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International
Journal
Of Modern Engineering Research (IJMER)

Analytical Expression of The Concentration of Reaction Kinetics of Carbon Dioxide with Phenyl Glycidyl Ether By TEA - CP - MS41 Catalyst

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ABSTRACT : Theoretical analysis corresponding to the reaction kinetics in a chemical reaction between carbon dioxide and phenyl glycidyl ether solution by TEA-CP-MS41 is presented. Analytical expressions pertaining to the concentration of carbon dioxide (CO_2), phenyl glycidyl ether solution (PGE) and flux are obtained in terms of reaction rate constants. In this paper, a powerful analytical method, called the New Homotopy perturbation method (NHPM) is used to obtain approximate analytical solutions for nonlinear differential equations. Furthermore, in this work the numerical simulation of the problem is also reported using Scilab/Matlab program. An agreement between analytical and numerical results is noted.

Keywords: Carbon Dioxide; Phenyl Glycidyl Ether Solution; TEA-CP-MS41; Nonlinear Differential Equations; New Homotopy perturbation method; Boundary Value Problems

I. INTRODUCTION

Carbon dioxide has the potential to provide a vast and cheap source of carbon. Turning it into useful products would also reduce its environmental impact as a green house gas. Carbon dioxide is used to produce carbonated soft drinks and soda water. Traditionally, the carbonation of beer and sparkling wine came about through natural fermentation, but many manufacturers carbonate these drinks with carbon dioxide recovered from the fermentation process. Scientists have shown that ionic liquids are selective catalysts for converting carbon dioxide into synthetic intermediates called cyclic carbonates, but it is difficult to separate and recycle the liquid catalyst.

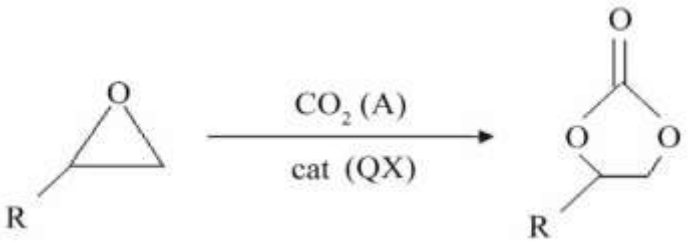
Recently, the chemical fixation of carbon dioxide has become an important research topic [1], because of the danger posed by global warming, and conversion of carbon dioxide into valuable substances is an extremely attractive solution. The synthesis of cyclic carbonates by the reaction of CO_2 with oxirane has been performed using Lewis acids, transition metal complexes, and organometallic compounds as catalysts at high pressure such as 10 - 50 atm [2,3]. Some papers about oxirane - CO_2 reactions have focused on the reaction mechanism, the overall reaction kinetics, and the effect of the catalyst on the conversion. But, because the diffusion may have an effect on the reaction kinetics [4] in the mass transfer accompanied by chemical reactions, we believe that it is worthwhile to investigate the effect that diffusion has on the reaction kinetics of the gas–liquid heterogeneous reaction such as the oxirane - CO_2 reaction.

Many organic and inorganic compounds including ammines, phosphines, quaternary ammonium salts, and alkali metal salts are known to catalyze the oxirane reaction [5]. The kinetics of the reaction between CO_2 and phenyl glycidyl ether (PGE) have been studied using catalyst TEA-CP-MS41 catalyst, The reaction rate constants were obtained using the measured absorption rate of and analyzed with the mass transfer mechanism associated with the chemical reactions.

Park et al. [6] investigated the chemical absorption of carbon dioxide and phenyl glycidyl ether solution containing the catalyst TEA-CP-MS41 catalyst in a heterogeneous system. To our knowledge no analytical solutions of this model have been reported. The purpose of this communication is to derive simple approximate analytical expression for the steady-state concentrations of CO_2, PGE and flux using the New Homotopy perturbation method.

