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Determining Kinetic Parameters of Cellulose and Lignin Pyrolysis by Gaussian Process Regression (GPR) Method

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Category

Research Article

Abstract

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Keywords

Cellulose, Lignin, Kinetic analysis, Thermogravimetry, Pyrolysis, Gaussian process regression fitting

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Determining kinetic parameters of cellulose and lignin pyrolysis by Gaussian process regression (GPR) method

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Abstract

The ignition and flame-spread processes in the forest and urban fires involve the pyrolysis reactions of biomass materials. One of the most common methods for estimating the fire performance of a material is the evaluation of kinetic parameters, i.e., activation energy (E), pre-exponential factor (A), and reaction model ($f(\alpha)$), from thermogravimetric analysis (TG) data. Typically, E is estimated based on an Arrhenius-type equation such as Kissinger, Kissinger-Akahira-Sunose (KAS), and Friedman equations. Then, its value is adjusted along with other parameters by assuming a reaction model, e.g., the n -order model. This study proposes a Gaussian process regression (GPR) method to determine more reliable kinetic parameters without any assumptions of reaction mechanisms. This paper studies both constant and variable kinetic parameters and compares the GPR method with the conventional methods that assume the n -order model. The results of numerically calculated conversion (α) indicated that the GPR model achieves the best fit with the experimental data.

Keywords: Cellulose; Lignin; Kinetic analysis; Thermogravimetry; Pyrolysis; Gaussian process regression fitting

Introduction

The ignition and flame spread on solid fuel are essential aspects of fire protection engineering [1]. The kinetic parameters of combustible materials are necessary to evaluate the thermal performance in fire modeling. Lignocellulosic biomass comprises three major components: cellulose, hemicellulose, and lignin. Cellulose accounts for the largest fraction of the biomass (40–50 wt%) and dominates as the primary fuel in fires, while lignin accounts for 10–40 wt% [2].

The kinetic study of cellulose and lignin is an essential first step in investigating fire performance. According to previous studies, a single-step reaction with constant activation energy can reasonably mimic the weight loss behavior of cellulose [3]. On the other hand, lignin has a more complex structure than cellulose and hemicellulose. Pyrolysis of lignin occurs over several stages, and its decomposition takes place over a wider temperature range [4]. Therefore, determining kinetics with one constant set of kinetic parameters is rather difficult. Hence, the variable kinetic parameters need to

be considered in the case of lignin pyrolysis.

Generally, a conventional method is performed to determine kinetic parameters through experimental and mathematical approaches. Microscale thermal-analysis experiments, such as thermogravimetry (TG), are standard scale-modeling techniques in kinetic studies because of their controllability and high accuracy. Typically, the masses of samples used in thermal-analysis experiments are in the unit of milligrams, much smaller than real-scale phenomena. The heating rates in typical TG experiments are low compared to the actual fire conditions. The slow heating rates and the small sample sizes can achieve the pure kinetic regime, where there is no significant intra-particle temperature gradient, and the chemical reactions are slower than heat transfer [4]. The pure kinetic regime is characterized by a small thermal Biot number (Bi) and a high pyrolysis number (Py), defined respectively as

$$Bi = \frac{hL}{\lambda} \quad (1)$$

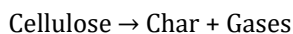
Nomenclature

A	Pre-exponential factor (1/s)	Py	Pyrolysis number (-)
Bi	Biot number (-)	R	Universal gas constant (J/mol·K)
c_p	Heat capacity (J/kg·K)	\dot{r}	Rate of pyrolysis reaction (kg/m ³ ·s)
$d\alpha/dt$	Normalized mass loss rate (1/s)	T	Temperature (K)
E	Activation energy (J/mol)	t	Time (s)
$f(\alpha)$	Reaction model (-)		
h	External heat transfer coefficient (W/m ² ·K)	<i>Greek symbols</i>	
L	Sample size (m)	α	Conversion (-)
n	Reaction order (-)	β	Heating rate (°C/min)
		λ	Thermal conductivity (W/m ² ·K)

$$Py = \frac{\lambda}{\dot{r} c_p L^2} \quad (2)$$

where h is the external heat transfer coefficient, L is the sample size, λ is the thermal conductivity, \dot{r} is the rate of pyrolysis reaction, and c_p is the heat capacity. The pure kinetic regime ensures that the sample has the same temperature as the surrounding fluid and allows the identification of different thermal decomposition steps [5].

The next step is a mathematical kinetic analysis based on the Arrhenius equation. For cellulose pyrolysis reaction, there have been many studies on the kinetics of cellulose pyrolysis over the past few decades. However, the exact definition of its reaction mechanism remains controversial. In the 1980s, Antal [6] proposed a single-step first-order model to describe the cellulose decomposition process.



