

# Pyrolysis of Hazelnut Shell: Kinetic Modeling And Simulation

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## ABSTRACT

Pyrolysis essentially is the thermal decomposition of organic matter under inert atmospheric conditions or in a limited supply of air, leading to the release of volatiles and formation of char. Modeling of pyrolysis implies the representation of the chemical and physical phenomena in a mathematical form. In this study, Differential Evolution (DE) algorithm is applied and global optimum set of kinetic parameters are found out by minimizing the least square error between the experimental data reported and the results of simulated model for hazelnut shell. Simulations are carried out to find the kinetic parameters of the proposed kinetic scheme. Experimental data of thermogravimetry of hazelnut shell at different heating rates are used in the simulation. A generalized best-fit kinetic model is presented which can be applied to a wide range of particle dimensions using only one set of kinetic parameters.

**Keywords:** *Pyrolysis; Hazelnut Shell; Kinetic modeling; Simulation; Differential Evolution.*

## INTRODUCTION

Decomposition of a compound, in the absence of oxygen, by the action of heat alone is known as pyrolysis. It is a promising route for the production of various organic gaseous products, charcoal and tar. Hazelnut shell is an important agricultural residue. It is necessary to understand the kinetics of pyrolysis in order to design a suitable pyrolysis reactor. In recent years thermo-gravimetric (TG) methods have been widely used to study the kinetics of various solid-state decomposition reactions. Dynamic TG has been widely applied in the study of various solid-state processes. The shape of the thermo-gravimetric curves is a function of the reaction kinetics and, hence, the information obtained from these curves is useful in evaluating the kinetic parameters. The study of pyrolysis is gaining increasing importance, as it is not only an independent process, but also a first step in the gasification or the combustion process [1, 2].

Balci et al. [3] performed the thermo-gravimetric experiments for the hazelnut shell and several kinetic models are proposed. In their experiments, particle size is kept constant of 0.91 mm and final pyrolysis temperature is varied up to only 850 °C. As particles are very fine, approximately 90% of the pyrolysis reactions are completed up to 450 °C. They also validated their models with the experimental data and found the best-fit model. Demirbas [4] performed the thermo-gravimetric experimental runs and presented the weight loss data for different particle sizes of ground hazelnut shell for various heating rates. An experimental technique comprising a simplified fast pyrolysis device for obtaining the pyrolysis products and kinetic parameters is presented. The effects of heating rate, particle size, reaction temperature and catalyst are studied by performing the experiments by varying respective parameters. 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 are not validated with any kinetic scheme. In other words kinetic modeling and validation of the results with theoretical models for these experiments is not reported.

Experimental and modeling studies have been conducted on pyrolysis by many researchers [1-10]. In spite of the numerous experimental studies existing on biomass pyrolysis and on kinetic modeling, there is no generally accepted model that can predict the pyrolysis rate and provide a priori information about final conversion over a wide range of particle size for a particular species of biomass.

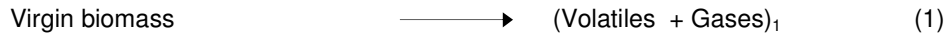
In the present study, kinetic model is developed and validated with the data reported in literature [1, 2]. To find the kinetic parameters of single step and two-step reaction models, an objective function based on the least square error between experimental data and simulated results has to be minimized. It is found that the objective function is highly nonlinear in nature and conventional

optimization techniques failed to yield global optimum result. One of the simple and highly successful population based search algorithms, Differential Evolution (DE) algorithm, is applied and global optimum set of kinetic parameters are found out. It is found that Differential Evolution algorithm is successfully applied to a number of optimization problems [11-15]. By using the proposed model of this study, it is possible to predict the pyrolysis rate for hazelnut shell over a wide range of particle dimensions using only one set of kinetic parameters.

## KINETIC MODELING

Different classes of mechanisms were proposed for the pyrolysis of wood and other cellulosic materials. The models are classified into three categories: one-step global models; one-stage multi-reaction models; and two-stage semi-global models. The first category of models considers pyrolysis as a single-step first order reaction.

