Full Length Article

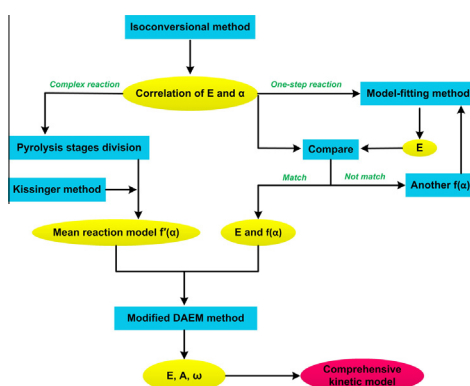# Kinetic modeling of biomass components pyrolysis using a sequential and coupling method

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HIGHLIGHTS

- Model-fitting method, isoconversional method and DAEM method were combined.
- Cellulose pyrolysis followed one-step Avrami-Erofeev nucleation model.
- Pyrolysis of hemicellulose and lignin contained three and two stages, respectively.
- Calculation method of DAEM with Am reaction model was developed for the first time.

GRAPHICAL ABSTRACT

ABSTRACT

This study proposed a sequential and coupling method to determine the comprehensive kinetic models for pyrolysis of cellulose, hemicellulose and lignin. Isoconversional method was employed to find the correlation between activation energy and conversion rate. Cellulose pyrolysis could be interpreted by one-step global reaction model, while pyrolysis of hemicellulose and lignin could be divided into three stages and two stages, respectively, in which competitive parallel reactions occurred. Coats-Redfern method and Kissinger method were subsequently used to obtain the reaction model f(α). Particularly, a new mean reaction model f'(α) was introduced to deal with the complex competitive parallel reactions. It was proposed that pyrolysis of cellulose followed Avrami-Erofeev (m = 2) nucleation model, while pyrolysis of hemicellulose and lignin could be described by reaction-order model. The other kinetic parameters and the contribution of each parallel reaction to devolatilization were further analyzed based on the modified distributed activation energy models. And the detailed kinetic models for pyrolysis of biomass components were finally obtained.

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1. Introduction

Biomass is the only renewable carbonaceous resource and is widely available in nature. Pyrolysis is recognized as a promising thermal-chemical technology because it can efficiently convert biomass into advanced fuels, which is significant for the substitution of the depleting fossil fuels [1]. Apparent kinetics for biomass pyrolysis could predict the products distribution and mass loss behavior of biomass sample in pyrolysis process, and provides valuable information for the reactor design and process optimization in biomass pyrolysis industry [2]. The main purpose for kinetic modeling is to build the correlation among reaction rate (k),

conversion rate (α) and reaction temperature (T). The Arrhenius type kinetic triplet, E (activation energy), A (pre-factor) and f(α) (kinetic equation or reaction model), is calculated to interpret the biomass pyrolysis behavior. It is believed that only with the appropriate kinetic modeling method can the kinetic model be comprehensive and the prediction be reliable [3]. Obviously, how to get a precise kinetic triplet is the key in kinetic modeling.

Model-fitting method and isoconversional method (also known as model-independent method) are the two major ways used in kinetic studies [4]. So far, model-fitting is the absolutely dominant method in the kinetic modeling for biomass pyrolysis. The kinetic parameters are calculated by forcible simulation of the thermogravimetry (TG) data with the presupposed reaction model f(α). Therefore, the reliability of kinetic parameters highly depends on the selection of f(α). However, in most studies, for the simplification of calculation procedure, the first-order reaction model was selected without enough verification. Another problem by using model-fitting method is the kinetic compensation effect (KCE) [5], i.e., numerous E and A can satisfy a single Arrhenius form reaction rate, while the actual ones cannot be determined. Isoconversional method could directly get the reliable value of E without the assumption of reaction model. However, how to determine f(α) is another important problem in pyrolytic kinetics, which is very crucial for understanding the decomposition form of biomass sample. For the nth-order reaction model, Kissinger [6] proposed a procedure to calculate the value of n. Recently, ICTAC (International Confederation for Thermal Analysis and Calorimetry) recommended using isoconversional method to first obtain the precise E, and the f(α) and A corresponding to this E value could be determined by checking KCE [3]. Moriana et al. [7] investigated the kinetics for pyrolysis of a hemicellulose sample. They applied Coats–Redfern method [8] to calculate E values under the assumptions of different reaction models, and then compared them with the one obtained from isoconversional method. The f(α) with the most matching E value with isoconversional result was selected as the proposed reaction model. Model-fitting method considers the selected pyrolysis stage as a one-step global reaction model and uses a single kinetic triplet to describe the devolatilization behavior. However, the actual pyrolysis process is very complex and involves both successive reactions and parallel reactions. The E value calculated from isoconversional method could change at different conversion rates. In the most cases of complex reaction, isoconversional method would obtain a correlation between E and α. And the variation tendency gives the information about reaction mechanism. Vyazovkin and Lesnikovich [9] pointed out that if E increased as reaction progressed, there is a competitive parallel reaction existed in the reaction. For these complex reaction systems, such as biomass pyrolysis, most of previous studies used simultaneous first-order reaction equations to solve the kinetic parameters (usually called semi-global reaction model). However, for each step in the reaction network, the reaction model was usually not discussed.

