

Optimization of Kinetic Parameters in Pyrolysis of Biomass Using Differential Evolution (DE)

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Pyrolysis, a first step in the biomass gasification, is the thermal decomposition of organic matter under inert atmospheric conditions, 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. Four different models are proposed based on different possible relation of activity of biomass with normalized conversion. The corresponding kinetic parameters of the above 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 using Differential Evolution (DE), a population based search algorithm. Among the four different models proposed in this study, *Model-3* gave the best agreement with the experimental data.

Keywords: *Biomass; Hazelnut Shell; Renewable Energy; Thermal Decomposition; Pyrolysis; Biomass Gasification; Reaction Mechanism; Thermogravimetry; Kinetics; Parameter Estimation; Modeling; Simulation; Optimization; Evolutionary Algorithm; Differential Evolution.*

1. INTRODUCTION

Decomposition of a compound, in the absence of oxygen, by the action of heat alone is known as pyrolysis. In the pyrolysis process, biomass gets decomposed by heat in the absence of oxygen, which results in the production of various organic gaseous products, charcoal and tar [1]. The examples for biomass include plants, saw dust, rice husk, wood, energy crops, agricultural and forestry wastes. Hazelnut shell is an abundantly available agriculture residue. A pilot plant scale

downdraft gasifier is 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]. 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. The shape of the thermo-gravimetric curves is a function of the reaction kinetics and, hence, these curves are very useful to identify the kinetic parameters [5].

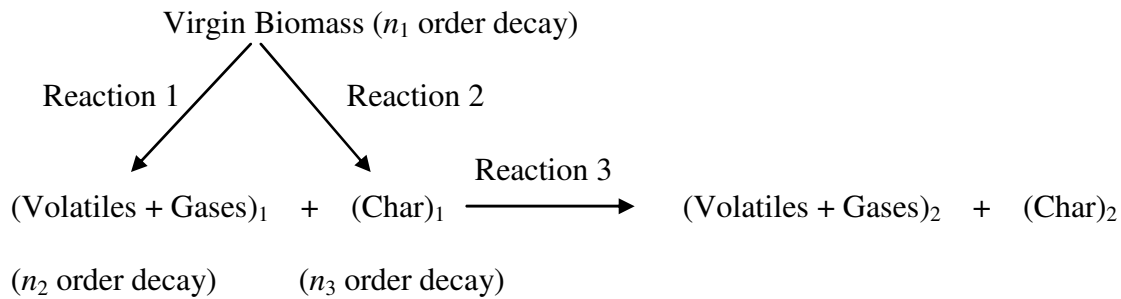
Balci et al. [5] performed the thermo-gravimetric experiments for the hazelnut shell and other lignocellulosic biomasses, and proposed several kinetic models. In these kinetic models, an exponential decrease of solid reactivity with respect to conversion level is proposed and the rate expression based 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 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 [1-13]. 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]. The present proposed model of this study 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

The pyrolysis reactions can be described by means of the following scheme proposed by Koufopoulos et al. [11, 12]. 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. (3).

$$r_1 = k_1 B^{n_1} \quad (1)$$

$$r_2 = k_2 B^{n_1} \quad (2)$$

$$r_3 = k_3 G_1^{n_2} C_1^{n_3} \quad (3)$$

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. (4)

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

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 10.0, 25.0, and 40.0 K/s [6].

To find the residual weight fraction theoretically, net rate of production of different species by reaction 1 and reaction 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).

$$W = B + C_1 \quad (5)$$

For simplicity, the order of reactions 1 and 2 are taken as 1.0. Then Eq. (1) and Eq. (2) reduce to Eq. (6) and Eq. (7) respectively.

$$\frac{dB}{dt} = -(k_1 + k_2)B \quad (6)$$

$$\frac{dC_1}{dt} = k_1B \quad (7)$$

So the change of residual weight fraction with time [Eq. (8)] obtained by addition of Eq. (6) and Eq. (7).