Shafizadeh [7] suggested a global mechanism involving two competitive first-order reactions leading to volatiles, a char, and a gaseous fraction, including water, carbon dioxide, and carbon monoxide. Agrawal [8] developed a model with three consecutive first-order reactions. The main drawback of these multistep reaction schemes is the difficulty in identifying and quantifying the formation of intermediate or active cellulose. Hence, many researchers usually consider the kinetic model based on a single-step reaction [9]. The assumption of the n -order reaction model is the most intensively used. In some other cases, cellulose pyrolysis is modeled using the nuclei-growth or Avrami-Erofeev mechanisms [10].

On the contrary, the assumption of a first-order reaction model for lignin pyrolysis can lead to an underestimation of the activation energy values [4]. The pyrolysis of lignin requires at least a three-step reaction to describe its complex process [11]. Consequently, developing a simple model with high accuracy has gained continuous interest among kinetics communities.

The present study proposes a Gaussian process

regression (GPR) model to achieve more reliable kinetic parameters without assuming any reaction models. The comparison of kinetic parameters obtained from conventional and GPR methods is presented and evaluated through the fit error%.

The structure of this work is as follows: we shall first introduce the TG experiment to obtain the weight loss data and then compare the constant kinetic parameters between conventional and GPR methods for cellulose pyrolysis. Then, we discuss the necessity of the GPR method to determine the variable kinetic parameters of lignin pyrolysis.

Experimental

The cellulose filter papers (100% cotton linter cellulose, Advantec) and lignin powder (catalog number 24101-32, Kanto Chemical) were investigated using a TG analyzer (Rigaku STA8122 External PC). The 5 ± 0.5 mg of cellulose was heated from room temperature to 700 K at heating rates of 5, 10, 20, and 30 °C/min. The 5 ± 0.5 mg of lignin was heated from room temperature to 1000 K at heating rates of 3, 5, 10, 20, and 30 °C/min under the inert atmosphere (helium gas, flow rate 100 mL/min) to avoid any oxidation reaction.

Additionally, the scale effect of initial mass was examined by conducting the TG experiments at various sample masses (2.5, 5, and 10 mg) for a heating rate of 10 °C/min to confirm that the condition is within the pure kinetic regime. Note that the cellulose was used as a test sample for the scale test. Calculating the sample size as $L = (m_i/\rho)^{1/3}$ where m_i is the initial mass, and ρ is the density, Eqs. (1) and (2) give the ranges of Bi and Py in the present experiment, as shown in Fig. 1. The resulting Bi numbers are low enough ($Bi < 0.1$), and Py numbers are high enough ($Py > 10$) for the present experimental conditions to fall within the pure kinetic regime.

Figs. 2(a) and 2(b) confirm that the heat transfer inside the particle does not influence the reaction rate within the pure kinetic regime; the definition of conversion, α , is given in the next section. We, therefore, ignore the initial-mass effects in the following discussion.

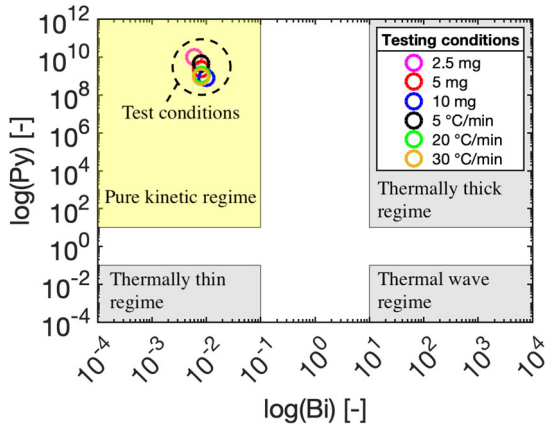


Fig. 1. The Pyrolysis and Biot numbers, Eqs. (1) and (2), are used to determine the pyrolysis regime of cellulose.

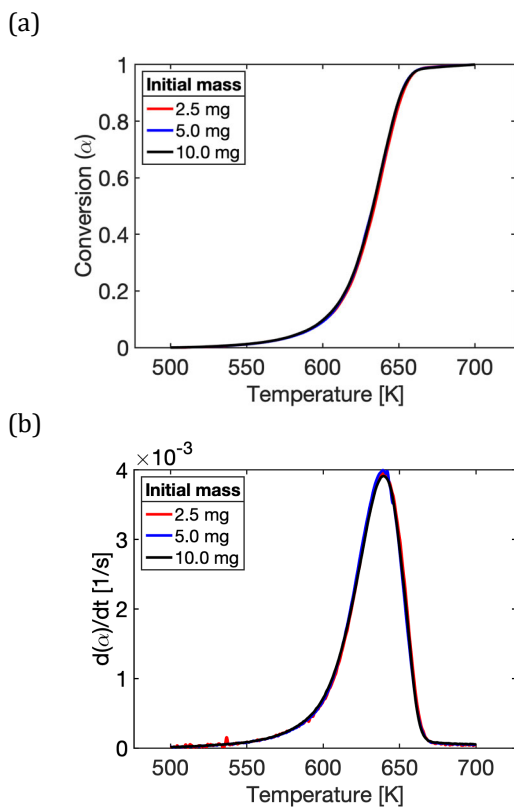


Fig. 2. Normalized (a) TG and (b) DTG curves of cellulose pyrolysis at the different initial masses of 2.5, 5, and 10 mg for the heating rate of 10 °C/min.

