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Published in:
Proceedings of 11th International Conference on Applied Energy Part 1

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 0291

A PARALLEL REACTION KINETIC MODEL BASED ON WEIBULL DISTRIBUTION FOR BIOMASS PYROLYSIS

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ABSTRACT

Pyrolysis as the key stage of biomass thermochemical conversion processes draws increasing attention in past decades. Developing a kinetic model of biomass decomposition or bio-production is crucial for biomass pyrolysis process optimization and reactor design. In this paper, a novel kinetic model based on Weibull distribution is developed with the assumption of parallel reaction scheme during pyrolysis. The model is solved by an improved differential evolution algorithm and validated by the thermogravimetric analysis data of alpha cellulose, cardboard, and whitepaper. All the predicted results show good agreements with the corresponding experimental data. The present work provides a new model framework of biomass pyrolysis using Weibull distribution.

Keywords: biomass pyrolysis, kinetic model, Weibull distribution, parallel reaction

1. INTRODUCTION

Over the past few decades, biofuels and bio-based chemicals production from biomass through thermochemical conversion processes have attracted considerable attention [1]. Pyrolysis, as the key stage of biomass thermochemical conversion technologies, plays a dominant role in bio-production [2]. Understanding of biomass pyrolysis mechanism will benefit the process optimization and reactor design for bio-products. Some modeling works have been developed for this purpose.

Thermogravimetric analysis (TGA) and the Arrhenius theory have been mostly used in modeling biomass pyrolysis for the description of biomass decomposition and bio-production [3]. The widely used calculation method is the model-fitting method, which assumes the reaction order in advance and then fits (mostly in linear fit) the data from TGA in isothermal or no-isothermal condition to obtain the kinetic parameters [4]. However, the model-fitting method is not able to achieve a wide range of the conversion rate parameters. To make the parameters more reliable in a wide range of conversion, another method called isoconversional method, i.e., model-free method, has been developed, since it does not have to assume the reaction order in advance [5]. The activation energy at the conversion degree can be determined by a series of TGA data under different heating rates. Both the widely known methods for kinetic modeling are reviewed in literature [2,6].

Besides the Arrhenius theory, some statistical distributions (e.g. Weibull distribution, Gauss distribution) have been utilized in the description of biomass pyrolysis process in different approaches [7]. The distributed activation energy model (DAEM) applies Weibull or Gauss distribution for accounting a large number (normally around 25) of simultaneous parallel reactions to make the model closer to the reality. In general, the fitting goodness is positively related to the number of reactions. As a result, DAEM shows more accurate fits but sacrifices the computational cost, as seen in [8]. Weibull distribution has also been used to represent the mass loss rate of biomass pyrolysis directly. A Weibull mixture model was developed by mixing the major components decomposition rates, which are described via Weibull distribution [9]. The parameters of each Weibull function are obtained separately, and then mixed together by the weight fraction of the corresponding components. Both the DAEM and Weibull mixture model are successfully used in modeling biomass pyrolysis.

In this paper, a novel kinetic model using Weibull distribution is developed with the assumption of several parallel reactions during biomass pyrolysis. Different from the DAEM, the number of assumed reactions in the

Selection and peer-review under responsibility of the scientific committee of the 11th Int. Conf. on Applied Energy (ICAE2019).

new Weibull distribution-based model are largely reduced, so that the computation cost decreases a lot. Different from the Weibull mixture model, the Weibull parameters and the weights in the new Weibull distribution-based model are solved via an improved differential evolution (DE) algorithm. The prediction of the new model shows good agreements with TGA data of alpha cellulose, cardboard, and whitepaper. Therefore, it provides another view of modeling biomass pyrolysis process, and a universal model based on Weibull distributions for the description of biomass pyrolysis via a reaction progress factor will be further developed.

