

# Kinetic Modeling for Pyrolysis of Hazelnut Shell: Optimal Parameter Estimation using Differential Evolution (DE)

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Pyrolysis is the thermal decomposition of organic matter under inert atmospheric conditions or in the presence of a limited supply of air, leading to the release of volatiles and formation of char. In the proposed kinetic model of this study, the kinetic scheme of biomass decomposition by two competing reactions giving gaseous volatiles and solid charcoal is used. Two different models are proposed based on different relation of activity of biomass with normalized conversion: (1) the activity is taken as unity, (2) rate of change of activity decreases with normalized conversion. The corresponding kinetic parameters of the above two models are estimated 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. As the above objective function is highly nonlinear, complex in nature, and traditional optimization techniques failed to yield the global optimum set of kinetic parameters, Differential Evolution (DE), a population based search algorithm, is employed. *Model -2*, which considers the variation of activity of biomass with the normalized conversion, gave the best agreement with the experimental data.

**Keywords:** *Pyrolysis; Kinetics; Modeling; Simulation; Optimization; Differential Evolution.*

## 1. INTRODUCTION

Pyrolysis is a process of degradation of biomass by heat in the absence of oxygen, which results in the production of various organic gaseous products, charcoal and tar [1]. Hazelnut shell is an important agriculture residue. It is necessary to understand the kinetics of pyrolysis in order to design a suitable pyrolysis reactor. A pilot scale downdraft gasifier is reported to have used to investigate gasification potential of hazelnut shells with successful operation [2]. 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 [3, 4].

Balci et al. [5] performed the thermo-gravimetric experiments for the hazelnut shell and other lignocellulosic biomasses, and proposed several kinetic models. In the kinetic model, an exponential decrease of solid reactivity with respect to conversion level is proposed and the rate expression based on first-order decomposition of the reactive solid is defined in terms of fractional conversion. Arrhenius relation of rate constant is replaced with an expression, where rate constant is expressed as a function of extent of reaction. Demirbas [6] performed the thermogravimetric

experimental runs and presented the weight loss data for different particle sizes of ground hazelnut shell and 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. 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 theoretical models for these experiments are not reported in the literature.

Experimental and modeling studies have been conducted on pyrolysis by many researchers [1-13]. Kinetic modeling of lignocellulosic biomass by method of least squares is performed by Varhegyi et al. [14] by using thermogravimetry data. Experiments are performed on large wood particles and mathematical model is presented for the packed bed pyrolysis [15]. Thermogravimetric data has been generated to study the kinetics of isothermal degradation of wood [16]. As mentioned earlier though the kinetic model proposed by Balci et al. [5] is simplest in nature, the rate expression is based on first-order decomposition of the reactive solid. In the present study, kinetic model developed by Balci et al. [5] is modified and used for the hazelnut shell biomass of 0.180 mm. Instead of apparent decomposition rate expression, kinetic scheme proposed by Koufopoulos et al. [11,12] and validated by many researchers for various biomasses [3,4,7-10,13,17] is applied. Model simulation results are validated with the data reported in literature [6]. Proposed model includes the rate of change of activity with respect to solid reactant conversion in pyrolysis of Hazelnut Shell biomass. Reaction rate constant is expressed as a function of extent of reaction, which has replaced the Arrhenius relation of rate constant with temperature. 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. A population based search algorithm, Differential Evolution (DE), which is simple and robust and has proven successful record, is employed for optimization in the present case. It may be noted that Differential Evolution algorithm has been successfully applied to a number of optimization problems [18-22]. By using the proposed model of this study, it is possible to predict the pyrolysis rate for hazelnut shell.

## **2. KINETIC MODELING AND SIMULATION**

Different classes of mechanisms were proposed for the pyrolysis of wood and other lignocellulosic materials. The models are classified into three categories; one-step global models; one-step multi-reaction models; and two-stage semi-global models. The first category of models considers pyrolysis as a single-step first order reaction [23].

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 constituents of pyrolysis products, namely volatiles, gases and char [Reactions (1) & (2)]. The third class 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 & gases, and char of different compositions. 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 increase [5].

