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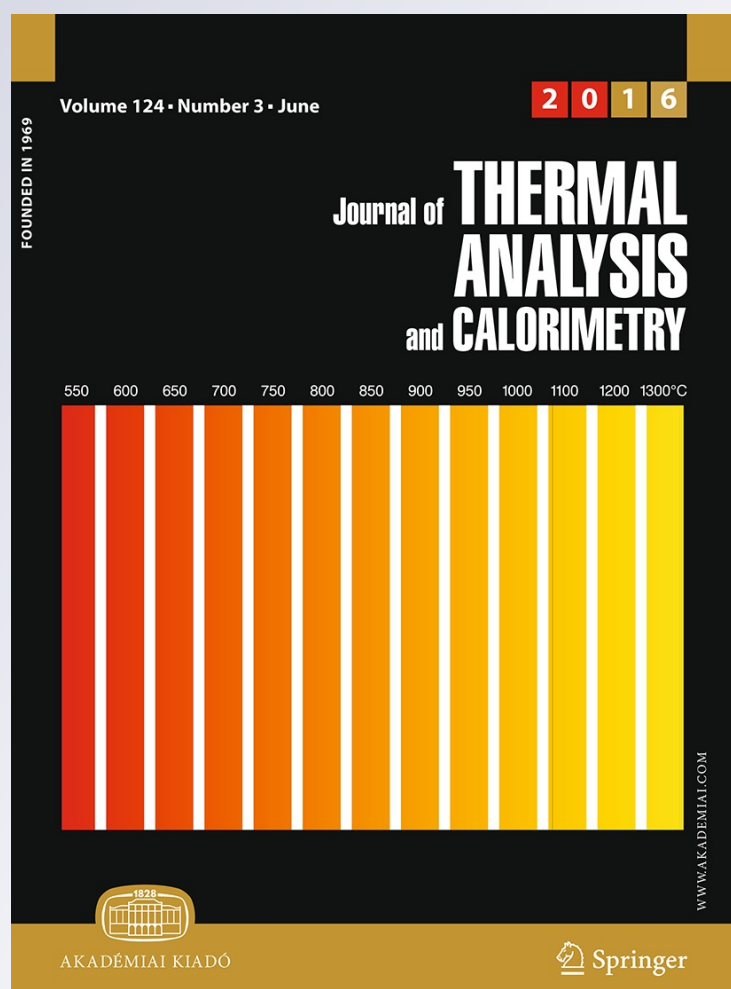
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Error evaluation on pyrolysis kinetics of sawdust using iso-conversional methods

Jinxing Wang¹ · Haibo Zhao¹ 

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Abstract Pyrolysis behavior and kinetic properties of sawdust with the heating rates (β) of 5, 10, 15 and 20 °C min⁻¹ in nitrogen atmosphere were analyzed by using a thermogravimetric analyzer. The results showed that organics of sawdust mainly decomposed at 250–400 °C, and greater heating rate can move the peak of differential thermogravimetric curves toward higher temperature. Two iso-conversional methods, Flynn–Wall–Ozawa (FWO) method and Kissinger–Akahira–Sunose (KAS) method, were employed to analyze the non-isothermal pyrolysis kinetics of sawdust, and the range of apparent activation energies for sawdust pyrolysis is between 101.53 and 114.83 kJ mol⁻¹ using FWO method and is between 95.94 and 114.87 kJ mol⁻¹ using KAS method. Error limit from heating rate was first proposed to examine the reliability of two iso-conversional methods, and the error from heating rate cannot exceed the range of ± 20 kJ mol⁻¹ in this study. Overall, these results suggested that the experimental results and kinetic parameters provided useful information for the design of pyrolytic processing system using sawdust as feedstock, and error limits demonstrated the precision of these obtained apparent activation energies.

