

## Mathematical Modeling

1. First order model
2. Kinetic reaction scheme model
3. ODE solver
4. Reaction order determination
  - a. Differential method
  - b. Integral method

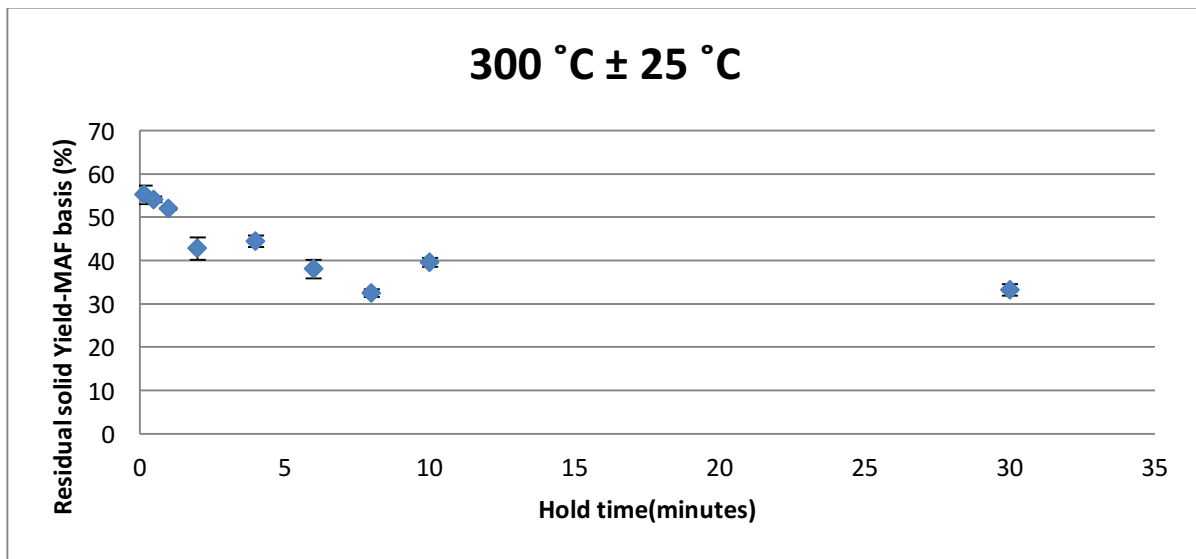
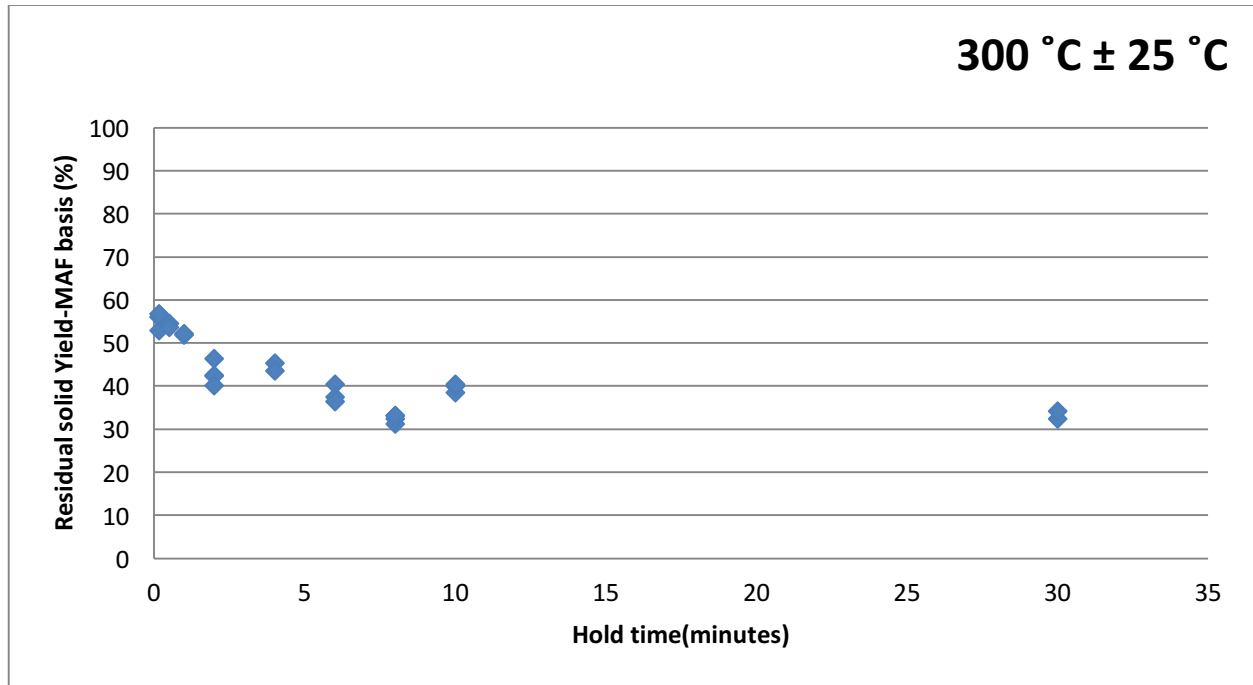
## Data generated

Residual solid vs hold time data is collected over a temperature range of 400, 500, 600 & 700 °C.