$$\frac{dW}{dt} = -k_1 B \quad (8)$$

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

$$T = (HR)t + T_0 \quad (9)$$

where

T_0 Initial Temperature

HR Heating Rate

Differentiating Eq. (9) would result in

$$dT = (HR)dt \quad (10)$$

Using Eq. (8) and Eq. (10), the relations of change of residual weight fraction with temperature can be found, which is given by Eq. (11).

$$\frac{dW}{dT} = -k_1 B \frac{1}{HR} \quad (11)$$

Using Eq. (6) and Eq. (10), the relation of change of biomass weight fraction with temperature can be found, which is given by Eq. (12).

$$\frac{dB}{dT} = -(k_1 + k_2) B \frac{1}{HR} \quad (12)$$

Arrhenius relation of kinetic constants with temperature is given by Eq. (13) and Eq. (14) respectively for reaction 1 and reaction 2.

$$k_1 = A_1 \exp\left(\frac{-E_1}{RT}\right) \quad (13)$$

$$k_2 = A_2 \exp\left(\frac{-E_2}{RT}\right) \quad (14)$$

Values of the Frequency factor and Activation energy of both reactions are found by minimizing the objective function as given by Eq. (15).

$$F(A_1, E_1, A_2, E_2) = \sum_{j=1}^n (W_{\text{exp},j} - W_{\text{cal},j})^2 \quad (15)$$

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. (15) 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 [18]. 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 on natural phenomenon such as Genetic Algorithms (GAs), Differential Evolution (DE), etc. [22-24] have 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 by taking Eq. (15) as an objective function to be minimized to find the global optimum set of kinetic parameters. 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, 25, 26].

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 [18, 24]. Based on these heuristics, the values of DE key parameters for the present problem are set as follows:

$$NP = 40, 80, 200, 300$$

$$CR = 0.9$$

$$F = 0.5$$

To find the theoretical value of the residual weight fraction (W), Forward finite difference technique [27, 28] is applied to Eq. (11) to Eq. (14) with the following initial conditions.

At time $t=0$

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

3. RESULTS AND DISCUSSION

Table-1 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 10.0, 25.0, and 40.0 K/s for a sample size of 0.180 mm. The kinetic parameters are found by minimizing the error between experimental and theoretical residual weight fraction. Kinetic parameters are used to find the residual weight fraction and the results are compared with experimental data as shown in Fig. 2.

For the heating rate values of 10, 25 and 40 K/s, model predictions are exactly matching with the experimental values in the temperature range of 600 to 650 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 up to a certain residual weight fraction value. This residual weight fraction value is 0.55, 0.47 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 is decreasing with progress in conversion. In the Model described above [Eq. (5) to Eq. (15)], 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. (13) and Eq. (14).

The activity of solid reactant is expected to decrease with the extent of reaction due to the changes in chemical and pore structure of solid. Based on the above observations, various other models are proposed in which activity decreases as a function of either conversion or activity itself, which are 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 $\left(z = \frac{1-W}{1-W_{\text{final}}}\right)$ as given by Eq. (16).

$$\frac{-da}{dz} = \beta z^n \quad (16)$$

Here β corresponds to a deactivation rate constant. Decrease of activity of solid with conversion is obtained by the integration of Eq. (16) taking activity to be unity when $z = 0$ and is shown by Eq. (17).

$$a = 1 - \left(\frac{\beta}{n+1} \right) z^{n+1} \quad (17)$$

Activity approaches zero when dimensionless conversion (z) goes to unity. So variation of reaction rate constants with conversion are obtained, and are given by Eq. (18) and Eq. (19).

$$k_1 = A_1 (1 - z^{n+1}) \exp\left(\frac{-E_1}{RT}\right) \quad (18)$$

$$k_2 = A_2 (1 - z^{n+1}) \exp\left(\frac{-E_2}{RT}\right) \quad (19)$$

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

Model 3: In this Model, the deactivation process is considered to be directly proportional to activity itself, as given by Eq. (20).

$$\frac{-da}{dz} = \beta a \quad (20)$$

Integration of Eq. (20) and considering the activity to be unity when $z = 0$, yields the reaction rate constants as given by Eq. (21) and Eq. (22):

$$k_1 = A_1 \exp\left[-E_1 \left(\frac{1 + \beta' T z}{RT} \right)\right] \quad (21)$$

$$k_2 = A_2 \exp\left[-E_2 \left(\frac{1 + \beta' T z}{RT} \right)\right] \quad (22)$$

$$\text{where } \beta' = \frac{\beta R}{E} \quad (23)$$

This Model predicts an increase of activation energy of pyrolysis with conversion.

