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Short Communication

Sensitivity analysis of three-parallel-DAEM-reaction model for describing rice straw pyrolysis

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HIGHLIGHTS

- ▶ The three-parallel-DAEM-reaction model was successfully applied to describe rice straw pyrolysis.
- ▶ The kinetic parameters of the model were estimated by using the pattern search methods.
- ▶ The local sensitivity of the model to various parameters was analyzed in the first time.
- ▶ The parameters related to cellulose decomposition are more sensitive than other parameters.

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ABSTRACT

The three-parallel-DAEM-reaction model was used to study the slow pyrolysis kinetics of rice straw based on thermogravimetric analysis (TGA) data. The kinetic parameters of the model were calculated using the pattern search method. A comparison between the predicted DTG data and experimental values showed good agreement. The influences of the kinetic parameters on the model for describing the experimental data of rice straw were analyzed by means of local parametric sensitivity analysis. The results indicated that the frequency factor and the mean value of the activation distribution for cellulose decomposition affect the model more strongly than other parameters, followed by the corresponding parameters for hemicellulose and lignin. The sensitivity of the model to the standard deviations of the activation energy distributions for all pseudocomponents is very slight.

1. Introduction

Biomass has great potential as a clean, renewable energy source that could dramatically improve our environment, economy and energy security. Therefore, the research on biomass energy conversion has attracted more and more attention in the world. Biomass can be converted to more valuable energy forms via a number of processes including thermal, biological, and mechanical processes (Bridgwater, 2012). Pyrolysis is a well-established thermal processing method for converting biomass into a liquid fuel that can substitute for fuel oil and make valuable chemicals (Bridgwater, 2012).

Biomass pyrolysis kinetics is required for the design and optimization of pyrolytic reactors (White et al., 2011). Furthermore, biomass pyrolysis kinetics can produce submodels that can be coupled with transport phenomena to describe the practical conversion process (Calonaci et al., 2010).

Lignocellulosic biomass has a complex internal structure and contains three main components: hemicellulose, cellulose and lignin. Many models have been used to describe the pyrolysis kinetics of lignocellulosic materials (Bates and Ghoniem, 2012). The three-parallel-DAEM-reaction model is by far the most comprehensive model for analyzing the pyrolysis kinetics of lignocellulosic biomass (Varhegyi et al., 2011). The model assumes that lignocellulosic biomass contains three independently reacting pseudocomponents (hemicellulose, cellulose and lignin), and their pyrolysis kinetic behaviors can be described by the distributed activation energy model (DAEM). However, the sensitivity analysis of the model for describing biomass pyrolysis kinetics is still missing. This is the scope of this work.

2. Experimental section

As a large agricultural country, China has huge potential of lignocellulosic biomass resource availability in the form of crop residues.

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Rice is the second largest agricultural crop in China, and about 200 million tons of rice straw are produced annually (Wang et al., 2010). About 50% of rice straw can be used for bioenergy production according to the literature (Jiang et al., 2012). Therefore, rice straw, one representative type of lignocellulosic biomass, was used as the experimental material in this work. The rice straw samples were obtained from a farm located in Zibo, Shandong Province, China. The samples were used after screening to 100 mesh and dried for 12 h at 378 K to remove moisture. Elemental composition and lower heating value of rice straw are presented in Table 1.

Slow pyrolysis of rice straw was performed using the thermogravimetric equipment Netzsch STA 449 C, which allows the measurement of mass changes and thermal effects. To achieve pyrolysis conditions, a nitrogen atmosphere was used. The flow rate of nitrogen was set to 25 mL min^{-1} for the purge gas and 14 mL min^{-1} for the protective gas. Around 5 mg samples were spread on a Pt–Rh crucible. Thermogravimetric measurements were performed from room temperature to 900 K at the heating rate of 10 and 20 K min^{-1}.

3. Three-parallel-DAEM-reaction model applied to biomass pyrolysis kinetics

In the three-parallel-DAEM-reaction model, it is assumed that lignocellulosic biomass contains three independently reacting pseudocomponents (hemicellulose, cellulose and lignin), and therefore, that the global thermal decomposition behavior reflects the individual behavior of these pseudocomponents, weighted by the composition. It is further assumed that the pyrolysis kinetics of each pseudocomponent can be described by the DAEM (Varhegyi et al., 2011).

The equation of the model is given below:

$$\begin{aligned}\frac{d\alpha(T)}{dT} &= c_1\int_0^\infty \frac{k_{0,1}}{\sqrt{2\pi}\sigma_1\beta}\exp\left[-\frac{E}{RT}-\frac{k_{0,1}}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)dT-\frac{(E-E_{0,1})^2}{2\sigma_1^2}\right]dE\\ &+c_2\int_0^\infty \frac{k_{0,2}}{\sqrt{2\pi}\sigma_2\beta}\exp\left[-\frac{E}{RT}-\frac{k_{0,2}}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)dT-\frac{(E-E_{0,2})^2}{2\sigma_2^2}\right]dE\\ &+c_3\int_0^\infty \frac{k_{0,3}}{\sqrt{2\pi}\sigma_3\beta}\exp\left[-\frac{E}{RT}-\frac{k_{0,3}}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)dT-\frac{(E-E_{0,3})^2}{2\sigma_3^2}\right]dE\end{aligned} \quad (1)$$

In the above equation, α is the conversion degree, T is the temperature, β is the heating rate, E is the activation energy, R is the universal gas constant, k_0 is the frequency factor, E_0 is the mean value of the activation energy distribution, σ is the standard deviation of the activation energy distribution, c is the fraction of volatiles produced by a certain pseudocomponent, and the subscripts 1, 2 and 3 indicates the values related to hemicellulose, cellulose, and lignin, respectively.

