Fuel 232 (2018) 147–153

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The effect of chemical reaction kinetic parameters on the bench-scale pyrolysis of lignocellulosic biomass

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ARTICLE INFO

Keywords:
Lignocellulosic biomass
Beech
Kinetic parameters
Pyrolysis
FireFOAM

ABSTRACT

The pyrolysis of lignocellulosic biomass has received extensive attention due to its potential as an alternative and renewable energy source. The chemical reaction kinetic parameters, obtained by micro-scale thermogravimetric experiments and optimized by the Shuffled Complex Evolution method, are one of the key factors to represent the pyrolysis process. The bench-scale Fire Propagation Apparatus experiment with sample size of 0.1 m × 0.1 m is conducted to investigate the scale effect of these parameters during the pyrolysis process in a N_2 environment. These optimized parameters are applied to the pyrolysis model based on Gypro considering the three-component parallel reaction mechanism, moisture and volume change to simulate the bench-scale experiment based on FireFOAM coupled with the dynamic mesh technology. Eventually, the predicted results agree well with experimental data, validating the effectiveness of the current parameters. Moreover, the effects of chemical reaction kinetic parameters from different references or models are further analyzed based upon the predicted results.

1. Introduction

Sustainable heat and power generation from lignocellulosic biomass are at the center of scientific and industrial interest due to the increasing awareness of the limited availability of fossil fuels and the environmental impact of pollutants generated by conventional energetic systems [1]. Pyrolysis, as the first step in the thermal chemical conversion of lignocellulosic biomass materials [2], is a thermal degradation of organic matrix to obtain an array of solid, liquid and gas products in an inert environment and has been extensively studied in recent decades [3,4]. Knowledge of pyrolysis kinetics can help provide better understanding and planning of important industrial processes because pyrolysis is not only an independent energy conversion method but also part of gasification and combustion processes [5–7].

Wood, as the main representative of lignocellulosic biomass, is a composite material, constituted by a mixture of hemicellulose, cellulose, lignin and extractives, with proportions and chemical structures affected by the specific species type and also growth conditions [1]. An accurate description of wood pyrolysis accordingly includes numerous reactions. Such a broad range of reactions increases both the complexity of these models and the computational cost, since reactions will occur over different characteristic times, affecting the overall stiffness of the system of equations [8]. However, the computational cost and accuracy need to be balanced, and researchers inevitably have to apply simplified models to overcome this challenge [9]. Therefore, the primary pyrolysis reactions of wood can be modeled by taking into account the thermal behavior of the main components (hemicellulose, cellulose and lignin) and their relative contribution in the chemical composition [1]. Then a three-component parallel reaction mechanism with linear or nonlinear dependence on species concentrations [10], for the fractions of the hemicellulose, cellulose and lignin [11], is widely applied to describe dynamic thermogravimetric curves of wood pyrolysis [12]. One main advantage of the three-component parallel reaction mechanism is that such a model can be applied to a variety of biomass types, since they typically differ by mass fractions of hemicellulose, cellulose and lignin [13]. These three components are all handled individually so that it is relatively easy to adjust their fractions and take into account their influence in the model [14]. However, a practical point of concern and criticism of using the three-component parallel reaction mechanism is that it requires more input parameters (e.g. activation energy, pre-exponential factors, reaction order, etc.), which might be obtained directly by experiments or indirectly from

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https://doi.org/10.1016/j.fuel.2018.05.140
Received 9 April 2018; Received in revised form 25 May 2018; Accepted 27 May 2018

other assumptions and models [8]. Ding et al. emphasized that 15 parameters would be needed to fully describe the pyrolysis kinetics based on micro-scale thermogravimetric (TG) experiments [12]. These parameters can be estimated by common optimization approaches, such as Genetic Algorithms (GA) [15] or Shuffled Complex Evolution (SCE) method [16], fitting well with TG experimental data.

However, the applicability of these optimized parameters, namely the scale effect, should be further verified on the larger scale experiments coupled with these more complex pyrolysis models. Towards this assessment, the Fire Propagation Apparatus (FPA) was applied in our experiment with a sample size of 0.1 m × 0.1 m × 0.01 m in a nitrogen atmosphere. This study provides a thorough examination of whether the optimized kinetic parameters can be used from the micro-scale TG experiment to a bench-scale FPA experiment for prediction and/or extrapolation of lignocellulosic biomass pyrolysis. The present study was motivated by the background discussed above and took advantage of a modified version of FireFOAM [17] within the OpenFOAM toolbox which is a free, open source CFD software released and developed primarily by OpenCFD Ltd to simulate the pyrolysis process [18]. Note that most of the thermophysical input parameters applied in the simulation were obtained from direct property measurements [19] to provide as much information as we can to understand the physics and chemistry of lignocellulosic biomass pyrolysis. Furthermore, different sets of reaction kinetic parameters involved in the simulation were analyzed for their effects on the predicted results compared with experimental data.

