Kinetics and Thermodynamic Analysis of Recent and Ancient Buried Phoebe zhennan Wood

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ABSTRACT: Kinetics and thermogravimetric analysis of recent Phoebe zhennan wood (RZ) and ancient buried P. zhennan wood (ABZ) were investigated under a nitrogen atmosphere at different heating rates of 5, 10, 15, and 20 K/min. The activation energy values were estimated based on the Flynn−Wall−Ozawa model-free method, and then, the Coats−Redfern model-fitting method was used to predict the reaction mechanism. The best model of RZ for regions 1 and 2 was based on the diffusional and reaction order (second-order) mechanism, respectively, while a diffusional (Jander equation) mechanism is the best model for ABZ. The change in enthalpy and activation energy of the RZ was lower than that of the ABZ at different conversion rates. When the conversion rate was less than 0.4, the RZ may require lower thermal decomposition reaction energy, but the overall energy of thermal decomposition reactions and the degree of disorder was not much different.

1. INTRODUCTION

With the diminishing of reservoirs of fossil fuels and the increasing demand for energy and chemicals, the renewable and environmentally energy resources become more and more popular.1 Biomass is one of the most potential renewable resources for power and heat generation with huge reserve.2−4 The utilization of biomass has positive effects on the environment and will decrease dependency on the limited fossil fuels.5 Wood is one of the main renewable solid energy resources. Phoebe zhennan (Family: Lauraceae, Category: Phoebe) is widely cultivated in Sichuan Province, China, and many buried P. zhennan wood is found there.6 Buried wood is a common and unexploited resource in forests,7 the formation of which is mostly through two ways:7 disastrous events leading to a rapid burial, given by examples as landslides, earthquakes, and floods8 or litter deposition and overgrowth by ground vegetation caused by the gradual burial of deadwood.9−11 At the same time, buried wood is generally considered to be the major precursor of coal.12−15 Recent and ancient buried wood are expected to play a more important role in the energy mix of the future.16 Pyrolysis has been developed extensively as a promising platform for biofuels or chemical production from various types of biomass,17 and with best industrial perspectives for the process, conditions can be optimized to maximize the yields of gas, liquid, and char.5 The major content of biomass is cellulose, hemicellulose, and lignin, which determined its pyrolysis behavior and the yields of pyrolysis products both quantitatively and qualitatively.18 The major content of ancient buried P. zhennan wood (ABZ) is different from recent P. zhennan wood (RZ) because the cellulose and hemicellulose of...
ABZ degraded after the transformation of the natural environment.19

As one of the most common techniques, thermogravimetric analysis (TGA) is usually used for biomass pyrolysis analysis.20−24 Numerous works on kinetic studies of wood have been reported in literature studies.18,25−33 Various isoconversional methods such as Kissinger,30 Kissinger–Akahira–Sunose,34 Flynn–Wall–Ozawa (FWO),17,34 Starink,1 and Friedman methods18,25,34 were used to calculate the kinetic parameters, while the Criado method,31 the Avrami equation,28,35 and the Coats–Redfern (CR) method26 were used to predict the reaction mechanism. It was found that the main mechanisms of wood were three-dimensional diffusion,28 random nucleation with one nucleus mechanisms,31 and reaction order (2nd to 3rd).26

However, there are rarely studies comparing the pyrolysis of recent and ancient buried wood. In this study, kinetics and TGA of ABZ and RZ were investigated under a nitrogen atmosphere at different heating rates of 5, 10, 15, and 20 K/min. The activation energy ($E_a$) values were estimated at different conversion rates based on the FWO model-free method, and then, the CR model-fitting method was used to predict the reaction mechanism. Thermodynamic parameters such as change in enthalpy ($\Delta H$), change of the Gibbs free energy ($\Delta G$), and change of reaction entropy ($\Delta S$) were also calculated. The thermodynamic parameters provide basis for further applications of the thermochemical conversion of ABZ and RZ as a potential feedstock.

2. RESULTS AND DISCUSSION

2.1. TGA. The derivative thermogravimetry (DTG) curves and the change in conversion rate ($\alpha$) with the temperature of RZ and ABZ at different heating rates (5, 10, 15, and 20 K/min) under a nitrogen environment are showed in Figure 1. There was only one obvious peak of RZ and ABZ at 598−625 and 627−652 K, respectively, when the maximum weight loss rate occurred, which related to the decomposition of hemicellulose and cellulose, while lignin is decomposed in the whole temperature range without characteristic peaks.18 It was found that the total mass of RZ and ABZ was 67.0 and 63.5%, respectively.

