```
% ****************************************************************
%
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%
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%  please give appropriate credit to the authors by citing "Hydrothermal
%  carbonization kinetics of lignocellulosic agro-wastes: experimental data and
%  modeling".
%
% ****************************************************************


clear all
close all
clc

global c_v0 tspan Ca Cl Cb Cd tspan2 k1 k2 k3 k4 k5 n

lb=[];
ub=[];

options = optimset('Algorithm','levenberg-marquardt','Display','off');

% loop for the estimation of the parameters of the reaction kinetics
for i=1:3 % calculate the parameters for three different temperatures (for olive
trimmings: T=180°C, T=220°C, T=250°C

    if i==1 % T = 180°C

        % temperature in K
        temperatura_1=180+273.15;


        % Experimental data for the concentrations
        Ca=[0.4830  0           0           0           0           0       0
]/(0.031*12); %biomass
        Cl=[0       0.0313      0.0577      0.0815      0.0736      0.0384
0.0499]/(0.031*12); %liquid
        Cb=[0       0.4501      0.4185      0.3928      0.3981      0.4297
0.4222]/(0.031*12); %primary+secondary char
        Cd=[0       0.0015      0.0068      0.0087      0.0113      0.0149
0.0109]/(0.031*12); %gas1+gas2
        % time instants corresponding to the experimental measurements
        tspan=[0 0.27 0.77 1.27 3.27 6.27 8.27];

        c_v0(1)=Ca(1);  % biomass
        c_v0(2)=0;      % liquid
        c_v0(3)=0;      % secondary char
        c_v0(4)=0;      % primary char
        c_v0(5)=0;      % gas 1
        c_v0(6)=0;      % gas 2

        % Initial guess for the parameters used in the reaction kinetics
```

```
        % This initial guess has been obtained as a result of a nonlinear
optimization process
        % based on a reduced model with only 5 independent parameters, fixing k4=0.

        k1 = 0.2;
        k2 = 0.0300;
        k3 = 1.0;
        k4 = 0;
        k5 = 0.1;
        n  = 1.1;

        % initial guess for the parameters written as a vector
        par0=[k1,k2,k3,k4,k5,n];
    end

    if i==2 % T = 220°C

        % temperature in K
        temperatura_2=220+273.15;


        % Experimental data for the concentrations
        Ca=[0.4830  0           0           0           0           0       0
]/(0.031*12); %biomass
        Cl=[0       0.0676      0.0670      0.0959      0.0928      0.0788
0.0617]/(0.031*12); %liquid
        Cb=[0       0.4075      0.4001      0.3713      0.3656      0.3761
0.3913]/(0.031*12); %primary+secondary char
        Cd=[0       0.0080      0.0159      0.0158      0.0246      0.0281
0.0300]/(0.031*12); %gas1+gas2
        % time instants corresponding to the experimental measurements
        tspan=[0 0.36 0.86 1.36 3.36 6.36 8.36];

        c_v0(1)=Ca(1);  % biomass
        c_v0(2)=0;      % liquid
        c_v0(3)=0;      % secondary char
        c_v0(4)=0;      % primary char
        c_v0(5)=0;      % gas 1
        c_v0(6)=0;      % gas 2

        % Initial guess for the parameters used in the reaction kinetics
        % This initial guess has been obtained as a result of a nonlinear
optimization process
        % based on a reduced model with only 5 independent parameters, fixing k4=0.

        k1 = 0.3;
        k2 = 0.07;
        k3 = 1.1;
        k4 = 0;
        k5 = 0.15;
        n  = 1.5;


        % initial guess for the parameters written as a vector
        par0=[k1,k2,k3,k4,k5,n];
    end
```

```
    if i==3 % T = 250°C

        % temperature in K
        temperatura_3=250+273.15;


        % Experimental data for the concentrations
        Ca=[0.4830  0           0           0           0           0       0
]/(0.031*12); %biomass
        Cl=[0       0.0813      0.0940      0.1156      0.1161      0.0936
0.1096]/(0.031*12); %liquid
        Cb=[0       0.3861      0.3638      0.3367      0.3330      0.3508
0.3379]/(0.031*12); %primary+secondary char
        Cd=[0       0.0156      0.0252      0.0307      0.0339      0.0359
0.0355]/(0.031*12); %gas1+gas2
        % time instants corresponding to the experimental measurements
        tspan=[0 0.47 0.97 1.47 3.47 6.47 8.47];

        c_v0(1)=Ca(1);  %biomass
        c_v0(2)=0;      %liquid
        c_v0(3)=0;      %secondary char
        c_v0(4)=0;      %primary char
        c_v0(5)=0;      %gas1
        c_v0(6)=0;      %gas2

        % Initial guess for the parameters used in the reaction kinetics
        % This initial guess has been obtained as a result of a nonlinear
optimization process
        % based on a reduced model with only 5 independent parameters, fixing k4=0.