Data obtained was filtered by removing the outliers.

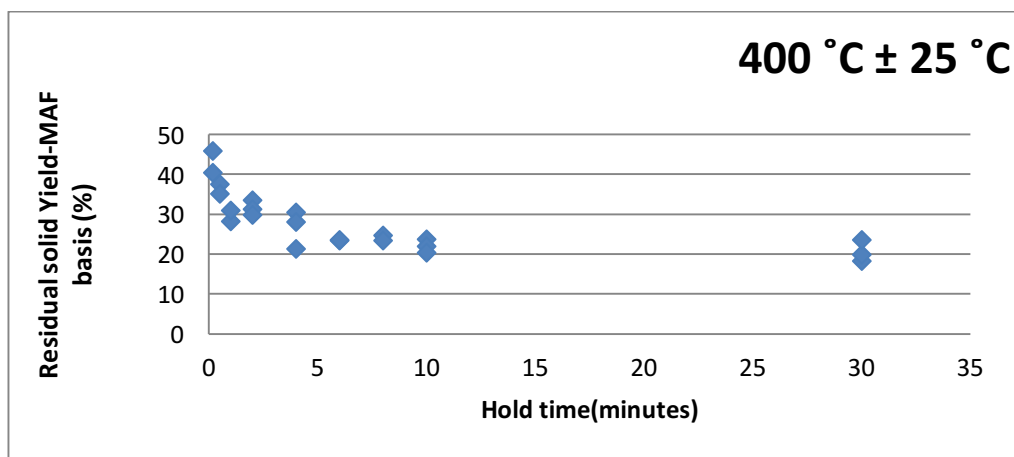
Hold time(mins)	% Residual solid yield(MAF basis)
0.1667	52.7729
0.1667	55.9805
0.1667	56.7660
0.5	54.4998
0.5	53.5553
1	51.7697
1	52.1714
2	42.2515
2	42.4806
2	46.3238
2	40.0580
4	45.3269
4	43.5123
6	40.3193
6	37.4201
6	36.2920
8	31.1744
8	33.0860
8	32.3597
8	33.0860
10	38.4173
10	39.8824
10	40.2891
30	32.3012

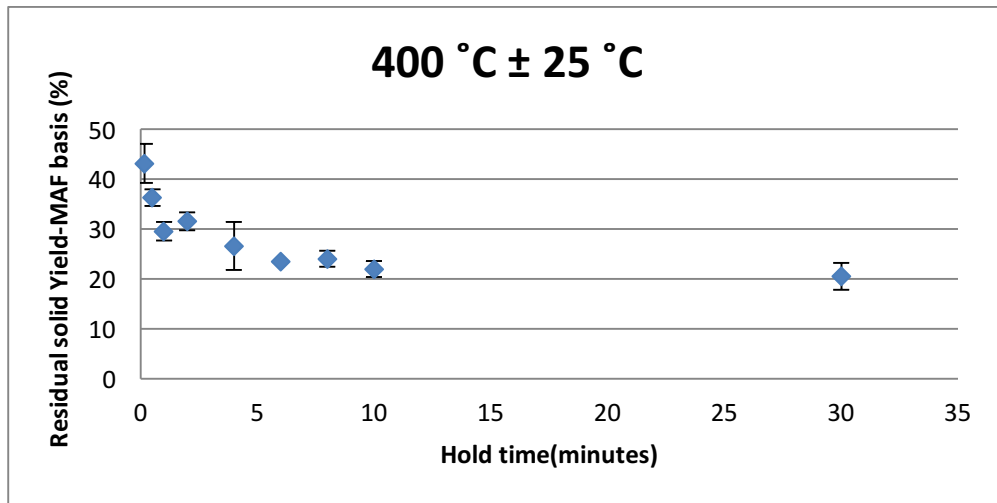
30	34.1617
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S No.	Hold time(mins)	% Residual solid yield(ash free basis)
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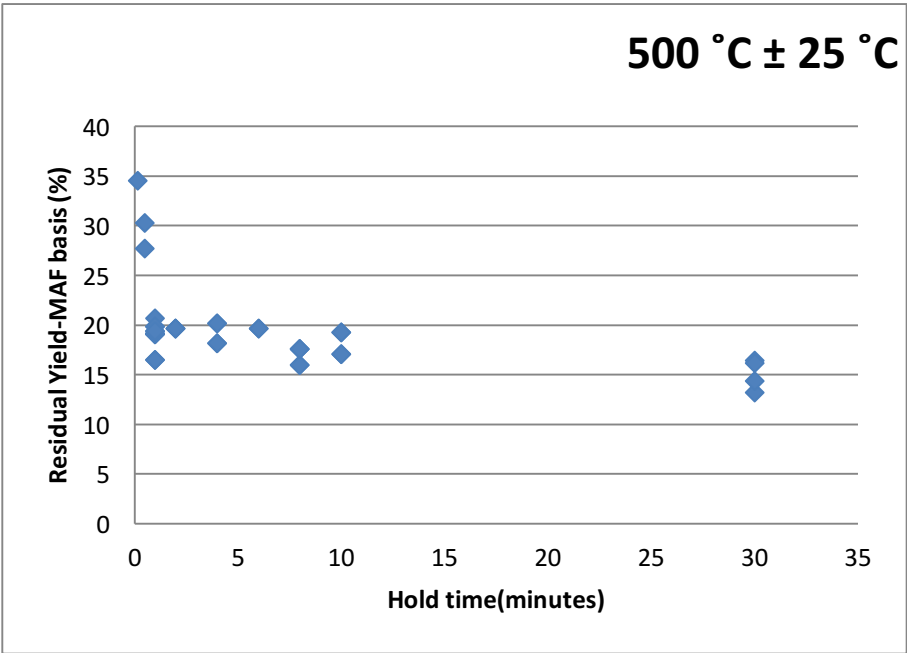
1	0.1667	45.8806
2	0.1667	40.3393
3	0.5	37.4648
4	0.5	35.0780
5	1	28.1814
6	1	30.8573
7	2	33.4374
8	2	31.2522
9	2	29.8405
10	4	30.4821
11	4	27.9544
12	4	21.2122
13	6	23.3201
14	6	23.5024
15	8	24.6001
16	8	23.3815
17	10	23.6287
18	10	21.9118
19	10	20.3694
20	30	18.1536
21	30	19.8741
22	30	23.4523