Figure 1. Pyrolytic decomposition at different heating rates: (a) DTG (RZ), (b) DTG (ABZ), (c) $\alpha$(RZ), and (d) $\alpha$(ABZ).

Figure 2. Comparative DTG and TG curves between RZ and ABZ at the heating rate of 20 K/min: (a) DTG and (b) $\alpha$. 
The DTG curves of RZ and ABZ show the same trend under different heating rates: slower heating rates correspond to larger peak mass loss rate values while taking place at lower temperatures. The main components of wood are cellulose, hemicellulose, and lignin, which are the main organic polymers decomposed during wood pyrolysis. Because of the different chemical properties and structures of the three components, their pyrolytic properties are also different. The literature shows that hemicellulose decomposed easily, but lignin was the hardest to decompose. The temperature of mainly weight loss of hemicellulose and cellulose was 493–588 and 588–673 K, respectively, while the maximum mass loss rate happened at 541 and 628 K. Lignin decomposed with a very low mass loss rate under the whole temperature range. The intersection decomposition temperature of hemicellulose and cellulose is about 588 K, which corresponds to the conversion rates 0.4 of RZ and 0.25 of ABZ. The corresponding temperature at the conversion rate 0.8 of RZ and ABZ is 630 and 658 K, respectively. Therefore, the degradation process can be divided into two regions. The temperature is less than 588 K in region 1, in which hemicellulose is mainly pyrolyzed, while cellulose are responsible for the main pyrolysis in region 2 where the temperature is above 588 K. The conversion rates of 0.4 and 0.25 are the dividing points of RZ and ABZ, respectively. The DTG and the change in α with the temperature between RZ and ABZ at 20 K/min are shown in Figure 2. It can be clearly seen that the α of ABZ at the same temperature is smaller than that of RZ, which can be explained by the degradation of cellulose and hemicellulose during the burial process of ABZ. The char residual of ABZ is greater than of RZ at 970 K; this is due to the deposition of natural mineral inside the ABZ, which could not be decomposed under 970 K.

2.2. Kinetic Analysis Based on the FWO Method. The plots of ln β versus 1/T at different conversion rates by the FWO method for RZ and ABZ are shown in Figure 3a,b, respectively. Then, Ea is calculated by the slopes (−1.052Ea/R) corresponding to various conversion rates, which are listed in Table 1 and shown in Figure 4.

The temperature of mainly weight loss of hemicellulose and cellulose was 493–588 and 588–673 K, respectively, while the maximum mass loss rate happened at 541 and 628 K. Lignin decomposed with a very low mass loss rate under the whole temperature range. The intersection decomposition temperature of hemicellulose and cellulose is about 588 K, which corresponds to the conversion rates 0.4 of RZ and 0.25 of ABZ. The corresponding temperature at the conversion rate 0.8 of RZ and ABZ is 630 and 658 K, respectively. Therefore, the degradation process can be divided into two regions. The temperature is less than 588 K in region 1, in which hemicellulose is mainly pyrolyzed, while cellulose are responsible for the main pyrolysis in region 2 where the temperature is above 588 K. The conversion rates of 0.4 and 0.25 are the dividing points of RZ and ABZ, respectively. The DTG and the change in α with the temperature between RZ and ABZ at 20 K/min are shown in Figure 2. It can be clearly seen that the α of ABZ at the same temperature is smaller than that of RZ, which can be explained by the degradation of cellulose and hemicellulose during the burial process of ABZ. The char residual of ABZ is greater than of RZ at 970 K; this is due to the deposition of natural mineral inside the ABZ, which could not be decomposed under 970 K.

