The kinetic analysis of lignite and waste biomass during co-combustion process by general distributed activation energy model

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Abstract: In this work, the new general distributed activation energy model (G-DAEM) was employed to obtained kinetic parameters during co-combustion process. Four pseudo-components for both lignite and waste biomass were optimized and the simulation results demonstrated excellent match. The results suggested that the G-DAEM is an effective and comprehensive kinetic model for complex solid-state thermal reaction. Assume the pre-frequency factor A is not a fixed number, the real kinetic mechanism may be obtained by the G-DAEM method.

1. Introduction
Co-combustion of coal and waste biomass is regarded as an attractive choose to increase the share of renewable fuels in the energy market. This technology not only reduces fossil fuel consumption, but also saves initial investment for treating waste biomass [1]. Co-combustion can in principle, be applied to any type of biomass utilized with coal for thermal power production [2, 3].

Unfortunately, there is a significant difference between the combustion behavior of coal and biomass, and obtaining the kinetic parameters of co-combustion is crucial to further optimize combustion. There are many kinetics methods, including iso-conversional methods [4], Coast-Redfern models [5] and DAEM [6], etc. Compared to other kinetic models, the advantage of the DAEM model is effective and comprehensive, especially for complex solid-state thermal reaction system [7]. The calculation results can provide some meaningful parameters, including the pseudo-component distribution, the reaction characteristic and energy barrier [8], which are helpful to further explore the kinetic mechanism.

However, the frequency factor was considered as a constant in DAEM model. In fact, the frequency factor \( A = A_0T^m \) is a function temperature in some reactions [9]. Recently, Lin et al. [10] proposed a new General distributed activation energy model (G-DAEM) which set the A to a non-constant number. This novel model was successfully applied to co-pyrolysis kinetics of bagasse and sewage sludge. They claimed that the G-DAEM method is more likely to accord with the real kinetic mechanism. In this work, we try to employ this new G-DAEM to obtain the kinetic parameters during co-combustion of coal and waste biomass.
2. Materials and method

2.1. Materials
In this work, the lignite was selected from paper mill industrial power plant. And the waste biomass (WB) was a mixture of herb residue components which was provided from a traditional Chinese medicine manufacturer in Dongguan (Guangdong Province, China). The samples of lignite and WB were air-dried at 105 °C for 36 h, and then crushed and sieved into the desired particle size (<178 μm). Their characteristics were presented in Table 1. The WB was added to lignite at weight ratio of 0, 10%, 30%, 50%, 70%, 90% and 100%, which were named as lignite, 90L10W, 70L30W, 50L50W, 30L70W, 10L90W and WB, respectively.

Table 1. Characteristics of lignite and WB on dry basis (wt. %).

| Samples       | Ultimate analysis | Proximate analysis |
|---------------|-------------------|--------------------|
|               | C     | H     | O     | N     | S     | Volatile | Fixed carbon | Ash      |
| Lignite       | 61.49 | 5.14  | 24.28 | 0.76  | 0.06  | 65.68    | 26.04        | 8.28     |
| Waste biomass | 40.97 | 6.73  | 45.57 | 1.36  | 0.12  | 77.60    | 17.14        | 5.26     |

2.2. Experimental setup
The combustion process was performed on METTLER TOLEDO thermogravimetric analyzer. The process was heated from 100°C to 1100°C in air atmosphere with a flow rate of 50 ml/min, at a heating rate of 15°C/min and 25°C/min. The initial weights of all samples were 6± 0.5 mg. All the tests were carried out at least twice to ensure the reproducibility.

2.3. Theory of G-DAEM kinetics model
Recently, Lin et al. [10] proposed a general distributed activation energy model (G-DAEM) to modifying the calculation process. More detailed derivation can be found in this reference. The integral form of the Arrhenius dynamics formula is:

\[ \int_0^\alpha d\alpha = \frac{1}{\beta} \int_0^\alpha A \exp \left( \frac{-E}{RT} \right) dT \]

where \( \alpha \) is the conversion rate, %; \( f(\alpha) \) is the mechanism function; \( G(\alpha) \) is the integral model function form; \( \beta \) is the heating rate, K/min; \( A \) is the frequency factor, min\(^{-1}\); \( E \) is the activation energy, kJ/mol; \( R \) is the universal gas constant, 8.314 kJ/mol·K.

