

Kinetic Modeling, Simulation, and Optimization of Pyrolysis

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Abstract

Thermal decomposition of organic matter under inert atmospheric conditions, leading to the release of volatiles and formation of char is called as pyrolysis. It is also a first step in the biomass gasification. To design of a suitable pyrolysis reactor, understanding of kinetic parameters is essential. In the proposed kinetic model of this study, biomass decomposition is represented as a decomposition of its main three components namely cellulose, hemicellulose and lignin. Each component is modeled as decomposition by two competing reactions giving gaseous volatiles and solid charcoal is used. Logarithmic Differential Evolution (LDE) is used to find the kinetic parameters by minimizing the square of the error between the reported experimental data of thermogravimetry of hazelnut shell and simulated model predicted values of residual weight fraction. Logarithmic DE, an improved version of simple DE, incorporates logarithmic initialization and logarithmic mutation to take care of wide ranges of variable values. Logarithmic DE is found to yield better kinetic parameters in terms of objective function and gave better fit with experimental data.

INTRODUCTION

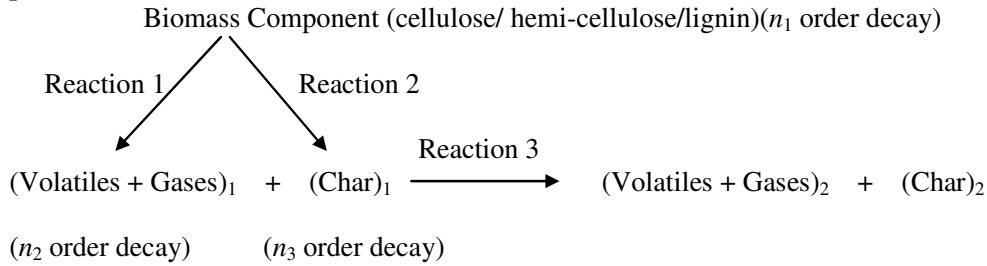
Decomposition of a compound, in the absence of oxygen, by the action of heat alone to produce various organic gaseous products, charcoal and tar, is known as pyrolysis [1]. Pyrolysis is not only an independent process, but also a first step in the gasification or the combustion process. Hazelnut shell is an abundantly available agriculture residue. Dogru et al. [2] used a pilot plant scale downdraft gasifier to investigate gasification potential of hazelnut shells. It is necessary to understand the kinetics of pyrolysis in order to design a suitable pyrolysis reactor. Balci et al. [3] proposed several kinetic models for hazelnut pyrolysis and validated by thermo-gravimetric experiments. In these kinetic models, the rate expression based on first-order decomposition of the reactive solid is defined in terms of fractional conversion. Demirbas [4] performed thermo-gravimetric experimental runs and presented the weight loss data for different particle sizes of ground hazelnut shell and for various heating rates. Kinetic analysis has also been carried out but the expression for the kinetic constants with respect to temperature is not developed, and the experimental data validation with theoretical models for these experiments is not reported in the literature. Experimental and modeling studies have been conducted on pyrolysis by many researchers [1-10]. In our previous studies [10, 11], a population based search algorithm, Differential Evolution (DE), which is simple and robust and has proven successful record, is employed for estimation of kinetic parameters. However, for some problems simple DE gave poor population distribution for cases where the range of limits was very wide (more than three orders of magnitude). Hence simple DE is modified first by including the logarithmic initialization (LIDE). The algorithm is further improved by incorporating the logarithmic mutation also and named as logarithmic DE (LDE) [12].

In the present study, Biomass decomposition is represented as a sum of decomposition of its components cellulose, hemi-cellulose and lignin. For each component, a kinetic model based on two competing reactions giving gaseous volatiles and solid charcoal is used. To find kinetic parameters of proposed model, an objective function based on least square error between experimental data and simulated results has to be minimized. The objective function minimization is carried out by Logarithmic DE. Model simulation results are validated with the data reported in literature [4].