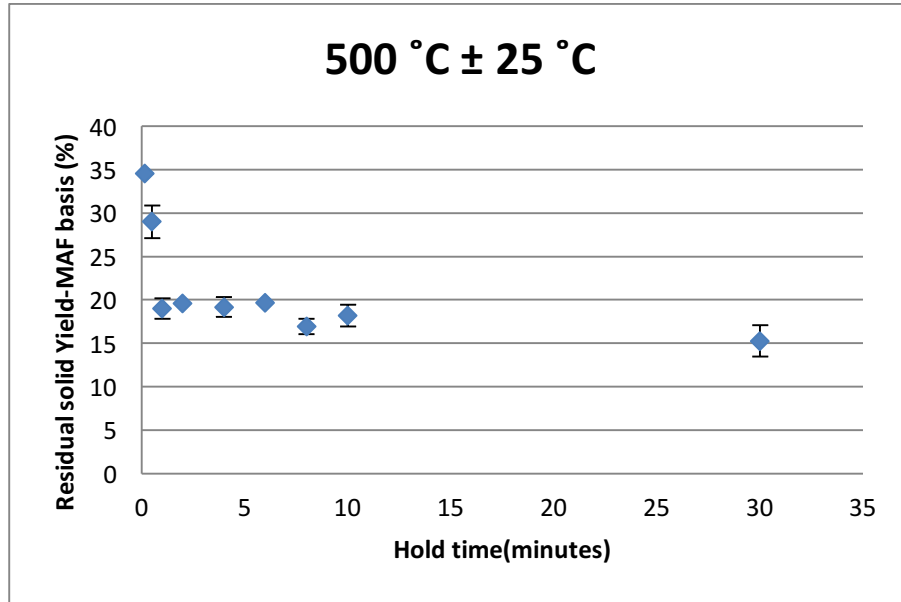




Date	Hold time(mins)	% Residual Solid yield(ash free basis)
1	0.1667	34.56593
2	0.5	27.68427
3	0.5	30.29278
4	1	20.6717
5	1	19.8155
6	1	19.1567
7	1	19.0985
8	1	16.4723
9	1	19.1255
10	1	19.4266
11	1	19.81546
12	1	19.15669
13	1	19.09855
14	1	16.4723
15	1	19.1255
16	1	19.42664
17	2	19.6209
18	2	19.62091
19	2	19.62091
20	4	20.17485
21	4	18.17479
22	4	20.17485
23	4	18.17479
24	6	19.65257
25	6	19.65257
26	8	17.6086

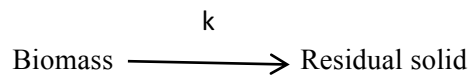
27	8	15.98978
28	8	17.60865
29	8	15.98978
30	8	17.60865
31	10	19.28572
32	10	17.10301
33	10	19.28572
34	10	17.10301
35	30	16.4300
36	30	16.1886
37	30	13.1905
38	30	14.38916





### First Order model

#### 1 First order linear fit



Let us use the following chemical equation:

The decrease in the concentration of biomass overtime can be written as:

$$-dC_A / dt = kC_A$$

Rearrangement yields the following:  $dC_A / C_A = -k dt$

Integrate the equation, which yields:  $\ln C_A = -kt + C$

Evaluate the value of C (the constant of integration) by using boundary conditions. Specifically, when  $t = 0$ ,  $C_A = C_{A0}$ .  $C_{A0}$  is the original starting concentration of A.

Substituting into the equation, we obtain:  $\ln [C_A] = -k(0) + C$ .

Therefore,  $C = \ln C_{A0}$

We now can write the integrated form for first-order kinetics, as follows:

$$\ln C_A = -kt + \ln C_{A_0}$$

This last equation can be rearranged into several formats, such as:

$$\ln (C_A / C_{A_0}) = -kt$$

$$C_A / C_{A_0} = 1-X$$

Where X is the conversion of biomass to residual solid

$$\text{Therefore, } \ln (1-X) = -kt$$

The graph of  $\ln(1/(1-X))$  vs t gives straight line with slope k, i.e rate constant..