Parallel reactions:



Secondary Interactions:



The second category of models discuss those mechanisms, which consider simultaneous and competing first order reactions in which virgin wood decomposes into different constitutes of pyrolysis products, namely volatiles, gases and char (Reactions (1) & (2)). The third class of models considers pyrolysis to be a two-stage reaction, in which the products of the first reaction (volatiles and gases) further reacts with the char produced by second reaction to produce volatile and gases of different composition. Thus the primary pyrolysis products participate in secondary interactions (reaction 3) causing a modified final product distribution. As particle size increases, the residence time of the volatiles inside the solid increases and the effect of secondary reactions also increased [3].

Based on unit surface area of solid in gas-solid system, the kinetic equations for the mechanism shown above are as follows [4].

$$r_1 = k_1 B^{n_1} \left( \frac{SA}{V} \right) \quad (4)$$

$$r_2 = k_2 B^{n_2} \left( \frac{SA}{V} \right) \quad (5)$$

$$r_3 = k_3 G_1^{n_3} C_1^{n_3} \left( \frac{SA}{V} \right) \quad (6)$$

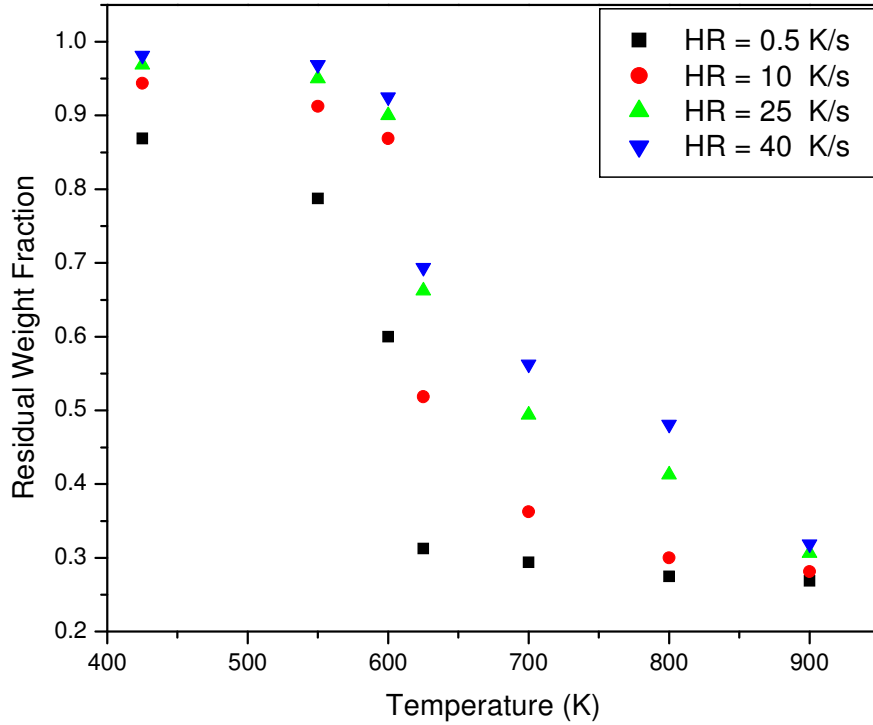
Where,

$r_i$	Rate of Reaction i	;	V	Volume of the Particle
$k_1$	Kinetic constant of reaction 1	;	B	Concentration of Biomass
$k_2$	Kinetic constant of reaction 2	;	$C_1$	Concentration of Charcoal 1
$k_3$	Kinetic constant of reaction 3	;	$G_1$	Concentration of Volatile Component 1
SA	Surface Area of the Particle			

Table-1 shows the net rate of production of the different species by chemical reactions in terms of the rate of reactions.

**Table-1. Net Rate of Production of the Different Species by Chemical Reactions in Terms of the Rates of Reactions 1 to 3**

Species	$R_x$ (kg/sec)
Biomass B	$-r_1 - r_2$
$(\text{Volatiles + Gases})_1 G_1$	$r_1 - r_3$
$(\text{Char})_1 C_1$	$r_2 - r_3$
$(\text{Volatiles + Gases})_2 G_2$	$r_3$
$(\text{Char})_2 C_2$	$r_3$



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

Thermogravimetry data of hazelnut shell is reported as % weight loss versus temperature in the literature [4]. The data has been recalculated in terms of residual weight fraction, replotted and shown in Fig. 1. The hazelnut shell sample of size 0.180 mm is used and experimental run is performed for the heating rate of 0.5, 2.0, 10.0, 25.0 and 40.0 K/s [4].

