

Effect of the addition of cornstalk to coal powder/coal tar combustion

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Abstract Thermogravimetry (TG) and differential thermal analysis were used to investigate combustion behavior with the addition of cornstalk to coal powder and coal tar at three different heating rates: 5, 10, and 15 °C min⁻¹. Different reaction kinetic mechanisms with the classical Arrhenius model were used to treat TG data. The first-order combustion model fitted the data well. The combustion characteristics of the two masses were analyzed according to combustion characteristics parameters such as ignition temperature, peak temperature at maximum weight loss rate, and burnout temperature, among others. By calculation, a uniform trend of decreasing activation energies was observed with the addition of cornstalk. The rate of coal powder and coal tar combustion process was also greatly improved.

Keywords Coal powder · Coal tar · Cornstalk · Combustion · Kinetics model · TG

Introduction

Despite environmental issues and competition from alternative fuels, coal remains to play a major role in the world's energy usage. In China, coal is currently one of the main energy resources. It is dominantly used in

thermoelectricity generation and coke production industries. In the coking process, the main by-product is coal tar, which accounts for 3–4% of the total raw material of coal. The composition of coal tar differs from process to process, mainly due to the different raw materials and treatments used during its production [1]. Recent studies have shown that burning biomass with fossil has a positive effect both on the environment and the economics of power generation [2–5].

Biomass and coal blend combustion is a promising combustion technology. Numerical studies on co-firing coal with biomass have been presented [6–8]. The co-combustion of coal and biomass at different proportions has also been examined. For example, Zhang and Shi [9] found that a small biomass mass fraction can be attributed to a decrease in activation energy of the mixture, whereas a small one is attributed to an increase in the frequency factor of the reaction. Min studied the combustion characteristics of biomass and coals with different ranks [10]. Demirba argued that coal co-firing is successful with up to 20% biomass mix [1]. However, significant development work is required before large-scale implementation can be realized. Issues related to the successful implementation of coal biomass blend combustion have been identified. In comparison, relatively little information on the effect of coal tar-biomass co-firing on activation energy and pre-exponential has been published. Coal tar is a complex mixture composed almost entirely by aromatic compounds, whose total number is estimated to be around 1,000 [11]. It contains harmful chemicals such as polycyclic aromatic hydrocarbons, phenolic compounds, and sulfur, which damage the environment. In this study, its kinetics is studied using a thermogravimetric analysis system.

The straw mixed up burning technology is a biomass burning technology that has emerged in recent years. In

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Table 1 Coal powder combustion stage and peak temperature

	Heating rate/°C min ⁻¹	Tem. scope/°C	Peak tem./°C	Tem. scope/°C	Peak tem./°C
Coal powder	5	300–550	500		
	10	350–600	525		
	15	360–700	620		
Coal powder + 20% cornstalk	5	200–470	280, 425	480–600	490
	10	200–450	310, 440	540–600	510
	15	200–510	316, 445	510–620	330

Table 2 Coal powder, coal tar, cornstalk properties and ultimate analysis data

	Elemental analysis/%					
	C	H	O	N	S	Others
Coal powder	59.40	4.04	9.12	0.72	0.83	25.89
Coal tar	90.39	5.37	1.20	0.96	0.72	1.36
Cornstalk	43.67	5.99	35.62	0.28	0.15	14.29

China, a large volume of cornstalk is produced every year but is of little use. As a green energy source, the cornstalk has a number of good properties in terms of ignition and burnout, and low pollution output. Grammelis et al. [12] and Muthuraman et al. [13] indicated that the co-combustion of biomass and coal to generate electricity is feasible and can reduce environmental pollution of NO_x, SO₂, and CO₂. Tillman posited that co-firing coal with clean wood wastes does not create ash deposition problems [14]. Better properties of ignition and burnout can be achieved when coal powder/coal tar is mixed with biomass.

In this study, a thermogravimetric analyzer was used to obtain information on the combustion behavior of coal powder/coal tar in coexistence with cornstalk. The effect of the addition of cornstalk on coal powder/coal tar combustion in the air environment was studied. The apparent activation energy (*E*) and pre-exponential factor (*A*) for combustion kinetics were gathered. The data showed that cornstalk can efficiently improve coal powder/coal tar combustion properties (Table 1).