The kinetic equations for the mechanism, discussed above are represented by Eq. (4) through Eq. (6).

$$r_1 = k_1 B^{n_1} \quad (4)$$

$$r_2 = k_2 B^{n_2} \quad (5)$$

$$r_3 = k_3 G_1^{n_3} C_1^{n_3} \quad (6)$$

where,

- $r_i$  Rate of reaction  $i$
- $k_i$  Kinetic Constant of reaction  $i$
- $B$  Concentration of Biomass
- $C_1$  Concentration of Charcoal 1

$G_1$  Concentration of volatile component 1

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 [6]. The data has been recalculated in terms of residual weight fraction, where, residual weight fraction is defined as given by Eq. (7)

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

The recalculated experimental data are plotted and shown in Fig. 1. The hazelnut shell sample of size 0.180 mm is used and experimental runs are performed for different heating rates of 0.5, 2.0, 10.0, 25.0, and 40.0 K/s [6]. As shown in Fig. 1, biomass sample would get heated for a longer time period in case of lower heating rate than that for higher heating rates. So the residual weight fraction value is the least at all temperatures for the lowest heating rate (0.5 K/s). It also shows that the amount of charcoal produced finally, is almost independent of the heating rate. However, Demirbas [6] found that amount of volatiles and tarry materials formed depend upon the heating rate, and reported that higher heating rate gave lesser amount of gaseous products and higher amounts of tarry materials.

To find the residual weight fraction theoretically, net rate of production of different species by reaction 1 and reaction 2 [Eq. (1) and Eq. (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 as given by Eq. (3)] is neglected. The residual weight fraction can be calculated using Eq. (8).

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

For simplicity the order of reactions 1 and 2 are taken as 1.0. Then Eq. (4) and Eq. (5) reduce to Eq. (9) and Eq. (10) respectively.

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

$$\frac{dC}{dt} = k_2B \quad (10)$$

So the change of residual weight fraction with time [Eq. (11)] obtained by addition of Eq. (9) and Eq. (10).

$$\frac{dW}{dt} = -k_1 B \quad (11)$$

To find temperature ( $T$ ) at a particular time ( $t$ ), following equation [Eq. (12)] can be used [3, 4, 7-9],

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

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 relations of change of residual weight fraction with temperature can be found, which is given by Eq. (14).

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

Using Eq. (9) and Eq. (13), the relation of change of biomass weight fraction with temperature can be found, which is given by Eq. (15).

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

Arrhenius relation of kinetic constants with temperature is given by Eq. (16) and Eq. (17) respectively for reaction 1 and reaction 2.

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

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

Values of the Frequency factor and Activation energy of both reactions are found by minimizing the objective function as given by Eq. (18).

$$F(A_1, E_1, A_2, E_2) = \sum_{j=1}^n (W_{exp,j} - W_{cal,j})^2 \quad (18)$$

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 [13] found the kinetic parameters for isothermal pyrolysis of beech wood saw dust by minimizing the square of error between the experimental data reported by Koufopoulos et al. [12] and model predicted values. A MATLAB optimization subroutine '*fminsearch*', which is based on simplex search method, is used for optimization. When the same inbuilt MATLAB optimization function is used to find the kinetic parameters by minimizing the Eq. (18) for non-isothermal pyrolysis of hazelnut shell in the present study, it yielded different converged values of frequency factor and activation energies as optimum with different initial guesses. It indicates that the present objective function is highly nonlinear and complex in nature, having local optima (non-concave). 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. Unfortunately, none of the traditional algorithms are guaranteed to find the global optimum solution. In the recent past, nontraditional search and optimization techniques (Evolutionary Computation) based in natural phenomenon such as Genetic Algorithms (GAs) [24] and Differential Evolution (DE) has been developed to overcome these problems. One such population based search algorithm, Differential Evolution (DE), which is simple & robust and has proven successful record, is applied to Eq. (18) to find the global optimum set of frequency factor and Activation energy of both reactions [Eq. (1) and Eq. (2)]. The crucial idea behind DE is scheme for generating trial parameter vectors. Basically, DE adds weighted difference between two population vectors to a third vector. The key parameters of control in DE are: *NP*- the population size, *CR*-the cross over constant, and *F* the weight applied to random differential (scaling factor). The details of DE algorithm and pseudo code are available in literature [18-22].

The key parameters of DE (*NP*-population size; *CR*-crossover constant; and *F*-scaling factor) are problem dependent. However, certain guidelines and heuristics are available for the choice of these parameters [24]. Based on these heuristics, the values of DE key parameters for the present problem are set as follows:

$NP = 10 \text{ times the Number of variables}$

$CR = 0.9$

$F = 0.5$

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

At time  $t=0$

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

### **3. RESULTS AND DISCUSSION**

Table-1 shows the kinetic parameters of reaction 1 ( $A_1$  and  $E_1$ ) and reaction ( $A_2$  and  $E_2$ ) for the heating rates of 0.5, 10.0, 25.0, 40.0 K/s for a 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 experimental data as shown in Fig. 2.