Model-4: For further improvement of *Model-3* to incorporate the non-linear variation, change of activity is expressed as follows:

$$\frac{-da}{dz} = \beta \alpha z^n \quad (24)$$

From this model, the variation of apparent rate constant is found as given by Eq. (25) and Eq. (26).

$$k_1 = A_1 \exp \left[-E_1 \left(\frac{1 + \beta' T z^{n+1}}{RT} \right) \right] \quad (25)$$

$$k_2 = A_2 \exp \left[-E_2 \left(\frac{1 + \beta' T z^{n+1}}{RT} \right) \right] \quad (26)$$

where

$$\beta' = \left(\frac{\beta}{n+1} \right) \frac{R}{E} \quad (27)$$

This Model also predicts an increase in activation energy with fractional conversion. For a special case of $n=0$, *Model-4* reduces to *Model-3*.

Values of the Frequency factors (A_1 and A_2), Activation Energies (E_1 and E_2), deactivation rate constant (β) and power of fractional conversion (n) of both reactions are found by minimizing the objective function as given by Eq. (28) is minimized and the global optimum set of kinetic parameters is found out.

$$F(A_1, E_1, A_2, E_2, \beta, n) = \sum_{j=1}^n (W_{\text{exp},j} - W_{\text{cal},j}) \quad (28)$$

It may be noted that Eq. (28) is a modified and an improved version of Eq. (15), which takes into account of the changes that are incorporated in *Models 2-4*. Using Differential Evolution algorithm, the objective function [Eq. (28)] is minimized and the global optimum set of kinetic parameters is found out. To find the theoretical value of residual weight fraction (W), forward finite difference technique is applied to Eq. (11), Eq. (12), Eq. (18) and Eq. (19) for *Model-2*. Eq. (21) and Eq. (22) are used to find the residual weight fraction of the biomass for *Model-3* along with Eq. (11) and Eq. (12). For values of theoretical value of W in *Model-4*, Eq. (25) and Eq. (26) are used in combination with Eq. (11) and Eq. (12). 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 ($A_1, E_1, A_2, E_2, n, \beta$) for *Model-1* to 4 for heating rates of 10, 25 and 40 K/s for the ground hazelnut shell biomass sample of 0.180 mm size and reported in Table-2. For heating rate value of 10 K/s, *Model-2* gives minimum value of objective function amongst various proposed models. Whereas *Model-3* fits better and gives minimum objective function value for the heating rate of 25 and 40 K/s. It could be deceptive to go totally by objective function value (the sum of the square of the difference between experimental and model simulated value) for comparing the performance of various models because of the reasons given below. The objective function values obtained for *Model-2* and *Model-3* are 0.01949137 and 0.028003858 respectively for heating rate value of 10 K/s (Table-2). For the temperature values of 600, 625 and 700K, *Model-2* simulated values are exactly matching with experimental data; for the temperature values of 550, 800, and 900 K, *Model-3* predictions are much better than *Model-2* predictions; and for the temperature value of

425 K, both *Model-2* and *Model-3* are predicting same value (Fig. 3). However, *Model-3* predictions and trends obtained of residual weight fraction better represent the experimental data in the entire temperature range in spite of having a higher objective function value over *Model-2*. Kinetic parameters reported in Table-2 are used to find residual weight fraction which is compared with the experimental data as shown in Fig. 3, Fig. 4 and Fig. 5 for the heating rate of 10, 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. Fig. 4 and Fig. 5 show that *Model-3* predictions fit better with the experimental data amongst the simulated results with various models in the entire temperature range for the heating rate values of 25 and 40 K/s. The objective function value is least for *Model-3* and reported in Table-2 for the heating rate values of 25 and 40 K/s.