Distributed activation energy model (DAEM) is a new method used in the kinetic modeling of biomass pyrolysis, and essentially belongs to the model-fitting method. Since DAEM does not need to select the linear interval and directly simulates the data of entire process, it usually obtains a satisfied fitting precision. DAEM assumes the whole reaction is composed of infinite number of parallel reactions, and their activation energies could be integrally described by a continuous probability function, e.g. Gaussian function. For a simple reaction process, a single Gaussian function is enough to precisely fit the distribution of activation energy. While for a complex reaction system like biomass pyrolysis or even pyrolysis of biomass components (especially hemicellulose and lignin), which contains totally different types of parallel reaction, such as

degradation reaction and condensation reaction, a total function f (E) with two Gaussian functions [10–12] or multi-Gaussian functions [13,14] is necessary to get a good fitting performance. And this type function also overcomes the intrinsic symmetry of single Gaussian function.

It is well-known that studying the pyrolysis behaviors of the three major components, cellulose, hemicellulose and lignin, individually, is a feasible way to simplify the complicated pyrolysis reaction network of biomass. The kinetics of the three major components pyrolysis have been intensively studied by using the model-fitting, isoconversional and DAEM methods. For example, López-González et al. [15] analyzed the pyrolysis kinetic of cellulose, hemicellulose and lignin using Coats-Redfern method. Chen et al. [16] obtained the activation energies for the three components pyrolysis using an isoconversional method. Cai et al. [13] investigated the thermal kinetic of the three components by DAEM method. However, kinetic analysis based on the combination of these methods is seldom performed. In order to get a comprehensive kinetic model with mechanism scheme, a sequential and coupling method was proposed to unravel the complex reaction of pyrolysis process. Isoconversional method was introduced to calculate the E values under a series of conversion rates. Based on the variation tendency between E and α, the whole pyrolysis process was divided into different stages according to the reaction models. The KCE in the model-fitting methods with different reaction models was used to determine f(α), which was further substituted into the modified DAEM equation to conduct the non-linear simulation to obtain the kinetic triplet for the entire reaction stage. Comprehensive kinetic models for pyrolysis of the three biomass components were finally proposed.

2. Experimental

2.1. Materials

Microcrystalline cellulose (FMC BioPolymer, Belgium), beechwood xylan (Sigma-Aldrich, USA) and organosolv lignin (Sigma-Aldrich, USA) were selected as the model compounds for cellulose, hemicellulose and lignin, respectively, for the following pyrolysis process and kinetic modeling.

2.2. Experimental procedure

Pyrolysis of biomass components were performed on a TA-Q500 thermogravimetric analyzer (TA Instruments, USA) with non-isothermal method. Four linear heating rates, 5 °C/min, 10 °C/min, 20 °C/min and 40 °C/min, from 25 °C to 800 °C were chosen to get the data of solid mass loss. Pure nitrogen was used as carrier gas (40 mL/min) and provided the inert reaction environment. The weight of the sample was 2 mg in each TG experiment.

The solid conversion rate was defined as Eq. (1), where m_0 and m_∞ were the solid mass before and after pyrolysis, respectively, and m_T was the solid mass at the reaction temperature of T.

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

3. Results and discussion

3.1. Thermogravimetric analysis

For pyrolysis of biomass components under different heating rates, their char yield (Y_{char}), maximum weight loss rate ($(dm/dT)_{max}$), the temperature corresponding to the maximum weight loss (T_m) and the initial decomposition temperature for