by exothermic combustion of carbon particles in carbide slag. The thermal decomposition kinetic parameters in the second and third stages in terms of activation energies were calculated by Kissinger and FWO peak maximum evolution isoconversional methods. The obtained activation energy values were similar, indicating that both methods were suitable for solving the thermal decomposition kinetics of carbide slag.

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