Experimental

Materials and preparations

Sample preparation

The coal powder studied in the current study is a kind of bituminous coal produced from Shanxi Province, China. The particle sizes are between 450 and 495 μm. Coal tar, another material used, is also from Shanxi Province. Coal

tar is a black liquid with high viscosity. The cornstalk from Beijing in North China was crushed by a disintegrator after it was naturally dried and ground into fragments between 490 and 833 μm. For every sample, about 20 mass% of cornstalk was added to the coal powder/coal tar and uniformly mixed to see the effect of cornstalk on coal powder/coal tar combustion. The results of industry analysis by Elementar Vario Micro Cube and elementary analysis of the three samples are shown in Table 2.

Results and discussion

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed with a Shimadzu DTG-60 H thermogravimeter analysis system. TG and DTA curves were obtained using the following experimental conditions: air atmosphere; flow rate: 30 mL min⁻¹; mass of coal powder/coal tar sample: 4–6 mg; heating rates: 5, 10, and 15 °C min⁻¹; and temperature range: 25–800 °C. Prior to the experiments, the TG/DTA equipment was calibrated, and experiments were repeated at least twice to insure repeatability and accuracy.

Kinetic theory

Various reaction models such as those of Arrhenius [16–18], Coats–Redfern [18–21], and Horowitz–Metzger [22, 23] were used to describe solid fuel (coal, lignin) combustion by different researchers.

Coal tar is a kind of black and high-viscosity liquid containing more than 100 compounds. It is a material whose

properties are between liquids, such as crude, and between solids, such as coal and asphaltene. Theoretically, the combustion of coal tar can be initiated whenever oxygen comes into contact with it when the temperature reaches a certain degree. However, the reaction process is exceedingly complex, and many competing processes contribute to the thermal analysis curves. Coal tar from different sources also expresses different combustion characterizations.

Due to the complex nature of coal tar, its combustion is often assumed to be a single reaction in which all coal tar components are regarded as one group (a coal tar mixture). Therefore, the overall rate of coal tar disintegration is given by the sum of the rates of all elementary individual reactions. This approach has been accepted by most researchers [1, 24]. In the current study, we also adopt this method: all reactions involved in the combustion process are lumped into one. We use the Coats–Redfern method used by many researchers [13–16, 25] to determine combustion kinetics. Therefore, the coal tar combustion rate equation can be expressed as

$$dx/dt = \kappa(1 - \alpha)^n \tag{1}$$

where dx/dt is the combustion conversion rate, n is the assumed reaction order, the correct order leading to the best linear plot (usually the first-order linear rate is assumed), κ is the reaction rate constant, and $(1 - \alpha)^n$ is a function that proceeds from the reaction of the samples' characteristics.

The extent of conversion α is defined by the following expression:

$$\alpha = (W_0 - W_t)/(W_0 - W_F) \tag{2}$$

where W_0 and W_F are the initial and final sample masses (weight%), and W_t is the sample mass at time t . The temperature dependence of the reaction rate constant κ can be expressed by the Arrhenius equation:

$$\kappa = Ae^{-E/RT} \tag{3}$$

where A is the pre-exponential factor in min^{-1} and E is the apparent activation energy in J mol^{-1} .

The heating rate (β , min^{-1}) can be expressed as

$$\beta = dT/dt \tag{4}$$

Therefore, Eq. 1 can be rewritten as follows:

$$\frac{1}{f(\alpha)}d\alpha = \frac{A}{\beta}e^{-E/RT}dT \tag{5}$$

Integrating Eq. 5,

$$h(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)}d\alpha = \frac{A}{\beta} \int_0^T e^{-E/RT}dT \tag{6}$$

For Eq. 6, many forms of alpha functions (kinetic laws) can be envisioned, such as nucleation and growth, power

law, or diffusion-controlled process [7, 21, 26]. The right-hand side of Eq. 6 has no exact integral, but Eq. 7 can be obtained when this term is expanded into an asymptotic series. Higher-order terms are ignored by the numerical approach.

$$h(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)}d\alpha = ART^2 \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) / (\beta E) \tag{7}$$

Taking the natural logarithms of both sides of Eq. 7 and assuming that $2RT/E \ll 1$, we obtain the following:

$$\ln\left(\frac{h(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \tag{8}$$

Such trace for biomass tar has been presented in an earlier paper [10].

In the current study, only the power law is considered with assumed power values (reaction orders): $n = 0.5, 1, 1.5,$ and 2 .

A suitable reaction order can be selected, taking into account the correlation coefficient. From the slope ($-E/R$) and intercept (y) of the regression line obtained using TG data, E and A are calculated.

