Characterization of Cornstalk and Bituminous Coal Based on Kinetic and Thermodynamic Parameter for Co-pyrolysis

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Abstract. The pyrolysis characteristic of bituminous coal (BC) and raw cornstalk (RC) were investigated through thermogravimetric analysis from environment temperature to 900 °C with 5, 15 and 25 °C/min. The distributed activation energy model (DAEM) was applied to estimate the kinetic parameters of samples. The average activation energy ($E_a$) of BC, RC and the blended sample ($m_{BC}/m_{RC}=6/4$) were 304.56, 207.77 and 226.26 kJ/mol, respectively. The heat energies of the experiment to be needed was lower than that of calculation during co-pyrolysis, comparing with the theoretical calculation $E_a$. To further researcher the thermal behavior during co-pyrolysis, the closeness of change in Enthalpy ($\Delta H$) values vs. $E_a$ values for the blend indicated that activated complex formation may be favored because of lower potential energy barrier. Moreover, Gibbs free energy ($\Delta G$) for the blend varied from 108.40 to 275.93 kJ/mol, the pyrolysis process was converted to disordered-state from ordered-state, considering the changes of Entropies ($\Delta S$) loss.

Keywords. Co-pyrolysis; thermogravimetric analysis; kinetic model; thermodynamic analysis.

1. Introduction
Coal is the most important source of energy, accounts for 67.5% of primary energy structure, almost 75% of electricity generation, and 60% of civilian commercial energy in China, so it is clear that application of coal contributes great to China’s economic development [1]. Low rank coals (bituminous and lignite coal), can be regarded as an abundant (41.18% of the total coal reserve) and inexpensive resource, which play a great role in the utilization of chemicals and energy in this century. Unfortunately, comparing the high rank coal, the inherent limitations of low rank coal greatly restrict their large-scale application, for instance high oxygen content, low calorific values and high ash content. Meanwhile, the inefficiency and uncleanness of low rank coal consumption has been focused attention on the sustainability environmental and economic problem under the excessive growth of its consumption, such as global climate warming, NOx and SOx emissions [2]. The major challenge for mankind is that how to deal with the conflict of environment problems and requirement for energy. To cope with this clash, the direct way is shrinkage fossil fuel consumption and increases the utilization of renewable resources. Biomass is a clean and renewable energy with near-zero carbon emission, which is an abundant and low-cost source to promise among alternative energy sources for fossil fuels [3]. Nevertheless, there are some deficiencies for biomass, such as lower density, lower calorific value, scattered distribution, prominently limit its extensive utilization [4]. Compared with biomass, the
advantage of coal, such as higher density, higher calorific value, concentrated distribution, is favorable for recovering the imperfection of biomass. Meanwhile, advanced coal pyrolysis technology has been achieved widespread industrialization and reveals high complementarity with utilization of biomass [5]. Meanwhile, there is an interesting opportunity to reduce the trouble of coal in resource utilization to assure environment issues [6]. Therefore, it makes sense to further study on coal and biomass during co-pyrolysis process.

Co-pyrolysis is an essential step of co-thermochemical conversion for coal and biomass, which effect on the product regularity of distribution and characteristic under physicochemical evolution [7]. The characteristics of pyrolysis products is depending on the kinds of feedstock (softwood, hard wood, wastes of forestry and agriculture) which has different structural composition, for instance, the oil could be changed for desired compounds due to phenolic, alcohols, ketones and esters components formed by lignin, cellulose and hemicellulose during co-pyrolysis process between selective biomass and coal [8]. Meanwhile, the ordering of co-pyrolysis char structure is increased by addition of cellulose, the disordering degree of microstructure structure is promoted by hemicellulose when the co-pyrolysis between biomass model compounds with coal on char structure transformation is researched [9]. Moreover, several reports showed that the inherent alkali and alkaline earth metals (AAEMs) in biomass could be used to reduce the catalyst cost in coal pyrolysis industry as natural catalyst [10]. With some studies, it is found that tar cracking converted into gas, and repolymerization formed into secondary tar and char because biomass char was also served as catalyst [11]. It is significance that the biomass could supply cheaper catalysts during biomass and coal industrialization as a potential provider [12].