2. METHODS AND MATERIALS

2.1 Parallel reaction kinetic model description

The parallel reaction kinetic model assumes the pyrolysis progress of biomass is made up by several parallel reactions, each reaction corresponding to the decomposition of one compound, and all the reactions are independent of each other [10]. The mechanism is shown in Fig. 1, the overall conversion degree of the pyrolysis process α is the sum of each compound conversion degree α_i, as expressed as:

$$\frac{m}{m_0} = \alpha = \sum_i^n w_i \cdot \alpha_i \quad (1)$$

$$\frac{d\alpha}{dt} = -\sum_i^n w_i \cdot \frac{d\alpha_i}{dt} \quad (2)$$

Where m is the observed mass at time t, w_i is the mass fraction of the compound of $i\text{-}th$ reaction.

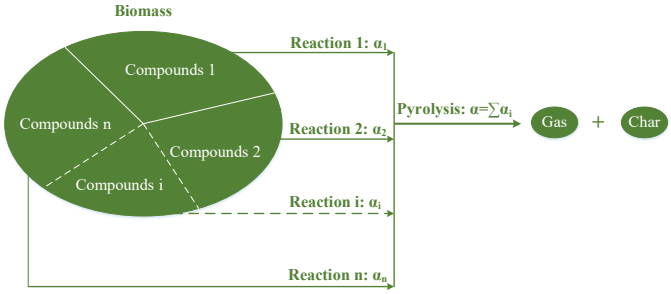

Fig 1 Reaction scheme of the parallel reactions model

To avoid the choice of the reaction orders, Weibull distribution is chosen to describe the conversion rate for each reaction instead of Arrhenius expression [11]. The conversion degree and the reaction time obey the Weibull distribution function, which can be expressed:

$$\alpha_i = 1 - exp\left[-\left(\frac{t-\gamma_i}{\eta_i}\right)^{\beta_i}\right] \quad (3)$$

$$\frac{d\alpha_i}{dt} = \frac{\beta_i}{\eta_i}\left(\frac{t-\gamma_i}{\eta_i}\right)^{\beta_i-1} exp\left[-\left(\frac{t-\gamma_i}{\eta_i}\right)^{\beta_i}\right] \quad (4)$$

Where β_i, η_i and γ_i are the shape, scalar and location parameters for the compound of $i\text{-}th$ reaction, respectively. Since the reaction time t accounts from the beginning of the pyrolysis process, the location parameter γ_i always equal to zero.

Moreover, the reaction time (t) and temperature (T) always in a linear relationship in the thermogravimetric analysis $\mathrm{T} = T_0 + \xi \cdot t$, the conversion degree function to time can be transient to the temperature function:

$$\alpha_i = 1 - exp\left[-\left(\frac{T-T_0}{\xi\eta_i}\right)^{\beta_i}\right] \quad (5)$$

$$\frac{d\alpha_i}{dt} = \frac{\beta_i}{\xi\eta_i}\left(\frac{T-T_0}{\xi\eta_i}\right)^{\beta_i-1} exp\left[-\left(\frac{T-T_0}{\xi\eta_i}\right)^{\beta_i}\right] \quad (6)$$

The overall conversion degree and rate can be summarized as:

$$\alpha = \sum_{i=1}^n w_i \cdot \left\{1 - exp\left[-\left(\frac{T-T_0}{\xi\eta_i}\right)^{\beta_i}\right]\right\} \quad (7)$$

$$\frac{d\alpha}{dt} = \sum_{i=1}^n w_i \cdot \left\{\frac{\beta_i}{\xi\eta_i}\left(\frac{T-T_0}{\xi\eta_i}\right)^{\beta_i-1} exp\left[-\left(\frac{T-T_0}{\xi\eta_i}\right)^{\beta_i}\right]\right\} \quad (8)$$

An improved differential evolution (DE) algorithm with constraint of weight parameters is implemented to estimate the kinetic parameters in equation (7), (8). The objective function to and the constraints are summarized in equation (9), (10).