        k1 = 0.5;
        k2 = 0.1;
        k3 = 1.4;
        k4 = 0.0000;
        k5 = 0.2;
        n  = 2;

        % initial guess for the parameters written as a vector
        par0=[k1,k2,k3,k4,k5,n];

    end

    % run the nonlinear lsq algorithm of Matlab to find the best set of parameters
    paropt(i,:) = lsqnonlin(@minimiz,par0,lb,ub,options);

    % compute the obtained error
    lsq(i) = minimiz(paropt(i,:));

    % plot the results
    if i==1 % T = 180°C

        tspan2=0:0.01:max(tspan);

        [t,c_v] = ode45(@lsqparafit2,tspan2,c_v0,' ',paropt(i,:));
```

```
paropt_180=paropt(i,:)
lsq_180=lsq(i);
c=c_v(:,3)+c_v(:,4)+c_v(:,1);
g=c_v(:,5)+c_v(:,6);

%vectors to plot the line "time residence=0"
v=tspan;
z=[0.11 0.22];
z_c=[0.4701 0.4500]/(0.031*12);
z_g=[0 0.0003]/(0.031*12);
x=[0.27 0.27];
y=[0 1];

%carbon recovery values of solid and gas at each residence time
Cc_0_180=c(28);
Cc_05_180=c(78);
Cc_1_180=c(128);
Cc_3_180=c(328);
Cc_6_180=c(628);
Cc_8_180=c(828);

Gg_0_180=g(28);
Gg_05_180=g(78);
Gg_1_180=g(128);
Gg_3_180=g(328);
Gg_6_180=g(628);
Gg_8_180=g(828);

%calculate the errors between experimental and modeled carbon
%recovery values for solid and gas
errore_0_180=abs(((Ca(2)+Cb(2))-(c(28)))/(Ca(2)+Cb(2)))*100
errore_05_180=abs(((Ca(3)+Cb(3))-(c(78)))/(Ca(3)+Cb(3)))*100
errore_1_180=abs(((Ca(4)+Cb(4))-(c(128)))/(Ca(4)+Cb(4)))*100
errore_3_180=abs(((Ca(5)+Cb(5))-(c(328)))/(Ca(5)+Cb(5)))*100
errore_6_180=abs(((Ca(6)+Cb(6))-(c(628)))/(Ca(6)+Cb(6)))*100
errore_8_180=abs(((Ca(7)+Cb(7))-(c(828)))/(Ca(7)+Cb(7)))*100

err_0_180=abs(((Cd(2))-(g(28)))/(Cd(2)))*100
err_05_180=abs(((Cd(3))-(g(78)))/(Cd(3)))*100
err_1_180=abs(((Cd(4))-(g(128)))/(Cd(4)))*100
err_3_180=abs(((Cd(5))-(g(328)))/(Cd(5)))*100
err_6_180=abs(((Cd(6))-(g(628)))/(Cd(6)))*100
err_8_180=abs(((Cd(7))-(g(828)))/(Cd(7)))*100

%plot the results
figure();
plot (tspan2,c_v(:,1)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,2)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,3)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,4)/Ca(1), 'LineWidth',3.0);
```

```
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;
        plot (tspan2,c_v(:,5)/Ca(1),'LineWidth',3.0);
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;
        plot (tspan2,c_v(:,6)/Ca(1), 'LineWidth',3.0);
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;

        plot(x,y,'--','LineWidth',3.0,'Color','k');
        set(gca,'fontsize', 26);
        x_leg=xlabel('Time [h]', 'fontsize', 26,'fontweight','bold');
        set(x_leg,'fontsize',26, 'fontweight','bold');
        y_leg=ylabel('Carbon recovery [-]', 'fontsize', 26, 'fontweight','bold');
        set(y_leg,'fontsize',26,'fontweight','bold');
        h_leg=legend({'Biomass','Liquid','Secondary char','Primary char','Gas
1','Gas 2'},'Location','east');
        set(h_leg,'fontsize',26,'fontweight','bold');
        axis([0.0 max(tspan) 0.0 1.0]);
        yticks([0 0.2 0.4 0.6 0.8 1.0]);
        yticklabels({'0.0','0.2','0.4','0.6','0.8','1.0'});