According to previous studies, it is important to obtain the pyrolysis products from raw material decomposition by different conditions of pyrolysis. Regarding co-pyrolysis of coal and biomass, some researchers put forward that the impact of co-pyrolysis occurred synergistic with non-linear relationship [13]. Shui et al. [14] stated that the thermochemical conversion of analogous coal model compound improved to 4.3% at 360 °C, blending 10% lignin, this result from that the aliphatic C-C bonds of model compounds were attacked by phenoxy radicals derived from lignin. And then mechanism of phenoxy radical was further verified for positive synergetic effect between Shenfu Sub-bituminous coal and sawdust during co-pyrolysis process [15]. However, some reports support the opposite results [16]. The different conclusions for co-pyrolysis process are determined by process conditions and the characteristic of raw material (physical properties as well as chemical compositions). The process condition refers to reactor types, pyrolysis temperature, heating rate, reaction pressure and residence time.

To investigate the thermal degradation processes and mechanisms, thermogravimetric analysis (TGA) can be employed as an efficient tool, which is widely used in physical chemistry, thermal analysis and material research in relatively wide range of temperatures. Some different models have been established to keep a watchful eye on chemical reactions, such as distributed activation energy model (DAEM), the Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), master-plots and so on [17]. Moreover, the pyrolysis activation energy of single or mixture fuel reaction could be acquired after the kinetic data inputted a kinetic reaction model. Furthermore, an information about the pyrolysis characteristics and kinetic analysis has a great importance for design and operation of co-physicochemical conversion during the co-pyrolysis process, which is very necessary for product yield and performance promotion.

In the foreseeable future, coal is still considered to be major energy resources in China. Meanwhile, more than 8.2 billion tons of agricultural residues (rice straw, wheat straw, cornstalk and cotton straw) could be produced annually in China, and 35% of which is cornstalk, most of which is burned or discarded, leading to a series of environmental pollution [18]. There is a focused opportunity to combine biomass and coal during co-pyrolysis process, and the result of that not only reasonably utilizes biomass resources but also solves environmental problems [19]. In this paper, the thermal characteristics of raw cornstalk (RC) and bituminous coal (BC) in TGA were investigated to further study the co-pyrolysis behaviors of coal and biomass. RC is blended with BC at different weight ratio,
and the pyrolysis behaviors of blends are studied through TGA under a non-isothermal atmosphere. Meanwhile, the difference of weight loss between the blend and raw material during the same pyrolysis process was investigated except heating rate. Furthermore, thermal decomposition kinetic parameters and thermodynamic parameters (Enthalpy, Entropy change and Gibbs free energy) of blend were determined by DAEM and thermodynamic equations, respectively.

### 2. Materials and Methods

#### 2.1. Samples

Bituminous coal (BC) was obtained from Yima colliery (Henan province, China), the biomass feedstock used in this study was raw cornstalk (RC) from farm which produced a great deal of cornstalk annually. The particle size of samples was about 0.18-0.25 mm, and drying at 105 °C for 24 h. The coal ratio of the blends (CR) was 0%, 20%, 40%, 60%, 80%, 100%, respectively.

The proximate and ultimate analyses of BC and RC were shown in Table 1. In addition, hemicellulose, cellulose and lignin of RC were 19.93, 32.43 and 14.72 wt.%, which were obtained by following NREL/TP-510-42618 [20]. The mineral composition of BC, RC and blends ash was obtained by inductively coupled plasma-atomic emission spectrometry (213DFOG/ASDWE, Japan) as shown in Table 2. As shown in Table 2, the contents of AAEMs in ash of RC were higher than that of BC, K2O, Na2O and CaO in the ash of RC was 15.85, 43.21 and 47.25 mg/g, respectively.

#### 2.2. Methods

The non-isothermal thermal analysis of each sample was achieved based on thermogravimetric analyzer (TGAQ50, USA) with platinum crucible. To ensure that mass and heat transfer smoothly, 10 mg of material was added in the sample crucible putted in thermogravimetric analyzer. Before experiment the N2 was leaded into the furnace to maintain an inert atmosphere at flow rate of 40 mL/min. And then the material was heated from room temperature to 900 °C under non-isothermal conditions at 5, 15 and 25 °C/min, respectively, the material mass was recorded simultaneously. Each experiment was tested for three times to make sure the reliability of experimental results.