KINETIC MODELING & SIMULATION

The kinetics of thermal decomposition of biomass materials is complicated, as it involves a large number of reactions in parallel and series. Biomass mainly consists of three components: cellulose, hemi-cellulose and lignin. In the present study, the pyrolysis process is described by the independent reactions corresponding to the decomposition of the constituent components cellulose, hemi-cellulose and lignin. The pyrolysis reactions of each component are described by means of the scheme proposed by Koufopoulos et al. [8, 9]. This model indicates that the biomass decomposes to volatiles, gases and char. The volatiles and gases may further react with char to produce different types of volatiles, gases and char where the compositions are different. Therefore, the primary

pyrolysis products participate in secondary interactions (Reaction 3), resulting in a modified final product distribution.



The kinetic equations for the mechanism, shown above are represented by Eq. (1) through Eq. (7).

$$r_{1i} = k_{1i} B_i^{n_1} \quad (1)$$

$$r_{2i} = k_{2i} B_i^{n_1} \quad (2)$$

$$r_{3i} = k_{3i} G_{1i}^{n_2} C_{1i}^{n_3} \quad (3)$$

where,

- i Biomass component: cellulose, hemi-cellulose and lignin
- r_{1i} Rate of reaction 1 for i^{th} component
- r_{2i} Rate of reaction 2 for i^{th} component
- k_{1i} Kinetic Constant of reaction 1 for i^{th} component
- k_{2i} Kinetic Constant of reaction 2 for i^{th} component
- B_i Concentration of i^{th} component of Biomass
- C_{1i} Concentration of Charcoal 1 for i^{th} component
- G_{1i} Concentration of volatile component 1 for i^{th} component

To find the kinetic parameters of the above-mentioned reactions, the square of the error between the reported experimental data of thermogravimetry of hazelnut shell and theoretical values of residual weight fraction is minimized. Thermogravimetry data of hazelnut shell is reported as % weight loss versus temperature [4]. The data has been recalculated in terms of residual weight fraction, where, residual weight fraction is defined as given by Eq. (4)

$$\text{Residual Weight Fraction } (W) = \frac{(\text{Residual Weight})}{(\text{Initial Weight})} \quad (4)$$

The recalculated experimental data of 0.180 mm size and for heating rate of 10.0, 25.0 and 40.0 K/s are plotted and shown in Fig. 1. To find the residual weight fraction theoretically, net rate of production of different species by reaction 1 & 2 in terms of rate of reactions are found. Due to small size (0.180 mm) of the hazelnut shell sample taken in the experiments, the secondary reaction [reaction 3] is neglected. The residual weight fraction is calculated using Eq. (5).

$$W_{\text{total}} = W_C + W_H + W_L \quad (5)$$

$$W_i = B_i + C_{1i} \quad \text{for } i = \text{cellulose, hemi-cellulose and lignin} \quad (6)$$

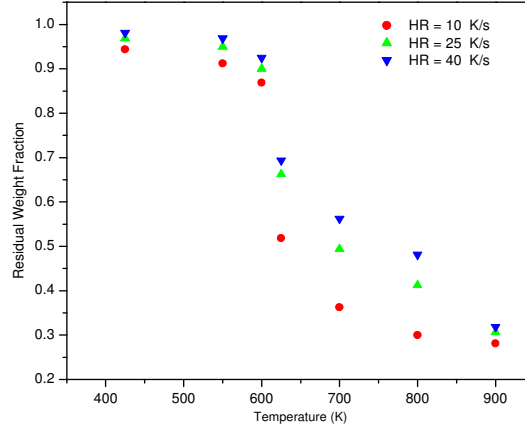


Fig. 1 Residual Weight Fraction versus Temperature (K) for Various Heating rates

For simplicity, the order of reactions 1 and 2 are taken as 1.0. Then Eq. (1) and Eq. (2) reduce to Eq. (7) and Eq. (8) respectively.

$$\frac{dB_i}{dt} = -(k_{1i} + k_{2i})B_i \quad (7)$$

$$\frac{dC_{1i}}{dt} = k_{1i}B_i \quad (8)$$

So change of residual weight fraction with time [Eq. (9)] obtained by addition of Eq. (7) & Eq. (8).

$$\frac{dW_i}{dt} = -k_{1i}B_i \quad (9)$$

To find temperature (T) at a particular time (t), following equation [Eq. (10)] is used [3, 4, 7-9],

$$T = (HR)t + T_0 \quad (10)$$

where

T_0 Initial Temperature
 HR Heating Rate

Differentiating Eq. (10) would result in

$$dT = (HR)dt \quad (11)$$

Using Eq. (9) and Eq. (11), the relations of change of residual weight fraction with temperature can be found, which is given by Eq. (12).