Kinetic analysis methods

We base our analysis on the following equation:

$$\frac{d\alpha}{dt} = A(\alpha)f(\alpha)e^{-\frac{E(\alpha)}{RT}} \tag{3}$$

Here, α is the conversion that is defined as

$$\alpha(t) = \frac{m_i - m(t)}{m_i - m_f} \tag{4}$$

where $m(t)$, m_i , and m_f are the instantaneous, initial, and final masses, respectively. The conversion ranges from 0 to 1 as the reaction progresses from initiation to completion. The purpose of the kinetic analysis is to determine $A(\alpha)$, $E(\alpha)$, and $f(\alpha)$.

The knowledge of the reaction model $f(\alpha)$ has been studied over the past decade. The frequently used reaction models to describe the cellulose pyrolysis process include two major types: the n -order reaction and nuclei-growth models as shown in Eqs. (5) and (6), respectively.

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

$$f(\alpha) = n(1 - \alpha)(-\ln(1 - \alpha))^{\frac{n-1}{n}} \tag{6}$$

According to the study of Dollimore [10], the cellulose decomposition process relates to the random nucleation and nucleus growth mechanism, which can be well described by the plot of Eq. (6). However, Eq. (6) gives $f(0) = 0$, leading to the trivial solution, $\alpha = 0$, of Eq. (3) with the initial condition of $\alpha = 0$ at $t = 0$. A reasonable non-zero initial condition of α must be specified to remedy the problem, but such information is usually unavailable. Thus, Eq. (6) is not discussed in this paper. On the other hand, the n -order reaction model (Eq.(5)) has been widely used in previous studies [5, 12].

Results and discussion with constant A and E for cellulose pyrolysis

The case with constant A and E for cellulose pyrolysis is first discussed. The following briefly summarizes the previous conventional methods and the proposed GPR method.

Kissinger method

The Kissinger method assumes the first-order reaction, i.e., $f(\alpha) = 1 - \alpha$, to determine A and E . The basic equation of this method can be derived from taking the derivative of Eq. (3), giving $d^2\alpha/dT^2$ (note that $dT = \beta dt$, where β is the heating rate). The maximum reaction rate occurs when the second derivative is zero. After rearranging, Eq. (7) can be obtained.

$$\ln \frac{\beta}{T_{max}^2} = \ln \frac{AR}{E} - \frac{E}{RT_{max}} \tag{7}$$

where T_{max} is the temperature at the maximum reaction rate. The value of E is determined from the slope of the plot of $\ln(\beta/T_{max}^2)$ against $1/T_{max}$ as shown in Fig. 3, giving $E = 147.41$ kJ/mol. The y -intercept of the plot yields $A = 5.35 \times 10^{11}$ /min.

Although Eq. (7) is derived by assuming the first-order reaction model, the reaction order is often adjusted by fitting the experimental normalized DTG curves with Eq. (3). The best-fit value of n was 0.78, as shown in Fig. 4 and Table 1.

Table 1. The determined kinetic parameters and fit error% of TG curves for cellulose pyrolysis.

Parameters	Constant A and E				
	n optimized			A , E , and n optimized	GPR
	Kissinger	KAS	Friedman		
E [kJ/mol]	147.41	160.07	156.60	183.06	152.65
A [1/min]	5.35×10^{11}	5.94×10^{12}	3.46×10^{12}	5.00×10^{14}	–
n	0.78	0.85	0.85	0.94	–
Fit error%	3.63	1.99	3.63	2.27	0.94

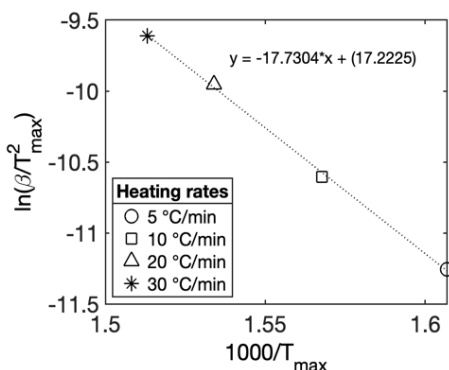


Fig. 3. Arrhenius-type linear regression of cellulose pyrolysis according to the Kissinger method, Eq. (7).