#### 2.3. Kinetic Model

2.3.1. Distributed Activation Energy Model. To explore the mechanism of pyrolysis reaction, it was assumed that a series of irreversible, parallel, independent and first-order thermal decomposition reactions occur simultaneously in the pyrolysis system. However, the distributed activation energy model (DAEM) has an advantage to research pure solid fuel pyrolysis [21]. The distribution function
routinely is assumed as follows:

\[
\alpha(t) = 1 - \int_0^t \exp(-A) \int_0^T \exp\left(-\frac{E_a}{RT}\right) f(E_a) dE dT
\]

where \( \alpha(t) \) is the extent of conversion degree with time, meaning the ratio of the quality of volatiles produced at any time to the total volatile at the end of the pyrolysis process, \( T \) is the absolute temperature, \( A \) satisfies the frequency factor according to the activation energy value and \( f(E_a) \) is a distribution curve of \( E_a \). And \( m_0, m_t \) and \( m_\infty \) represents the initial quality of raw material, the quality at time \( t \) and the final quality until the end of pyrolysis reaction. The function of \( f(E_a) \) represented by equation (3) [22]:

\[
\int_0^\infty f(E_a) dE_a = 1
\]

In this paper, \( f(E_a) \) and \( A \) are estimated by Miura’s method for RC and BC with different heating rates. Then the \( E_a \) and \( A \) are also obtained at the same \( \alpha(t) \) for each fuel sample. The \( f(E_a) \), \( E_a \) and \( A \) are obtained from the following equation (4) [23].

\[
\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE}{E}\right) + 0.6075 - \frac{E_a}{RT}
\]

This function shows that temperature plays an important role, and different temperatures affect the point of slope and intercept which needs to fit linear, where the \( \beta \) is heating rate. Meanwhile, increased pyrolysis temperature could lead to the increase of the conversion rates at every heating rate.

2.3.2. Thermodynamic Analysis. Besides activation energy, enthalpy (\( \Delta H \)), Entropy (\( \Delta S \)) and Gibbs free energy (\( \Delta G \)) play an important role for the thermodynamic system as thermodynamic parameters. For pyrolysis, enthalpy means the total energy consumption used for thermal decomposition of raw material to char, oil and gas. Moreover, the degree of randomness is represented by entropy in a system. The change of \( \Delta G \) is the total energy increase of the pyrolysis system at the approach of formation of the activated complex [24]. The relation of \( \Delta H, \Delta G \) and \( \Delta S \) can be described in equations (5)-(7) [25]:

\[
\Delta H = E_a - RT
\]

\[
\Delta G = E_a + R \cdot T \ln\left(\frac{K_B \cdot T}{h \cdot A}\right)
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T}
\]

where, \( K_B \) is Boltzmann constant (\( 1.381\times10^{-23} \text{ J/K} \)), \( h \) is Plank constant (\( 6.626\times10^{-34} \text{ J s} \)).

3. Results and Discussion

3.1. Thermogravimetric Experiments

3.1.1. Effect of Biomass Ratio. The characteristic pyrolysis of fuels (parent and blended samples) were researched by TGA at different heating rates to further estimate the nature of pyrolysis. The mass ratios of coal in the blended samples were 100%, 80%, 60%, 40%, 20% and 0%, respectively.
Description of the pyrolysis process of the blended samples at 5 °C/min was shown in figure 1 with thermogravimetry (TG) and different thermogravimetry (DTG) plot. TG curve could reveal the weight loss of the sample, and DTG profile was obtained by taking the derivative of every point of TG curve, indicating the decomposition rate of sample. As shown in figure 1b, the thermal decomposition of biomass could be differentiated three parts from DTG. The first part mainly represented the loss of light volatiles and moisture, occurred in the temperature range of ambient temperature to 180 °C. The second one was from 180 °C to 450 °C, at which the reaction rate attained maximum on account of cellulose, hemicellulose and a part of lignin decomposed. The ether bond and glucosidic bond linked Hemicellulose and Cellulose was breakage with dealkylation, decarbonylation and decarboxylation reactions under lower temperature due to weak bond. The strong peak existed particularly maximum in the DTG curve from the whole pyrolysis process. The last part represented that the char occurred continuous decomposition with slow rate from 450 °C to the end, and the rate of degradation was much slower than the previous stage.