Keywords Sawdust · TG · Pyrolysis kinetic · Error limit · Iso-conversional method

Introduction

Biomass has been recognized as a potential renewable energy source and potentially neutral in relation to global warming [1, 2]. In recent years, the utilization of biomass has received considerable attention because supplies of fossil fuels are dwindling and price just as energy demand continues to soar [3]. For adequately utilizing biomass, thermochemical process plays an important role in rejuvenation of biomass into energy [4]. It is acknowledged that thermochemical reactions in a reactor are complicated processes including pyrolysis, gasification and combustion [5]. Among these thermochemical patterns, biomass pyrolysis has attached the most attention because it can convert biomass directly into chemicals and fuels with high efficiency in the absence of oxygen, which can be utilized more efficiently in an environment-friendly manner [3]. Also, pyrolysis process has been considered as a fundamental step in combustion or gasification of biomass [6], which enhances the significance of cognizing biomass pyrolysis process.

Thermogravimetric (TG) analysis has been used extensively over the years to investigate the thermal events during pyrolysis of biomass, and it provides quantitative results regarding the mass loss of a sample as a function of increasing temperature or time under isothermal or non-isothermal conditions [7–10]. Besides, the TG analysis technique can allow for the estimation of effective kinetic parameters for various decomposition reactions and it has been investigated by numerous researchers [11–16]. A detailed knowledge and understanding of the thermogravimetric analysis and the devolatilization kinetics will help in planning, designing and operation of the industrial pyrolysis processes [3, 8]. Regarding this subject, many methods have been introduced to different researches [11, 17–20]. For example, Yan et al. [21] used a distributed

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activation energy model (DAEM) to analyze kinetic parameters for the pyrolysis process of bamboo stick. Papageorgiou et al. [20] analyzed thermal degradation kinetics of a polypropylene copolymers by using Kissinger–Akahira–Sunose (KAS) method. Yu et al. [22] used a modified three-parallel-reactions model to calculate thermal decomposition kinetics of *Echinodontium taxodii*. Zhu et al. [5] employed three iso-conversional methods to identify the kinetic triple of textile waste. Among them, iso-conversional methods [11, 12, 17, 23], which do not require knowledge of the reaction mechanism, have been widely accepted to study reaction kinetics of pyrolysis because of its operational simplicity. Flynn–Wall–Ozawa (FWO) method [5, 11, 23] and KAS method [20, 24] as two representative iso-conversional methods have been generally adopted to analyze the pyrolysis kinetics of biomass using TG data from different heating rates. However, little information is available about the effect of heating rate on the obtained kinetic parameters, although it has been discovered that a greater heating rate can delay the mass loss rate of pyrolysis [2, 5, 6, 13, 14, 25]. Our interest is to develop a novel method to calculate the error limit from heating rate and to evaluate the precision of these obtained apparent activation energy.

In this work, pyrolysis characteristics of sawdust as a representative biomass were analyzed using TG in nitrogen atmosphere. Based on TG data at four heating rates (β) of 5, 10, 15 and 20 °C min⁻¹, pyrolysis kinetics were analyzed through FWO method and KAS method, and the apparent activation energies were calculated with different conversion levels. Besides, error limit was introduced in this study to estimate the effect of heating rate on the apparent activation energy. It is anticipated that this study will be useful in evaluating the reliability of these obtained apparent activation energies using iso-conversional methods and will further direct the design of pyrolytic processing system using biomass as feedstock.

Experimental

Materials

Sawdust as a typical type of biomass was selected in this study. The sample was crushed and sieved into particles with a size range of 0.1–0.2 mm, which was dried for 24 h at 105 °C before experiments. The elemental composition and proximate analysis are based on ASTM D5373 criterion and GB212-91/GB212-84 criterion, respectively. Table 1 summarizes the proximate and ultimate analysis and lower heating value of sawdust, and its ash analysis is listed in Table 2. Note that M_{ad} , FC_{ad} , V_{ad} and A_{ad} in Table 1 represent moisture, fixed carbon, volatile matter and ash, respectively. Generally,

cellulose, hemicellulose and lignin are regarded as three primary components of sawdust [26].