        figure();

        [ax,h1,h2]=plotyy(tspan2,c/Ca(1),tspan2,g/Ca(1));
        hold on
        axis(ax(1),[0 max(tspan)+0.5 0 1])
        axis(ax(2),[0 max(tspan)+0.5 0 0.2])
        set(ax(1),'YTick',0:0.2:1.0)
        set(ax(2),'YTick',0:0.04:0.2)
        set(ax(2),'YTicklabel',0.00:0.04:0.2)
        set(ax,{'ycolor'},{'none';'none'})
        set(ax,{'fontsize'},{24;24}) %asse y2
        set(ax,{'fontweight'},{'bold';'bold'})
        set(ax(1),'YTickLabel',['0.0';'0.2';'0.4';'0.6';'0.8';'1.0'])
        set(ax(2),'YTickLabel',['0.00';'0.04';'0.08';'0.12';'0.16';'0.20'])
        h1.LineWidth=2.0;
        h2.LineWidth=2.0;
        h2.LineStyle='--';

        [px,z1,z2]=plotyy(v,(Cb+Ca)/Ca(1),v,Cd/Ca(1));
        z1.Marker = 'o';
        z2.Marker = 'o';
        z1.MarkerEdgeColor='b';
        z2.MarkerEdgeColor='r';
        z1.MarkerSize=14;
        z2.MarkerSize=14;
        z1.LineStyle = 'none';
        z2.LineStyle = 'none';

        hold on
        plot(z,z_c/Ca(1),'bo','MarkerSize',14);
        axis(px(1),[0 max(tspan)+0.5 0 1])
        axis(px(2),[0 max(tspan)+0.5 0 0.2])
        set(px(1),'YTick',0:0.2:1.0)
        set(px(2),'YTick',0:0.04:0.2)
```

```
        set(px,{'ycolor'},{'none';'none'})
        set(px,{'fontsize'},{24;24})
        set(px,{'fontweight'},{'bold';'bold'})
        set(get(ax(1),'Ylabel'),'String','Carbon recovery in solid [-]')
        set(get(ax(2),'Ylabel'),'String','Carbon recovery in gas [-]')
        set(get(ax(2),'Ylabel'),'fontweight','bold')
        set(ax,{'ycolor'},{'black';'black'})
        set(get(ax(1),'Ylabel'),'Fontsize', 28)
        set(get(ax(2),'Ylabel'),'Fontsize', 28)
        set(px(1),'YTickLabel',['0.0';'0.2';'0.4';'0.6';'0.8';'1.0'])
        set(px(2),'YTickLabel',['0.00';'0.04';'0.08';'0.12';'0.16';'0.20'])
        hold on
        z3=plot(x,y,'--','LineWidth',2.0,'color','k');
        x_leg=xlabel('Time [h]');
        set(x_leg,'fontsize',28);
        h_leg2=legend([h1;h2;z1;z2],{'predicted data - solid','predicted data -
gas','experimental data - solid','experimental data - gas'},'Location','east');
        set(h_leg2,'fontsize',24,'fontweight','bold');

    end


    if i==2 % T = 220°C

        tspan2=0:0.01:max(tspan);

        [t,c_v] = ode45(@lsqparafit2,tspan2,c_v0,' ',paropt(i,:));

        paropt_220=paropt(i,:) %
        lsq_220=lsq(i);
        c=c_v(:,3)+c_v(:,4)+c_v(:,1);
        g=c_v(:,5)+c_v(:,6);

        %vectors to plot the line "time residence=0"
        v=tspan;
        z=[0.11 0.22 0.27];
        z_c=[0.4701 0.4500 0.4501]/(0.031*12);
        x=[0.36 0.36];
        y=[0 1];

        %carbon recovery values of solid and gas at each residence time
        Cc_0_220=c(37);
        Cc_05_220=c(87);
        Cc_1_220=c(137);
        Cc_3_220=c(337);
        Cc_6_220=c(637);
        Cc_8_220=c(837);

        Gg_0_220=g(37);
        Gg_05_220=g(87);
        Gg_1_220=g(137);
        Gg_3_220=g(337);
        Gg_6_220=g(637);
        Gg_8_220=g(837);

        %calculate the errors between experimental and modeled carbon