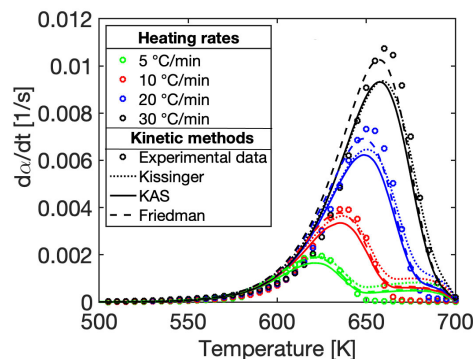


Fig. 4. Fitting of normalized DTG curves to optimize n for the Kissinger, KAS, and Friedman methods.

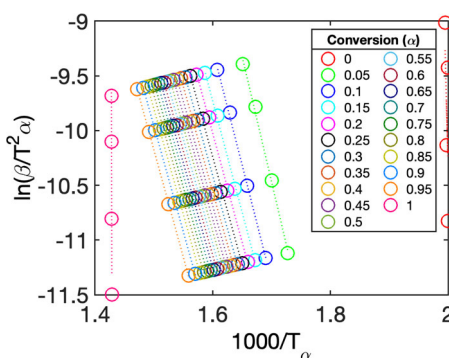


Fig. 5. Arrhenius-type linear regression of cellulose pyrolysis according to the KAS method, Eq. (8).

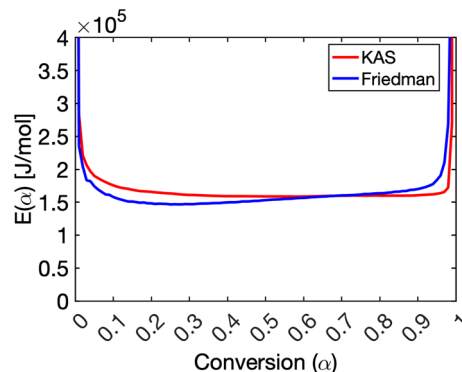


Fig. 6. E as a function of α of cellulose pyrolysis from the KAS and Friedman methods.

Kissinger-Akahira-Sunose (KAS) method

The rearrangement and integration of Eq. (3) give the KAS equation as follows

$$\ln \frac{\beta}{T_\alpha^2} = \ln \frac{A_\alpha R}{E_\alpha g(\alpha)} - \frac{E_\alpha}{RT_\alpha} \tag{8}$$

where $g(\alpha)$ is the integral form of the reaction model. T_α and E_α are the temperature and activation energy at a given conversion. The slope of KAS plots provides the activation energy for each specified conversion value, as presented in Fig. 5. The regression lines are plotted in Fig. 5 with an interval of 0.05, as suggested by Vyozovkin et al. [13]. It is noticeable that the regression lines within the conversion ranges of 0.05 and 0.95

are parallel, which means that the slope is nearly constant along each conversion step. However, linear regression of conversion below 0.05 and over 0.95 (boundary regions) approaches a vertical line, leading to significantly high activation energies in these regions, as shown in Fig. 6. Nevertheless, the sharp changes in the narrow regions can only have limited influences on the kinetic analysis and are therefore negligible in most cases [14–16]. Thus, the median value was used to obtain the constant E , giving $E = 160.07$ kJ/mol. Assuming an n -order reaction, the best-fit value of the reaction order was $n = 0.85$, as shown in Fig. 4 and Table 1. The pre-exponential factor (A) can be derived from the y -intercept of Eq. (8). The value of A is influenced

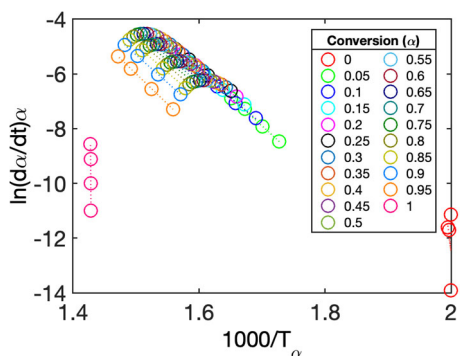


Fig. 7. Arrhenius-type linear regression of cellulose pyrolysis according to the Friedman method, Eq. (9).

by the value of n as $g(\alpha)$ in Eq. (8) includes n ; $n = 0.85$ yielded $A = 5.94 \times 10^{12}/\text{min}$.

Friedman method

The Friedman method is one of the most common differential methods derived from directly taking the logarithm of Eq. (3), giving Eq. (9) as

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln A_\alpha f(\alpha) - \frac{E_\alpha}{RT_\alpha} \quad (9)$$

At each given α , the value of E_α from the Friedman method can be determined from the slope of the plot $\ln(d\alpha/dt)_\alpha$ against $1/T_\alpha$, as presented in Fig. 7. Similar to the KAS method, the median activation energy is used, giving $E = 156.60$ kJ/mol. The best-fit value of n and A equal 0.85 and $3.46 \times 10^{12}/\text{min}$, as reported in Fig. 4 and Table 1.