### Activation Energy

The relationship between the rate constant k and the temperature is given by the Arrhenius equation given by the expression;

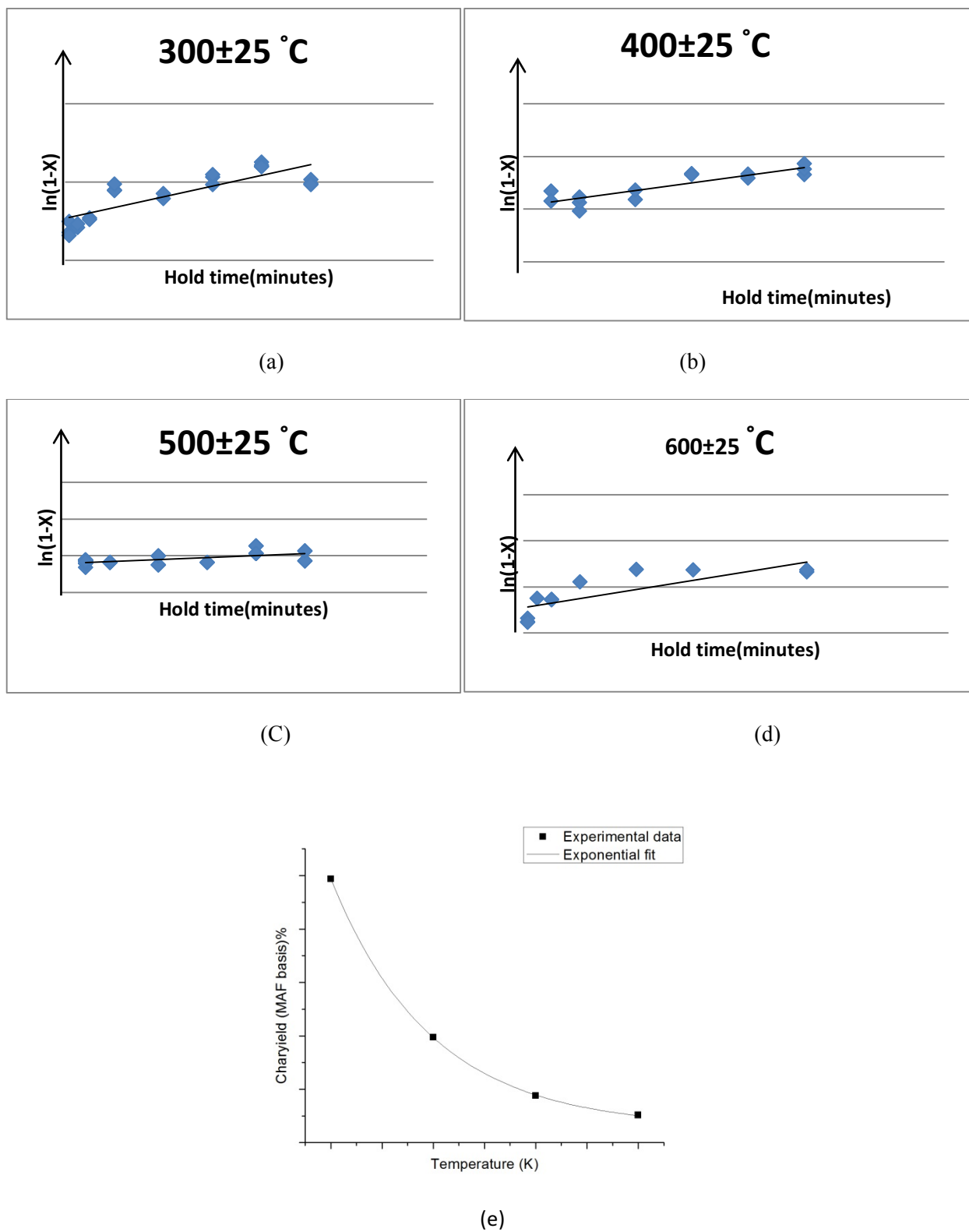
$$k = A \exp^{-\left(\frac{E_a}{RT}\right)} \quad (4)$$

Where A is the frequency factor and  $E_a$  is the apparent activation energy. The rate constants were calculated from Figure which is the slopes from the graph and are given in Table 5. To determine the activation energy, an Arrhenius graph of  $\ln k$  vs  $1/T$  ( $K^{-1}$ ) was plotted which an Arrhenius plot is obtained and the activation energy also obtained from the slope of the graph (Figure 4.3) using Equation 4 to obtain Equation 5

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

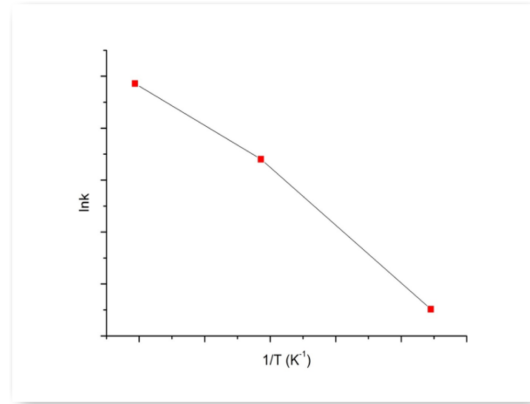
This is equivalent to  $y = mx + c$  and therefore the slope from the graph of  $\ln k$  vs  $1/T$  ( $K^{-1}$ ) is equivalent to  $E_a/R$ , which means  $E_a = \text{slope} \times R$ .