2. Mathematical formulation of the problem and analysis

The rate-determining step is the attack of the anionic portion of the catalyst on the oxirane. The importance of this portion of the catalyst can be explained by this mechanism, whereby the overall reaction between CO_2 and PGE to form the 5-membered cyclic carbonate is as follows:



The complete mathematical formalism of this problem is given in Park et al. [6]. The overall reaction of equation (1) consists of two consecutive steps: i) a reversible reaction between PGE (B) and THA-CP-MS41 (QX) to form an intermediate complex (C_1) and ii) irreversible reaction between C_1 and CO_2 (A) to form QX and 5-membered cyclic carbonate (C):

$$B + QX \underset{k_2}{\overset{k_1}{\rightarrow}} C_1 \tag{1a}$$

$$A + C_1 \overset{k_3}{\leftrightarrow} C + QX \tag{1b}$$

The reaction rate of CO_2 under the condition of a steady state approximation to form C_1 is presented as follows:

$$r_A = \frac{C_B S_t}{\frac{1}{k_1} + \frac{1}{K_1 k_3 C_A} + \frac{C_B}{k_3 C_A}} \tag{2}$$

where, C_A is the concentration of CO_2, C_B is the concentration of PGE, k_1 is the Forward reaction rate constant in eqn. (1a), k_2 is the Backward reaction rate constant in eqn. (1a), K_1 is the Forward reaction rate constant in eqn. (1b). S_t is the surface area of catalyst. The mass balance of CO_2 and PGE, using film theory accompanied by chemical reactions and boundary conditions are given as follows:

$$D_A \frac{d^2 C_A}{dz^2} = r_A \tag{3}$$

$$D_B \frac{d^2 C_B}{dz^2} = r_A \tag{4}$$

$$\begin{aligned} &C_A = C_{Ai}; \quad \frac{dC_B}{dz} = 0 \ \text{ when } z = 0 \\ &C_A = C_{AL}; \quad C_B = C_{Bo} \ \text{ when } z = z_L \end{aligned} \tag{5}$$

where, z is the distance, z_L is the film thickness, D_A, D_B are the diffusivity of CO_2 and PGE respectively. We introduce the following set of dimensionless variables:

$$x = \frac{z}{z_L},\ a = \frac{C_A}{C_{Ai}},\ b = \frac{C_B}{C_{Bo}},\ \alpha_1 = \frac{z_L^2 S_t C_{Bo} K_1 k_3}{D_A},\ \ \alpha_2 = \frac{z_L^2 S_t C_{Ai} K_1 k_3}{D_B},$$

$$\beta_1 = \frac{C_{Ai} K_1 k_3}{k_1},\ \ \beta_2 = \frac{C_{Bo} K_1 k_3}{k_1}$$

where $a, \text{and } b$ represent dimensionless concentrations, and x is the distance parameter. We get the dimensionless nonlinear equations as follows:

$$\frac{d^2 a}{dx^2} - \frac{\alpha_1 ab}{1 + \beta_1 a + \beta_2 b} = 0 \tag{6}$$

$$\frac{d^2b}{dx^2} - \frac{\alpha_2 ab}{1+\beta_1 a+\beta_2 b} = 0 \tag{7}$$

Now the initial and boundary conditions are represented as follows:

$$a = 1,\ \frac{db}{dx} = 0 \quad \text{when } x = 0$$
$$a = k,\ b = 1 \quad \text{when } x = 1 \tag{8}$$

The dimensionless flux is given by [6]

$$\beta = -\left(\frac{da}{dx}\right)_{x=0} \tag{9}$$

3. Solution of Boundary Value Problem Using New Homotopy Perturbation Method

In this paper, New Homotopy perturbation method is used to solve non linear differential equations. The basic principle of this method is described in Appendix A and detailed derivation of dimensionless concentration of CO_2 and PGE, from the nonlinear Equations (6) and (7) are described in Appendix B. This method is the most effective and convenient ones for both linear and non-linear equations. Perturbation method is based on assuming a small parameter. Recently, many authors have applied the New Homotopy perturbation method (NHPM) to solve the non-linear boundary value problem in physics and engineering sciences. Recently this method is also used to solve some of the non-linear problem in physical sciences. This method is a combination of Homotopy in topology and classic perturbation techniques. The HPM [7-18] is unique in its applicability, accuracy and efficiency. The New HPM [19, 20] uses the imbedding parameter p as a small parameter, and only a few iterations are needed to search for an asymptotic solution. The analytical expression of concentration (see Appendix B) of the substrate is as follows:

$$a(x) = \cosh\left(\sqrt{\alpha_1 m}\, x\right) + \frac{k - \cosh\left(\sqrt{\alpha_1 m}\right)}{\sinh\left(\sqrt{\alpha_1 m}\right)} \sinh\left(\sqrt{\alpha_1 m} x\right) \tag{10}$$