Apparatus and procedure

The non-isothermal pyrolysis experiments of sawdust were carried out on a simultaneous thermal analysis (WCT-1D). The corresponding TG and differential thermogravimetry (DTG) pyrolysis curves were obtained through monitoring weight variation as a function of time. The TG baselines were corrected by subtraction of predetermined baselines which were obtained under identical conditions except for the absence of a sample. The microbalance of the TG apparatus has a nominal sensitivity of 0.1 µg. A sample of approximate 20 mg was designated and loaded into a plate crucible made of Al₂O₃. Each sample was heated to 100 °C over 10 min and was maintained at 100 °C for 5 min for sample drying. Then, the sample was heated to 1000 °C for pyrolysis by four heating rates (β), i.e., 5, 10, 15 and 20 °C min⁻¹. Note that four heating rates (5, 10, 15, 20 °C min⁻¹) were determined to satisfy the requirement that the logarithm of heating rates is approximatively uniform. The gas flow into the TG was controlled using an electronic mass flow regulator, and the ambient atmosphere during temperature-programmed pyrolysis was provided by gas unit. Note that 40 mL min⁻¹ was selected as the continuous nitrogen flow and it has been demonstrated that the flow rate can ideally eliminate the influence of gas diffusion. The pyrolysis kinetics was then determined by monitoring the mass change of the sample at four different heating rates.

Results and discussion

The TG and DTG curves during the sawdust pyrolysis at four heating rates (5, 10, 15 and 20 °C min⁻¹) are shown in Figs. 1, and 2, respectively. It is found that the mass loss mainly occurs between 250 and 450 °C. Also, it can be seen that the main mass loss stages could be distinguished gradually with the increase in heating rate, which is consistent with the previous achievements [5, 6, 25]. This result indicates that heating rate can influence the pyrolysis progress because of the difference of mass and heat transfer, and further determine the kinetic parameters. Hence, it is necessary to research the effect of heating rate on the apparent activation energy in order to precisely evaluate the reliability of iso-conversional methods. Correspondingly, the DTG curves have two obvious mass loss peaks, which should be related to the difference of degradation between cellulose and hemicellulose. Furthermore, the DTG peaks move toward higher temperature and the absolute values of DTG peaks decrease with the increase in heating rate. The most reasonable explanation is that a greater heating rate delays the

Table 1 Proximate analysis, ultimate analysis (on mass%, as received) and lower heating value of the sawdust

| Sample | Proximate/mass%, as received | | | | LHV (MJ/kg, db) | Ultimate/mass%, d.a.f | | | | |
|---------|------------------------------|-----------|----------|----------|-----------------|-----------------------|------|------|------|-------|
| | M_{ad} | FC_{ad} | V_{ad} | A_{ad} | | C | H | N | S | O |
| Sawdust | 6.88 | 16.26 | 74.99 | 1.87 | 18.14 | 47.46 | 5.06 | 0.18 | 0.06 | 38.49 |

Table 2 Ash analysis of the sawdust (on mass%, as received)

| Sample | Component analysis/mass% | | | | | | | | | | Else elements |
|---------|--------------------------|---------|--------|--------|-------|---------|-----------|-----------|-------|-------|---------------|
| | Al_2O_3 | SiO_2 | K_2O | SO_3 | CaO | TiO_2 | Mn_2O_3 | Fe_2O_3 | CuO | ZnO | |
| Sawdust | 6.59 | 17.62 | 36.37 | 12.31 | 13.31 | 7.24 | 0.78 | 4.37 | 0.74 | 0.24 | 0.43 |