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 models consider 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 by 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 Models, which consider the kinetic scheme of biomass decomposition by two competing reactions giving volatile gaseous and solid charcoal products, better represent the thermogravimetry results than apparent decomposition rate expression.
- Evolutionary algorithms such as Differential Evolution have a better global perspective than the traditional optimization techniques for the cases where the objective function to be optimized is highly complex and non-linear in nature.
- For lower heating rate (10 K/s) *Model-2*, which predicts a decrease of frequency factor of pyrolysis rate constants with conversion, gave best results when compared with experimental data amongst various proposed models.
- For higher heating rate (25 and 40 K/s), which predicts an increase of activation energy of pyrolysis rate constants with conversion, gave best results when compared with experimental data amongst various proposed models.
- An interesting phenomenon is observed that objective function value (the sum of the square of the difference between experimental and model simulated value) should not be

the only criteria for deciding the best fit model as it may be fitting with few experimental data points exactly and vary widely for rest of the experimental data points.

- To decide the best fit model not only the objective function value but the trends obtained using optimum parameters has to be carefully examined for each data point.

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
SA	Surface area of the particle
t	Time
T_0	Initial Temperature
V	Volume of the particle
W	Residual Weight Fraction

W_{exp} Experimental value of the residual weight fraction

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

z Normalized Conversion

Greek Letters

β Deactivation Rate Constant

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

Table-2. Kinetic Parameters of reaction 1 and reaction 2 for the pyrolysis of hazelnut shell

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

Heating Rates (K/s)	Kinetic Parameters				Objective Function Value [Eq. (15)]
	A_1	E_1	A_2	E_2	
10	9.99999870e+014	1.830963883e+005	9.99999870e+014	1.860584981e+005	0.020025030
25	5.771498789e+014	1.780711826e+005	9.99999870e+014	1.818287369e+005	0.028319044
40	9.99999870e+014	1.789020459e+005	9.99999870e+014	1.784195956e+005	0.046808721

Table-2. Kinetic Parameters of reaction 1 and reaction 2 for the pyrolysis of hazelnut shell

Kinetic Parameters								
Heating Rate (K/s)	Model	A_1 (1/s)	E_1 (J/mol)	A_2 (1/s)	E_2 (J/mol)	β	n	Objective Function Value [Eq. (15) for Model-1 and Eq. (28) for Model-2 to 4]
10.0	1	9.99999870e+014	1.830963883e+005	9.99999870e+014	1.860584981e+005	-	-	0.020025030
	2	8.101628677e+014	1.820082250e+005	6.525157449e+014	1.839203710e+005	-	8.354	0.019491337
	3	1.631473979e+014	1.687529179e+005	3.817607903e+014	1.770171303e+005	4.000	-	0.028003858
	4	9.998664072e+014	1.830208026e+005	8.531165618e+014	1.849042580e+005	4.000	10.000	0.023827228
25.0	1	5.771498789e+014	1.780711826e+005	9.99999870e+014	1.818287369e+005	-	-	0.028319044
	2	4.802800875e+014	1.771581429e+005	7.671474063e+014	1.805251955e+005	-	6.891	0.027951533
	3	2.826228910e+011	1.348690973e+005	3.820552102e+010	1.273586962e+005	5.504	-	0.016778276
	4	3.466431937e+014	1.755514367e+005	8.786262004e+014	1.812851772e+005	6.831	9.459	0.028126398
40.0	1	9.99999870e+014	1.789020459e+005	9.99999870e+014	1.784195956e+005	-	-	0.046808721
	2	9.928115823e+014	1.789845779e+005	9.928071716e+014	1.785507511e+005	-	7.445	0.111616604
	3	1.354623177e+012	1.375183991e+005	2.255813493e+011	1.320127398e+005	10.000	-	0.017888651
	4	9.99999870e+014	1.788643021e+005	9.99999870e+014	1.783705206e+005	4.000	10.000	0.045454113