The G-DAEM fundamental equation is:

\[ \sigma = \frac{1}{\beta} \int_0^\sigma \exp \left[ \frac{A}{\beta} \psi_u(E,T) \right] f(E_u,\sigma) dE \]

Where \( \psi_u(E,T) \) is the general Boltzmann factor integral, and is described by:

\[ \psi_u(E,T) = \int_0^T \exp \left( \frac{-E}{RT} \right) \frac{-E}{RT} dT \int_0^1 \exp \left( \frac{-u}{R} \right) du' \]

In this study, the \( m \) and \( u' \) of Lin’s results [10] were used to approximate \( \psi_u(E,T) \). The density distribution \( f(E_u,\sigma) \) is assumed as a unite of four normal distribution function \( f(E_u,\sigma) \):

\[ f(E_u,\sigma) = \sum_{i=0}^{4} c_i f(E_{u,i},\sigma), \sum_{i=0}^{4} c_i = 1 \]

To acquire high goodness of fit, the objective function (O.F.) is defined as:
\[ O.F. = 1 - \alpha_{adj}^2 = \frac{SSE}{\text{dof}_{\text{Error}}} = \frac{dof_{\text{Total}}}{\sum_{i=1}^{n} \left( \frac{\alpha_{i}}{dT} - \frac{\alpha_{i,\text{init}}}{dT} \right)^2} \times 100\% \]  

where the sum of squared error is defined as SSE, and the total sum of squares is defined as SST, and the degree of freedom of error and the degree of freedom of total are defined as dof_{\text{Error}} and dof_{\text{Total}}, respectively.

3. Results and discussion

3.1. Combustion thermal behavior analysis

Figure 1 displayed the individual combustion curve of lignite and WB with 25°C/min heating rate, respectively. As a low-rank coal, the main combustion region of lignite was characterized by only one stage. This was consistent with previous studies [11]. When lignite heated by TGA furnace, small adsorbed molecules and side chains with lower bond energy were precipitated out. The light volatiles were released rapidly due to increasing temperature. Once the accumulated volatiles began to burn, the coke and char were also ignited at the same time. Therefore, the decomposition of volatiles and concurrent oxidation of char and fixed carbon were overlapped, forming a broad and flat weight loss peak in the DTG curve, which was not as distinct as that of WB. This peak occurred between 350 and 600°C, with a maximum weight loss rate (-7.79%/min) at 432 °C.

In the case of WB, a slight shoulder and three weight loss peaks were observed during its combustion process. Because of the oxygen adsorption and initial oxidation on a solid surface, small amounts of protein and lipids contained in WB were decomposed. As a result, a pre-combustion mass shoulder from 220 to 258 °C was detected (center at 238°C, -5.01%/min). The subsequent combustion process could be divided into three main regions which were centered at 314°C, 454°C and 572 °C, respectively. The second DTG peak located in the first stage which extended from 260 to 400 °C. In fact, WB consists of herbaceous plant and belongs to a kind of lignocellulosic waste biomass. The cleavage of the glycosidic bonds and branch-chain structure of hemicellulose and cellulose were considered as the main causes of this peak. The value of DTG reached -20.87%/min which was much bigger than other loss peaks and lignite, indicating hemicellulose and cellulose were the main components of WB.

The second stage extended from 400 to 505°C with a gentle loss peak (DTG, -3.82%/min) which revealed the decomposition of remaining cellulose and lignin. It is generally known that lignin is a high
molecular aromatic compound composed of phenylpropane units. The decomposition of lignin is through the breakage of β-O-4 linkages at a relatively slow burning rate [12]. Thus, a plain region was observed in this combustion stage.

The third combusting zone extended from 505 to 624°C, attributing to the combustion of previous products (tar and coke mainly) and fixed carbon as well as the decomposition of ash. It was worth noting that due to the significant release of combustible components, the proportion of ash in the remaining solids increased. The minerals’ catalytic effect was evident which could promote solid combustion [13], leading to a steep and narrow mass loss peak (DTG₄, -7.25%/min). The above analysis showed that the combustion behavior of WB was more complex than that of lignite, thus maybe some synergistic effects could be expected.