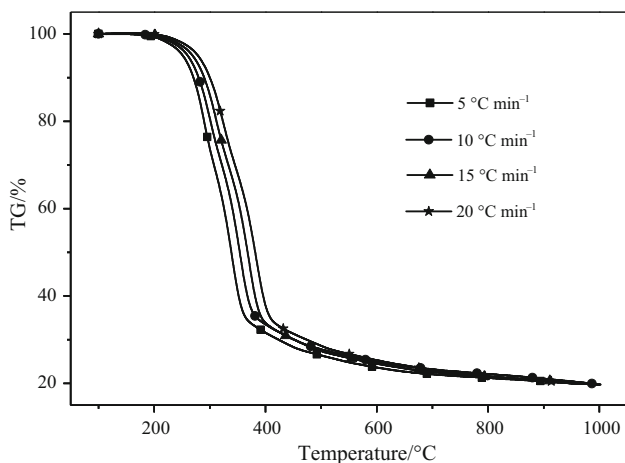


Fig. 1 TG curves of sawdust at different heating rates (β)

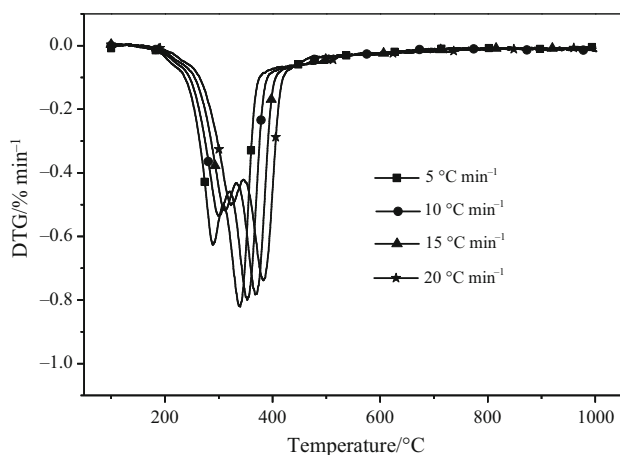


Fig. 2 DTG curves of sawdust at different heating rates (β)

release of part volatile and reduces the amount of volatile release at specific temperature (based on Table 1, approximate 90 % of organic volatile components can release promptly when temperature attain 450 °C).

Pyrolysis kinetics

The degree of conversion (α) of the pyrolysis process, which describes the change in sample mass, can be expressed as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{1}$$

where m_0 , m_t and m_∞ are the sample masses at the beginning, at time t , and the end of the pyrolysis stage, respectively.

The rate of conversion ($d\alpha/dt$) is often expressed using an Arrhenius-type expression [13].

$$\frac{d\alpha}{dt} = A \exp\left(\frac{E_\alpha}{RT}\right) f(\alpha) \tag{2}$$

where A (s^{-1}), E_α ($kJ mol^{-1}$), R ($kJ mol^{-1} K^{-1}$) and T (K) are the pre-exponential factor, the activation energy, the universal gas constant and the sample absolute temperature, respectively. $f(\alpha)$ represents the kinetic model that describes the rate of conversion dependence on the conversion, e.g., an n -order reaction model [27–30]: $f(\alpha) = (1 - \alpha)^n$.

Under a constant heating rate ($\beta = dT/dt$), the time dependence of the conversion rate can be used to rewrite the differential form [Eq. (3)] or the integral form [Eq. (4)] of the pyrolysis kinetic expression.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_\alpha}{RT}\right) f(\alpha) \tag{3}$$

$$g(\alpha) = \int_0^T \frac{A}{\beta} \exp\left(\frac{-E_\alpha}{RT}\right) dT \tag{4}$$

A variety of algebraic equations were derived to illustrate these models in a mathematical manner with relevant assumptions [24, 31]. This iso-conversional method involves carrying out a series of experiments at different heating rates. In this study, the FWO method [13] and the KAS method [24] as two of typical iso-conversional methods were employed as two typical iso-conversional methods without knowledge of reaction mechanism. The

following sections will detail the FWO method and the KAS method to determine the apparent activation energies for sawdust pyrolysis. In order to demonstrate the precision of these obtained kinetic parameters, the error limits from different heating rates were analyzed according to Eq. (3).