![Figure 3](https://dx.doi.org/10.1021/acsomega.0c02395)

Table 1. Ea Calculated by the FWO Method

| α    | Ea (kJ mol⁻¹) | R² | ln A (s⁻¹) | α    | Ea (kJ mol⁻¹) | R² | ln A (s⁻¹) |
|------|--------------|----|------------|------|--------------|----|------------|
| 0.1  | 191.32       | 0.95961 | 42.07     | 0.1  | 208.83       | 0.96859 | 45.17     |
| 0.15 | 173.59       | 0.97431 | 37.98     | 0.15 | 203.27       | 0.98189 | 43.46     |
| 0.2  | 171.09       | 0.98004 | 37.41     | 0.2  | 196.42       | 0.98579 | 41.63     |
| 0.25 | 170.08       | 0.98272 | 37.18     | 0.25 | 195.09       | 0.99063 | 41.09     |
| 0.3  | 169.29       | 0.98846 | 37.01     | 0.3  | 193.70       | 0.99234 | 40.61     |
| 0.35 | 169.30       | 0.99267 | 37.01     | 0.35 | 193.29       | 0.99495 | 40.39     |
| 0.4  | 167.75       | 0.99199 | 36.70     | 0.4  | 166.69       | 0.99121 | 39.73     |
| 0.45 | 166.69       | 0.99086 | 39.59     | 0.45 | 168.64       | 0.99652 | 39.30     |
| 0.5  | 166.17       | 0.99232 | 39.60     | 0.5  | 186.21       | 0.99507 | 38.80     |
| 0.55 | 166.41       | 0.99278 | 39.63     | 0.55 | 192.02       | 0.94043 | 39.98     |
| 0.6  | 166.84       | 0.99383 | 39.73     | 0.6  | 183.53       | 0.99103 | 38.28     |
| 0.65 | 167.57       | 0.99464 | 39.91     | 0.65 | 181.05       | 0.99234 | 38.38     |
| 0.7  | 168.84       | 0.99725 | 40.39     | 0.7  | 185.39       | 0.99472 | 39.30     |
| 0.75 | 171.09       | 0.99854 | 41.44     | 0.75 | 188.51       | 0.99788 | 39.20     |
| 0.8  | 175.13       | 0.99725 | 38.96     | 0.8  | 192.84       | 0.99960 | 40.91     |
| average | 170.49 |          |            | average | 192.54 |          |            |
content of ABZ is 7.28% higher than that of RZ. Among the three components, hemicellulose started its decomposition easily and lignin was the most difficult one to decompose, so the $E_a$ of ABZ is always higher than that of the RZ at different conversion rates because of the lower hemicellulose content of ABZ.

2.3. Reaction Mechanism Estimation. The $E_a$ of RZ and ABZ at different heating rates in regions 1 and 2 was calculated by the CR method. The plots of $\ln(g(\alpha)/T^2)$ versus $1/T$ by eq 7 at 5 K/min for RZ and ABZ based on various reaction mechanisms (Table 5) are showed in Figure 5 and 6, respectively, and the method of heating rates 10, 15, and 20 K/min was the same. Tables 2 and 3 show the $E_a$ calculated by the slopes for RZ and ABZ, respectively. If the average $E_a$ of the four different heating rates is close to $E_a$ obtained by the FWO method, then this mechanism plays an important role in this region.

In region 1, the average $E_a$ of RZ calculated by the diffusional model (D1, D2, D3, and D4) is about 160 kJ mol$^{-1}$, which is close to the value (173.2 kJ mol$^{-1}$) obtained by the FWO method, and the value of $R^2$ is nearly 1. Then, diffusion should be responsible to the reaction in region 1 of RZ. Many literatures reported similar results of a diffusion-controlled mechanism for wood decomposition. The possible diffusion mechanism is that solid-state reactions often occur between crystal lattices or with molecules that must permeate into lattices where motion is restricted and may depend on lattice defects. Moreover, a product layer may increase where the reaction rate is controlled by the movement of the reactants or products from the reaction interface. In region 2, the estimated $E_a$ based on the reaction order model R2 is 167.65 kJ mol$^{-1}$, which is close to the $E_a$ (168.08 kJ mol$^{-1}$) acquired by the FWO method, and the value of $R^2$ is 0.993. The reaction can be classified as the reaction order mechanism R2. In this region, the reaction rate is proportional to the concentration, amount, or remaining fraction of the reactant raised in a particular reaction order. Ding et al. reported a similar reaction order mechanism of beech wood. Similarly, the most appropriate mechanism of ABZ corresponding the regions 1 and 2 is shown in the diffusional model D3. The pre-exponential factors A based on the appropriate reaction mechanism are shown in Table 1.