The combustion of volatile matter released chemical energy to heat the remaining carbon coke. The more volatile matter, the more heat it can provide to ignite the coke. And due to the highly cross-linked aromatics with stronger conjugated double bonds in lignite, the ignition temperature of lignite (349°C) was much higher than WB (275°C). However, the Burnout temperature of lignite (604°C) was 20°C lower than WB (624°C), suggesting that lignite has a very short burning process. Due to the high reactivity of WB, the combustible substances combusted concentrated around 314°C (DTG₂, -20.87%/min/min).

3.2. The analysis of general distributed activation energy model (G-DAEM)
The G-DAEM considers the case that the frequency factor is a function of temperature, replacing the temperature integral of DAEM by its general type. In fact, the DAEM (m=0 in Eq. (3)) is a special form of G-DAEM. The 15°C/min heating rate was chosen for optimizing by numerical training use G-DAEM method, and the influence of m on the modelling process is analyzed.

| Fitting parameter | Radj² of dα/dT_m = 0 | Radj² of dα/dT_m = 0.5 | Radj² of dα/dT_m = 1 |
|-------------------|----------------------|----------------------|----------------------|
| Lignite           | 99.994%              | 99.994%              | 99.999%              |
| 90L10W            | 99.992%              | 99.993%              | 99.992%              |
| 70L30W            | 99.999%              | 99.996%              | 99.998%              |
| 50L50 W           | 99.998%              | 99.994%              | 99.993%              |
| 30L70 W           | 99.995%              | 99.981%              | 99.981%              |
| 10L90 W           | 99.994%              | 99.993%              | 99.996%              |
| WB                | 99.991%              | 99.993%              | 99.996%              |

As displayed in Table 2, the adjusted coefficient of determination $R_{adj}^2$ for all samples exceeded 99.980% which indicated the high accuracy of G-DAEM. And all were higher than that of Lin data [10] which clearly demonstrated the applicability of this method in complex thermal processes. It is worth noting that the $R_{adj}^2$ improved when increasing the value of m in Lin et al. [10], while this phenomenon was only observed on lignite and WB in this work. The $R_{adj}^2$ of Blends had only minor differences which didn’t affect the calculation accuracy. As a matter of fact, most of the published literatures acquiescently maintained the pre-exponential factor as a constant to reduce optimized computing capacity. However, for complex reaction systems, the real kinetic mechanism may be obtained by the G-DAEM method before the thermodynamic characteristics are fully understood.

Set $E_0$, $\sigma$ and $c$ (proportion) as labels of X-axis, Y-axis and Z-axis, the 3D features of pseudo-components were shown in Figure 2. It is well known that hardly decomposable substances need high activation energies. The $E_0$ of pseudo-components with different m value were lined from low to high. And the pseudo-component decomposed more intensively and react explosively, the smaller $\sigma$ is. The $c$ represents the proportion of pseudo-component in the total decomposition. The activation energy
distribution \( f(E) \) was exhibited in Figure 3. As shown in Figure 3, the effect of different mixing ratios and \( m \) values on the distribution \( f(E) \) curve were obvious.

Figure 2. The characteristics of activation energy distribution in 3D projection.

Figure 3. The profile of activation energy distribution for \( m = 0, m = 0.5 \) and \( m = 1 \).

In order to distinguish it from DAEM (\( m=0 \)), the G-DAEM with \( m=0.5 \) was analyzed to illustrate mechanism evolution. As shown in Figure 2, the lignite was composed of four pseudo-components and their corresponding \( E_0 \) were 152.32 kJ/mol, 187.27 kJ/mol, 202.66 kJ/mol and 220.71 kJ/mol, respectively. For WB, the \( E_0 \) of four pseudo-components were 169.25 kJ/mol, 182.53 kJ/mol, 222.26 kJ/mol and 260.91 kJ/mol, respectively. The \( E_{\text{mean}} \) of WB was 202.66 kJ/mol which was low compared to lignite (214.24 kJ/mol), indicating the WB required less energy input to complete the entire combustion process.