From the figure 4.3 slope and intercept can be obtained



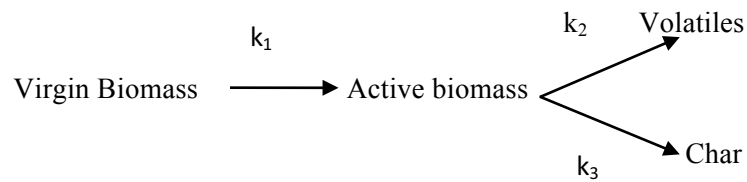
**Figure 4.2** a,b,c,d Graphs represents liner fit for first order rate equation at 400 °C, 500 °C, 600 °C & 700 °C probe temperature respectively. ( e ) charyield data at various temperatures 400 °C, 500 °C, 600 °C & 700





**Figure 4.3** Arrhenius plot of  $\ln k$  vs  $1/T$  ( $K^{-1}$ ) for hydrolysis of biomass to residue

#### Kinetic Reaction model



**Figure 4.3 2:** Koufopoulos model for biomass pyrolysis

$$\frac{d\rho_w}{dt} = -k_1 \rho_w \quad (1)$$

$$\frac{d\rho_a}{dt} = k_1 \rho_w - (k_2 + k_3) \rho_a \quad (2)$$

$$\frac{d\rho_c}{dt} = v_c k_1 \rho_a \quad (3)$$

**Assumptions:**

- 1)  $k_1 \gg k_2 \& k_3$
- 2) Selectivity is constant

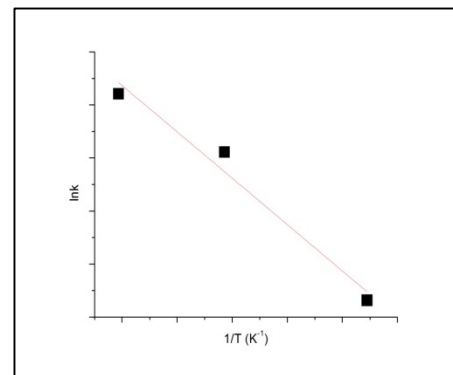
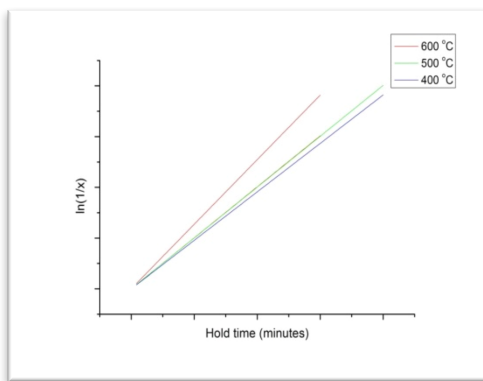
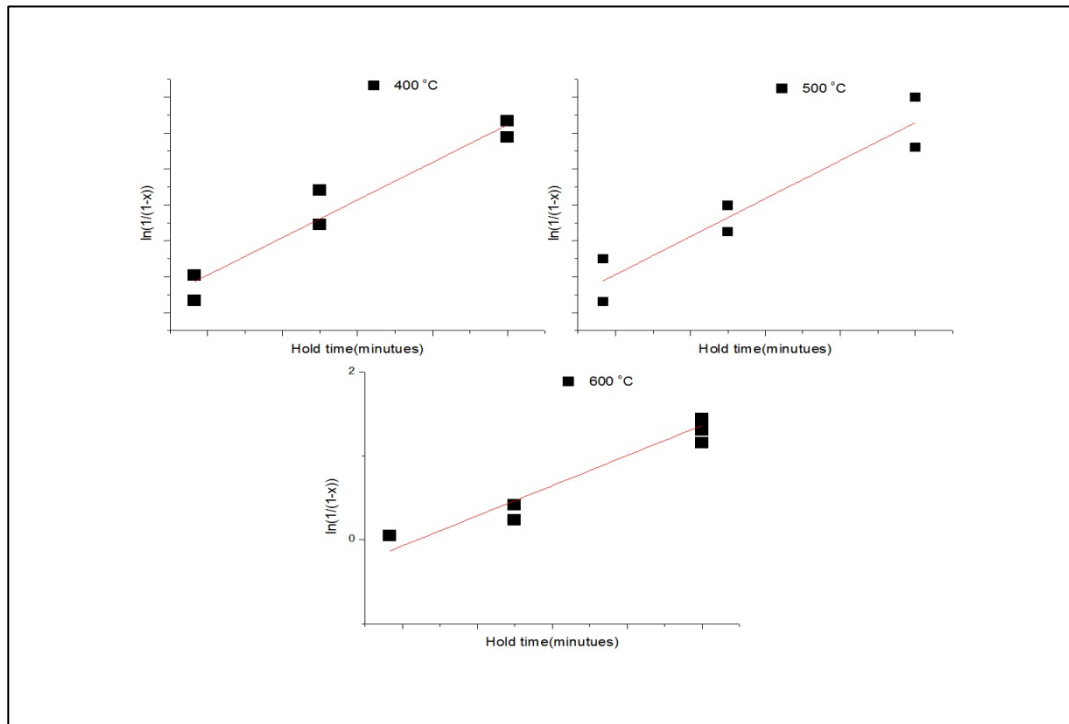
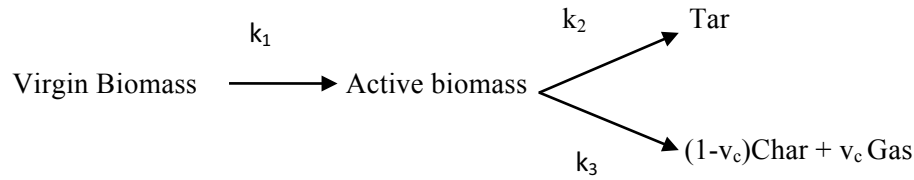


