



Thermogravimetric kinetics of lignocellulosic biomass slow pyrolysis using distributed activation energy model, Fraser–Suzuki deconvolution, and iso-conversional method



Mian Hu^a, Zhihua Chen^a, Shengkai Wang^b, Dabin Guo^a, Caifeng Ma^a, Yan Zhou^a, Jian Chen^a, Mahmood Laghari^{a,c}, Saima Fazal^a, Bo Xiao^a, Beiping Zhang^a, Shu Ma^{a,*}

^a School of Environmental Science & Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

^b Yuannan Chihong Zn&Ge Co., Ltd, Qujing 655011, China

^c Faculty of Agricultural Engineering, Sindh Agriculture University, Tandojam 70060, Sindh, Pakistan

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ABSTRACT

Pyrolysis kinetics of pine wood, rice husk and bamboo (*Bambusa chungii*) were studied via thermogravimetric analysis technique under low heating rates. The result of model-free procedure showed that the lignocellulosic pyrolysis according to one-step reaction model is dominated by the diffusion effects. However, the complex features of variations are caused by the mechanism changes, which are hard to be determined. The distributed activation energy model (DAEM) kinetic results indicated that the activation energy distribution for pseudo components follows the orders of: $E_0(\text{lignin}) > E_0(\text{cellulose}) > E_0(\text{hemicelluloses})$, $\sigma(\text{lignin}) > \sigma(\text{hemicelluloses}) > \sigma(\text{cellulose})$. The Fraser–Suzuki deconvolution fits better with the experimental data than DAEM. The pyrolysis mechanism of pseudo components after deconvolutions follows the theoretical models: third order model $f(\alpha) = (1 - \alpha)^3$ for hemicelluloses and lignin, random scission model $f(\alpha) = 2(\alpha^{1/2} - \alpha)$ for cellulose. The apparent activation energy for pseudo hemicelluloses is 162.84 ± 26.45 kJ/mol for pine wood, 168.63 ± 28.47 kJ/mol for rice husk and 154.55 ± 26.49 kJ/mol for bamboo, respectively. The E_x value increases with the conversion with little deviation to its mean value. Similar E_x vs. α dependencies also are observed for pseudo celluloses, which has E_x of 188.14 ± 24.42 kJ/mol for pine wood, 206.71 ± 24.88 kJ/mol for rice husk and 190.45 ± 23.79 kJ/mol for bamboo, respectively.

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1. Introduction

Biomass is considered as a potential renewable energy source in the future with the depletion of fossil fuel reserves and corresponding environment problem [1–3]. The conversion of biomass into liquid, gas fuels and other energy-related end products has spurred the growth of research and development efforts worldwide. Lignocellulosic biomass (LB), which mainly includes forest wastes, agricultural residues, etc, contributes a vast majority of untapped biomass raw feedstock [4–6]. Slow pyrolysis is regarded as a promising treating method, which is suitable to convert LB into bio-fuels (such as bio-oil and syngas), adsorbent bio-char and various chemicals [7,8]. The development of pyrolysis

processes for LB conversion and proper equipment design is based on the knowledge of pyrolysis mechanisms and significant pyrolysis parameters [9,10].

Thermogravimetric analysis (TGA) has been widely used to study the apparent kinetics of LB pyrolysis attributes to the high-precision in weight loss recording, perfectly suitable for low heating rates condition [11–13]. Based on the TGA, the pyrolysis kinetic parameters and mechanisms can be estimated using two main procedures: model-free and model based. The model-free procedure can estimate the kinetic parameters (i.e. apparent activation energy and pre-exponential factor) accurately without knowing the pyrolytic mechanism (model) by combining the iso-conversional methods, master-plots methods and energy compensation effects. And the accurate mechanisms can be determined by inverse computing using the kinetic parameters [14]. However, the actual reaction mechanism of biomass pyrolysis is extremely complex mainly due to the highly heterogeneous of the pyrolysis process and amorphous morphologies of its components especially for

* Corresponding author at: School of Environmental Science & Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan, Hubei 430074, China.

E-mail address: mashu@hust.edu.cn (S. Ma).

hemicelluloses and lignin [15]. The model-free procedure, which is only suitable for a single reaction, is appropriate for apparent activation energy estimation but is not considered to be used for mechanism identification during the whole pyrolysis process [5,16]. The model based procedure can realize the pyrolysis kinetic prediction with a known mechanism, via a fitting which the corresponding kinetic parameters can be estimated directly with the experimental data. The three-parallel-reaction (TPR) model is the most suitable mechanisms for LB pyrolysis in model-free procedure which considers three main pseudo components (hemicelluloses, cellulose and lignin) reacts independently to volatiles and char. Based on the TPR model, the pyrolysis of LB can be separated into three single reactions correspond to each pseudo component.