For $n = 1$:

$$\ln\left(-\frac{\ln(1 - \alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right) - \frac{E}{RT} \tag{9}$$

For the other n values ($1/2, 3/2, 2$),

$$\ln\left[-\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{10}$$

when $n = 1$, $\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right)$ is plotted as a function of $\frac{1}{T}$, and if $n \neq 1$, $\ln\left[-\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ is plotted as a function of $\frac{1}{T}$. From the slope ($-E/R$) and intercept (y) of the regression line obtained using TG data, E and A are calculated.

Results and discussion

Selection of the reaction order

Using the data from Table 3, we obtained the least straight line using the best squares method. The linear correlations for the identified rectilinear portions of different reaction orders are shown in Table 4 for a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$, air flow rate of 30 mL min^{-1} , and cornstalk amount of 20% (mass). From Table 5, the regression coefficient for the combustion of tar in the presence of a cornstalk is in the range of 0.96–0.99 for $n = 1$, which is better than that for $n = 0.5, 1.5,$ and 2 . The results reveal that this is the best

Table 3 Coal tar combustion stage and peak temperature

	Heating rate/°C min ⁻¹	Tem. scope/°C	Peak tem./°C	Tem. scope/°C	Peak tem./°C
Coal tar	5	200–400	345	400–550	540
	10	260–435	385	435–680	570
	15	275–450	425	450–680	615
Coal tar + 20% cornstalk	5	200–360	325	330–540	460
	10	200–380	340	340–600	475
	15	200–390	350	400–600	495

Table 4 Kinetic parameters of coal powder in coexistence of cornstalk (heating rate, 5, 10, and 15 °C min⁻¹; flow rate of air, 30 mL min⁻¹; amount of cornstalk, 20 mass% in total mass)

	Heating rate/°C min ⁻¹	E_a /kJ mol ⁻¹	A /min ⁻¹	E_a /kJ mol ⁻¹	A /min ⁻¹
Coal powder	5	40.4	3.7×10^2		
	10	53.1	1.8×10^4		
	15	57.9	5.0×10^3		
		Stage1		Stage2	
Coal powder + cornstalk	5	20.5	8.7×10^{-1}	22.5	5.0×10^0
	10	24.9	1.1×10^1	27.6	2.0×10^1
	15	30.7	4.9×10^2	31.1	4.6×10^2

Table 5 Correlation coefficient for different reaction orders (heating rate, 5 °C min⁻¹; flow rate of air, 30 mL min⁻¹; amount of cornstalk, 20 mass% in total mass)

	Correlation coefficient			
	$n = 0.5$	$n = 1$	$n = 1.5$	$n = 2$
Coal powder	0.9719	0.9373	0.9347	0.9207
Coal powder + 20% cornstalk	0.8443	0.9416	0.9212	0.9360
Coal tar	0.0594	0.7512	0.6893	0.5111
	0.0142	0.5617	0.4236	0.0531
Coal tar + 20% cornstalk	0.0500	0.9648	0.6652	0.7236
	0.5081	0.8505	0.7927	0.7576
	0.7113	0.9136	0.9056	0.9019

reaction order for the two assumed selections. Therefore, the first-order model for tar combustion was adopted in the current study. Comparing tar combustion behavior in the absence and presence of cornstalk, combustion kinetics was not affected by the presence of cornstalk. The reaction mechanism was difficult to identify because the coal tar combustion process is very complex. It proceeds in several stages such as delocalization or transfer of electrons in chemical bonds; diffusion of atoms, free radicals, or ions; heat transfer to the reaction zone in case of endothermic

reaction; and formation of a new solid phase such as carbon, impurities, and catalysts. For the tar combustion process, the rate-limiting step is not confined to nor occurs only at the reactant surface. In this condition, all molecules, whether on the surface or in the bulk, may have equal probability per unit time of reaction. This is the case when the change from the reactant to the solid product phase involves little rearrangement of the reactant atoms. The reaction has a homogeneous mechanism. Therefore, it has an approximate reaction order of one, that is, $d\alpha/dt = \kappa(1 - \alpha)$.