Figure 6: (a) Liner fit for first order devolatalization of biomass (b) Arrhenius plot of  $\ln(k)$  vs  $1/T$  ( $K^{-1}$ ) for hydrolysis of biomass to char

### 4.3 Model Development

Biomass kinetics is modeled using Broido-Shafizadeh scheme (Broido and Weinstein, 1971; Bradbury and Shafizadeh, 1979), extended to include secondary reactions (Liden et al., 1988): In most cases, kinetic models consist of a one-step global reaction whose data are estimated to best fit experimental weight loss curves. The main drawback of these kinetic models is that they are generally based on the assumption of a constant ratio of the final volatile to char yield. Consequently, they cannot predict, even from the qualitative point of view, the dependence of product yields on reactor temperature and heating rate, which is of fundamental importance in reactor design and operation. Contrary to primary reactions, very few studies (Di Blasi, 1993) have been made to quantify the extent of secondary reactions.



**Figure 4.3** Biomass pyrolysis model by Miller and Bellan [23].

The following assumptions are made in modelling of biomass pyrolysis: (1) Heat and momentum transfer effects are neglected; (2) Reaction volume is considered constant; (3) No particle shrinkage and surface regression;

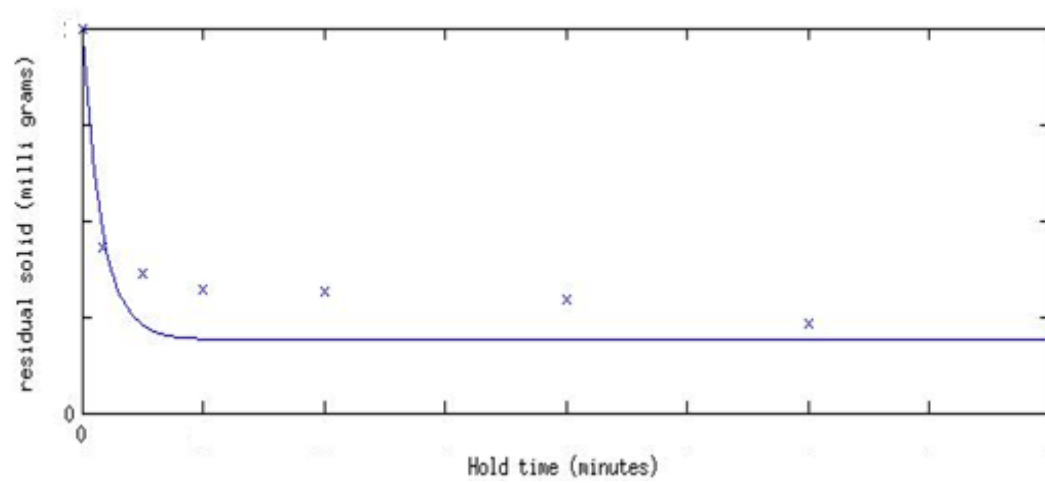
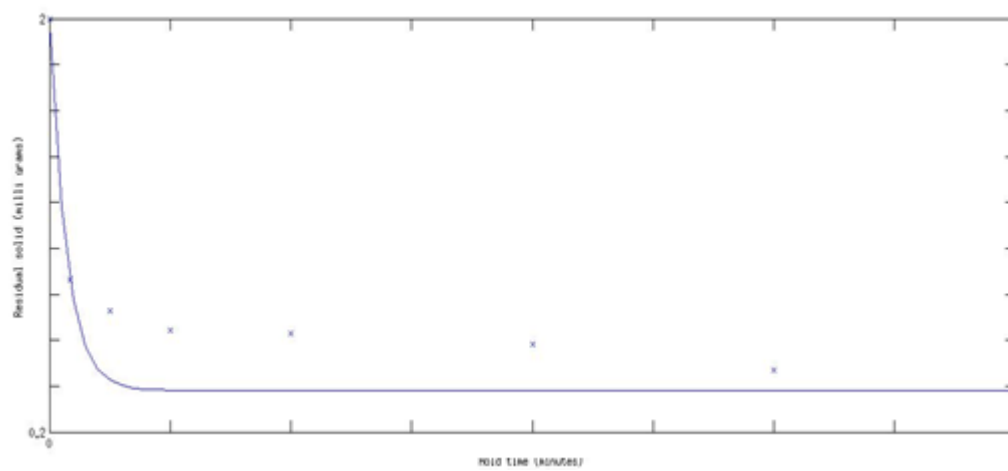
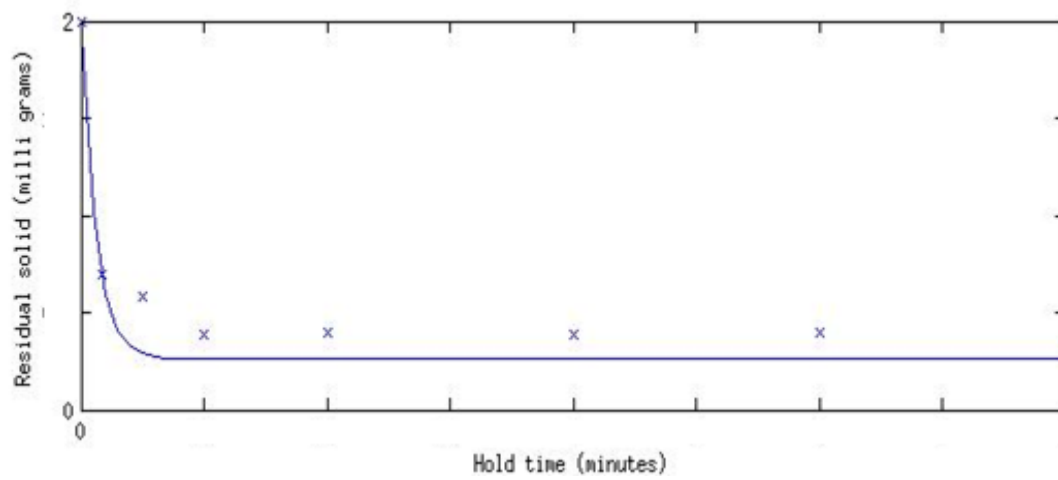
This model of ordinary differential equations describes the most general case of biomass pyrolysis i.e when internal heat transfer and momentum transfer are neglected and chemical kinetics is considered. Simplified versions are used when certain processes are no longer controlling.