2.4. Thermodynamic Parameter Calculation. Thermodynamic parameters such as change in enthalpy ($\Delta H$), change in Gibbs free energy ($\Delta G$), and change in entropy ($\Delta S$) were calculated at different conversion rates, as shown in Table 4. The comparison of $E_a$, $\Delta H$, $\Delta G$, and $\Delta S$ of RZ and ABZ at different conversion rates are shown in Figure 7.

Enthalpy is the state function of a chemical reaction that reflects reactions from heat absorbed or released and chemical bond dissociation under constant pressure. The changes in enthalpies ($\Delta H$) revealed that the energy difference between the reagent and the activated complex agreed with the activation energies. The variation in $\Delta H$ as well as the respective $E_a$ changes represented the residual carbonaceous material. It can be seen from Figure 7 that the $\Delta H$ of RZ and ABZ was positive, which showed that the pyrolysis of RZ and ABZ was all endothermic. The change in $\Delta H$ and $E_a$ of the RZ and ABZ samples at different conversion rates presented similar patterns. The $\Delta H$ and $E_a$ of the RZ were generally lower than that of the ABZ samples, indicating that the ABZ requires generally higher energy to decompose at each mass conversion.

The change in reaction entropy ($\Delta S$) is associated with the formation of complex activated species, and it is also a measure of disorder. The varied $\Delta S$ showed that the biomass has a high degree of arrangement and had a physical and/or chemical process. The $\Delta S$ of both RZ and ABZ was positive (Table 4), indicating that the disorder degree of RZ and ABZ formed through bond dissociation was higher than that of initial reactants. When the conversion rate was less than 0.4, the $\Delta S$ of RZ showed lower values than ABZ, but the difference is inconspicuous when conversion rate was more than 0.4. Comparatively, the higher value of $\Delta S$ means that the ABZ are more activated and disordered and exhibit low thermal stability to the RZ when the conversion rate was less than 0.4.
The changes in the Gibbs free energy (ΔG) showed the total energy increase of the system at the approach of the reagents and the formation of the activated complex. It is a comprehensive evaluation of the heat flow and disorder change, and a higher value of ΔG indicates a lower favorability of the reaction. The Gibbs free energy of RZ was close to the values of the ABZ samples when the conversion rate was less than 0.4. The RZ sample had a lower Ea and enthalpy compared with the ABZ, but the difference of the Gibbs free energies was not significant when the conversion rate was less than 0.4. Thus, with respect to reaction energies, the RZ sample may require lower energy, but no notable difference of overall energy that would require overcoming both the thermal decomposition reactions and the degree of disorder was observed.

### 3. CONCLUSIONS

TGA of RZ and ABZ under a nitrogen atmosphere at different heating rates of 5, 10, 15, and 20 K/min was investigated in this study. A model-fitting method (CR) and a model-free method (FWO) were used. The Ea values were estimated at different conversion rates based on the FWO, and then, the CR was used to predict the reaction mechanism.

The pyrolysis was divided into two regions with the same divided temperature of about 588 K. The best model of RZ for regions 1 and 2 was based on the diffusional and reaction order.
### Table 3. $E_a$ Values of ABZ Calculated by the CR Method with Different Reaction Models