For the heating rate of 10, 25 and 40 K/s, model predictions are exactly matching the experimental values in the temperature range of 600 to 750 K. The rate of pyrolysis is initially very less for all three heating rates. With an increase in temperature, the apparent rate of reaction is increasing very fast. The rate of reaction remains constant upto a certain residual weight fraction value. This residual weight fraction value is 0.6, 0.52 and 0.35 for the heating rates of 40, 25 and 10 K/s respectively. It indicates that during the process of pyrolysis the reactivity of biomass remains constant for lower heating rate (10 K/s) and is decreasing with progress in conversion for higher heating rates (25 K/s and 40 K/s). In the Model described above [Eq. (8) to Eq. (18)], change of activity with respect to conversion is assumed to be negligible. Thus, activity is taken as unity throughout the pyrolysis. Let us denote it as *Model-1*, which is given below:

**Model-1:** Rate constants are taken as a function of temperature (Arrhenius relation of kinetic constant with temperature) only, which is represented by Eq. (16) and Eq. (17).

The activity of the solid reactant is expected to decrease with the extent of reaction due to changes in chemical and pore structure of solid. Based on the above observations, a model is proposed in which activity decreases as a function of conversion, which is briefly described below:

**Model-2:** In this Model, the rate of change of activity with respect to normalized conversion

$\left(\frac{-da}{dz}\right)$  is expressed as a function of normalized conversion  $\left(z = \frac{1-W}{1-W_{final}}\right)$  as given by Eq. (19).

$$\frac{-da}{dz} = \beta z^n \quad (19)$$

Here  $\beta$  corresponds to a deactivation rate constant. Decrease of activity of solid with conversion is obtained by the integration of Eq. (19) taking activity to be unity when  $z=0$  and is shown by Eq. (20).

$$a = 1 - \left(\frac{\beta}{n+1}\right) z^{n+1} \quad (20)$$

Activity approaches zero when dimensionless conversion ( $z$ ) goes to unity. So variation of reaction rate constants with conversion are obtained, and given by Eq. (21) and Eq. (22).

$$k_1 = A_1 (1 - z^{n+1}) \exp\left(\frac{-E_1}{RT}\right) \quad (21)$$

$$k_2 = A_2 (1 - z^{n+1}) \exp\left(\frac{-E_2}{RT}\right) \quad (22)$$

The implication of this model is a decrease of frequency factor of pyrolysis rate constants with conversion.

Values of the Frequency factors ( $A_1$  and  $A_2$ ), Activation Energies ( $E_1$  and  $E_2$ ), and power of fractional conversion ( $n$ ) of both reactions are found by minimizing the objective function given below [Eq. (31)] is minimized and the global optimum set of kinetic parameters is found out.

$$F(A_1, E_1, A_2, E_2, \beta, n) = \sum_{j=1}^n (W_{exp,j} - W_{cal,j}) \quad (31)$$

Using the Differential Evolution algorithm, the objective function [Eq. (31)] is minimized and the global optimum set of kinetic parameters is found out. To find the theoretical value of the residual weight fraction ( $W$ ), forward finite difference technique is applied to Eq. (14), Eq. (15), Eq. (21) and Eq. (22) for *Model-2*. Initial conditions used to solve the above-mentioned first order differential equations are:

At time  $t=0$

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

Simulations are performed to find the kinetic parameters of reaction 1 and reaction 2 ( $A_1$ ,  $E_1$ ,  $A_2$ ,  $E_2$ ,  $n$ ) for *Model-1* and 2 for heating rate of 25 K/s for the ground hazelnut shell biomass sample of 0.180 mm size. Using the kinetic parameters found by minimizing the objective function [Eq. (31)], residual weight fraction is found and compared with the experimental data as shown in Fig. 3 and Fig. 4 for the heating rate of 25 and 40 K/s respectively.

In *Model-1*, the change of activity with conversion is neglected. In this Model, neither the activation energy nor the frequency factor changes with conversion. As discussed earlier in this paper this approach gives significant deviations between the experimental and predicted values of the residual weight fraction for the hazelnut shell biomass. This is essentially due to the changes in the chemical composition and physical properties of solid reactant with extent of reaction.