Table 1 summarizes the kinetic parameters obtained from the conventional methods. The accuracy of the kinetic parameters was evaluated by numerically integrating Eq. (3) and comparing it with the experimental data. Then, the fit error% defined in Eq. (10) was computed to quantify the accuracy.

$$\text{Fit error}\% = \sqrt{\frac{\sum_{i=1}^N (\alpha_{i,exp} - \alpha_{i,cal})^2}{N}} \times 100 \quad (10)$$

where $\alpha_{i,exp}$ and $\alpha_{i,cal}$ are the experimental and the calculated conversion, respectively. N is the number of data points considered. The adjustment of the n value provides the satisfactory fit error% values. Among the conventional methods tested, the kinetic parameters from the KAS method yielded the least fit error% (1.99%).

Optimization of E , A , and n

The kinetic parameters (E , A , and n) can be optimized by fitting the DTG curves, as shown in Fig. 8. After the optimization process, the values of kinetic parameters obtained from the different methods arrived at the same results regardless of the initial estimate: E

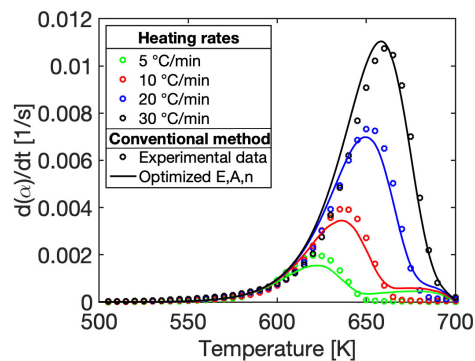


Fig 8. Fitting of normalized DTG curves to optimize E , A , and n .

$= 183.06$ kJ/mol, $A = 5.00 \times 10^{14}/\text{min}$, and $n = 0.94$. When Eq. (3) was integrated and compared with experimental data, the fit error% was 2.27%. Interestingly, the optimized E , A , and n did not improve the fit error% compared to the KAS method, although they can fit the DTG curve with higher accuracy.

Gaussian process regression (GPR) method

GPR is a powerful non-parametric technique used mainly in non-linear regression problems [17, 18]. The GPR uses a mean function and a covariance (kernel) function to define a probability distribution of functions over the input data, allowing it to provide the uncertainty of the predictions. This study applied the GPR model through the “fitrgp” function in the MATLAB R2021b program using the zero-mean function and the squared exponential kernel function with its default kernel parameters.

Analysis of the present data shows that Eq. (3) is sufficient to model the pyrolysis reactions of cellulose and lignin, i.e., the reaction model f depends only on α . With constant E and A , $Af(\alpha)$ can be expressed as $(d\alpha/dt)/e^{-E/RT}$. The activation energy E can then be determined by the non-linear least squares (NLS) method, as shown in Fig. 9. When the value of E equals 100 kJ/mol, the plotted $Af(\alpha)$ values are different for different heating rates, as shown in Fig. 9(a). On the other hand, the curves in Fig. 9(b) use the determined E of 152.65 kJ/mol from the NLS method can represent the same reaction model and minimize the difference among the various heating rates. However, there are some fluctuations in the reaction model at low conversion ($\alpha = 0-0.05$) and high conversion because the assumption of constant E is not valid during these stages. The fluctuation at high conversion is insignificant since the reaction rate approaches zero at high conversion. Therefore, the GPR method is applied to extrapolate the data only at low conversion, as shown in Fig. 10. Fig. 11 is the master plot to compare the experimentally obtained reaction model with kinetic models. It can be noticed that the experimental data share some similarities with the random chain scission model [14,

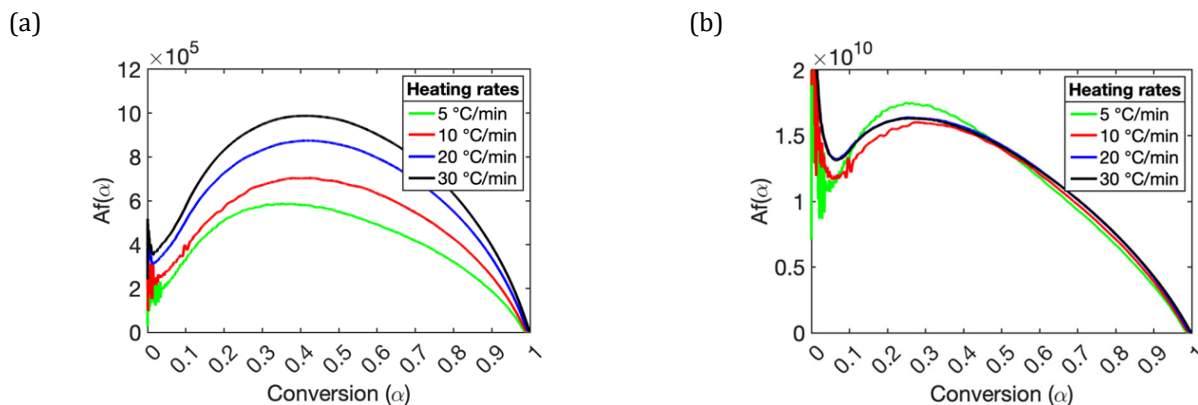


Fig. 9. Experimental reaction model, $Af(\alpha)$ as a function of conversion (α) of cellulose pyrolysis with (a) $E = 100$ kJ/mol and (b) $E = 152.65$ kJ/mol.