FWO method and KAS method

By the kinetic method, it is usually expected to derive an appropriate kinetic description of the process in terms of the E_x . The iso-conversional methods (the FWO and KAS methods in this work) involve carrying out a series of experiments at different heating rates. More detailed explanation can be found in the literature [11, 23].

The FWO method and the KAS method are the iso-conversional, integral methods. The FWO method is based on Eq. (5) using Doyle's approximation [12, 23], and the KAS method is based on Eq. (6) [32, 33].

$$\ln \beta = \ln \left[\frac{AE_x}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E_x}{RT_x} \quad (5)$$

$$\ln(\beta/T_x^2) = \ln \left[\frac{AR}{E_x g(\alpha)} \right] - \frac{E_x}{RT_x} \quad (6)$$

For Eq. (5), $\ln \beta$ and $-1052/(RT_x)$ corresponding to each heating rate are fitted into a straight line at each degree of conversion (α). The slope, ($E_x/1000$), represents the apparent activation energy term, while the intercept is a coupled expression of the reaction model in the integral form, $g(\alpha)$, the apparent activation energy, E_x , and the frequency factor, A . For Eq. (6), a plot of $\ln(\beta/T_x^2)$ versus $1/T_x$, obtained from thermal curves recorded at several heating rates, is a straight line whose slope allows evaluation of the apparent activation energy.

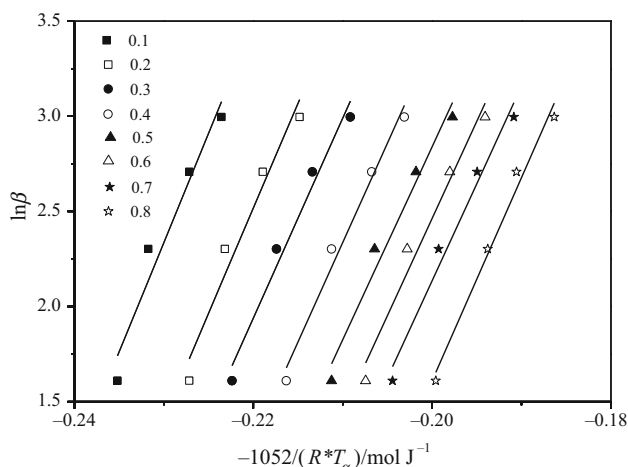


Fig. 3 Iso-conversional plot of FWO method at different values of conversion

Error limit of different heating rate

As above mentioned, different apparent activation energies can be obtained when different heating rates were adopted. Hence, calculating kinetic parameters would be restricted and the error limit from heating rate needs to be estimated first.

For differential form of the pyrolysis kinetic expression, substituting $f(x) = (1 - \alpha)^n$ [27–30] into Eq. (3) and taking a natural logarithm, the below equation yielded.

$$\ln \frac{d\alpha}{dT} = \ln \frac{A}{\beta} - \frac{E_x}{RT} + n \ln(1 - \alpha) \quad (7)$$

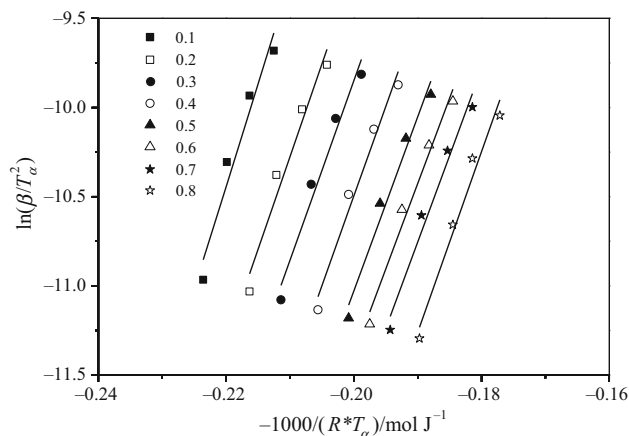


Fig. 4 Iso-conversional plot of KAS method at different values of conversion

Table 3 Kinetic parameters obtained by TG data at different heating rates using FWO method and KAS method