| RZ     | model name | $E_a$ (kJ/mol) | $R^2$ | $E_a$ (kJ/mol) | $R^2$ | $E_a$ (kJ/mol) | $R^2$ | $E_a$ (kJ/mol) | $R^2$ | average value |
|--------|------------|----------------|-------|----------------|-------|----------------|-------|----------------|-------|---------------|
| region 1 | R0         | 74.07          | 0.999 | 68.75          | 1.000 | 69.49          | 1.000 | 69.02          | 1.000 | 70.33         |
|        | R1         | 85.50          | 1.000 | 79.43          | 0.999 | 80.25          | 0.998 | 79.74          | 0.999 | 81.23         |
|        | R2         | 98.09          | 0.998 | 91.19          | 0.996 | 92.10          | 0.994 | 91.57          | 0.995 | 93.24         |
|        | R3         | 111.85         | 0.995 | 104.04         | 0.992 | 105.04         | 0.988 | 104.48         | 0.991 | 106.35        |
|        | N1         | 85.50          | 1.000 | 79.43          | 0.999 | 80.25          | 0.998 | 79.74          | 0.999 | 81.23         |
|        | N2         | 22.29          | 1.000 | 20.18          | 0.999 | 20.36          | 0.997 | 20.16          | 0.998 | 20.75         |
|        | N3         | 14.39          | 1.000 | 12.77          | 0.999 | 12.88          | 0.996 | 12.71          | 0.997 | 13.19         |
|        | D1         | 157.46         | 0.999 | 146.95         | 1.000 | 148.56         | 1.000 | 147.67         | 1.000 | 150.16        |
|        | D2         | 167.40         | 1.000 | 153.71         | 1.000 | 155.37         | 1.000 | 154.47         | 1.000 | 157.06        |
|        | D3         | 172.43         | 1.000 | 160.94         | 1.000 | 162.66         | 0.999 | 161.73         | 0.999 | 164.44        |
|        | D4         | 167.27         | 1.000 | 156.12         | 1.000 | 157.80         | 0.999 | 156.89         | 1.000 | 159.52        |
|        | C1         | 79.64          | 1.000 | 73.95          | 1.000 | 74.73          | 0.999 | 74.24          | 0.999 | 75.64         |
|        | C2         | 81.56          | 1.000 | 75.75          | 1.000 | 76.54          | 0.999 | 76.05          | 0.999 | 77.47         |
|        | F2         | 14.70          | 0.847 | 12.99          | 0.813 | 13.03          | 0.794 | 12.91          | 0.805 | 13.41         |
|        | F3         | 38.72          | 0.905 | 35.43          | 0.890 | 35.65          | 0.878 | 35.47          | 0.886 | 36.32         |
| region 2 | R0         | 59.59          | 0.985 | 57.07          | 0.981 | 60.38          | 0.991 | 60.49          | 0.992 | 59.38         |
|        | R1         | 104.76         | 0.999 | 100.85         | 0.998 | 106.08         | 0.999 | 106.28         | 0.999 | 104.49        |
|        | R2         | 168.03         | 0.995 | 162.22         | 0.996 | 170.03         | 0.992 | 170.33         | 0.991 | 167.65        |
|        | R3         | 247.41         | 0.986 | 239.23         | 0.989 | 250.22         | 0.981 | 250.65         | 0.981 | 246.88        |
|        | N1         | 104.76         | 0.999 | 100.85         | 0.998 | 106.08         | 0.999 | 106.28         | 0.999 | 104.49        |
|        | N2         | 28.30          | 0.998 | 26.88          | 0.997 | 28.53          | 0.999 | 28.55          | 0.999 | 28.06         |
|        | N3         | 18.74          | 0.998 | 17.63          | 0.999 | 18.83          | 0.998 | 18.83          | 0.998 | 18.51         |
|        | D1         | 129.11         | 0.988 | 124.25         | 0.984 | 131.01         | 0.992 | 131.30         | 0.993 | 128.92        |
|        | D2         | 153.71         | 0.993 | 148.08         | 0.991 | 155.92         | 0.997 | 156.26         | 0.997 | 153.49        |
|        | D3         | 185.35         | 0.998 | 178.75         | 0.996 | 187.92         | 0.999 | 188.33         | 0.999 | 185.09        |
|        | D4         | 164.13         | 0.995 | 158.18         | 0.993 | 166.46         | 0.998 | 166.82         | 0.998 | 163.90        |
|        | C1         | 79.95          | 0.996 | 76.79          | 0.993 | 80.98          | 0.998 | 81.14          | 0.998 | 79.72         |
|        | C2         | 87.71          | 0.997 | 84.32          | 0.996 | 88.84          | 0.999 | 89.00          | 0.999 | 87.47         |
|        | F2         | 98.51          | 0.966 | 95.04          | 0.971 | 99.40          | 0.957 | 99.52          | 0.956 | 98.12         |
|        | F3         | 206.96         | 0.969 | 200.19         | 0.974 | 209.04         | 0.961 | 209.36         | 0.960 | 206.39        |