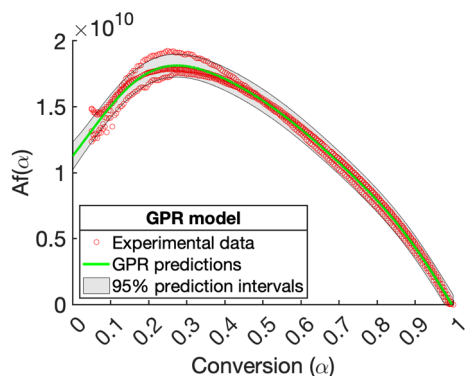


Fig. 10. Experimental reaction model, $Af(\alpha)$, as a function of conversion (α) of cellulose pyrolysis obtained from the GPR method.

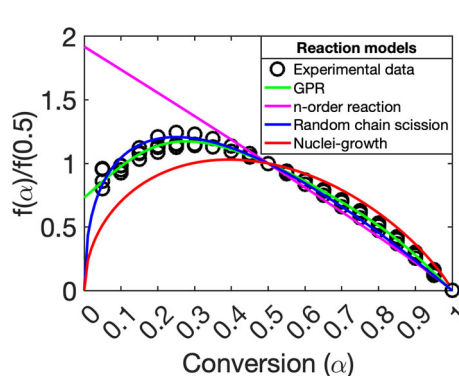


Fig. 11. Master plot corresponding to the different kinetic models of cellulose pyrolysis.

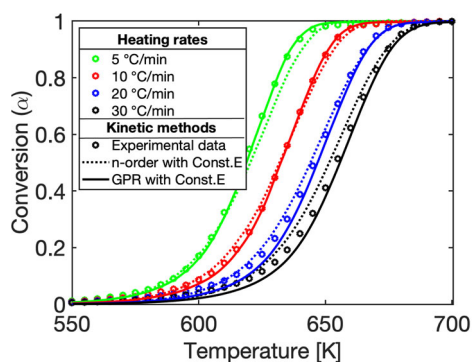


Fig. 12. Transient calculation of cellulose TG curves using constant kinetic parameters obtained from conventional and GPR methods.

19], which can be summarized in three steps as follow:

Step 1: Short fragments are released after a random splitting of bonds close to the chain end. The cellulose chains at initial reaction times are still too long, and the fragments are not short enough to evaporate. Thus, it can result in a low reaction rate during the initial period.

Step 2: The cellulose chains are sufficiently

fragmented even without changes in the rate of bond scission; a greater fraction of the scissions will lead to volatilization. Therefore, the mass-loss rate suddenly increases during $\alpha = 0.1-0.3$.

Step 3: The reaction model decreases for $\alpha > 0.3$ because of fuel consumption.

Transient calculation of conversion (α)

The transient calculation of α was lastly done to re-check the accuracy of kinetic parameters from the GPR method by numerically integrating Eq. (3). Fig. 12 shows the simulated α curves using kinetic parameters from the KAS and GPR methods, shown with the dotted and solid lines, respectively. The fit error% between the simulated and experimental α is summarized in Table 1. The results confirm that the GPR method can produce the best-fit results with the least fit error% (0.94%).

Results and discussion with constant and variable A_α and E_α of lignin pyrolysis

The thermal degradation of lignin occurred through the multistep reactions; hence, lignin pyrolysis is a good example to compare the accuracy between the

Table 2. The determined kinetic parameters and fit error% of TG curves for lignin pyrolysis.

Parameters	Constant A and E				
	n optimized			$A, E,$ and n optimized	GPR
	Kissinger	KAS	Friedman		
E [kJ/mol]	189.70	137.50	127.32	127.81	146.30
A [1/min]	1.55×10^{18}	8.16×10^{11}	1.40×10^{11}	1.25×10^{11}	-
n	25.62	6.83	6.34	6.45	-
Fit error%	29.94	6.15	4.85	5.38	3.55

Parameters	Variable A_α and E_α			
	n optimized			GPR
	Kissinger	KAS	Friedman	
E [kJ/mol]	-	-	-	-
A [1/min]	-	-	-	-
n	-	7.70	1	-
Fit error%	-	3.55	4.09	2.48

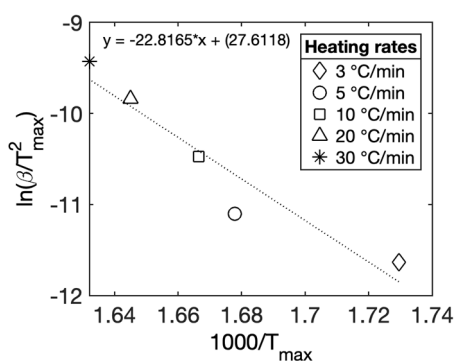


Fig. 13. Arrhenius-type linear regression of lignin pyrolysis according to the Kissinger method, Eq. (7).