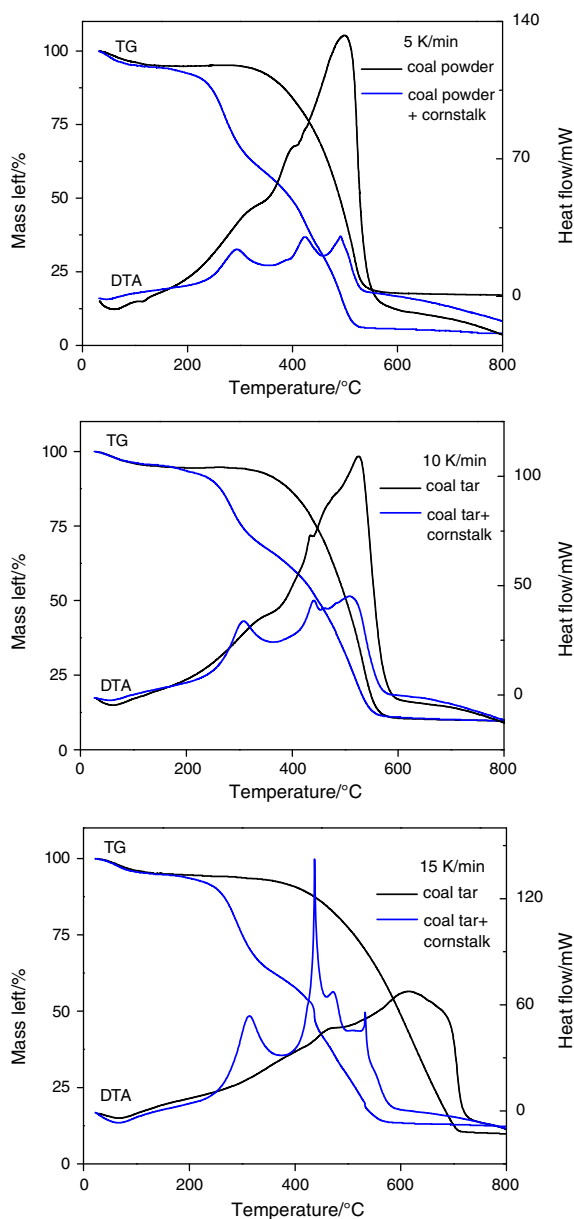


Fig. 1 TG–DTA curves of coal powder without/with cornstalk (heating rate 5, 10, 15 K min⁻¹)

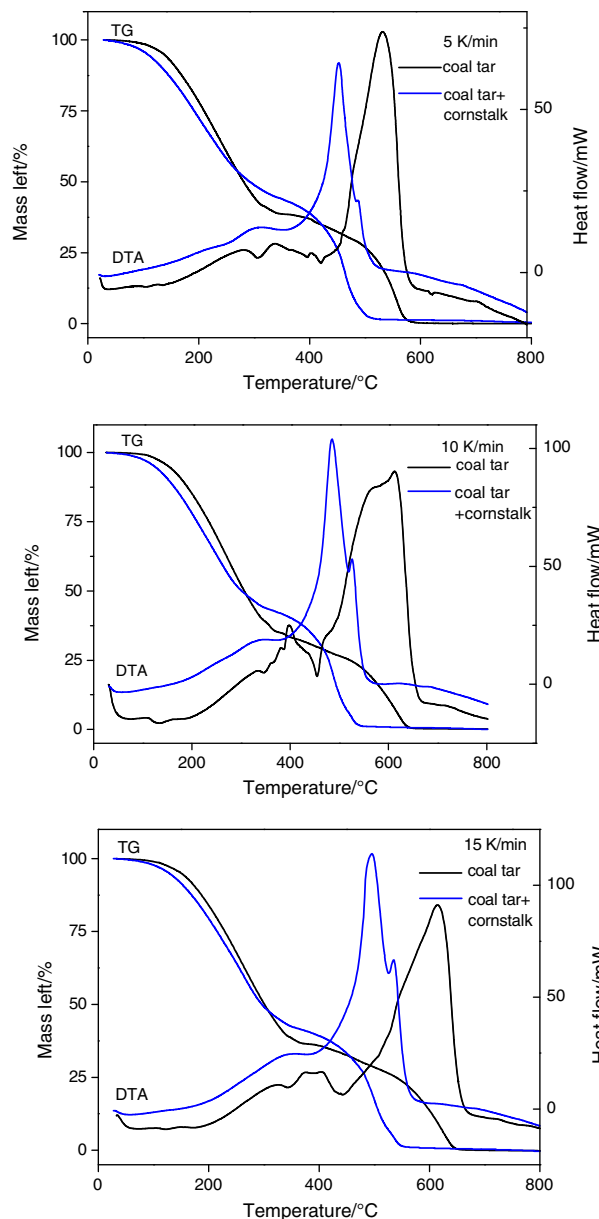


Fig. 2 TG–DTA curves of coal tar without/with cornstalk (heating rate 5, 10, 15 K min⁻¹)