$$\frac{d\rho_w}{dt} = -k_1 \rho_w \quad (1)$$

$$\frac{d\rho_a}{dt} = k_1 \rho_w - (k_2 + k_3) \rho_a \quad (2)$$

$$\frac{d\rho_c}{dt} = v_c k_1 \rho_a \quad (3)$$

Where  $\rho_w$ ,  $\rho_a$ ,  $\rho_c$  are densities of biomass, active biomass and char produced respectively.



Matlab code to generate the fit:

### One parameter fit model:

```
function dx = f(t,x)
global b;
dx(1,1) = -b(1)*x(1)*x(2);
dx(2,1) = -b(1)*x(1)*x(2);
end

function S = Sfun1D(b)
% computation of an error function for an ODE model
% INPUT: b - vector of parameters
global tdata xdata x0;
%% numerical integration set up
tspan = [0:0.1:max(tdata)];
[tsol,xsol] = ode23(@f,tspan,x0);
%% plot result of the integration
plot(tdata,xdata,'x','MarkerSize',10);
hold on
plot(tsol,xsol(:,1));
hold off
drawnow
%% find predicted values x(tdata)
xpred = interp1(tsol,xsol(:,1),tdata);
%% compute total error
S = 0;
for i = 1:length(tdata)
S = S + (xpred(i)-xdata(i) )^2;
end
end
function paramfit1D
% main program for fitting parameters of an ODE model to data
% error function is defined in the file Sfun1D.m
clearvars -global
global tdata xdata x0 b;
%% declaring data for the model
% time - x values
tdata(1) = 0; xdata(1) = 3.1;
tdata(2) = 5; xdata(2) = 2.35;
tdata(3) = 10; xdata(3) = 2;
tdata(4) = 20; xdata(4) = 1.6;
tdata(5) = 30; xdata(5) = 0.8;
tdata(6) = 40; xdata(6) = 0.45;
tdata(7) = 50; xdata(7) = 0.25;
%% initial conditions
x0(1) = 3.1;
```

```

x0(2) = 7.57;
%% initial guess of parameter values
b(1) = 0.007;
%% minimization step
[bmin, Smin] = fminsearch(@Sfun1D,b);
disp('Estimated parameters b(i):');
disp(bmin)
disp('Smallest value of the error S:');
disp(Smin)
end