It can be seen from Fig. 3 and Fig. 4 that *Model-2* predictions fit better with the experimental data in comparison with *Model-1* in the temperature range of 600 to 850 K. And also *Model-2* yielded a minimum value of the objective function. The changes in chemical structure of the solid with extent of reaction might cause a decrease in frequency factor of pyrolysis, which is predicted by *Model-2*.

#### **4. CONCLUSIONS**

In the present study, kinetic model developed by Balci et al. [5] is modified and used for the hazelnut shell biomass of 0.180 mm. Instead of apparent decomposition rate expression, kinetic scheme proposed by Koufopoulos et al. [11, 12] and validated by many researchers for various biomasses [3, 4, 7-10, 13] is applied. Present proposed model considers the kinetic scheme of biomass decomposition by two competing reactions giving volatile gaseous and solid charcoal products. Model simulation results are validated with the data reported in literature [6]. Proposed Model includes the rate of change of activity with respect to solid reactant conversion in pyrolysis of Hazelnut Shell biomass. Reaction rate constant is expressed as a function of extent of reaction, which has replaced the Arrhenius relation of rate constant with temperature. The proposed kinetic model is simulated and the global optimum values of the kinetic constant are found by minimizing the least square of the error between the experimental data reported by Demirbas [6] and the results of the simulated model using a population based search algorithm for optimization,

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

- Present proposed Model, based on the kinetic scheme of two competing reactions, predicts the rate of pyrolysis of hazelnut shell biomass different heating rates.
- Activation energy, frequency factor, and  $n$  (power value of the conversion) values found using Differential Evolution algorithm are global optimum values.
- For all heating rate values, the objective function values of *Model-2* is lesser than *Model-1*.

*Model-2* that gave the better agreement in comparison with *Model-1* predicts the decrease of frequency factor of pyrolysis rate constants with  $n^{\text{th}}$  power of conversion.

## NOTATIONS

$a$	Activity of biomass
$B$	Concentration of Biomass
$C_1$	Concentration of Charcoal 1
$CR$	Crossover constant
$F$	Scaling Factor
$G_1$	Concentration of volatile component 1
$HR$	Heating Rate
$k_1$	Kinetic constant of reaction 1
$k_2$	Kinetic constant of reaction 2
$k_3$	Kinetic constant of reaction 3
$NP$	Population size
$r_i$	Rate of reaction $i$
$t$	Time
$T_0$	Initial Temperature
$W$	Residual Weight Fraction
$W_{\text{exp}}$	Experimental value of the residual weight fraction
$W_{\text{cal}}$	Calculated value of the residual weight fraction (predicted from Model)
$z$	Normalized Conversion

## Greek Letters

$\beta$  Deactivation Rate Constant

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

Heating Rates (K/s)	Kinetic Parameters				Objective Function Value [Eq. (18)]
	$A_1$	$E_1$	$A_2$	$E_2$	
10	3.126212282e+017	2.119155645e+005	4.884784208e+017	2.170600379e+005	1.055828051e-002
25	4.431990932e+017	2.112252859e+005	7.528231491e+017	2.140353804e+005	9.143317659e-003
40	6.357624068e+017	2.112073401e+005	8.712775417e+017	2.115595805e+005	1.446749337e-002

**Table-2. Kinetic Parameters of reaction 1 and reaction 2 for the pyrolysis of hazelnut shell for HR = 25 K/s**

Kinetic Parameters	Models (Heating Rate = 25 K/s)	
	1	2
$A_1$ (1/s)	4.431990932e+017	9.038448373e+016
$E_1$ (J/mol)	2.112252859e+005	2.022444059e+005
$A_2$ (1/s)	7.528231491e+017	2.003540437e+017
$E_2$ (J/mol)	2.140353804e+005	2.072401639e+005
$n$		6.715746798e-002
Objective Function Value [Eq. (31)]	9.143317659e-003	6.689873600e-003

**Table-3. Kinetic Parameters of reaction 1 and reaction 2 for the pyrolysis of hazelnut shell for HR = 40 K/s**

Kinetic Parameters	Models (Heating Rate = 40 K/s)	
	1	2
$A_1$ (1/s)	6.357624068e+017	1.583557976e+017
$E_1$ (J/mol)	2.112073401e+005	2.044863309e+005
$A_2$ (1/s)	8.712775417e+017	2.171158310e+017
$E_2$ (J/mol)	2.115595805e+005	2.059366146e+005
$n$		3.718162996e-002
Objective Function Value [Eq. (31)]	1.446749337e-002	6.676316000e-003