| Iso-conversional method | α | Intercept | $E_x/\text{kJ mol}^{-1}$ | R^2 |
|-------------------------|----------|-----------|--------------------------|---------|
| FWO method | 0.1 | 28.74763 | 114.83 | 0.97492 |
| | 0.2 | 26.81317 | 110.44 | 0.97895 |
| | 0.3 | 25.04746 | 105.04 | 0.98746 |
| | 0.4 | 24.27828 | 104.49 | 0.99133 |
| | 0.5 | 23.14501 | 101.53 | 0.98623 |
| | 0.6 | 22.91095 | 102.24 | 0.98542 |
| | 0.7 | 22.58278 | 102.12 | 0.98929 |
| | 0.8 | 23.0116 | 107.02 | 0.99256 |
| KAS method | 0.1 | 14.83926 | 114.87 | 0.97529 |
| | 0.2 | 11.53215 | 103.85 | 0.98017 |
| | 0.3 | 10.29357 | 100.72 | 0.98478 |
| | 0.4 | 9.62618 | 100.62 | 0.98755 |
| | 0.5 | 8.49389 | 97.62 | 0.98721 |
| | 0.6 | 7.80122 | 95.94 | 0.98917 |
| | 0.7 | 7.66335 | 96.93 | 0.98668 |
| | 0.8 | 8.01738 | 101.47 | 0.98592 |

Table 4 Error limit from heating rate by the iso-conversional methods

| α | $\varepsilon_{\alpha} _{\beta=10^{\circ}\text{C min}^{-1}} / \text{kJ mol}^{-1}$ | | | $\varepsilon_{\alpha} _{\beta=15^{\circ}\text{C min}^{-1}} / \text{kJ mol}^{-1}$ | | | $\varepsilon_{\alpha} _{\beta=20^{\circ}\text{C min}^{-1}} / \text{kJ mol}^{-1}$ | | |
|----------|--|---------|---------|--|---------|---------|--|---------|---------|
| | $n = 1$ | $n = 2$ | $n = 3$ | $n = 1$ | $n = 2$ | $n = 3$ | $n = 1$ | $n = 2$ | $n = 3$ |
| 0.1 | -7.93 | -8.15 | -8.36 | -8.41 | -8.65 | -8.89 | -8.65 | -9.02 | -9.39 |
| 0.2 | -13.25 | -15.61 | -17.98 | -13.14 | -15.45 | -17.77 | -13.32 | -15.69 | -18.07 |
| 0.3 | 9.11 | 5.991 | 2.88 | 9.46 | 6.511 | 3.55 | 9.51 | 7.291 | 5.07 |
| 0.4 | 2.4 | 2.72 | 3.03 | 0.11 | -1.04 | -2.1 | -2.76 | -4.08 | -5.4 |
| 0.5 | -3.56 | -1.65 | 0.26 | 5.31 | 5.15 | 4.98 | 1.07 | 0.19 | -0.68 |
| 0.6 | -5.37 | -4.16 | -2.93 | 2.02 | 4.56 | 7.11 | 8.39 | 10.11 | 11.84 |
| 0.7 | -12.59 | -14.24 | -15.91 | 4.94 | 12.05 | 19.15 | 7.14 | 12.69 | 18.24 |
| 0.8 | 17.7 | 15.65 | 3.59 | 17.07 | 12.18 | 7.28 | 5.92 | 16.96 | 8.41 |

For each heating rate, $\ln(A/\beta)$ can be considered as a constant. The derivative equation [Eq. (8)] states that the reaction rate at constant extent of conversion is only a function of temperature with a specific reaction order (n). The simplified equation [Eq. (9)] can be obtained.

$$E_{\alpha} = \frac{d[n \ln(1 - \alpha) - \ln \frac{dx}{dT}]}{d(RT)^{-1}} \tag{8}$$

$$E_{\alpha} = RT^2 \times \left[\frac{d(\ln \frac{dx}{dT})}{dT} - n \frac{d \ln(1 - \alpha)}{dT} \right] \tag{9}$$