The unknown parameters of the model were determined by evaluating the experimental derivative thermogravimetric (DTG) data using least squares nonlinear methods. Therefore, the objective function based on the DTG data was defined by the following equation:

$$O.F. = \sum_{j=1}^{2}\sum_{i=1}^{n_d}\left[\left(\frac{d\alpha}{dT}\right)_{\exp,ij}-\left(\frac{d\alpha}{dT}\right)_{\mathrm{cal},ij}\right]^2 \quad (2)$$

where the subscript i refers to the data points used, nd is the number of data points, $(d\alpha/dT)\exp, ij$ represents the experimental values at the heating rate j ($j = 1$ represents 10 K min^{-1}, and $j = 2$ represents 20 K min^{-1}), and $(d\alpha/dT)$cal, ij represents those calculated by Eq. (1) for a given set of parameters.

Table 1
Analytical characteristics of rice straw (dry ash free basis).

C (% by wt)	H (% by wt)	N (% by wt)	O[a] (% by wt)	LHV (MJ kg^{-1})
45.52	6.29	0.99	47.20	15.35

[a] Calculated by difference.

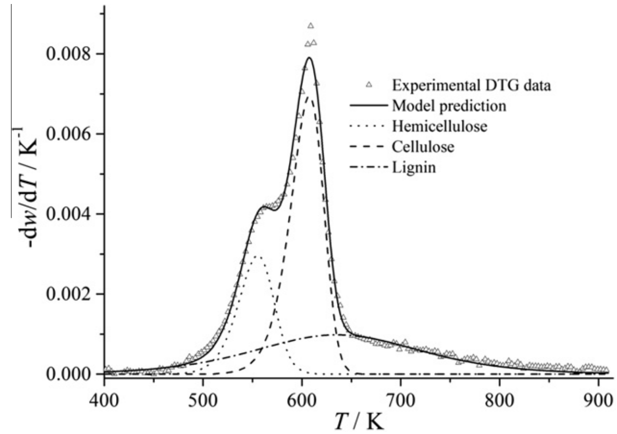

Fig. 1. Experimental and predicted DTG curves of rice straw pyrolysis at the heating rate of 10 K min^{-1}.

There are many methods which have been used for solving the above optimization problem, such as the differential evolution algorithm (Santos et al., 2012), the direct search method (Gunes and Gunes, 2002), the simulated annealing method (Mani et al., 2009), the flexible simplex method (Conesa et al., 1995), the Multistart algorithm (Kirtania and Bhattacharya, 2012), and the pattern search method (Cai and Liu, 2008; Cai et al., 2011). The pattern search method is a derivative-free, direct search method and superior to other direct search methods in both robustness and number of function evaluations (Lewis et al., 2000). Therefore, the pattern search method was used to estimate the model parameters. For this purpose, a program was developed in MATLAB for the implementation of the parameter estimation.

The model parameters estimated from the above method were used to generate a DTG curve which was compared with the experimental one by the fit quality parameter. The fit between the experimental and estimated data can be found out by the fit quality parameter stated below:

$$\mathrm{FP}(\%) = 100\frac{\sqrt{O.F./n_d}}{\sum_{j=1}^{2}(d\alpha/dT)_{m,j}} \quad (3)$$

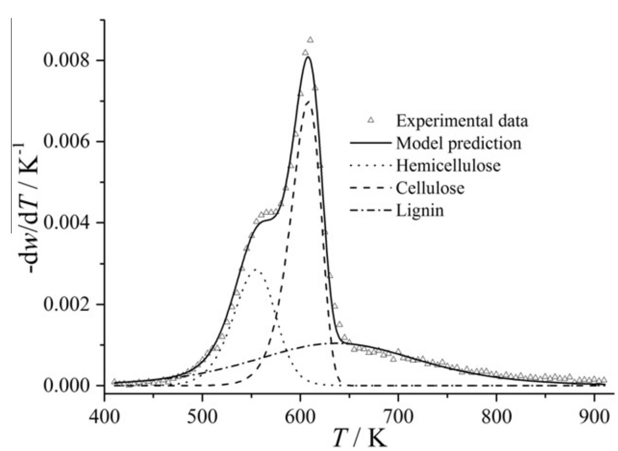

Fig. 2. Experimental and predicted DTG curves of rice straw pyrolysis at the heating rate of 20 K min^{-1}.