The pyrolysis parameter of blend was shown in table 3. The thermal decomposition of BC and RC was initialized at around 215 °C and 184 °C in table 3, respectively. At the end of pyrolysis process, the highest residue mass for BC was about 82.50%, and the lowest residue mass for RC was 30.12%. Decreasing the ratio of BC in the blend caused a decrease in the pyrolysis residue mass. Further, it was shown that there were three peaks for blended samples from DTG curve affected by both coal and RC during co-pyrolysis process, and the blended samples maintained fundamentally the same position and shape comparing with individual pyrolysis on the temperature axis [26]. However, the CR affected the maximum reaction rate and peak height of the curves especially (dw/dt)_{max,1}, and the reaction rate of blends were ordered by CR-80% > CR-60% > CR-40% > CR-20%. Increasing the RC ratio in the blend, the maximum devolatilization rate of the peaks was higher due to the more organic volatiles thermal decomposition.

3.1.2. Effect of Heating Rate. Heating rate of pyrolysis process is also a significative factor in the fuel thermal decomposition, which could change the product distribution. Figure 2 showed the DTG and TG curves of the blend (CR-60%) at several heating rates. According to TG profile, heating rate led to more thermal decomposition of the blend while heating rate reduction result in lower decomposition. It can be seen from the DTG profile that the peak of DTG for RC shifted to positive side at 25 °C/min compared to 5 °C/min at horizontal coordinate axis. This resulted from existed a temperature gradient between inner core and outer surface of RC which promoted the heat transfer to postpone the thermal decomposition process under higher heating rate [27]. The temperature gradient of sample could be seen linear along the cross-section at lower heating rate, leading to small temperature difference from the inner core to ambient of a particle of sample. Similar phenomenon was reported in previous literatures [28].

![Figure 1](image-url)

**Figure 1.** (a) TG profiles for BC, RC and the blends at 5 °C/min; (b) DTG profiles for BC, RC and the blends.
Table 3. The pyrolysis parameters of blends at different ratio.

| Samples | \( T_i \) (°C) | \( T_1 \) (°C) | \((\text{dw/dt})_{\text{max},1}\) (wt.%/min) | \( T_2 \) (°C) | \((\text{dw/dt})_{\text{max},2}\) (wt.%/min) | \( T_e \) (°C) | \( Y \) (%) |
|---------|----------------|----------------|--------------------------------|----------------|--------------------------------|-------------|---------|
| BC      | 215            | 517            | 0.0094                         | 569            | 82.50                          |
| CR-80%  | 211            | 310            | 0.0809                         | 511            | 0.0277                         | 572         | 71.50  |
| CR-60%  | 207            | 318            | 0.1661                         | 504            | 0.0368                         | 583         | 60.57  |
| CR-40%  | 201            | 316            | 0.3039                         | 508            | 0.0512                         | 575         | 49.39  |
| CR-20%  | 198            | 314            | 0.3431                         | 510            | 0.0671                         | 570         | 39.81  |
| RC      | 184            | 309            | 0.3500                         | 448            | 30.12                          |

Note: \( T_i \), initial decomposition temperature; \( T_1 \), temperature of the higher DTG peak; \((\text{dw/dt})_{\text{max},1}\) reaction rate of the higher DTG peak; \( T_2 \), temperature of the lower DTG peak; \((\text{dw/dt})_{\text{max},2}\), reaction rate of the lower DTG peak; \( T_e \), terminated temperature of the pyrolysis; \( Y \), pyrolysis residue mass.

As shown in figure 2b, it was found that the DTG peak was higher with increasing heating rate. In addition, the pyrolysis behavior had an important relationship with heating rate, so that pyrolysis products (tar and gas) from secondary reactions could be influenced by heating rate. There was more free radical generated from volatile components reach a specified temperature in a short time at higher heating rate, and then secondary reactions should be sufficient both released gas and tar species owing to the free radical as medium. In the end, the DTG peaks moved slightly on the temperature axis because of interaction between BC and RC.

Scanning Electron Microscope (SEM) images of pyrolysis char will contribute to the understanding the structure of products affected heating rates under the pyrolysis conditions. Figure 3 show the changing of char under different heating rate for SEM with blend (CR-60%) at 900 °C. As can been seen from figure 3, the more pores been formed with increase of heating rate. Amount of volatile materials formation started with inner core of fuel due to temperature gradient at higher heating rate, and then which was sprayed from the particle to create the pore as well as volcanic eruption. Based on the SEM images obtained, this result indicated that high heating rate enhanced the degree of vehement impact by rapid formation and evolution of volatile in pyrolysis process.