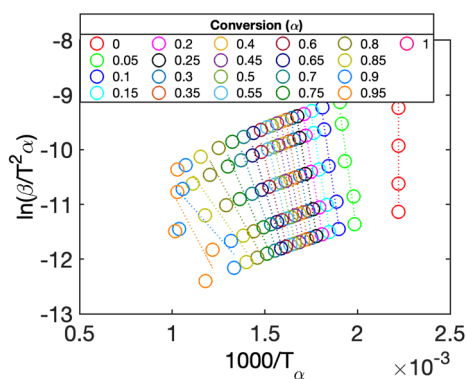


Fig. 14. Arrhenius-type linear regression of lignin pyrolysis according to the KAS method, Eq. (8).

constant and variable kinetic parameters.

Kissinger method

The activation energy derived from the slope of the Kissinger plot is 189.70 kJ/mol, as shown in Fig. 13. Fitting with the experimental DTG data gives $A = 1.55 \times 10^{18}$ /min and $n = 25.62$. The set of parameters leads to the high fit error% of 29.94%, as shown in Table 2. This high error might be because the Kissinger method only allows the determination of constant kinetic parameters at the maximum reaction rate, which is more suitable for the one-step reaction than the multistep reaction of lignin pyrolysis. The R^2 value (0.912) of the Kissinger plot in Fig. 13 is indeed not as good as that for cellulose (0.999) in Fig. 3.

Kissinger-Akahira-Sunose (KAS) method

The activation energy for each specified conversion value can be obtained by the slope shown in Fig. 14. It

can be revealed that the linear regression at high conversions shows inconsistencies with the value of R^2 less than 0.8. This poor fitting confirms that the pyrolysis of lignin undergoes multi-stage reactions and E_α highly depends on the α values, as expressed in Fig. 15. Therefore, this study considered both constant ($E = 137.50$ kJ/mol) and variable activation energy in the case of lignin pyrolysis.

Assuming the n -order reaction model, the best-fit value of the reaction order for constant parameters is $n = 6.83$, giving $A = 8.16 \times 10^{11}$ /min. The best fit of reaction order for variable parameters was $n = 7.70$, as shown in Table 2 and Fig. 16.

Friedman method

The E_α at a given conversion can be derived from the slope of the Friedman plot in the same way as cellulose pyrolysis. The linear regression in Fig. 17 also points out the poor fitting at high conversion. Hence,

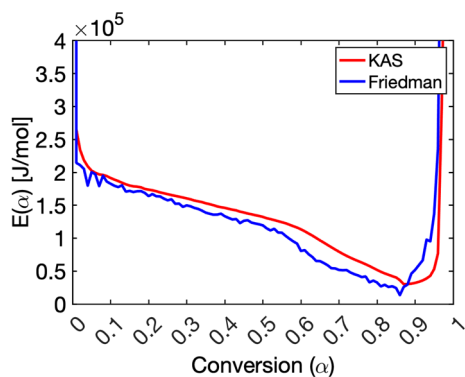


Fig. 15. E as a function of α of lignin pyrolysis from KAS and Friedman methods.

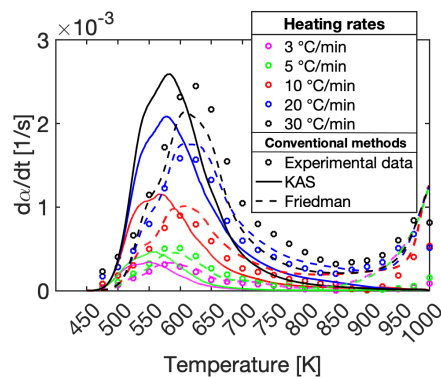


Fig. 16. Fitting of normalized DTG curves to optimize n for the KAS and Friedman methods in the case of variable kinetic parameters.

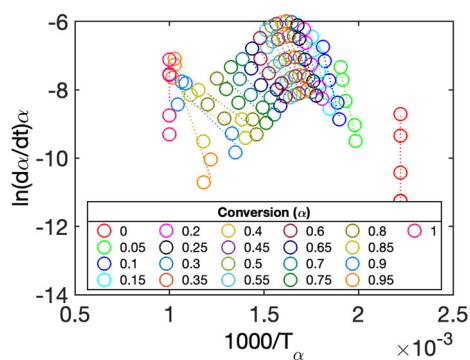


Fig. 17. Arrhenius-type linear regression of lignin pyrolysis according to the Friedman method, Eq. (9).

