Kinetic Analysis of the Main Temperature Stage of Fast Pyrolysis

Xiaoxiao Yang, Yuying Zhao, Lanshu Xu and Rui Li*

College of materials science and technology, Beijing Forestry University, 100083, Beijing, China
Email: 13020021531@163.com

Abstract. Kinetics of the thermal decomposition of eucalyptus chips was evaluated using a high-rate thermogravimetric analyzer (BL-TGA) designed by our research group. The experiments were carried out under non-isothermal condition in order to determine the fast pyrolysis behavior of the main temperature stage (350-540ºC) at heating rates of 60, 120, 180, and 360ºC min⁻¹. The Coats-Redfern integral method and four different reaction mechanism models were adopted to calculate the kinetic parameters including apparent activation energy and pre-exponential factor, and the Flynn-Wall-Ozawa method was employed to testify apparent activation energy. The results showed that estimation value was consistent with the values obtained by linear fitting equations, and the best-fit model for fast pyrolysis was found.

1. Introduction
In view of the important role that fast pyrolysis plays in thermal conversion process of biomass, a great need exists for robust comprehensive biomass pyrolysis mechanism that could predict product speciation and yields as well as optimize process conditions. Non-isothermal thermogravimetric analysis (TGA) is the most common method to investigate the kinetics, but heating rates often confined to lower than 120 °C min⁻¹ due to commercial instrument limitation, which is quite different from fast biomass pyrolysis case. In the present work, we investigated fast pyrolysis behavior of eucalyptus chips tested by a high-rate thermogravimetric analyzer (BL-TGA) designed by our group at different heating rates (60, 120, 180, and 360 °C min⁻¹) under nitrogen atmosphere, and determined the kinetic parameters of the main temperature stage through the Coats-Redfern integral method and four different reaction mechanism models (RO1, RO2, R2, D1). The Flynn-Wall-Ozawa method was used to testify apparent activation energy and determine the best-fit model.

2. Experimental
2.1. Materials
Eucalyptus obtained from Guangxi Province, China were air-dried and sliced into sheets with a area of 50 mm×10 mm and thickness of 2 mm. which has the chemical composition as Table 1.
Table 1. Chemical composition of eucalyptus chips.

| Sample          | Moisture (%) | Ash (%) | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|-----------------|--------------|---------|---------------|------------------|------------|
| Eucalyptus chips | 5.8          | 0.3     | 41.02         | 20.21            | 30.43      |

2.2. Fast Pyrolysis Kinetic Analysis

Under non-isothermal conditions, the actual temperature can be expressed in terms of the initial temperature $T$ and the heating rate $\beta$ as follows:

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

Where $T$ is the temperature, $A$ is the pre-exponential factor, $E$ is the apparent activation energy, and $R$ is the universal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$), $\alpha$ is the mass-loss rate, expressed by $\alpha = M_0 - M_t / M_\infty - M_\infty$. $M_0$ is the initial mass of the sample, $M_t$ is the mass at a given time $t$, and $M_\infty$ is the final mass of the sample and $f(\alpha)$ is the reaction model.

The integral function was defined:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$

Combination of (1) and (2) gives,

$$G(\alpha) = \frac{A}{\beta} \int_0^T \exp \left(-\frac{E}{RT}\right) dT$$

Through the approximate induction of integration with respect to temperature, Coats-Redfern equation is derived as follows and $E$ and $A$ can be calculated through fitting the linear curve:

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

Flynn-Wall-Ozawa formula was obtained by the transformation of equation (3):

$$\log \beta = \log \frac{AE}{RG(\alpha)} - 2.315 - 0.4567 \frac{E}{RT}$$

Flynn-Wall-Ozawa method can directly determine value $E$, which avoided calculation error caused by different assumptions of reaction mechanism models select in Coats-Redfern equation.

Different reaction mechanism models $G(\alpha)$ elucidating fast pyrolysis process of eucalyptus chips were presented in Table 2, which will be put into equation (4). The best-fit model was selected by using the Flynn-Wall-Ozawa method through the comparison of apparent activation energies obtained by two methods.