```

```
%recovery values


errore_0_220=abs(((Ca(2)+Cb(2))-(c(37)))/(Ca(2)+Cb(2)))*100
errore_05_220=abs(((Ca(3)+Cb(3))-(c(87)))/(Ca(3)+Cb(3)))*100
errore_1_220=abs(((Ca(4)+Cb(4))-(c(137)))/(Ca(4)+Cb(4)))*100
errore_3_220=abs(((Ca(5)+Cb(5))-(c(337)))/(Ca(5)+Cb(5)))*100
errore_6_220=abs(((Ca(6)+Cb(6))-(c(637)))/(Ca(6)+Cb(6)))*100
errore_8_220=abs(((Ca(7)+Cb(7))-(c(837)))/(Ca(7)+Cb(7)))*100

err_0_220=abs(((Cd(2))-(g(37)))/(Cd(2)))*100
err_05_220=abs(((Cd(3))-(g(87)))/(Cd(3)))*100
err_1_220=abs(((Cd(4))-(g(137)))/(Cd(4)))*100
err_3_220=abs(((Cd(5))-(g(337)))/(Cd(5)))*100
err_6_220=abs(((Cd(6))-(g(637)))/(Cd(6)))*100
err_8_220=abs(((Cd(7))-(g(837)))/(Cd(7)))*100


%plot the results
figure();
plot (tspan2,c_v(:,1)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,2)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,3)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,4)/Ca(1), 'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,5)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,6)/Ca(1), 'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;


plot(x,y,'--','LineWidth',3.0,'Color','k');
set(gca,'fontsize', 26);
x_leg=xlabel('Time [h]', 'fontsize', 26,'fontweight','bold');
set(x_leg,'fontsize',26, 'fontweight','bold');
y_leg=ylabel('Carbon recovery [-]', 'fontsize', 26, 'fontweight','bold');
set(y_leg,'fontsize',26,'fontweight','bold');
h_leg=legend({'Biomass','Liquid','Secondary char','Primary char','Gas
1','Gas 2'},'Location','east');
set(h_leg,'fontsize',26,'fontweight','bold');
axis([0.0 max(tspan) 0.0 1.0]);
yticks([0 0.2 0.4 0.6 0.8 1.0]);
yticklabels({'0.0','0.2','0.4','0.6','0.8','1.0'});


figure();
```

```
        [ax,h1,h2]=plotyy(tspan2,c/Ca(1),tspan2,g/Ca(1));
        hold on
        axis(ax(1),[0 max(tspan)+0.5 0 1])
        axis(ax(2),[0 max(tspan)+0.5 0 0.2])
        set(ax(1),'YTick',0:0.2:1.0)
        set(ax(2),'YTick',0:0.04:0.2)
        set(ax(2),'YTicklabel',0.00:0.04:0.2)
        set(ax,{'ycolor'},{'none';'none'})
        set(ax,{'fontsize'},{24;24}) %asse y2
        set(ax,{'fontweight'},{'bold';'bold'})
        set(ax(1),'YTickLabel',['0.0';'0.2';'0.4';'0.6';'0.8';'1.0'])
        set(ax(2),'YTickLabel',['0.00';'0.04';'0.08';'0.12';'0.16';'0.20'])
        h1.LineWidth=2.0;
        h2.LineWidth=2.0;
        h2.LineStyle='--';

        [px,z1,z2]=plotyy(v,(Cb+Ca)/Ca(1),v,Cd/Ca(1));
        z1.Marker = 'o';
        z2.Marker = 'o';
        z1.MarkerEdgeColor='b';
        z2.MarkerEdgeColor='r';
        z1.MarkerSize=14;
        z2.MarkerSize=14;
        z1.LineStyle = 'none';
        z2.LineStyle = 'none';


        hold on
        plot(z,z_c/Ca(1),'bo','MarkerSize',14);
        axis(px(1),[0 max(tspan)+0.5 0 1])
        axis(px(2),[0 max(tspan)+0.5 0 0.2])
        set(px(1),'YTick',0:0.2:1.0)
        set(px(2),'YTick',0:0.04:0.2)
        set(px,{'ycolor'},{'none';'none'})
        set(px,{'fontsize'},{24;24})
        set(px,{'fontweight'},{'bold';'bold'})
        set(get(ax(1),'Ylabel'),'String','Carbon recovery in solid [-]')