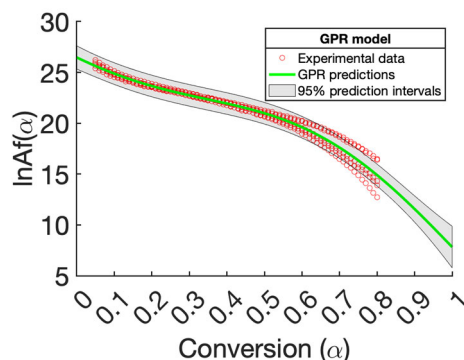


Fig. 18. $\ln A f(\alpha)$ as a function of α of lignin pyrolysis from the GPR method using constant activation energy.

E_α is not constant throughout the process, as shown in Fig. 15. The values of E_α obtained from both KAS and Friedman methods are likely to follow the same trends, but E_α from the KAS method is less noisy because the KAS method originated from the integration of Eq. (3).

Assuming the n -order model, the best fit of reaction order for constant parameters is $n = 6.34$, yielding $A = 1.40 \times 10^{11}/\text{min}$. However, in the case of variable E_α , the optimization process of n obtained from the Friedman method cannot be performed because there is no freedom to adjust the n value. The term of the reaction model, $f(\alpha)$, cancels itself. Thus, the unity n value is used according to the assumption of the first-order reaction model, yielding the fit error of 4.09% as shown in Table 2.

Gaussian process regression (GPR) method

The constant activation energy ($E = 146.30$ kJ/mol) with the GPR method can improve the accuracy of kinetic parameters with a decreasing fit error of 3.55% compared to the conventional optimized process, as summarized in Table 2. This indicates the importance of a reliable reaction model. Nevertheless, owing to the strong dependence of E_α on α for the lignin pyrolysis, the high uncertainty of the predicted model can be

noticed as shown with the wider grey area in Fig. 18.

Therefore, the variable E_α should be considered to narrow the 95% prediction intervals and to enhance a more precise reaction model. The variable E_α below $\alpha = 0.05$ and over $\alpha = 0.95$ was first extrapolated using the GPR method; then, the value of variable $A(\alpha)f(\alpha)$ was further obtained, as presented in Fig. 19. The sensitivity of the variable kinetic parameters obtained by the GPR method on the input data is also tested. When the input data were perturbed by 1%, the changes in the kinetic parameters were less than 1.1% for $E(\alpha)$ and $A(\alpha)f(\alpha)$.

Transient calculation of conversion (alpha)

The transient calculation of lignin-pyrolysis residual mass loss was lastly done by numerical integration of Eq. (3), similar to cellulose. The results of the simulated TG curves are shown in Fig. 20. The lignin degraded through the multi-stage reactions. The first step occurs at low temperatures below 800 K. In contrast, the second reaction occurs mainly at temperatures over 900 K. In the low-temperature range, the difference among different heating rates is not as apparent as cellulose, reflecting the complicated nature of lignin degradation reactions. Nonetheless, the comparison between the

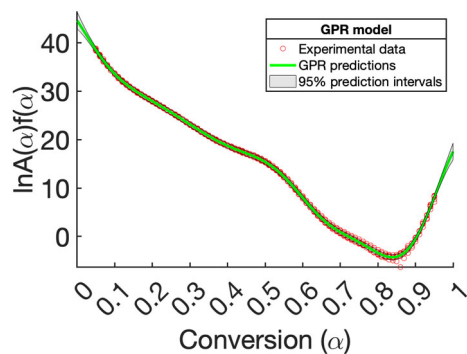


Fig. 19. $\ln A(\alpha)f(\alpha)$ as a function of α of lignin pyrolysis from the GPR method using variable activation energy.

conventional method by assuming the n -order reaction model and the GPR method confirms that the GPR method with variable E_α can reduce the fit error% to 2.48%, as summarized in Table 2.

Conclusions

Reaction models for describing cellulose and lignin pyrolysis kinetics are developed through the GPR approach. The advantage of this method is the ability to predict the reaction model without any assumptions. Furthermore, GPR can predict the reaction model outside the given dataset. Therefore, this approach avoids the noisy data at the boundary area and the risks of choosing an improper kinetic model. The results confirm that the GPR model accomplishes the minimum fit error of 0.94% for cellulose pyrolysis and 2.48% for lignin pyrolysis. This proposed method is useful for studying the pyrolysis of natural materials, for which it is difficult to identify a reliable reaction model because of their complexity.

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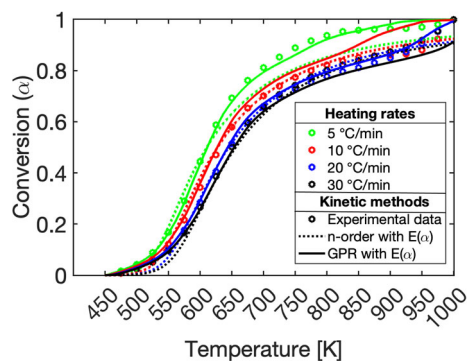


Fig. 20. Transient calculation of lignin TG curves according to variable kinetic parameters obtained from conventional and GPR methods.

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