$$b(x) = \frac{\cosh\left(\sqrt{\alpha_2 m} x\right)}{\cosh\left(\sqrt{\alpha_2 m}\right)} - \frac{\tanh\left(\sqrt{\alpha_2 m}\right)}{\sqrt{\alpha_2 m_2}\cosh\left(\sqrt{\alpha_2 m}\right)} \cosh\left(\sqrt{\alpha_2 m}\right) + \frac{\sinh\left(\sqrt{\alpha_2 m} x\right)}{\sqrt{\alpha_2 m_2}\cosh\left(\sqrt{\alpha_2 m} x\right)} \tag{11}$$

From eqn. (9), we obtain the flux as,

$$\beta = -\left(\frac{k - \cosh\left(\sqrt{\alpha_1 m}\right)}{\sinh\left(\sqrt{\alpha_1 m}\right)} \sqrt{\alpha_1 m}\right) \tag{12}$$

where, $m = \dfrac{1}{1+\beta_1+\beta_2}$

4. Results and Discussion

Eqns. (10) and (11) represent the new closed and simple approximate analytical expressions of the normalized concentrations of CO_2 and PGE for all values of parameters $\alpha_1, \alpha_2, \beta_1, \beta_2$ and *k*. The current response is given in eqn. (12). The concentration profiles of CO_2 and PGE are shown in Figures 1, 2 and 3. The concentration of CO_2 increases when the normalized parameter *k* increases. The concentration of CO_2 decreases when the parameters β_1 increases (refer Figures 2). In Figure 3, the concentration of PGE decreases when the normalized parameter α_2 decreases. Eqn. (12) represents the normalized flux. The value of flux decreases as the parameter β_1 increases and it increases when the parameter α_1 increases. (refer Figures 4 and 5). The value of flux increases as surface area of catalyst S_t increases (refer Figures 6) and it increases when the parameter k_l increases (refer Figures 7).

II. CONCLUSIONS

This paper presents a theoretical treatment of carbon dioxide and phenyl glycidyl ether solution in chemical reaction. Also, we have discussed the mathematical models of CO_2 absorption into the PGE solution. We have solved the nonlinear differential equations both analytically and numerically. The approximate analytical expressions for the steady state concentrations of CO_2 and PGE are obtained for all values of parameters using the

New Homotopy perturbation method. These theoretical results are useful to evaluate the overall reaction rate constant and enhancement factor of CO_2. A satisfactory agreement with the numerical result is noted.

ACKNOWLEDGEMENTS

This work is supported by the Department of Science and Technology (EMR/2015/002279),Government of India. The authors are thankful to Mr. S. Mohamed Jaleel, Founder and Chairman of Sethu Institute of Technology, Kariapatti, Tamilnadu and Dr. A. Senthilkumar, Principal and Dr. P.G. Jansi Rani, Dean, & The Head of the Department, Sethu Institute of Technology, Kariapatti, Kariapatti, Tamilnadu for their constant encouragement.

Appendix A

Basic idea of new Homotopy perturbation method

To illustrate the basic ideas of the Homotopy perturbation method, we consider the following nonlinear differential equation:

$$A(u) - f(r) = 0, \qquad r \in \Omega \tag{A.1}$$

with the boundary conditions

$$B\left(u, \frac{\partial u}{\partial n}\right) = 0, \qquad r \in \Gamma, \tag{A.2}$$

where A is a general differential operator, B is a boundary operator, $f(r)$ is a known analytical function, and Γ is the boundary of domain Ω.

The operator *A* in (A.1) can be rewritten as a sum of *L* and *N* , where of *L* and *N* are linear and nonlinear parts of *A*, respectively, as follows:

$$L(u) + N(u) - f(r) = 0.$$

By the Homotopy technique, we construct the Homotopy

$$H(v,p) = (1-p)(L(v) - L(u_0)) + p(A(v) - f(r)) = 0, \tag{A.3}$$

which is equivalent to

$$H(v,p) = L(v) - L(u_0) + pL(u_0) + p(N(v) - f(r)) = 0, \tag{A.4}$$

where

$$v(r,p) : \Omega \times [0,1] \to \Re,$$

$$p \in [0,1], r \in \Omega,$$

p is an embedding parameter, u_0 is an initial approximation of (A.1), which satisfies the boundary conditions. As p changes from zero to unity, $v(r,p)$ changes from u_0 to $u(r)$.

