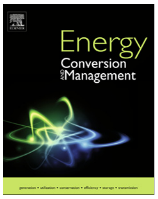
Energy Conversion and Management 146 (2017) 124–133

Contents lists available at ScienceDirect

Energy Conversion and Management

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



Thermal decomposition of rape straw: Pyrolysis modeling and kinetic study via particle swarm optimization

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ARTICLE INFO

Article history:
Received 26 February 2017
Received in revised form 29 April 2017
Accepted 9 May 2017

Keywords:
Biomass
TGA
Non-isothermal
Kinetic parameters
Activation energy

ABSTRACT

The aim of this work is to implement an efficient and robust optimization approach for parameter estimation of pyrolysis kinetic model to study the pyrolysis of a typical agricultural residue. Thermogravimetric profiles of rape straw were obtained at a wide heating range of 10, 20, 30 and 40 °C/min in an inert atmosphere of nitrogen and the thermal decomposition process was studied in detail. First, three different kinetic methods (Friedman, KAS and OFW) were applied for activation energy determination. The activation energies ranged from 191.16 kJ/mol to 264.31 kJ/mol. Then, the reaction mechanism and pre-exponential factor were analyzed by using the generalized master-plots method. It is found that at conversion level higher than 0.4 the rape straw decomposition was governed by 3-D diffusion model and it tended to high order reaction model at lower conversion. Finally, a multi-component parallel reactions scheme incorporated into the Particle Swarm Optimization (PSO) technique was presented to determine kinetic parameters. The kinetic triplets and other stoichiometric parameters were optimized against profiles for heating rates of 20 and 30 °C/min. The optimized activation energy value is 156.41 kJ/mol, 211.26 kJ/mol and 57.84 kJ/mol for hemicellulose, cellulose and lignin, respectively. These results are in conformity with results reported in previous literatures. Meanwhile, the obtained pre-exponential factors values also lie in the reasonable range of $\ln A_i = 25.32\text{–}39.14$ ln/s according to intrinsic transition-state theory. Furthermore, cross-validated results show that the optimized parameters can be applied not only to conditions where they were obtained, but also to conditions beyond (10 and 40 °C/min), indicating that the derived results are appropriate to simulate and predict rape straw pyrolysis under various heating rates, which will be useful for further design and sizing of biomass thermochemical process reactors.

1. Introduction

Agricultural residues, as major biomass raw feedstock, is generated as byproduct from agricultural plants harvest every year all over the world. The huge amount of biomass residues not only cause land occupation problems but also lead to air pollution during incineration. On the other way around, due to the serious energy crisis and environment deterioration worldwide, agricultural residual biomass is considered as an ideal alternative and renewable source of energy in the future [1]. Among the sundry techniques for biomass utilization, one of the promising and widely applicable way is pyrolysis [2]. As a key part of biomass thermochemical conversion technology and the first step in a gasification or combustion process, pyrolysis research and its application have attracted wide attention [3–6]. By means of pyrolysis, residual biomass can be converted into useful energy holders (bio-oil), adsorbent bio-char, and various useful chemicals [7].

For the purpose of biomass pyrolytic conversion, kinetic analysis and determination of significant pyrolysis model parameters are very important, as they could help to describe practical conversion processes, as well as optimizing the design of proper and efficient reactors [8,9]. In previous literatures, various reaction schemes have been developed to describe pyrolysis process, such as the single global reaction scheme [10], distributed activation energy model (DAEM) [11], independent parallel reactions scheme [12] and consecutive reaction model [13]. However, the modeling process appear to be difficult or even impractical when using these complex reaction schemes, because the model involves a great many unknown kinetic parameters that cannot be simply obtained by traditional integral and differential model-free methods. Therefore, optimization techniques have been employed to parameterize kinetic schemes in previous literatures, while studies of biomass pyrolysis kinetics by using optimization methodologies still

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http://dx.doi.org/10.1016/j.enconman.2017.05.020
0196-8904/

remains few. Saha et al. used the Genetic Algorithms (GA) to optimize the kinetic parameters for plastic thermal decomposition [14]. Grønli et al. considered the kinetic study of wood thermal decomposition via the least-squares method [15]. Ding et al. investigated the pyrolysis kinetic parameters of beech by employing Shuffled Complex Evolution (SCE) [16]. However, there have been rarely few studies reported for the adoption of Particle Swarm Optimization (PSO) methodology in biomass pyrolysis analysis, even though the PSO algorithm has been proved to be an efficient global optimum in various research fields [17,18]. Particle swarm optimization is a population based global search technique invoking natural behavior of particles, inspired by social behavior of bird flocking or fish schooling. PSO algorithm uses the velocity and position search model, the position of each particle represents a candidate solution of space, a certain number of particles make up the population for searching the solution space, the velocity of the particle is used to update the particle position, and the fitness function is used to evaluate the position of the particles. At the beginning of the search, the velocity and position of each particle in the population are initialized, and then they are improved and adjusted by iterations.