$$\frac{dW_i}{dT} = -k_{1i}B_i \frac{1}{HR} \quad (12)$$

Using Eq. (7) and Eq. (11), the relation of change of biomass weight fraction with temperature can be found, which is given by Eq. (13).

$$\frac{dB_i}{dT} = -(k_{1i} + k_{2i})B_i \frac{1}{HR} \quad (13)$$

Arrhenius relation of kinetic constants with temperature is given by Eq. (14) and Eq. (15) respectively for reaction 1 and reaction 2.

$$k_{1i} = A_{1i} \exp\left(\frac{-E_{1i}}{RT}\right) \quad (14)$$

$$k_{2i} = A_{2i} \exp\left(\frac{-E_{2i}}{RT}\right) \quad (15)$$

Values of the Frequency factor and Activation energy of both reactions are found by minimizing the objective function as given by Eq. (16).

$$F(A_{1i}, E_{1i}, A_{2i}, E_{2i}) = \sum_{j=1}^n (W_{\text{exp},j} - W_{\text{cal},j})^2 \quad (16)$$

where,

W_{exp}	Experimental Value of the residual weight fraction
W_{cal}	Calculated value of the residual weight fraction (predicted from Model)

Sheth and Babu [10] found that the kinetic parameter estimation of the non-isothermal pyrolysis of hazelnut shell is highly nonlinear and complex in nature. Most of the traditional optimization algorithms based on gradient methods have the possibility of getting trapped at local optimum depending upon the degree of non-linearity and initial guess. Sheth and Babu [10, 11] in their previous studies, Differential Evolution (DE) is applied to find the global optimum set of kinetic parameters. The details of DE algorithm and pseudo code are available in the literature [13-17]. However, DE gives poor population distribution for cases where the range of limits is very wide (more than three orders of magnitude). In the present case of kinetic parameter estimation, lower and upper limits of frequency factors are 10^{10} and 10^{18} respectively. Hence simple DE is modified first by including the logarithmic initialization (LIDE). The algorithm is further improved by incorporating the logarithmic mutation also and named as logarithmic DE (LDE). Optimum kinetic parameters are found by minimizing the objective function using simple DE, LIDE and LDE and obtained results are compared [12]. The key parameters of Logarithmic DE are Number of population (NP), Crossover Constant (CR) and Scaling Factor (F). The values used in the present case are: NP – 200, CR – 0.9 and F – 0.5. The limits of the frequency factors and activation energies are given below, which is chosen based on the available literature for kinetic modeling of different biomasses.

Limits of frequency factors (A_1 & A_2) = ($1.0e^{+10}$, $1.0e^{+18}$)

Limits of activation energies (E_1 & E_2) = ($1.0e^{+04}$, $3.0e^{+05}$)

To find the theoretical value of residual weight fraction (W), Forward finite difference technique [18, 19] is applied to Eq. (11) to Eq. (14) with the following initial conditions.

At time $t=0$

$$T_0 = 325 \text{ K}; \quad B = 1.0; \quad C_1 = 0.0; \quad G_1 = 0.0$$

RESULTS & DISCUSSION

The kinetic parameters are found by minimizing the error between experimental and theoretical residual weight fraction using logarithmic differential evolution. LDE gives different set of kinetic parameters with equal objective function value for its all 200 population points. Table-1 shows the kinetic parameters of reaction 1 (A_1 and E_1) and reaction 2 (A_2 and E_2) of decomposition of biomass components for the heating rate of 25.0 K/s for 4 different population points. It can be seen that for all 4 sets of kinetic parameters the objective function value is same. To validate kinetic parameters, residual weight fractions are found and compared with experimental data as shown in Fig. 2.