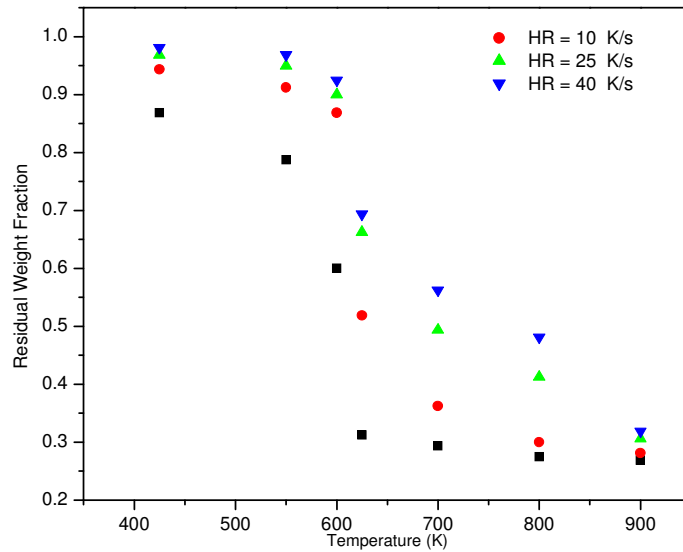


Fig. 1 Residual Weight Fraction versus Temperature (K) for Various Heating rates

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

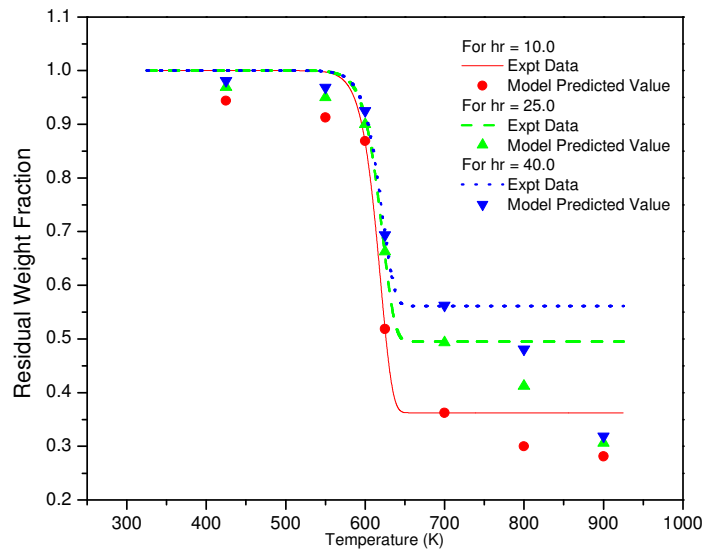


Fig. 2 Experimental and Theoretical Residual Weight Fraction for different Heating Rates (Model 1)

**Fig. 2 Experimental and Theoretical Residual Weight Fraction for different Heating Rates (*Model 1*)**

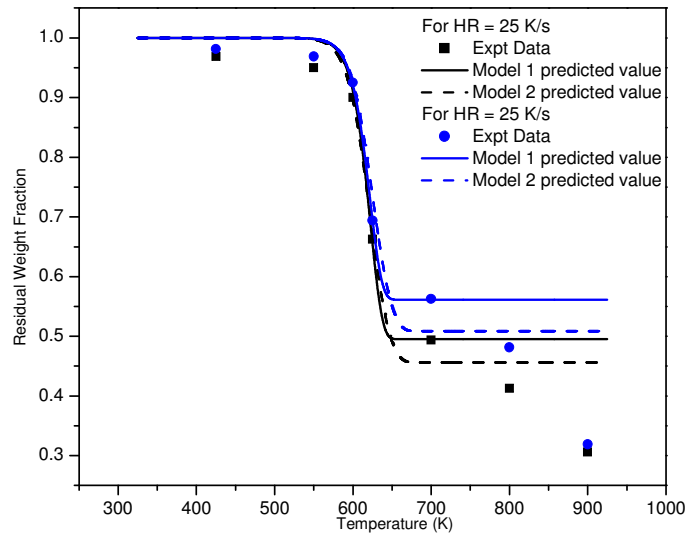


Fig. 3 Experimental and Theoretical Residual Weight Fraction for Heating Rates of 25 K/s and 40 K/s for Model 1 and 2

**Fig. 3 Experimental and Theoretical Residual Weight Fraction for Heating Rates of 25 K/s and 40 K/s for *Model 1* and 2**