2. Materials and methods

2.1. Sample preparation

Beech wood (*Fagus sylvatica*), native to temperate Europe and appropriate for furniture, tools and small household articles [13], is regarded as a typical lignocellulosic biomass and used in this study. The detailed elemental, proximate and biochemical analysis of beech wood can be found in our previous study [11]. Two different sample preparation methods were applied to the TG and FPA experiments, respectively. For the micro-scale TG experiment, the samples were milled to less than 0.2 mm prior to testing, to reduce the temperature gradients within the particles [11]. For the bench-scale FPA experiment, the wood was cut into 0.1 m × 0.1 m square pieces with 0.01 m thickness.

2.2. Thermogravimetric measurements

Studies on solid reactivity, useful for kinetic analysis, are mainly based on TG measurements [20]. A TA Instrument SDT Q600 thermal analyzer was used for the pyrolysis testing with the temperature range from 300 K to 1000 K. It should be noted that the sample had been dried at 80 °C for about 24 h to remove the free water prior to the pyrolysis testing. The detailed TG measurements had been introduced in [12]. TG curves were obtained at five heating rates (5, 10, 20, 60 and 80 K/min), as shown in Fig. 1.

The three-component parallel reaction scheme for the main components is established as:

$$hemicellulose \rightarrow \nu_h char + (1-\nu_h) volatiles \quad (1)$$

$$cellulose \rightarrow \nu_c char + (1-\nu_c) volatiles \quad (2)$$

$$lignin \rightarrow \nu_l char + (1-\nu_l) volatiles \quad (3)$$

where ν is the char yield for each reaction. The subscripts h, c, l denote hemicellulose, cellulose and lignin, respectively. The decomposition of each component is represented by [12]:

$$\frac{dY_i}{dt} = -Y_{i,0}\left(\frac{Y_i}{Y_{i,0}}\right)^{n_i} A_i \exp\left(-\frac{E_{a,i}}{RT}\right) \quad i = 1, 2, 3 \quad (4)$$

$$\frac{dY_{char}}{dt} = -\sum_{i=1}^{3} \nu_i \frac{dY_i}{dt} \quad (5)$$

where, for each component i, Y_i is the mass fraction, $Y_{i,0}$ is the initial mass fraction in the sample, A_i, E_i, and n_i are the Arrhenius kinetic triplet (activation energy, pre-exponential factor and reaction order, respectively), and Y_{char} is the char mass fraction. R is the universal gas constant.

Thus 15 parameters would be needed to fully describe the pyrolysis kinetics by providing appropriate values of $Y_{i,0}$, A_i, E_i, n_i, and ν_i. The number of unknown parameters in this case is large, and optimization algorithms have to be applied to estimate these values based on the limited TG data. The degree of difficulty in solving a global optimization problem is dependent on certain aspects, related to the dimensionality of the problem and the characteristics of the objective function to be optimized [21]. GA and SCE are the common optimization algorithms used for pyrolysis kinetics analysis. Compared to GA, SCE is preferred since it can reach the same level of agreement with the data as GA with considerably fewer function evaluations [16] and reproduce material pyrolysis properties within approximately 1% of the actual data value [22]. Moreover, SCE is based on the synthesis of four concepts that have proved successful for global optimization: a combination of probabilistic and deterministic approaches, a clustering algorithm, systematic evolution of a complex of points spanning the space in the direction of global improvement, and a competitive evolution algorithm [12,21]. Therefore, SCE was chosen as the reaction kinetic parameters optimization algorithm in this work. The detailed optimization process by SCE is described in [12]. From the TG curves at the five heating rates that were previously mentioned, the optimized values are listed in Table 1 and the predicted results compared with experimental data are shown in Fig. 1.

2.3. Fire propagation apparatus

A fire propagation apparatus [16] based on ASTM E-2058 was used to measure the mass loss rate of the prepared 0.1 m × 0.1 m × 0.01 m sample during pyrolysis, as shown in Fig. 2. The sample was placed horizontally in an aluminum dish, wherein the bottom and sides of each sample were wrapped with aluminum foil and ceramic fiber blanket to insulate the unexposed sides, so that only the top surface was exposed. These special procedures of sample preparation were taken to prevent heat loss to the sample holder so that the experimental results were apparatus-independent [23]. The sample was subject to an external radiant heat flux of 50 kW/m^2. Before the experiment, a water-cooled shield was used to protect the sample from exposure. Moreover, a quartz tube was used to shield the sample from room air entrainment. Nitrogen was supplied upward below the sample support at a flow rate of 100 L/min in the quartz tube to create a well-ventilated condition. The aim of FPA experiment was to provide bench-scale pyrolysis experimental data to compare with simulation results.

2.4. Density and moisture content measurement

The density measurement is based on the basic mass-volume method. The samples prepared for FPA experiment with the same sample volume (100 cm^3) were weighed by an electronic balance with precision of 0.01 g. After the FPA experiment, the residues were weighed to measure the density of char. Considering the final residue volume shrunk to about 70% of the original volume, the average char density could be computed based on the changed volume. Four different samples were measured and the results are listed in Table 2.

To measure the moisture content, four samples were dried in a drying oven and weighed every two hours until the mass change was less than 0.1 g. The final mass is listed in Table 2. Note that the optimized reactant compositions are based on dried sample of TG experiment, and then the proportions of reactants could be updated when