Table 2. Different reaction mechanism models of pyrolysis with various functions of $G(\alpha)$ and $f(\alpha)$.

| Reaction model                        | $G(\alpha)$          | $f(\alpha)$ | Reaction mechanism                        |
|---------------------------------------|-----------------------|-------------|-------------------------------------------|
| Chemical reaction                     | $-\ln(1-\alpha)$     | $1-\alpha$ | First-order reaction                       |
| Phase boundary reaction               | $(1-\alpha)^{-1}$ - 1 | $(1-\alpha)^2$ | Second-order reaction                      |
| Diffusion-controlled reaction          | $1-(1-\alpha)^{1/2}$  | $2(1-\alpha)^{1/2}$ | Two-dimensional, shrinking cylinder        |
|                                       | $\alpha^2$            | $1/2 \alpha$ | One-dimensional diffusion, parabolic law   |
3. Results and Discussion

3.1. Fast Pyrolysis Behaviour of the Main Temperature Stage

Figure 1 shows TG mass-loss curves and corresponding DTG analysis curves at different heating rates: 60, 120, 180 and 360 ℃min⁻¹. As shown in Figure 1, many peaks could be distinguished from the DTG curves at around 350-540 ℃, which indicated that main mass loss stages during fast pyrolysis. From DTG curve, we can conclude that the process could be mainly divided into four stages: moisture loss, the early stage of mass loss, the main stage of fast pyrolysis and charring. Table 3 showed the main temperature points of decomposition observed in DTG curves. Both curves and data could obviously illustrated that the most rapid mass loss stage shifted to higher temperature corresponding with increasing heating rates, which is the joint outcome of mainly different reaction conversion and slightly physically uniform heat transfer.

![Graph](image)

**Figure 1.** TG (left) and DTG (right) curves of eucalyptus chips at different heating rates.

**Table 3.** The main temperature points of decomposition.

| Heating rates β(℃ min⁻¹) | 60  | 120 | 180 | 360 |
|---------------------------|-----|-----|-----|-----|
| First temperature point T (℃) | 348.2 | 350.4 | 366.3 | 414.7 |
| Second temperature point T (℃) | 382.4 | 401.7 | 434.1 | 468.9 |
| Third temperature point T (℃) | 409.8 | 431.0 | 458.1 | 494.6 |
| Fourth temperature point T (℃) | 479.8 | 493.7 | 509.6 | 533.0 |

Moreover, as shown in Table 4, when the temperature reached the main stage of fast pyrolysis (350 ℃), the weight proportion at the heating rate of 60 ℃Cmin⁻¹ was the lowest observed, about 0.8174. The 360 ℃Cmin⁻¹ was the highest, about 0.9284. It indicated that samples had been consumed much more in low-temperature stage of lower heating rates, and consequently produce higher residue yield, about 0.3074 in case of 60 ℃Cmin⁻¹. This is attributed to that slow pyrolysis of low heating rates can lead to the formation of a large amount of carbon. From Figure 1, we can see the higher heating rates could heat the samples up to required temperature in a short time and reveal fast pyrolysis mechanism more perfectly.
Table 4. Mass loss process of fast pyrolysis.

| Temperature T (°C) | 200  | 350  | 540  | 650  |
|-------------------|------|------|------|------|
| 60                | 0.9240 | 0.8174 | 0.3475 | 0.3074 |
| 120               | 0.9343 | 0.8360 | 0.3342 | 0.2905 |
| 180               | 0.9507 | 0.9038 | 0.3910 | 0.2987 |
| 360               | 0.9723 | 0.9284 | 0.4622 | 0.2945 |

3.2. Kinetic Analysis of the Maximum Mass-loss Points

Coats-Redfern integral method and four kinds of reaction mechanism models (RO1, RO2, R2, D1) described in section 2.2 were applied to estimate the kinetic parameters of the maximum mass-loss points. The fitting straight lines of various reaction mechanism models at different heating rates were showed in Figure 2, and the corresponding kinetic parameters were summarized in Table 5.

As shown in Figure 2, the fitting straight lines had significant difference and their intercepts were utterly inconsistent at different heating rates. However, the lines simulated by the four different reaction mechanism models (RO1, RO2, R2, D1) had similar distribution order and their correlation coefficients were very high. The finding from A. V. Bridgwater also confirmed that the integral methods gave better fitting results. The specific parameters were shown in Table 5, the highest apparent activation energy values were obtained by the diffusion-controlled reaction model (D1), for which pre-exponential factor A also had the highest value. On the contrary, the corresponding values obtained by the phase boundary reaction model (R2) were the lowest, and the chemical reaction mechanism models (RO1, RO2) had similar apparent activation energy values. The changes of the apparent activation energy values calculated by the four different reaction mechanism models (RO1, RO2, R2, D1) at the maximum mass-loss points of different heating rates can be obviously observed in Figure 3. The trend of the change could be vividly presented and the apparent activation energies obtained by the chemical reaction mechanism models (RO1, RO2) had a slight change. The variation could be attributed to the mass and heat transfer limitations at different temperature points and heating rates.
Figure 2. Fitting straight lines of various reaction mechanism models at different heating rates.
**Table 5.** Kinetic parameters of various reaction mechanism models under different heating rates.