Figure 2. (a) TG profiles for the blend (CR-60%) at different heating rates; (b) DTG profiles for the blend.
3.2. Kinetics Analysis

Pyrolysis was a very complex physicochemical reaction process, much less co-pyrolysis process. In order to get insight into the co-pyrolysis between biomass and coal, the values of TGA were further analyzed to obtain activation energy ($E_a$) and pre-exponential factor ($A$) using the distributed activation energy model (DAEM) [29]. In this study, the pyrolysis temperature was ranged from environment temperature to 900 °C at 5, 15 and 25 °C/min, respectively. The Arrhenius plots was built, and calculating $\ln(\beta/T^2)$ versus $1/T$, those were linear fitting at a certain $\alpha$, and then $A$ and the $E_a$ were acquired directly according on slop and intercept of Eq.(4). The parameters of kinetics of samples were shown in table 4 at different conversion rate. Relative deviation ($R$) of fitting a straight line were with the narrow interval of 0.9503–0.9999 indicating these experimental points fitted well, and the result has very high accuracy.

As shown in table 4, the value of $A$ revealed variations in a wide range from $10^{15}$ to $10^{20}$ at different conversion rates, which suggested the complex reactions and composition of samples that appear during decomposition. Low $A (<10^9$ s$^{-1}$) may demonstrate mainly a surface reaction, however, if the reaction was not dependent on the surface area, the low $A$ may show a tight junctional complex. Alternatively, the higher $A$ ($\geq 10^9$ s$^{-1}$) indicated a simpler complex (loose junction complex) [30]. Moreover, the complex was expected to expand by interact more actively with near neighbors comparing the unimolecular. As shown in table 4, the value of $A$ for BC was $4.18 \times 10^{19}$ higher than that of RC, it was observed that there was more collision intensity of BC than that of RC during pyrolysis process. And the pyrolysis behavior indicated the complex nature and components for both BC and RC following multi-step degradation reaction chemistry.

The activation energy of samples at different conversion rate was shown in figure 4, with the conversion rate increasing, the activation energy increase. The activation energy of BC, RC and the
blended sample were about 258.94–370.36 kJ/mol, 175.0–248.84 kJ/mol and 133.07–332.17 kJ/mol, respectively. The mean activation energy of BC and RC were about 304.56 kJ/mol and 207.77 kJ/mol, respectively. As shown in figure 4, the theoretical calculation $E_a$ of the blended sample were obtained from the weighted average values of individual $E_a$ according on weight percentage of parent fuel, which were higher than the experimental values. The mean calculation $E_a$ and experimental $E_a$ were about 265.84 kJ/mol and 226.26 kJ/mol. The $E_a$ of experimental value for the blended sample was reduced by 14.89%.

![Figure 4](image)

**Figure 4.** Activation energy of samples at different conversion rate.

### Table 4. The parameters of kinetics of samples at different conversion rate.

| $\alpha$ | $E_a$ (BC) | $A$ (BC) | $R$ (BC) | $E_a$ (RC) | $A$ (RC) | $R$ (RC) | $E_a$ (CR-60%) | $A$ (CR-60%) | $R$ (CR-60%) |
|---|---|---|---|---|---|---|---|---|---|
| 0.1 | 258.94 | 2.38E+19 | 0.9804 | 175.00 | 3.75E+17 | 0.9953 | 133.07 | 3.00E+15 | 0.9999 |
| 0.2 | 269.81 | 6.45E+18 | 0.9968 | 185.97 | 3.66E+17 | 0.9998 | 165.51 | 4.27E+17 | 0.9552 |
| 0.3 | 263.24 | 6.12E+18 | 0.9916 | 197.92 | 1.25E+18 | 0.9993 | 198.06 | 2.71E+16 | 0.9616 |
| 0.4 | 269.61 | 6.35E+19 | 0.9947 | 202.57 | 1.80E+18 | 0.9983 | 202.01 | 2.32E+17 | 0.9567 |
| 0.5 | 279.18 | 1.06E+18 | 0.9763 | 203.67 | 5.57E+17 | 0.9971 | 226.13 | 8.25E+15 | 0.9992 |
| 0.6 | 312.55 | 4.27E+19 | 0.9669 | 205.14 | 5.98E+18 | 0.9959 | 233.94 | 2.32E+16 | 0.9503 |
| 0.7 | 349.50 | 1.23E+20 | 0.9855 | 219.74 | 3.75E+17 | 0.9878 | 236.59 | 1.30E+16 | 0.9857 |
| 0.8 | 367.86 | 1.26E+19 | 0.9790 | 231.08 | 5.57E+19 | 0.9994 | 308.84 | 1.08E+18 | 0.9996 |
| 0.9 | 370.36 | 9.69E+19 | 0.9847 | 248.84 | 1.75E+17 | 0.9994 | 332.17 | 4.63E+16 | 0.9691 |
| Mean | 304.56 | 4.18E+19 | 0.9460 | 207.77 | 7.40E+18 | 0.9971 | 226.26 | 2.07E+17 | 0.9691 |