        set(get(ax(2),'Ylabel'),'String','Carbon recovery in gas [-]')
        set(get(ax(2),'Ylabel'),'fontweight','bold')
        set(ax,{'ycolor'},{'black';'black'})
        set(get(ax(1),'Ylabel'),'Fontsize', 28)
        set(get(ax(2),'Ylabel'),'Fontsize', 28)
        set(px(1),'YTickLabel',['0.0';'0.2';'0.4';'0.6';'0.8';'1.0'])
        set(px(2),'YTickLabel',['0.00';'0.04';'0.08';'0.12';'0.16';'0.20'])
        hold on
        z3=plot(x,y,'--','LineWidth',2.0,'color','k');
        x_leg=xlabel('Time [h]');
        set(x_leg,'fontsize',28);
        h_leg2=legend([h1;h2;z1;z2],{'predicted data - solid','predicted data -
gas','experimental data - solid','experimental data - gas'},'Location','east' );
        set(h_leg2,'fontsize',24,'fontweight','bold');

end



    if i==3 % T = 250°C
```

```
tspan2=0:0.01:max(tspan);

paropt_250=paropt(i,:)

[t,c_v] = ode45(@lsqparafit2,tspan2,c_v0,' ',paropt(i,:));

lsq_250=lsq(i);
c=c_v(:,3)+c_v(:,4)+c_v(:,1);
g=c_v(:,5)+c_v(:,6);


v=tspan;
z=[0.161 0.22 0.27 0.36];
z_c=[0.4701 0.4500 0.4501 0.4075]/(0.031*12);
x=[0.47 0.47];
y=[0 1];

%Carbon recovery values at each residence time
Cc_0_250=c(48);
Cc_05_250=c(98);
Cc_1_250=c(148);
Cc_3_250=c(348);
Cc_6_250=c(648);
Cc_8_250=c(848);

Gg_0_250=g(48);
Gg_05_250=g(98);
Gg_1_250=g(148);
Gg_3_250=g(348);
Gg_6_250=g(648);
Gg_8_250=g(848);


%compute the carbon recovery errors for solid and gas
errore_0_250=abs(((Ca(2)+Cb(2))-(c(48)))/(Ca(2)+Cb(2)))*100
errore_05_250=abs(((Ca(3)+Cb(3))-(c(98)))/(Ca(3)+Cb(3)))*100
errore_1_250=abs(((Ca(4)+Cb(4))-(c(148)))/(Ca(4)+Cb(4)))*100
errore_3_250=abs(((Ca(5)+Cb(5))-(c(348)))/(Ca(5)+Cb(5)))*100
errore_6_250=abs(((Ca(6)+Cb(6))-(c(648)))/(Ca(6)+Cb(6)))*100
errore_8_250=abs(((Ca(7)+Cb(7))-(c(848)))/(Ca(7)+Cb(7)))*100

err_0_250=abs(((Cd(2))-(g(48)))/(Cd(2)))*100
err_05_250=abs(((Cd(3))-(g(98)))/(Cd(3)))*100
err_1_250=abs(((Cd(4))-(g(148)))/(Cd(4)))*100
err_3_250=abs(((Cd(5))-(g(348)))/(Cd(5)))*100
err_6_250=abs(((Cd(6))-(g(648)))/(Cd(6)))*100
err_8_250=abs(((Cd(7))-(g(848)))/(Cd(7)))*100


%plot the results
figure();
plot (tspan2,c_v(:,1)/Ca(1),'LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot (tspan2,c_v(:,2)/Ca(1),'LineWidth',3.0);
```

```
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;
        plot (tspan2,c_v(:,3)/Ca(1),'LineWidth',3.0);
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;
        plot (tspan2,c_v(:,4)/Ca(1), 'LineWidth',3.0);
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;
        plot (tspan2,c_v(:,5)/Ca(1),'LineWidth',3.0);
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;
        plot (tspan2,c_v(:,6)/Ca(1), 'LineWidth',3.0);
        set(gca,'fontsize', 26,'fontweight','bold');
        hold on;

        %plot line of transient time "t=0 h"
        plot(x,y,'--','LineWidth',3.0,'Color','k');
        set(gca,'fontsize', 26);
        x_leg=xlabel('Time [h]', 'fontsize', 26,'fontweight','bold');
        set(x_leg,'fontsize',26, 'fontweight','bold');
        y_leg=ylabel('Carbon recovery [-]', 'fontsize', 26, 'fontweight','bold');