(The R2 mechanisms, while the best model of ABZ was based on the diffusional (D3) mechanism. During the whole pyrolysis process, the $E_a$ of both RZ and ABZ gradually decreases first and slightly increases at last. The $E_a$ of ABZ was always higher than RZ, the average $E_a$ values of RZ are 173.2 and 168.09 kJ mol$^{-1}$ for regions 1 and 2, while the average $E_a$ values of ABZ are 200.9 and 189.96 kJ mol$^{-1}$ for regions 1 and 2, respectively. The $\Delta H$ and $E_a$ of the RZ at different conversion rates were lower than that of the ABZ samples, indicating that the ABZ requires higher energy to decompose at each mass conversion. When the conversion rate was less than 0.4, the RZ sample had a lower $E_a/\Delta H$, and $\Delta S$ compared with the ABZ, but the difference of $\Delta G$ was not significant, indicating that the RZ sample may require lower energy, but the overall energy of thermal decomposition reactions and the degree of disorder was not much different. The pyrolysis differences of ABZ and...
RZ could be attributed to the chemical component proportion of hemicellulose and cellulose.

4. MATERIALS AND METHODS

4.1. Materials. RZ and ABZ trees are both derived from Ya'an, Sichuan Province, China. Both the RZ and ABZ samples were placed in room temperature conditions for air drying until their weight became constant. The wood samples were milled to less than 0.2 mm for TGA.50

4.2. Thermogravimetric Measurements. Thermal analyzer instrument (NETZSCH TG 209 F1) was applied in the pyrolysis process from 300 to 970 K at a heating rate of 5, 10, 15, and 20 K/min. To maintain pyrolysis conditions, high purity nitrogen was used as the carrier gas. For each scan, approximately 7 to 10 mg of two samples were spread evenly in an aluminum crucible. During the heating, the mass of the wood sample and furnace temperature was recorded.

4.3. Kinetic Theory. The Kinetic equation for solid-state pyrolysis can be expressed based on the conversion rate as follows:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]

where \(\alpha\) is the conversion rate during pyrolysis, \(k(T)\) is the reaction rate constant which can be explained by the Arrhenius law, and \(f(\alpha)\) is the function of the reaction mechanism determined by the reaction type. Whereby, \(a\) and \(k(T)\) can be calculated with eqs 2 and 3, respectively.

\[
a = \frac{m_0 - m_i}{m_0 - m_f}
\]

(2)

where \(m_0\) is the initial mass of the sample; \(m_i\) is the mass of the sample during thermal degradation; and \(m_f\) is the final mass of the sample after pyrolysis.

The speed of the above thermal decomposition reaction depends on the size of reaction rate constant \(k(T)\). The dependence of \(k(T)\) on temperature is generally considered to comply with the Arrhenius law

\[
k(T) = A \exp\left(-\frac{E_a}{RT}\right)
\]

(3)

\(A\) is the pre-exponential factor, and \(E_a\) is the activation energy of the reaction. \(R\) is the universal gas constant, and \(T\) is the reaction absolute temperature.

For dynamic TGA in a nonisothermal experiment, the heating rate \(\beta = dt/dt\) into eqs 3 and 4 is obtained as

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E_a}{RT}\right)
\]

(4)

Equation 4 is the fundamental expressions of analytical methods used to calculate kinetic parameters on the basis of the TGA data.51

4.3.1. FWO Method. FWO is a model-free method developed by Flynn and Wall,52 as well as Ozawa.53 The \(E_a\) values for the degradation process were determined by the measurement of the temperatures corresponding to fixed conversion rates from experiments at different heating rates. This method can be used for determination of the \(E_a\) values without any knowledge of the reaction mechanisms. The FWO method is derived by Doyle’s approximation54 and can be expressed as

\[
\ln(\beta) = \ln\left(\frac{AE_a}{g(\alpha)R}\right) - 5.331 - 1.052\left(\frac{E_a}{RT}\right)
\]

(5)

where \(\beta\) is the heating rate, \(A\) is the pre-exponential factor, \(g(\alpha)\) is a function of the conversion, \(E_a\) is the activation energy, and