There mainly are three mechanisms for the TPR model calculation respectively corresponds to three methods. The first one is the order-based mechanism, in which the reaction mechanisms of hemicelluloses, cellulose and lignin are all assumed to n -th order reaction ($n = 1$ or $n \neq 1, n > 0$). The order-based mechanism is generally suitable for elementary reaction in a homogeneous reaction system and described by the collision or transition-state theories. The using of order-based mechanism in solid state material thermal decomposition kinetics, however, is semi-empirical without any physical meaning [17]. And the use of n -th order reaction even underestimates the apparent activation energy of pseudo lignin. The second one is distributed activation energy model (DAEM), in which each single reaction of pseudo components is considered as the combination of infinite first-order ($n = 1$). In DAEM, the apparent activation energy follows a probability density function (PDF) whose integration in the range of $(0, +\infty)$ equals to 1. However, the application of DAEM is more complicated while introducing comprehensive computational effort to the Computational Fluid Dynamics (CFD) coding, which is one of the most practical application technique for solid fuels thermo-chemical conversion [18]. The third method to treat the TPR model is the deconvolution. Through the deconvolution process, the reaction rate profiles (i.e. the DTG profile in TGA experiments) of LB pyrolysis can be separated into pseudo components profiles. The deconvolve profiles of pseudo components can be future inverting to the model-free procedures in order to study by their kinetics [19]. The used order-based TPR model and three-parallel DAEM had been investigated in numerous literatures [20–22]. However, studies of slow pyrolysis kinetic of LB by using deconvolution methods still remains few. Regarding to the deconvolution methods, the DTG profile of solid-state material can be separated using symmetric or asymmetric functions. The symmetric functions such Gaussian, Logistic, Lorentz functions have been investigated by Chen et al. [9] and Naya et al. [23], and the asymmetric Weibull, bi-Gaussian, Fraser–Suzuki functions have been used by Cai et al. [24] and Chen et al. [25]. Pérez-Maqueda et al. [20] considered that the asymmetric functions are more suitable for deconvolution procedures in TGA especially for the Fraser–Suzuki function.

To authors' knowledge, few studies have been reported for the LB slow pyrolysis using Fraser–Suzuki deconvolution. Our current research aims to study the slow pyrolysis of three representative lignocellulosic biomasses (pine wood, rice husk and bamboo) by combined using the DAEM, model-free and Fraser–Suzuki deconvolution procedures. It is anticipated that this study will provide a route for further kinetic analysis of lignocellulosic biomasses slow pyrolysis.

2. Materials and methods

2.1. Materials

The three used lignocellulosic biomass residues are powder of pine wood (sawdust), rice husk and bamboo (*Bambusa chungii*). Pine wood and bamboo were from a furniture factory and rice husk

was from a rice milling factory in Lingnan village, Jiangkou town, Guiping city, Guangxi province, China. The powders all have a particle size of <0.104 mm according to Tyler Standard Screen Scale (i.e. pass through 150 mesh sieve). The proximate analysis, ultimate analysis and chemical composition data of pine wood (PW), rice husk (RH) and bamboo (BB) are given in Table 1.

2.2. Thermo-gravimetric analysis of the fuels

Before the TGA experiments, the three kinds biomass are dried at 105 °C for 48 h to get the dried-basis samples, and then were stored in Low-Density Polyethylene bags for the subsequent experiments. The thermo-gravimetric analyses (TGA) of PW, RH and BB samples were performed under atmospheric pressure by using a TGA/DTA analyzer (SDT Q600, TA instruments, USA). Slow heating rates were guaranteed <50 °C/min [26]. 5–10 mg of samples were placed in alumina crucibles and heated from room temperature to 700 °C at rates of 5 °C, 10 °C and 20 °C/min, respectively. The argon (flow rate of 100 ml/min) was used as sweeping gas to maintain an anaerobic atmosphere for pyrolysis. Each TGA run at a heating rate was repeated at least three times until the mean standard deviation of weight loss is lower than 1%. In order to prevent the secondary reaction between the volatiles and char at higher temperature as weak as possible, the weight loss data of samples' in temperature ranges between 105 and 675 °C [27] is only used for kinetic study.

2.3. Pyrolytic kinetic modeling

2.3.1. Model-free procedure for single reaction kinetic

In linear non-isothermal TGA, solid-state material is heating at a constant heating rate ($\beta = dT/dt$, $K s^{-1}$). The conversion form of reaction rate according to Arrhenius law can be expressed as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

where E denotes the apparent activation energy, $J mol^{-1}$; A denotes pre-exponential factor, s^{-1} ; T is absolute temperature, K ; R is ideal gas constant, $8.3145 J mol^{-1} K^{-1}$; $f(\alpha)$ denotes the mechanism model which depends on the conversion, α . The conversion α (dimensionless), also is known as the normalized mass ($\alpha \in [0, 1]$) of the released volatiles, can be expressed as:

$$\alpha = 1 - x = (m_0 - m_T)/(m_0 - m_f) \quad (2)$$

where m_0 , m_T , and m_f denotes the normalized mass of the sample at the initial temperature (T_0), given temperature T and final temperature (T_f), respectively; x denotes the normalized mass remaining. The integral rearrangement of Eq. (1) gives:

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT = \frac{A}{\beta} \Psi(E, T) \quad (3)$$

where $g(\alpha)$ is an integral form of the $f(\alpha)$; $\Psi(E, T)$ is the so-called temperature integral which has no analytical solution but can be replaced with approximative formulas. The most common forms of $f(\alpha)$ and corresponding $g(\alpha)$ are listed in Table 2.

For single reaction, the iso-conversional methods (also called model-free) are believed to be accurate for apparent activation energy (E) estimation. The iso-conversional methods treat the E as a function of α . The E values at given α , E_α , can be estimated by using multiple heating rates without known $f(\alpha)$ or $g(\alpha)$. One of the most widely used iso-conversional methods is the Friedman method (Eq. (4)) which is rearranged from Eq. (1):

$$\ln \left[\beta_k \left(\frac{d\alpha}{dT} \right)_\alpha \right] = \ln [A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,k}} \quad (4)$$

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