For each degree of conversion (α), the error limit ($\varepsilon_{\alpha}|_{\beta=x}$) from heating rate can be calculated when n is assumed to be a certain value, as Eq. (10).

$$\varepsilon_{\alpha}|_{\beta=x} = E_{\alpha}|_{\beta=y} - E_{\alpha}|_{\beta=x} \tag{10}$$

$$E_{\alpha}|_{\beta=y} = R \cdot \left\{ T_{\alpha}^2 \cdot \left[\frac{d(\ln \frac{dx}{dT})}{dT} - n \frac{d \ln(1 - \alpha)}{dT} \right] \right\}_{\beta=y} \tag{11}$$

$$E_{\alpha}|_{\beta=x} = R \cdot \left\{ T_{\alpha}^2 \cdot \left[\frac{d(\ln \frac{dx}{dT})}{dT} - n \frac{d \ln(1 - \alpha)}{dT} \right] \right\}_{\beta=x} \tag{12}$$

In this work, the pyrolysis behavior with the heating rate of $5^{\circ}\text{C min}^{-1}$ should be least hindered by gaseous diffusion. The error limits were calculated when different n (1, 2, 3) is assumed, according to the result of $5^{\circ}\text{C min}^{-1}$.

Apparent activation energy E_{α}

In the present study, four different heating rates ($5, 10, 15$ and $20^{\circ}\text{C min}^{-1}$) were employed to calculate the apparent activation energies (E_{α}) using the FWO method and the KAS method. Eight conversions (α) were selected for the kinetic analysis corresponding to the sawdust pyrolysis. These conversions (α) include 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8. According to the FWO method and KAS method, straight lines are obtained and shown in Figs. 3, 4, respectively. The apparent activation energy (E_{α}) values

and linear correlation coefficient (R^2) shown in Table 3 for each degree of conversion and the corresponding intercept of linear fittings are also listed in this table. As shown in Table 3, the linear correlation coefficients for getting the activation energy are in the range of 0.97492–0.99256 and the fitting is good for every linear plot. The apparent activation energies for sawdust pyrolysis were calculated, and the range is between 101.53 and $114.83 \text{ kJ mol}^{-1}$ using FWO method and is between 95.94 and $114.87 \text{ kJ mol}^{-1}$ using KAS method.

Error limits from heating rate are calculated and listed in Table 4 with different reaction order ($n = 1, 2, 3$). Note that these error limits always maintain within the range of $\pm 20 \text{ kJ mol}^{-1}$, although these data do not express a clear rule. Besides, it should be pointed out that the kinetic parameters and error limits in this work were based on these experimental conditions. Sample quality, gas atmospheres and flow velocity can alter these results, and their effects on sawdust pyrolysis should be further studied in the following study.

Conclusions

This work conducts pyrolysis experiments of sawdust with the four heating rates (β) of $5, 10, 15$ and $20^{\circ}\text{C min}^{-1}$ in nitrogen atmosphere using a thermogravimetric analyzer and pyrolysis kinetics analysis through FWO method and KAS method. Error limit from heating rate was proposed to evaluate the precision of the obtained apparent activation energies. Following conclusions are made in this study.

1. Organics of sawdust mainly decomposed at $250\text{--}450^{\circ}\text{C}$, and greater heating rate can move the peak of differential thermogravimetric curves toward higher temperature.
2. FWO method and KAS method were employed to analyze the non-isothermal pyrolysis kinetic of sawdust,

and the range of apparent activation energies for sawdust pyrolysis is between 101.53 and 114.83 kJ mol⁻¹ using FWO method and is between 95.94 and 114.87 kJ mol⁻¹ using KAS method.

3. Error limits from heating rate were calculated, and the range cannot exceed the range of ± 20 kJ mol⁻¹. It is worth noting that this result mainly depends on the present experimental conditions.

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