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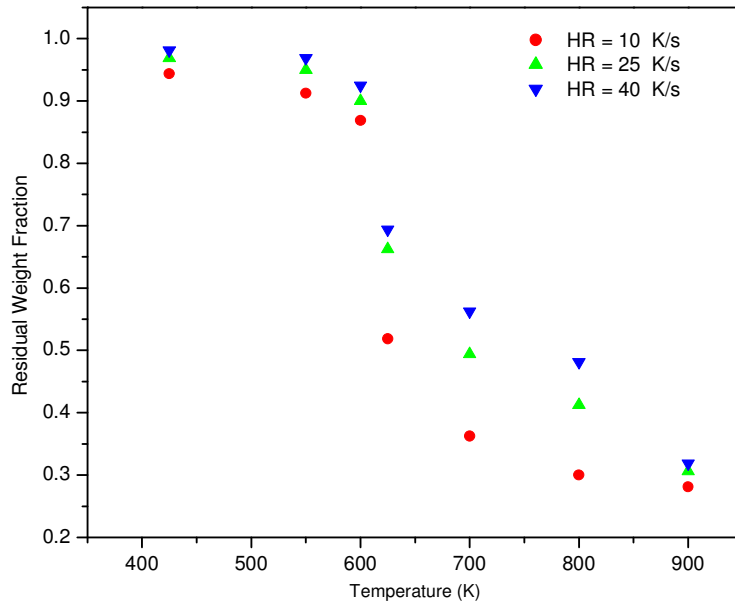


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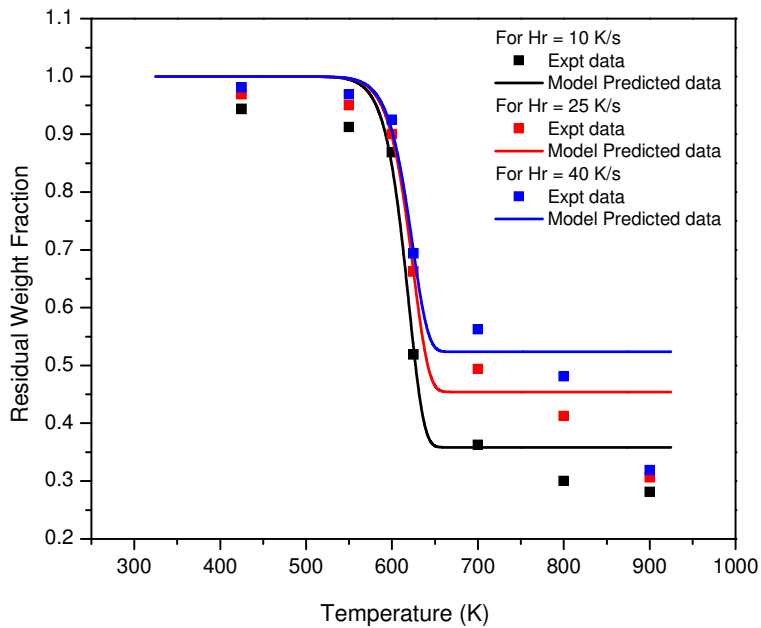