Table 6 Kinetic parameters of coal tar in coexistence of cornstalk (heating rate, 5, 10, and 15 °C min⁻¹; flow rate of air, 30 mL min⁻¹; amount of cornstalk, 20 mass% in total mass)

	Heating rate/°C min ⁻¹	Stage1		Stage2	
		E _a /kJ mol ⁻¹	A/min ⁻¹	E _a /kJ mol ⁻¹	A/min ⁻¹
Coal tar	5	4.1	2.3 × 10 ⁻¹	35.4	3.7 × 10 ²
	10	15.3	2.9 × 10 ³	39.5	5.8 × 10 ⁰
	15	18.2	1.1 × 10 ⁴	47.8	3.6 × 10 ²
Coal tar + cornstalk	5	3.4	3.9 × 10 ⁻¹	27.1	1.7 × 10 ²
	10	6.2	2.9 × 10 ¹	32.2	2.5 × 10 ²
	15	15.7	2.1 × 10 ³	34.3	6.1 × 10 ³

Combustion process

The main objective of the combustion experiment was to obtain sufficient data to establish the reaction kinetics and to determine the Arrhenius parameters. In the course of the present research, TG–DTA curves were produced for coal powder in coexistence with 20 mass% of cornstalk. Non-isothermal experiments were conducted from room temperature to 800 °C. The integrative plots of the TG–DTA curves in air environment of different heating rates are shown in Figs. 1 and 2, respectively.

Analysis of the derivative thermogravimetric curve of the coal powder showed that the reaction trends of the two conditions (coal powder, coal powder with cornstalk) are obviously different. A plausible explanation for this is that cornstalk combustion is divided into two stages followed by the burning of volatile and fixed carbon [21]. The third peak is mainly produced by the combustion of coal powder.

From the DTA curve, a wide and high peak appeared around 500 °C during coal powder combustion. In contrast, during coal powder with cornstalk combustion, three lower peaks appeared. For example, in Fig. 1, the DTA curve of coal powder mixed with cornstalk shows that the first peak corresponded to the combustion of the cornstalk volatile and easy pyrolytic volatile of coal powder from 200 to 350 °C. The second peak corresponded to the combustion of the fixed carbon of cornstalk and difficult pyrolytic volatile of coal powder from 350 to 470 °C.

The third was mostly due to the combustion of coal powder. When the heating rates of combustion were 5, 10, and 15 °C min⁻¹, the burnout temperatures of coal powder were 500, 530, and 615 °C, respectively. In comparison, the burnout temperatures of coal powder with cornstalk were 480, 510, and 540 °C, respectively, which are at least 20 °C lower than that of coal powder without cornstalk.

The summary of calculation results including the apparent activation energy (E) and the frequency factor (A) is shown in Table 4, which provides the quantitative explanation for the TG and DTA curves with and without cornstalk. The ignition of coal powder with cornstalk is concluded to be lower than that of coal powder. The table also shows that cornstalk can reduce E effectively. Possibly, cornstalk has a catalytic action on combustion. The frequency factor is shown in Table 6, which provides the quantitative explanation for the TG and DTA curves with and without cornstalk for coal tar combustion.

From Table 6, the apparent E of the volatilization stage is higher.

Conclusions

The thermogravimetric and derivative thermogravimetric analysis conducted in the present study provided valuable information on coal powder and coal tar combustion kinetics and mechanisms, especially in coexistence with cornstalk. By comparing the calculation result of different reaction orders, the first-order reaction model fitted the data well.

- (1) The co-combustion of coal powder/coal tar with cornstalk in a thermogravimetric analyzer showed distinctly different combustion characteristics depending on cornstalk proportion in the mixture.
- (2) By comparing the DTA curves of different heating rates, heating rate was found to have significant effects on combustion behavior such as combustion peak and burn-out temperatures. A higher heating rate caused the reactions to occur at higher temperatures, overlapped the subordinate reaction, and then caused the TG–DTA curves to change.
- (3) The coexistence of coal tar and cornstalk greatly improved the amount and speed of the combustion process for coal tar. The calculation results on E and A also provided quantitative explanation. The findings showed that advanced ignition and burnout can be achieved when coal tar is mixed with cornstalk.

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