        set(y_leg,'fontsize',26,'fontweight','bold');
        h_leg=legend({'Biomass','Liquid','Secondary char','Primary char','Gas
1','Gas 2'},'Location','east');
        set(h_leg,'fontsize',26,'fontweight','bold');
        axis([0.0 max(tspan) 0.0 1.0]);
        yticks([0 0.2 0.4 0.6 0.8 1.0]);
        yticklabels({'0.0','0.2','0.4','0.6','0.8','1.0'});

        figure();

        [ax,h1,h2]=plotyy(tspan2,c/Ca(1),tspan2,g/Ca(1));
        hold on
        axis(ax(1),[0 max(tspan)+0.5 0 1])
        axis(ax(2),[0 max(tspan)+0.5 0 0.2])
        set(ax(1),'YTick',0:0.2:1.0)
        set(ax(2),'YTick',0:0.04:0.2)
        set(ax(2),'YTicklabel',0.00:0.04:0.2)
        set(ax,{'ycolor'},{'none';'none'})
        set(ax,{'fontsize'},{24;24}) %asse y2
        set(ax,{'fontweight'},{'bold';'bold'})
        set(ax(1),'YTickLabel',['0.0';'0.2';'0.4';'0.6';'0.8';'1.0'])
        set(ax(2),'YTickLabel',['0.00';'0.04';'0.08';'0.12';'0.16';'0.20'])
        h1.LineWidth=2.0;
        h2.LineWidth=2.0;
        h2.LineStyle='--';

        [px,z1,z2]=plotyy(v,(Cb+Ca)/Ca(1),v,Cd/Ca(1));
        z1.Marker = 'o';
        z2.Marker = 'o';
        z1.MarkerEdgeColor='b';
        z2.MarkerEdgeColor='r';
        z1.MarkerSize=14;
        z2.MarkerSize=14;
        z1.LineStyle = 'none';
        z2.LineStyle = 'none';
```

```
        hold on
        plot(z,z_c/Ca(1),'bo','MarkerSize',14);
        axis(px(1),[0 max(tspan)+0.5 0 1])
        axis(px(2),[0 max(tspan)+0.5 0 0.2])
        set(px(1),'YTick',0:0.2:1.0)
        set(px(2),'YTick',0:0.04:0.2)
        set(px,{'ycolor'},{'none';'none'})
        set(px,{'fontsize'},{24;24})
        set(px,{'fontweight'},{'bold';'bold'})
        set(get(ax(1),'Ylabel'),'String','Carbon recovery in solid [-]')
        set(get(ax(2),'Ylabel'),'String','Carbon recovery in gas [-]')
        set(get(ax(2),'Ylabel'),'fontweight','bold')
        set(ax,{'ycolor'},{'black';'black'})
        set(get(ax(1),'Ylabel'),'Fontsize', 28)
        set(get(ax(2),'Ylabel'),'Fontsize', 28)
        set(px(1),'YTickLabel',['0.0';'0.2';'0.4';'0.6';'0.8';'1.0'])
        set(px(2),'YTickLabel',['0.00';'0.04';'0.08';'0.12';'0.16';'0.20'])
        hold on
        z3=plot(x,y,'--','LineWidth',2.0,'color','k');
        x_leg=xlabel('Time [h]');
        set(x_leg,'fontsize',28);
        h_leg2=legend([h1;h2;z1;z2],{'predicted data - solid','predicted data -
gas','experimental data - solid','experimental data - gas'},'Location','east' );
        set(h_leg2,'fontsize',24,'fontweight','bold');
    end

end

%Activation energy calculation
k_180=paropt(1,:);
k_220=paropt(2,:);
k_250=paropt(3,:);


k1=[k_180(1) k_220(1) k_250(1)];
k2=[k_180(2) k_220(2) k_250(2)];
k3=[k_180(3) k_220(3) k_250(3)];
k4=[k_180(4) k_220(4) k_250(4)];
k5=[k_180(5) k_220(5) k_250(5)];


T_180=temperatura_1;
T_220=temperatura_2;
T_250=temperatura_3;

T=[1/T_180 1/T_220 1/T_250];

%calculate the tendency line for k1
y_k1=polyfit(T,log(k1),1);
FX_k1=polyval(y_k1,T);

%calculate the tendency line for k2