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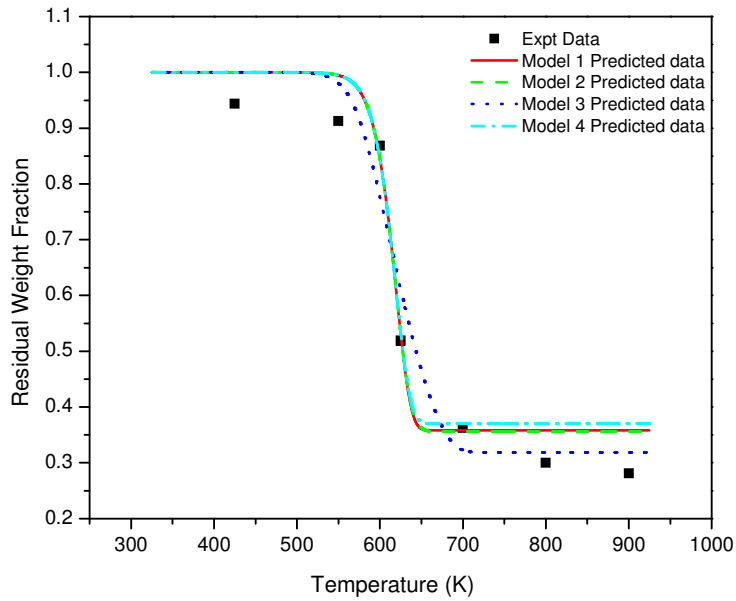


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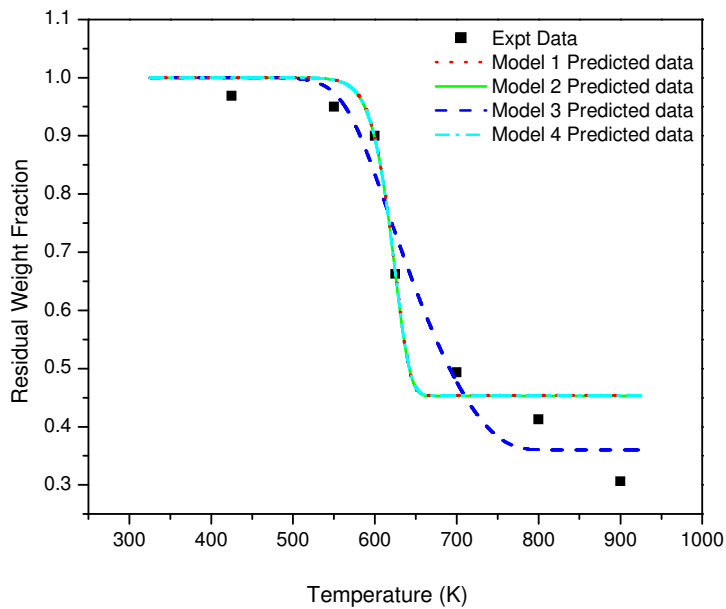


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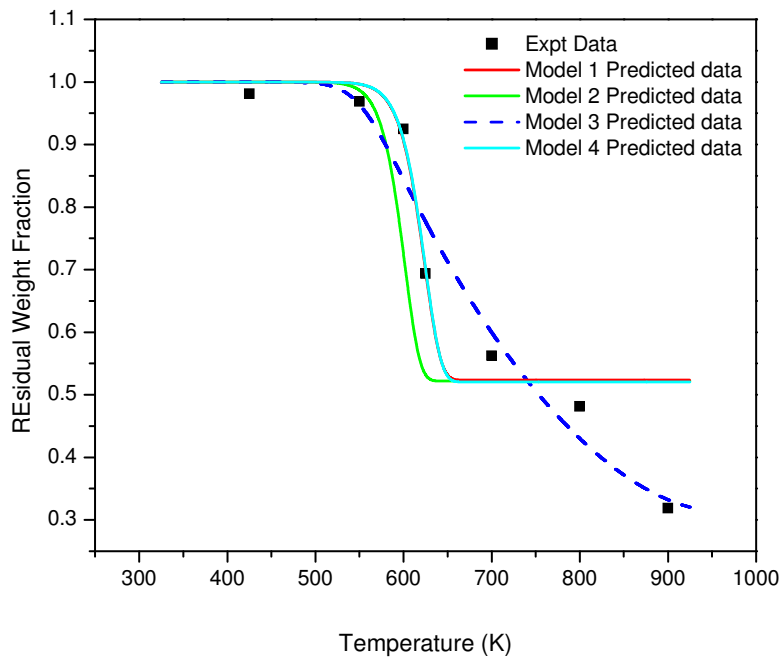


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