Table 5. Algebraic Expressions of \(g(\alpha)\) and \(f(\alpha)\) for the Common Reaction Mechanisms Used in Solid-State Reactions

| reaction mechanism | model name                                  | \(f(\alpha)\)                                      | \(g(\alpha)\)                              |
|--------------------|---------------------------------------------|--------------------------------------------------|-------------------------------------------|
| R0                 | zero order                                  | 1                                                | \(\alpha\)                                 |
| R1                 | first order                                 | \(1 - \alpha\)                                    | \(-\ln(1 - \alpha)\)                      |
| Rn                 | nth order                                   | \((1 - \alpha)^n\)                                | \(\frac{1}{(1 - \alpha)^{\frac{1}{n}}}/(1 - \alpha)\) |
| N1                 | Avrami eq 1                                 | \(2(1 - \alpha)[\ln(1 - \alpha)]^{1/2}\)         | \((-\ln(1 - \alpha))^{1/2}\)             |
| N2                 | Avrami eq 2                                 | \(3(1 - \alpha)[\ln(1 - \alpha)]^{1/3}\)         | \((-\ln(1 - \alpha))^{1/3}\)             |
| N3                 | Avrami eq 3                                 | \(4(1 - \alpha)[\ln(1 - \alpha)]^{1/4}\)         | \((-\ln(1 - \alpha))^{1/4}\)             |
| D1                 | one-dimensional diffusion                   | \(1/(2a)\)                                       | \(a^2\)                                   |
| D2                 | two-dimensional diffusion (Valensi equation) | \([-\ln(1 - a)]^{-1}\)                            | \((1 - a)\ln(1 - a) + a\)                |
| D3                 | three-dimensional diffusion (Jander equation) | \(3/2(1 - a)^{2/3}[1 - (1 - a)^{1/3}]\)          | \(1 - \frac{1}{(1 - a)^{1/3}}\)          |
| D4                 | three-dimensional diffusion (Ginstling–Brnushtein equation) | \(3/2[(1 - a)^{1/3} - 1]^{-1}\)                   | \(1 - 2/3\alpha - (1 - a)^{4/3}\)        |
| C1                 | contracting area                            | \((1 - \alpha)^{1/2}\)                            | \(1 - (1 - a)^{1/2}\)                     |
| C2                 | contracting volume                          | \((1 - \alpha)^{2/3}\)                            | \(1 - (1 - a)^{2/3}\)                     |

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R is the gas constant. Therefore, for different heating rates (β) and a given degree of conversion (α), a linear relationship is observed by plotting ln β versus 1/T, and the Eₚ is obtained from the slope of the straight line.55

4.3.2. CR Method. CR, a model-fitting method developing by Coats and Redfern,54 is extensively used to estimate the pre-exponential factor and activation energy to predict the order of reaction.56 First, various reaction mechanisms are assumed, mainly including reaction order, nucleation, diffusion, and contracting geometry models.57 CR is used to calculate the Eₚ from the assumed f(α) or g(α) forms. The Eₚ estimated by CR is compared to the previously obtained value by FWO to select the most appropriate reaction mechanism f(α) and then determine the pre-exponential factor A.58

The CR method is based on an asymptotic approximation 2RT/Eₚ close to 0, and then, the expression of eq 4 in logarithmic form is given as

\[
\frac{\ln g(α)}{T^2} = \ln \left( \frac{A R}{β E_a} \right) - \frac{E_a}{RT}
\]  

(6)

The plot of ln(g(α)/T²) versus 1/T gives a straight line, and the Eₚ was determined by the slope, when the reaction mechanism is assumed. Table 5 shows the common reaction mechanisms used in solid-state reactions.54,56,57

4.4. Thermodynamic Parameters. Thermodynamic parameters such as changes in enthalpy, Gibbs free energy, and entropy can be obtained from TGA.50 These parameters can be calculated based on kinetic data from the following equations.51,59–61

\[
ΔH = E_a - RT
\]  

(7)

\[
ΔG = E_a + RT_m \ln \left( \frac{K_b T}{h A} \right)
\]  

(8)

\[
ΔS = \frac{ΔH - ΔG}{T_m}
\]  

(9)

where K_b is Boltzmann constant (1.381 × 10⁻²³ J·K⁻¹), T_m is the maximum temperature at which maximum decomposition occurs, h is Planck’s constant (6.626 × 10⁻³⁴ J·s), and R is universal gas constant (0.008314 kJ·mol⁻¹·K⁻¹). The pre-exponential factor (A) and Eₚ at different conversion rates were calculated using the FWO and CR methods.

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