Note: $E_a,$ kJ/mol; $A,$ s$^{-1}$

3.3. Thermodynamic Parameters

At different heating rates, thermodynamic parameters were calculated by Equations (5)-(7) and the values for parameter were averaged at three heating rates. Thermodynamic corresponding results were presented in table 5. The $\Delta H$ illustrated the energy difference between the raw sample and the activated complex, and the values of $\Delta H$ for BC, RC and the blend increased with the increase of conversion rate. Based on table 5, it was indicated that there was the little change between the $\Delta H$ and $E_a$ ($\sim$6 kJ/mol) of fuels for the average values, revealing the lower potential energy barrier was beneficial to formation activated complex. Kaur et al. [31] reported similar result. The average values of $\Delta H$ for RC and BC was 202.78 kJ/mol and 297.81 kJ/mol, respectively. It was noticed that more heat energies were required to break the bonds of compound for BC than RC, which was accordant with $E_a$ [32]. The change in enthalpy for blend sample (CR-60%) at different heating rate was...
illustrated in figure 5. Enthalpy variation for blended sample was 133.07–332.17 kJ/mol, and the average value of $\Delta H$ for the blend (CR-60%) was about 220.79 kJ/mol. The pyrolysis theoretical calculation enthalpy of the blend (259.80 kJ/mol) was higher than experimental value of the blend.

| $\alpha$ | BC |  | RC | CR-60% |  |  |  |
|---|---|---|---|---|---|---|---|
|  | $\Delta H$ | $\Delta G$ | $\Delta S$ | $\Delta H$ | $\Delta G$ | $\Delta S$ | $\Delta H$ | $\Delta G$ | $\Delta S$ |
| 0.1 | 253.25 | 177.48 | 110.81 | 170.74 | 130.40 | 78.70 | 128.67 | 108.40 | 38.29 |
| 0.2 | 263.72 | 190.97 | 99.39 | 181.45 | 139.00 | 78.00 | 160.87 | 116.76 | 79.08 |
| 0.3 | 256.98 | 182.67 | 98.72 | 193.24 | 143.80 | 87.94 | 193.24 | 160.89 | 55.84 |
| 0.4 | 263.21 | 172.37 | 117.98 | 197.76 | 145.27 | 90.74 | 197.05 | 153.26 | 73.45 |
| 0.5 | 272.60 | 206.39 | 83.74 | 198.74 | 150.87 | 80.78 | 221.05 | 193.23 | 45.50 |
| 0.6 | 305.80 | 213.02 | 114.24 | 200.12 | 139.56 | 100.37 | 228.49 | 193.41 | 53.52 |
| 0.7 | 342.39 | 237.48 | 122.60 | 214.63 | 167.20 | 77.19 | 230.44 | 195.19 | 47.71 |
| 0.8 | 360.16 | 264.75 | 103.00 | 225.65 | 148.48 | 118.27 | 302.28 | 236.06 | 83.91 |
| 0.9 | 362.13 | 244.00 | 119.41 | 242.72 | 191.70 | 69.36 | 325.01 | 275.93 | 57.00 |
| Mean | 297.81 | 209.90 | 107.77 | 202.78 | 150.70 | 86.82 | 220.79 | 181.46 | 59.37 |

Note: $\Delta H$ and $\Delta G$, kJ/mol; $\Delta S$, kJ/(mol K).