Min:

$$\mathrm{O.F} = \sum_{j=1}^N \left\{\left[\alpha^{sim} - \alpha^{exp}\right]^2 + \lambda \times \left[\left(\frac{d\alpha}{dt}\right)^{sim} - \left(\frac{d\alpha}{dt}\right)^{exp}\right]^2\right\} \quad (9)$$

$$\text{s.t. } 0 < w_i < 1, i = 1,2,\dots,n$$
$$\sum_{i=1}^n w_i = 1 \quad (10)$$

Where j refers to the experimental data points used, N is the total number of the used data points; the superscript sim and exp denote the simulation results and experimental data, respectively. λ is the scale coefficient which is to balance the calculation error of the thermogravimetric(TG) prediction and the differential thermogravimetric (DTG) prediction in the same order of magnitude. The improved DE algorithm is coded in MATLAB 2018b, with the assumption of 3 parallel reactions of biomass pyrolysis.

2.2 Materials and characterization

The pyrolysis materials used are different type of lignocellulosic biomass: alpha cellulose, cardboard, and white paper. The proximate analysis (dry basis) was reported in Table 1. A simultaneous thermal analyzer (TA Instruments SDT Q600) was used tocharacterize the

pyrolysis behavior of each of three biomass samples (3-7 mg per sample). In each experiment, the sample was heated from the initial temperature 323 K to the final temperature 1273 K with the constant heating 10 K/min. More detailed experiments and materials information can be found in Ref. [3].

Table 1 Proximate analysis of the test biomass (dry based %)

Alpha Cellulose			Cardboard			White paper		
Volatile	Fixed carbon	Ash	Volatile	Fixed carbon	Ash	Volatile	Fixed carbon	Ash
93.2	6.8	0	78.7	11.9	9.4	81.9	13.1	4.9

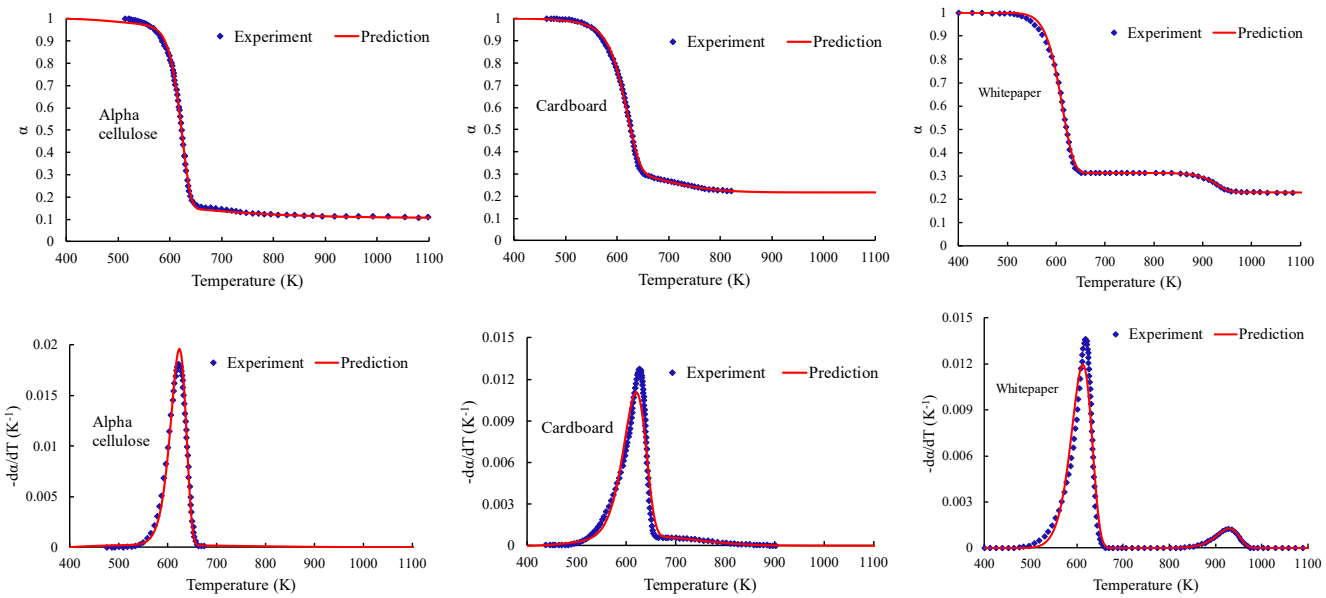

Fig 2 Comparison of experimental data and prediction results of various biomass pyrolysis