Where, residual weight fraction is defined as below.

$$\text{Residual Weight Fraction (W)} = \frac{(\text{Residual weight})}{(\text{Initial weight})} \quad (7)$$

As can be seen from Fig. 1 biomass sample would get heated for the longer time period than in the experimental run of higher heating rate. So the residual weight fraction value is least at all temperatures for the lowest heating rate run (0.5 K/s). It also shows that the amount of charcoal produced does not depend upon the heating rate of the experiments. But it is observed that amount of volatiles and tarry materials depend upon the heating rate. Higher heating rate experimental run shows the lesser amount of gaseous products and higher amounts of the tarry materials [4].

Residual weight fraction can be found out theoretically as follows. Hazelnut shell sample taken in the experiments is of very small size (0.180 mm) so the secondary reaction (reaction 3) can be neglected.

$$W = B + C_1 \quad (8)$$

For simplicity the order of the reaction 1 and 2 is taken as 1.0

$$\frac{dB}{dt} = -(k_1 + k_2)B \left( \frac{SA}{V} \right) \quad (9)$$

$$\frac{dC_1}{dt} = k_2 B \left( \frac{SA}{V} \right) \quad (10)$$

So change of residual weight fraction with time can be written as follows.

$$\frac{dW}{dt} = -k_1 B \left( \frac{SA}{V} \right) \quad (11)$$

To find the temperature ( $T$ ) at a particular time ( $t$ ) following equation can be used.

$$T = (HR)t + T_0 \quad (12)$$

Where

$T_0$  Initial Temperature  
 $HR$  Heating Rate

Differentiating Eq. (12) would result in

$$dT = (HR)dt \quad (13)$$

Using Eq. (11) and Eq. (13), the relation of change of residual weight fraction with temperature can be found.

$$\frac{dW}{dT} = -k_1 B \left( \frac{SA}{V} \right) \frac{1}{HR} \quad (14)$$

Using Eq. (9) and Eq. (13), the relation of change of biomass weight fraction with temperature can be found.

$$\frac{dB}{dT} = -(k_1 + k_2) B \left( \frac{SA}{V} \right) \frac{1}{HR} \quad (15)$$

Arrhenius relation of kinetic constant with temperature can be written as follows

$$k_1 = A_1 \exp \left( \frac{-E_1}{RT} \right) \quad (16)$$

$$k_2 = A_2 \exp \left( \frac{-E_2}{RT} \right) \quad (17)$$

## SIMULATION

Values of the Frequency factor and Activation energy of both reactions are found by minimizing the objective function given below.

$$F(A_1, E_1, A_2, E_2) = \sum_{j=1}^n (W_{\text{exp},j} - W_{\text{the},j}) \quad (18)$$

Where,

$W_{\text{exp}}$  Experimental value of the residual weight fraction  
 $W_{\text{the}}$  Theoretical value of the residual weight fraction

It is found that the objective function is highly nonlinear in nature and conventional optimization techniques failed to yield global optimum result. One of the simple and highly successful population based search algorithms, Differential Evolution (DE) algorithm, is applied to Eq. (18) and global optimum set of the Frequency factor and Activation energy of both reactions are found out.

To find the theoretical value of the residual weight fraction ( $W$ ), Forward finite difference technique is applied to the Eq.(14) to Eq. (17) with the following initial conditions.