y_k2=polyfit(T,log(k2),1);
FX_k2=polyval(y_k2,T);

%calculate the tendency line for k3
```

```
y_k3=polyfit(T,log(k3),1);
FX_k3=polyval(y_k3,T);

%calculate the tendency line for k4
y_k4=polyfit(T,log(k4),1);
FX_k4=polyval(y_k4,T);

%calculate the tendency line for k5
y_k5=polyfit(T,log(k5),1);
FX_k5=polyval(y_k5,T);

%calculate the slopes of the tendency lines
m_1=(FX_k1(end)-FX_k1(1))/(T(end)-T(1));
m_2=(FX_k2(end)-FX_k2(1))/(T(end)-T(1));
m_3=(FX_k3(end)-FX_k3(1))/(T(end)-T(1));
m_4=(FX_k4(end)-FX_k4(1))/(T(end)-T(1));
m_5=(FX_k5(end)-FX_k5(1))/(T(end)-T(1));

%calculate the pre-exponential factors
k10=exp(y_k1(2))
k20=exp(y_k2(2))
k30=exp(y_k3(2))
k40=exp(y_k4(2))
k50=exp(y_k5(2))

%calculate the activation energies [kJ/mol]
E_1=-m_1*0.00831
E_2=-m_2*0.00831
E_3=-m_3*0.00831
E_4=-m_4*0.00831
E_5=-m_5*0.00831


%plot ln kx vs 1/T and tendency lines
figure();
plot(T*1000,log(k1),'*b','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot(T*1000,FX_k1,'-b','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
x_leg=xlabel('1/T [1/K]');
set(x_leg,'fontsize',26,'fontweight','bold');
y_leg=ylabel('ln k');
set(y_leg,'fontsize',26,'fontweight','bold');

ylim([-8 1]);

plot(T*1000,log(k2),'*r','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot(T*1000,FX_k2,'-r','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
x_leg=xlabel('1/T [1/K]');
set(x_leg,'fontsize',26,'fontweight','bold');
y_leg=ylabel('ln k');
set(y_leg,'fontsize',26,'fontweight','bold');
```

```
ylim([-8 1]);

plot(T*1000,log(k3),'*g','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot(T*1000,FX_k3,'-g','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
x_leg=xlabel('1/T [1/K]');
set(x_leg,'fontsize',26, 'fontweight','bold');
y_leg=ylabel('ln k');
set(y_leg,'fontsize',26, 'fontweight','bold');


ylim([-8 1]);

plot(T*1000,log(k4),'*k','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot(T*1000,FX_k4,'-k','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
x_leg=xlabel('1/T [1/K]');
set(x_leg,'fontsize',26, 'fontweight','bold');
y_leg=ylabel('ln k');
set(y_leg,'fontsize',26, 'fontweight','bold');


ylim([-8 1]);

plot(T*1000,log(k5),'*y','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
hold on;
plot(T*1000,FX_k5,'-y','LineWidth',3.0);
set(gca,'fontsize', 26,'fontweight','bold');
x_leg=xlabel('1/T [1/K]');
set(x_leg,'fontsize',26,'fontweight','bold');
y_leg=ylabel('ln k');
set(y_leg,'fontsize',26,'fontweight','bold');


axis([1.85 2.27 -8 1])
```

```
function dc_v=lsqparafit2(t,c_v,par)

k1=par(1);
k2=par(2);
k3=par(3);
k4=par(4);
k5=par(5);
n=par(6);
```

```
dCa_dt=-k1*c_v(1)-k2*c_v(1)-k3*c_v(1);
dCl_dt=k1*c_v(1)-k4*c_v(2)-k5*c_v(2).^n;
dCsc_dt=k5*c_v(2).^n;
dCpc_dt=k3*c_v(1);
dCg1_dt=k2*c_v(1);
dCg2_dt=k4*c_v(2);


dc_v=[dCa_dt;dCl_dt;dCsc_dt;dCpc_dt;dCg1_dt;dCg2_dt];
```

```
function lsq=minimiz(par)
global c_v0 Ca Cl Cb Cd tspan

[t,c_v] = ode45(@lsqparafit2,tspan,c_v0,' ',par);

lsq=sum(abs(c_v(:,2)-Cl'))+sum(abs((c_v(:,3)+c_v(:,4))-
Cb'))+sum(abs((c_v(:,5)+c_v(:,6))-Cd'));


end
```