3. RESULTS

Fig 2 shows the comparison of experimental and predicted TGA results of alpha cellulose, cardboard and white paper at the heating rate 10 K/min. The number of the parallel reactions was set to 3 in advance for each type of biomass, all of the corresponding parameters can be seen in Table 2. Since alpha cellulose can be regard as single compound, the DTG shows only one significant peak at ~620 K, corresponding to the only dominated reaction. From the calculation results, the weight parameter w_i, shape parameter β_i and the scale parameter η_i of the dominated reaction are 0.8, 22.48 and 14.71, respectively. In addition, the DTG curve of cardboard also shows one sharp peak at ~620 K, probably due to the high cellulosic content [3]. The shape parameter of the reaction is very similar to alpha cellulose dominated reaction with the value 22.22, since the location of the peak is determined by the shape parameter. Another reaction of cardboard with the weight parameter 0.17 should not be neglected. The small peak at ~660 K is due to the larger shape parameter compared to Reaction 1, which is related to lignin, extractives or other added materials [3]. Nevertheless, it was not observed in the overall DTG curve, resulting from the lower weight fraction and the smaller scale parameter than those of the dominant reaction.

Different from alpha cellulose and cardboard, whitepaper shows 2 peaks in the DTG curve at the temperature of ~620 K and ~930 K, respectively. The second peak is probably due to the higher lignin content or other additives in the whitepaper, with the corresponding weight, shape and scale parameters 0.08, 53.1 and 22.42, respectively. The parameters of the first peak are very similar to those of the cardboard, probably because of the similar structure of cellulose inside. The parameters of Reaction 3 are nothing but demonstrating the residue inside the biomass, as the significant shape parameters (>200) indicate the reaction rate approximately to be zero. Weight parameter, as the key parameter of Reaction 3, is mostly related to the content of char and ash in the biomass. Reaction 3 can be considered as inert reaction of the residue inside biomass itself.

All the prediction results show the good agreements with the experimental data for the reasons that Weibull distribution is able to describe the mass loss process during pyrolysis, and the rationality of the parallel

reaction scheme assumption. Moreover, the improved DE algorithm which proposed by the authors is also crucial not only for purchasing the good parameters but also for keeping all the weight parameters sum up to 1 which maintains the consistency with the reality.

Table 2 Kinetic parameters obtained from the new model

Kinetic parameters		Biomass samples		
		Cellulose	Cardboard	Whitepaper
Reaction 1	w	0.09	0.17	0.08
	η	28.68	27.64	53.10
	β	1.67	2.81	22.42
Reaction 2	w	0.80	0.61	0.69
	η	22.48	22.22	21.50
	β	14.71	10.19	10.12
Reaction 3	w	0.11	0.22	0.23
	η	208.76	252.21	261.62
	β	12.79	28.31	3.51

4. CONCLUSIONS

A novel kinetic model based on Weibull distribution has been developed with the assumption of parallel reactions scheme during pyrolysis. Different from DAEM and Weibull mixture model, the new model describes the overall decomposition process directly using Weibull distribution, all the parameters are estimated by an improved differential evolution algorithm proposed by the authors. The predicted results show good agreements with experimental data due to the reasonable model description, reaction scheme assumption, and the algorithm implement. The new model doesn't need to assume the reaction orders in advance so that it is more reliable in the analysis of a wide range of conversion pyrolysis process. In addition, it is able to analyze real biomass without the knowledge of biochemical analysis, which can avoid experimental error, and enhance the applicability in various biomass. Moreover, since less number of parallel reactions used in the model, the computational cost is lower than the DAEM. The model shows another way for the description of biomass pyrolysis using Weibull distribution.

ACKNOWLEDGEMENT

Tianbao Gu acknowledges China Scholarship Council for the financial support of studying at Aalborg University.

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