Table-1. Kinetic Parameters of reaction 1 and reaction 2 for heating rate of 25 K/s

Population No.	Biomass Component	Kinetic Parameters				Objective Function Value [Eq. (16)]
		A_1 (1/s)	E_1 (J/mol)	A_2 (1/s)	E_2 (J/mol)	
1	Cellulose	8.92075e+014	2.925969e+005	3.180889e+016	2.253174e+005	8.12278e-02
	Hemi-cellulose	1.26343e+012	1.791043e+005	9.086669e+013	2.048196e+005	
	Lignin	1.21167e+015	1.354798e+005	2.426886e+012	2.346181e+005	
2	Cellulose	2.39570e+010	2.386905e+005	8.996826e+010	2.126407e+005	8.12278e-02
	Hemi-cellulose	9.23708e+011	1.775636e+005	4.218786e+010	2.425827e+005	
	Lignin	1.21167e+015	1.354798e+005	1.016640e+013	2.664622e+005	
3	Cellulose	1.39989e+012	2.642160e+005	1.790428e+011	2.109662e+005	8.12278e-02
	Hemi-cellulose	9.22649e+011	1.775580e+005	1.138944e+011	2.640481e+005	
	Lignin	1.21167e+015	1.354798e+005	4.121117e+012	2.841225e+005	
4	Cellulose	1.32158e+010	2.734741e+005	2.154280e+012	2.417867e+005	8.12278e-02
	Hemi-cellulose	9.50333e+011	1.777034e+005	2.609307e+013	2.287296e+005	
	Lignin	1.21167e+015	1.354798e+005	1.333182e+013	2.791724e+005	

Fig. 2 shows that the model predictions of residual weight fractions for all four population points are giving exactly the same trends. According to the Fig. 2, kinetic parameters reported in Table -1 are equally good but that is not true. It is therefore biomass composition and charcoal production is plotted against temperature to get more insight. Fig. 3 shows the biomass composition variation and charcoal production due to a particular component for the population no 1. It shows that Lignin decomposes prior to cellulose and hemi-cellulose, which is not true. As reported in the literature [1] hemi-cellulose decomposes first followed by cellulose and lignin during the pyrolysis. Moreover the charcoal production by lignin and hemi-cellulose is almost zero, which is not true again. Lignin produces maximum char yield due to its complex heavy hydrocarbon type molecular structure and releases least volatiles. So the kinetic parameters for population no 1 gives equally less objective function in terms of residual weight fraction but failed to explain the biomass decomposition of its components. It is therefore, to get the kinetic parameters, not only sum of square of error of residual weight fraction minimization but also the constraints related to the activation energies of each biomass component should be incorporated.

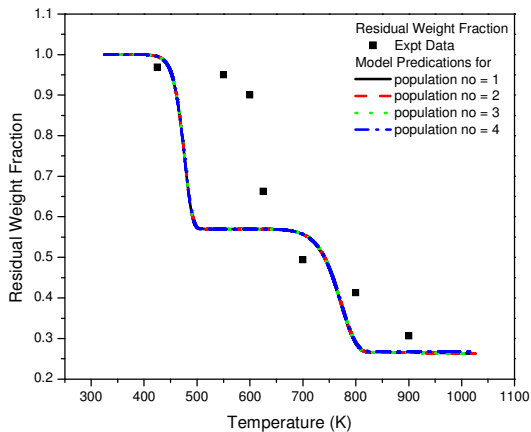


Fig. 2 Residual weight fraction variation with temperature (K)

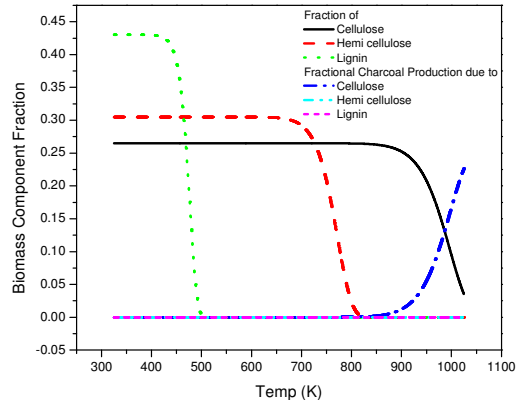


Fig. 3 Biomass composition variation and charcoal production with temperature (K) for population no 1.

CONCLUSIONS

Based on the results obtained and discussions in the earlier sections, the following conclusions are drawn.

- The kinetic model based on decomposition of its components is proposed. The kinetic scheme based on two competing reactions is incorporated for each biomass component.
- Model predicted values of the residual weight fraction matches well with the experimental data but failed to explain the biomass component decomposition.
- Constraints related to the activation energies are required to be found out and incorporated to find kinetic parameters.

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