As listed in Table 3, the \( E_{\text{mean}} \) of blends were between lignite and WB which were between 203.65 kJ/mol (10L90W) and 211.34 kJ/mol (90L10W). As shown in Figure 2, with increasing WB ratio in the blend, the value of \( E_0 \) was first increased from 153.85 kJ/mol to 181.27 kJ/mol and then decreased to around 168 kJ/mol. The \( E_{02} \) first decreased from 190.07 kJ/mol to 187.43 kJ/mol and then stabilized at about 181-182 kJ/mol. The \( E_{03} \) slightly increased between 218.66 kJ/mol and 222.56 kJ/mol which suggested co-combustion process had little effect on this pseudo-component. The value of \( E_{04} \) was basically stable at about 220 kJ/mol, then suddenly increased to 261.44 kJ/mol. Meanwhile, the \( \sigma_4 \) of 10L90C and WB became much small which meant the fourth pseudo-component in 10L90W and WB would go through an explosive reaction.
Table 3. The average activation energy $E_{0\text{mean}}$ of raw feedstock and blends.

| Sample/Item | m=0  | m=0.5 | m=1  |
|-------------|------|-------|------|
| log10($A_{\text{min}}$) (min$^{-1}$) | 15   | 16.2859 | 17.5719 |
| log10($A_{\text{max}}$) (min$^{-1}$) | 15   | 16.4779 | 17.9558 |
| Lignite      | 196.60 | 214.24 | 232.22 |
| 90L10W      | 193.94 | 211.34 | 228.82 |
| 70L30W      | 193.78 | 211.07 | 228.57 |
| 50L50W      | 192.01 | 209.36 | 226.65 |
| 30L70W      | 189.48 | 206.71 | 223.77 |
| 10L90W      | 186.83 | 203.65 | 220.33 |
| WB          | 185.92 | 202.66 | 219.35 |

As for the value of m=0 and m=1, the trend of $E_{0\text{mean}}$ for all samples were consistent with m=0.5. However, the $E_0$ variation of two pseudo-components was different. One was the $E_{01}$ for m=0 which increased firstly and then stabilized ($E_{01}$ for m=0 increased firstly and then decreased). And another was the $E_{01}$ for m=1 which first down and then remained basically stable. The $E_0$ variation of other pseudo-components showed a similar tendency to that of m=0.5.

The A-E compensatory effect was imported when the value of m was set as a non-zero number. The value of log$_{10}A$ was a constant (15) for m=0 while that varied from 17.57188 to 17.95576 for m=1. Therefore, the overall trend moved toward lower energy barrier region for m=0 and toward higher energy barrier for m=1 in X-Y surface as displayed in Figure.3. The average activation energy $E_{0\text{mean}}$ also showed the same trend. For instance, the $E_{0\text{mean}}$ of lignite and WB improved from 196.60 kJ/mol to 232.22kJ/mol and from 185.92 kJ/mol to 219.35 kJ/mol when increasing m from 0 to 1, respectively. However, as shown in Figure.3, the $E_{01}$ of 30L70W, 10L90W and WB samples had a slight decline when increasing m from 0.5 to 1. As mentioned above, the physical oxygen adsorption effect was visible when the sample contained high WB content. Therefore, the possible cause of this special case was the physical oxygen adsorption affected the first pseudo-component thermochemical decomposition. Although the pre-exponential factor of the G-DAEM was not a constant, this model was still composed and regrouped of multiple first-order reaction models. The nature characteristics of first-order could also be observed in G-DAEM.

But it must be clearly known that the kinetic parameters obtained by G-DAEM or DAEM were applicable to pseudo-components. In the actual reaction process, the combustion of components is not a completely isolated process, and there is no very clear boundary between them. Thus, the overlap of the actual reaction will occur definitely. To group reactions that are not a series into one virtual component. As a result, the G-DAEM may group reactions which are not the same first-order into one same pseudo-component. Therefore, the pseudo-component cannot be equated with the combusting of a certain type of actual substance in the sample. On the other hand, the pseudo-components in G-DAEM can accurately reflect the combustion characteristics of various substances contained in the sample. And G-DAEM can provide more abundant kinetic parameters compared to other kinetic models, especially the reaction concentration parameter $\sigma$. Low $\sigma$ means reaction proceed more explosively which can cause intense combustion and turbulence. These parameters had important reference value for designing and selecting burner when combusting this kind of fuel.

4. Conclusion
The G-DAEM was successfully applied to the co-combustion process, which proved again that G-DAEM was suitable for complex reaction systems. The activation energy distribution of four pseudo-components could accurately describe the change of activation energy in the combustion process. Considering the change of pre-exponential factor with temperature, the obtained kinetic parameters are closer to the actual mechanism. The G-DAEM provided an effective method to design and select burner for combusting specific fuel.
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