```

### Three parameters fit model:

```

function dx = f(t,x)
global b;
dx(1,1) = -b(1)*(( x(1)/b(3) ) - x(1) );
dx(2,1) = -b(1)*(50/49.78)*(( x(1)/b(3) ) - x(1) ) -
b(2)*x(2)*x(3);
dx(3,1) = -b(2)*x(2)*x(3);
end
function S = Sfun1D(b)
% computation of an error function for an ODE model
% INPUT: b - vector of parameters
global tdata xdata x0;
%% ODE model
% (nested function, uses parameters b(1) and b(2) of the main
function)
%% numerical integration set up
tspan = [0:0.1:max(tdata)];
[tsol,xsol] = ode23(@f,tspan,x0);
%% plot result of the integration
plot(tdata,xdata,'x','MarkerSize',10);
hold on
plot(tsol,(xsol(:,1)));
hold off
drawnow
%% find predicted values x(tdata)
xpred = interp1(tsol,xsol(:,1),tdata);
%% compute total error
S = 0;
for i = 1:length(tdata)
S = S + ( xpred(i)-xdata(i) )^2;
end
end
function paramfit1D
% main program for fitting parameters of an ODE model to data

```

```

% the model and the error function are defined in the file
Sfun1D.m
clearvars -global
global tdata xdata x0 b;
%% declare data for the model
% time - x value
tdata(1) = 0; xdata(1) = 3.1;
tdata(2) = 5; xdata(2) = 2.35;
tdata(3) = 10; xdata(3) = 2;
tdata(4) = 20; xdata(4) = 1.6;
tdata(5) = 30; xdata(5) = 0.8;
tdata(6) = 40; xdata(6) = 0.45;
tdata(7) = 50; xdata(7) = 0.25;
%% initial condition
x0(1) = 3.1;
x0(2) = 0;
x0(3) = 7.57;
%% initial guess of parameter values
b(1) = 0.043;
b(2) = 1.5;
b(3) = 0.5;
%% minimization step
[bmin, Smin] = fminsearch(@Sfun1D,b);
disp('Estimated parameters b(i):');
disp(bmin)
disp('Smallest value of the error S:');
disp(Smin)
end

```

### Order fit:

#### Differential Model:

Rate law can be written as

$$\left[ -\frac{dC_A}{dt} = kC_A^\alpha \right]$$

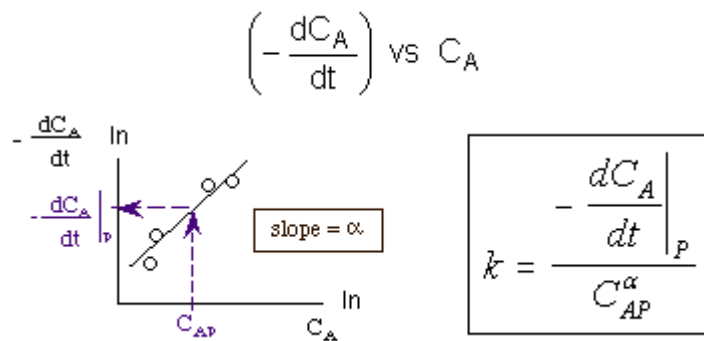
Taking the natural log of

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

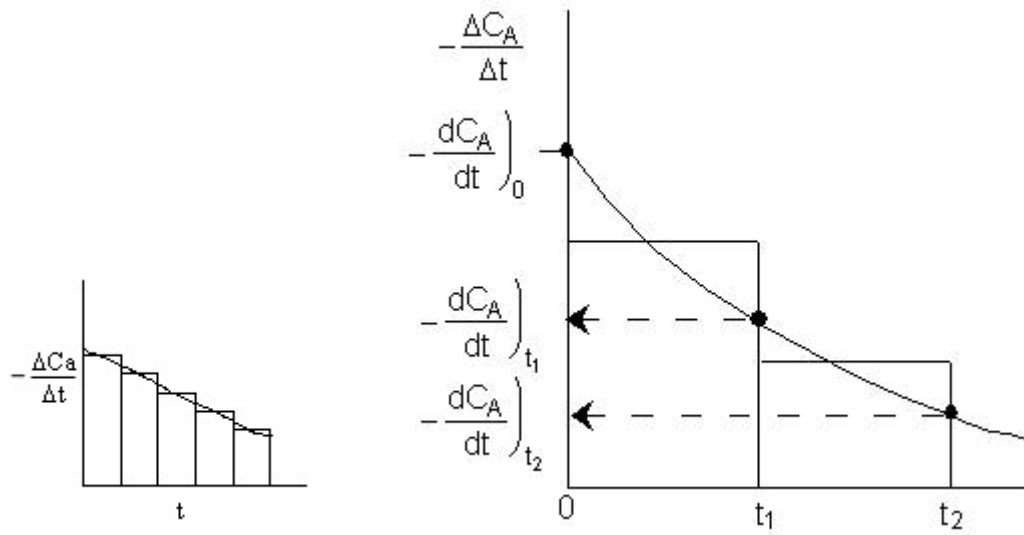
There are three ways to find the order of the reaction from concentration-time data

1. Graphical method
2. Polynomial
3. Finite difference method
4. Non-linear least square fit analysis

#### Graphical Method:







The reaction order can be found from a ln-ln plot and the slope gives us the order and the intercept gives rate constant.

#### Polynomial method:

Concentration

$$C_A = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4$$

$$\frac{dC_A}{dt} = a_1 + 2a_2t + 3a_3t^2 + 4a_4t^3$$