Rape straw is an important biomass energy source, and approximately 1.96×10^7 tons of rape straw is generated as byproduct in the harvest season in China annually [19]. Therefore, new studies are needed to understand its thermal decomposition characteristics. Since rape straw is an intricate lignocellulosic material, relatively complex reaction schemes should be adopted to describe its pyrolysis.

Therefore, the aim of this work is to present an efficient optimization methodology (PSO technique) for parameter estimation of pyrolysis kinetic model, thus better describing the thermal decomposition process of a representative agricultural residual biomass (rape straw). First, the activation energies were determined via three different iso-conversional kinetic models of Friedman, Kissinger-Akahira-Sunose and Ozawa-Flynn-Wall. Then, the reaction mechanism and pre-exponential factor were analyzed by using the generalized master-plots method. Finally, a multi-component parallel reactions scheme was incorporated into a global optimizer, Particle Swarm Optimization (PSO), to estimate the unknown model parameters. It is anticipated that our current work will provide a route for further kinetic analysis of pyrolysis of agricultural residues.

2. Materials and methods

2.1. Materials

The experimental materials (rape straw) used in this study were obtained from a biomass production workshop in a town of Zhengzhou City, Henan Province, China (34°39′49″North × 112°58′51″East). The rape straws were firstly cleaned and dried under the sun for 40 days in order to gain the air-dried basis (ADB) samples. The materials were then crushed, milled and passed through 150 mesh sieve to achieve a desired particle size below 125 μm according to Tyler Standard Screen Scale. The sample biomass were dried in 101A-4 electric forced air dry oven (Shanghai, China) at 105 °C for 48 h until their mass stabilizes, and then were sealed tightly in Ziploc bags for the subsequent experiments.

2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analyses of rape straw were performed in terms of global mass loss by using a NETZSCH STA 449 F3 Jupiter (NETZSCH, Germany) thermogravimetric analyzer, with a sensitivity of 0.001 mg. The rape straw particles were evenly placed in alumina crucibles and the initial sample mass was about 5 mg ± 0.5 mg. The samples were heated from room temperature to 900 °C at four different heating rates of 10, 20, 30 and 40 °C/min, respectively. Nitrogen (purity of 99.99%, flow rate of 60 ml/min) was continuously passed into the furnace for pyrolysis experiments. The mass change of the sample and the heat flux with respect to time and temperature were recorded by NETZSCH Proteus software. Table 1 presented the average and standard deviation of normalized mass for each heating rate. All tests were repeated three times and the repeatability is good, the mean standard deviation of mass loss is lower than 1%.

2.3. Kinetic analysis

TG provides a controllable atmosphere and heating rate, with negligible thermal gradients and transport effects during degradation of small solid samples [15]. The application of TG analysis is appropriate to obtain chemical kinetic parameters. The TG and DTG data were normalized using Eqs. (1) and (2). Where W means the normalized mass, m is the mass for each time and m_i is the initial mass, and the normalized DTG is represented by dW/dt:

$$W = \frac{m}{m_i} \tag{1}$$

$$\frac{dW}{dt} = \frac{dm}{dt}\left(\frac{1}{m_i}\right) \tag{2}$$

The basic rate equation applied in all studies of heterogeneous solid-state thermal decomposition kinetics is expressed as:

$$\frac{d\alpha}{dt} = kf(\alpha) = A\exp\left(\frac{-E_\alpha}{RT}\right)f(\alpha) \tag{3}$$

where α is sample conversion given by:

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty} \tag{4}$$

where W_0, W_t and W_∞ represent the normalized initial sample mass, the sample weight at time t, and the final sample weight, respectively.

The temperature dependence rate constant $k(T)$ is generally expressed by Arrhenius equation as follows:

$$k(T) = A\exp\left(\frac{-E_\alpha}{RT}\right) \tag{5}$$

where A is the pre-exponential factor (s^{-1}), E_α is the activation energy (kJ/mol), T is the absolute temperature (K), R is the gas constant (8.314 J/mol K) and $f(\alpha)$ is the reaction model.

For dynamic analysis of non-isothermal data, introducing the heating rate β (in K/min) into the equation and thus the final equation is given as:

$$\beta = \frac{dT}{dt} \tag{6}$$

$$\frac{d\alpha}{dT} = kf(\alpha) = \frac{A}{\beta}\exp\left(\frac{-E_\alpha}{RT}\right)f(\alpha) \tag{7}$$

2.3.1. Activation energy determination

In present study, the iso-conversional methods of Kissinger-Akahira-Sunose (KAS) [20,21], Ozawa-Flynn-Wall (OFW) [22,23], and Friedman [24], expressed by Eqs. (8)(10), respectively, are used.

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