As shown in table 5, $\Delta G$ for BC and RC during pyrolysis process were measured to be ranging from 177.48 to 264.75 kJ/mol and 130.40–191.70 kJ/mol. The average $\Delta G$ for the pyrolysis of BC and RC was 209.90 kJ/mol and 150.70 kJ/mol, respectively. Moreover, the average value of $\Delta G$ for BC was higher from the average value of $\Delta G$ for RC. The value of $\Delta G$ for the blend at different heating rates was represented in figure 6. To further comparison of the value of $\Delta G$ for the blend during co-pyrolysis, the average value of $\Delta G$ for theoretical calculation was obtained by weighted average. Experimental value and calculated $\Delta G$ for the blend was 186.22 kJ/mol and 220.79 kJ/mol. It was demonstrated that the heat energies were lower with blending both RC and BC during co-pyrolysis process.

![Figure 5](image1.png) ![Figure 6](image2.png)

**Figure 5.** Change in Enthalpy for blended sample as a function of conversion.

**Figure 6.** Change in Gibbs Energy for blended sample as a function of conversion.

As seeing in table 5, the average value of $\Delta S$ for BC, RC and the blend were 107.77, 86.82 and 59.37 J/(mol K), respectively. The low $\Delta S$ meant that the fuel was close to its own thermodynamic equilibrium, the activated complex need more time to be formed due to little reactivity [33]. In this situation, reactivity would be high and less reaction time was observed to form activated complex in
faster reaction system. It could be found that the reactivity of RC was lower than that of BC. Moreover, the reactivity of the blend was lower when RC was added into BC. Figure 7 represented the values of $\Delta S$ for the blend at different heating rate. The average value of $\Delta S$ for the blend (59.37 J/(mol K)) was lower than calculated value of that (99.39 J/(mol K)). It was declared that thermal behavior of blended sample was influenced greatly interaction between BC and RC during co-pyrolysis, and the pyrolysis process was converted to disordered-state from ordered-state due to the $\Delta S$ losses of samples.

Under co-pyrolysis conditions, the experimental value of $E_a$, $\Delta H$ and $\Delta G$ for blended sample were lower than theoretical calculation of that for the blended sample, the synergetic interaction occur between RC and BC. This phenomenon may be mainly caused by two reasons: (1) interaction between RC and BC by free radicals. According to the table 1, the H/C ratios of BC and RC are 0.41 and 1.66 respectively. It was shown that RC may provide more hydrogen radical as a hydrogen donor than BC during thermo-chemical conversion, due to higher H/C molar ratio for RC, especially in 200~500 ℃. Due to a higher H/C with RC, the thermal decomposition of coal was facilitated by cross-linking reactions of free radicals from RC with volatiles and char to promote the secondary reactions, preventing free radicals’ recombination, similar results were also reported in previous researches. (2) Catalytic effect on synergistic interactions. As shown in table 2, the ash of RC contained significant amount of AAEMs, especially Na$_2$O and K$_2$O. Na$_2$O and K$_2$O content in the ash of CR-60% was 31.43 mg/g and 16.78 mg/g, however, the theoretical calculation value of Na$_2$O and K$_2$O was 27.70 mg/g and 9.92 mg/g. The result supported that organic substance of the blend was further thermal degradation, and the thermal decomposition of BC was improved by the AAEMs. Furthermore, the nascent char of RC with a high catalytic activity improved tars to transform from volatiles to gases since its larger average pore size.

4. Conclusions
In this study, kinetics and thermodynamic behavior of BC, RC and the blended samples were investigated using TGA. The DTG curve of blended samples showed three dominating peaks during co-pyrolysis, and which maintained fundamentally the same position and shape on the temperature axis comparing with parent fuel. Peak of DTG for RC shifted to positive side of the horizontal coordinate axis to promote the heat transfer and secondary reactions account of higher heating rate. Moreover, average activation energy of the blend for kinetics analysis (226.26 kJ/mol) was lower than that of theoretical calculation. To further researcher the thermal behavior, thermodynamic parameters were also calculated and discussed. The variation trend of $\Delta H$ for the blend was close to $E_a$ at different conversion rate. The average $\Delta G$ for the pyrolysis of BC, RC and the blend was 209.90, 150.70 and 186.22 kJ/mol, respectively. The thermodynamic parameters demonstrated that the lower energy barrier of the blend to be need during co-pyrolysis, the synergetic interaction occurred between RC and BC causing by free radical and catalytic action.
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