At time  $t = 0$

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

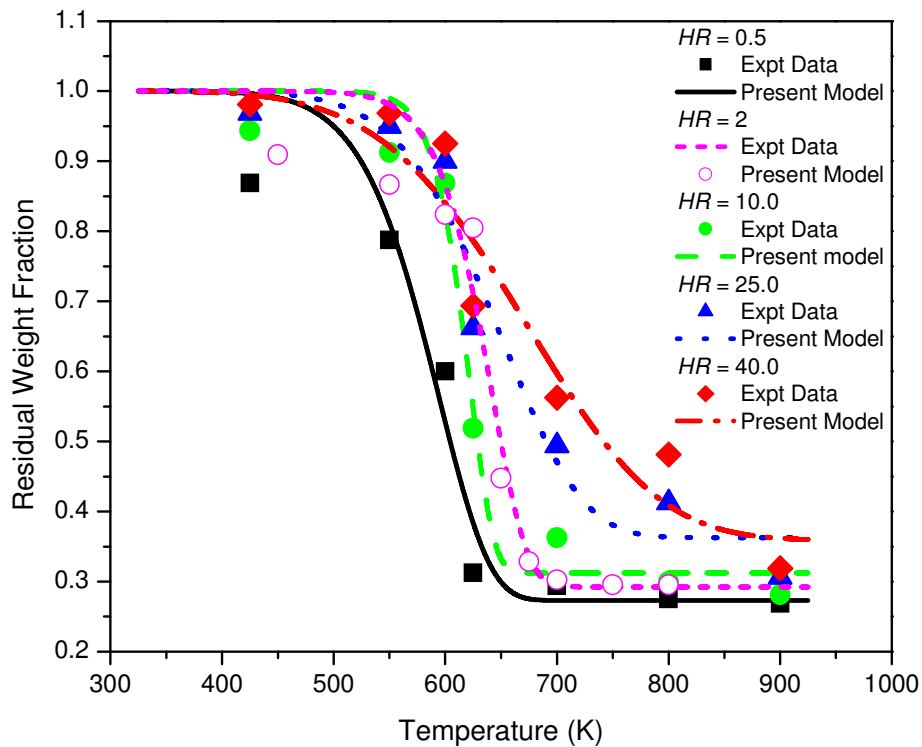
## RESULTS AND DISCUSSION

Table-2 shows the kinetic parameters of reaction 1 ( $A_1$  and  $E_1$ ) and reaction 2 ( $A_2$  and  $E_2$ ) for the heating rates of 0.5, 2.0, 10.0, 25.0, 40.0 K/s for the sample size of 0.180 mm. Using the kinetic parameters found by minimizing the error between experimental and theoretical residual weight fraction, Residual weight fraction is found and compared with the experimental data as shown in the Fig. 2.

**Table 2. Kinetic Parameters of reaction 1 and reaction 2**

Heating Rates (K/s)	Kinetic Parameters				Objective Function Value [Eq. (18)]
	$A_1$	$E_1$	$A_2$	$E_2$	
0.5	3.516348773e-02	5.617518496e+04	2.439624127e+02	1.044228968e+05	2.768564928e-02
2	4.705927035e+02	1.017063860e+05	9.197062353e+04	1.340870726e+05	3.439463864e-02
10.0	1.600607445e+08	1.536111418e+05	1.646238223e+06	1.344027308e+05	1.546313793e-02
25.0	2.566121987e-01	5.272973249e+04	4.722348418e-03	3.518546949e+04	1.923566054e-02
40.0	7.991504273e-03	3.512492732e+04	2.484965866e-04	2.016348896e+04	2.657827508e-02

Fig. 2 clearly shows that for the heating rate of 0.5 K/s, present model is fitting very well except for the value at 425 K. For the heating rate of 2 and 10 K/s, model predictions in the temperature range of 600 to 900 K are good. Although for the Heating rate of 25 and 40 K/s model is predicting the trend of decrease of residual weight fraction, the values are not matching exactly with the experimental values. For the heating rate of 0.5, 2 and 10 K/s, the rate of pyrolysis is initially very less.



**Fig. 2 Experimental and Theoretical Residual Weight Fraction for different Heating Rates**

An increase in temperature, the rate is increasing and remains almost constant upto a 30 % reduction in weight. It indicates that during the process of pyrolysis the reactivity of biomass is not decreasing. Whereas in the case of heating rate value equal to 25 and 40 K/s, after 70 % reduction in weight the rate starts decreasing. It clearly shows that the activity of biomass is decreasing with

progress in conversion for the heating rate of 25 and 40 K/s. Its value approaches zero when the conversion approaches to a maximum value.

## CONCLUSIONS

In the present study kinetic model is developed and validated with the data reported in literature [1, 2]. Using the data of Demirbas [4] for the pyrolysis of hazelnut shell by thermogravimetry experiments, kinetic parameters are found for the heating rates of 0.5, 2, 10, 25, and 40 K/s. The proposed kinetic model is simulated and the global optimum values of the kinetic constants are found by minimizing the least square of the error between the experimental data reported by Demirbas [4] and the results of the simulated model using Differential Evolution. Based on the results obtained and discussions in the earlier sections, the following conclusions are drawn.

- Present proposed model considers the reaction scheme based on unit surface area of solid in gas-solid system of pyrolysis.
- Activation energy and frequency factor values found using Differential Evolution algorithm are global optimum values.
- The present model predicts the rate of pyrolysis of hazelnut shell biomass of wide range of particle size.

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