| Heating rates $\beta$ (°C min$^{-1}$) | 60     | 120    | 180    | 360    |
|---------------------------------------|--------|--------|--------|--------|
| Maximum mass-loss points $T$ (°C)     |        |        |        |        |
| RO                                   | 382.4  | 401.7  | 434.1  | 468.9  |
| RO1                                  |        |        |        |        |
| RO2                                  |        |        |        |        |
| RO                                   |        |        |        |        |
| R2                                   |        |        |        |        |
| D1                                   |        |        |        |        |
| Fitting straight line equations       |        |        |        |        |
| RO                                   | $y = -8631.9x - 0.3934$ & $y = -8379.8x - 1.1345$ & $y = -8547.2x - 1.6956$ & $y = -8213.2x - 2.7187$ |
| RO1                                  | $y = -11294x + 3.9122$ & $y = -11553x + 3.8918$ & $y = 10802.0x + 1.7373$ & $y = -10380x + 0.4922$ |
| RO2                                  | $y = -7362.4x - 3.1584$ & $y = -7005.9x - 4.0085$ & $y = 7494.0x - 4.0039$ & $y = 7238.6x - 4.8611$ |
| D1                                   | $y = -13729x + 6.2628$ & $y = -12917x + 4.4907$ & $y = 14440.0x + 5.4852$ & $y = -14120x + 4.1427$ |
| Correlation coefficient R$^2$         |        |        |        |        |
| RO                                   | 0.9903 | 0.9976 | 0.9975 | 0.9935 |
| RO1                                  | 0.9909 | 0.9988 | 0.9966 | 0.9914 |
| RO2                                  | 0.9898 | 0.9950 | 0.9980 | 0.9943 |
| D1                                   | 0.9911 | 0.9950 | 0.9987 | 0.9958 |
| Apparent activation energy E (kJ mol$^{-1}$) |        |        |        |        |
| RO                                   | 71.77  | 69.67  | 71.06  | 68.28  |
| RO1                                  | 93.90  | 96.05  | 89.81  | 86.30  |
| RO2                                  | 61.21  | 58.25  | 62.31  | 60.18  |
| D1                                   | 114.14 | 107.39 | 120.05 | 117.39 |
| Pre-exponential factor A              |        |        |        |        |
| RO                                   | 6.8673E+03 | 6.4241E+03 | 5.6378E+03 | 3.9672E+03 |
| RO1                                  | 6.3896E+05 | 1.2819E+06 | 2.1187E+05 | 1.1888E+05 |
| RO2                                  | 3.8062E+02 | 3.1517E+02 | 5.0558E+02 | 4.2294E+02 |
| D1                                   | 7.9638E+06 | 2.5727E+06 | 1.1578E+07 | 5.9615E+06 |

**Figure 3.** Variation of the apparent activation energy for fast pyrolysis using four kinds of reaction models.
In order to find the best-fit models of biomass fast pyrolysis, the Flynn-Wall-Ozawa method was employed to verify the apparent activation energy. The specific parameters of the Flynn-Wall-Ozawa method were shown in Table 6 and the apparent activation energy \( E \) was 74.97 kJmol\(^{-1}\), which was similar to the apparent activation energies obtained by the first-order reaction model (RO1) of the Coats-Redfern method. This result accorded with other works presented in the literature comparing kinetic parameters determined by TGA and calculated by different methods. Moreover, as shown in Table 5, with the increase of the heating rates, the pre-exponential factor of RO1 slightly decreased, which could be caused by the heat transfer error between samples at different heating rates. The further study of heat transfer is in progress.

| method                    | Fitting straight line equation                      | Apparent activation energy \( E \) (kJ mol\(^{-1}\)) | Correlation coefficient \( R^2 \) |
|---------------------------|----------------------------------------------------|----------------------------------------------------|-----------------------------------|
| Flynn-Wall-Ozawa          | \( y = -4118.4x + 8.108 \)                         | 74.97                                              | 0.9730                             |

4. Conclusions

In this study, the fast pyrolysis of eucalyptus chips had been investigated under nitrogen atmosphere by means of BL-TGA at different heating rates (60, 120, 180 and 360ºCmin\(^{-1}\)). The fast pyrolysis behavior and reaction mechanism of the main temperature stage (350-540 ºC) were investigated, which indicated that kinetic analysis of fast pyrolysis under the condition of higher heating rates would be more comprehensive.

The maximum mass-loss points occurred at 382.4, 393.4, 434.1 and 468.9ºC respectively. Kinetic parameters were calculated by the Coats-Redfern integral methods using four reaction mechanism models and verified by the Flynn-Wall-Ozawa method.

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6. References

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