In this technique, the convergence of a solution depends on the choice of u_0, that is, we can have different approximate solutions for different u_0.

Let us decompose the source function as $f(r) = f_1(r) + f_2(r)$. If we take $L(u_0) = f_1(r)$ in (3), we obtain the following Homotopy:

$$H(v,p) = (1-p)(L(v) - f_1(r)) + p(A(v) - f(r)) = 0, \tag{A.5}$$

which is equivalent to

$$H(v,p) = L(v) - f_1(r) + p(N(v) - f_2(r)) = 0 \tag{A.6}$$

Obviously, from (A.6) we have

$$H(v,0) = L(v) - f_1(r) = 0,$$

$$H(v,1) = A(v) - f(r) = 0$$

As the embedding parameter p changes from zero to unity, $v(r,p)$ changes from $L^{-1}(f_1(r))$ to $u(r)$.

According to He's Homotopy perturbation method, we can first use the embedding parameter p as a small parameter and assume that the solution of (A.6) can be written as a Power series in *p* as follows:

$$v = v_0 + pv_1 + p^2v_2 + p^3v_3 + \cdots.$$

Setting $p = 1$, we get the approximate solution of (A.1)

$$u = \lim_{p \to 1} v = v_0 + pv_1 + p^2v_2 + p^3v_3 + \cdots$$

Appendix B

Solution of Non linear eqns. (6) and (7) Using New Homotopy Perturbation Method

In this Appendix, we indicate how eqns. (10) and (11) in this paper derived. To find the solution of eqns. (6) and (7) we first construct the Homotopy as follows:

$$(1-p)\left[\frac{d^2a}{dx^2} - \frac{\alpha_1 a(1)}{1+\beta_1(1)+\beta_2(1)}\right] + p\left[\frac{d^2a}{dx^2}(1+\beta_1 a+\beta_2 b) - \alpha_1 ab\right] = 0 \quad \text{(B.1)}$$

$$(1-p)\left[\frac{d^2b}{dx^2} - \frac{\alpha_2 (1)b}{1+\beta_1(1)+\beta_2(1)}\right] + p\left[\frac{d^2b}{dx^2}(1+\beta_1 a+\beta_2 b) - \alpha_2 ab\right] = 0 \quad \text{(B.2)}$$

We can write, (B.1) and (B.2) as follows:

$$(1-p)\left[\frac{d^2a}{dx^2} - \alpha_1 ma\right] + p\left[\frac{d^2a}{dx^2}(1+\beta_1 a+\beta_2 b) - \alpha_1 ab\right] = 0 \quad \text{(B.3)}$$

$$(1-p)\left[\frac{d^2b}{dx^2} - \alpha_2 mb\right] + p\left[\frac{d^2b}{dx^2}(1+\beta_1 a+\beta_2 b) - \alpha_2 ab\right] = 0 \quad \text{(B.4)}$$

The boundary conditions are,

$$a = 1,\ \frac{db}{dx} = 0 \quad \text{when } x = 0$$
$$a = k,\ b = 1 \quad \text{when } x = 1 \quad \text{(B.5)}$$

The approximate solutions of (B.3), (B.4) are,

$a = a_0 + p\,a_1 + p\,a_2 + p\,a_3 + \ldots\ldots$ (B.6)

$b = b_0 + p\,b_1 + p\,b_2 + p\,b_3 + \ldots\ldots$ (B.7)

Substituting eqns. (B.6) and (B.7) into eqns. (B.3) and (B.4) and comparing the coefficients of like powers of *p*

$$p^0 : \frac{d^2a_0}{dx^2} - \alpha_1 ma_0 = 0 \quad \text{(B.8)}$$

$$p^0 : \frac{d^2b_0}{dx^2} - \alpha_2 mb_0 = 0 \quad \text{(B.9)}$$

Solving the eqns. (B.8) and (B.9) and using the boundary conditions (B.5) and we can obtain the eqns. (10) and (11) in this term.

Appendix C

Scilab/Matlab program for the numerical solution of the system of nonlinear eqns. (6) & (7)

```
function pdex4
 m=0;
x=linspace(0,1);
t=linspace(0,100000);
sol = pdepe(m,@pdex4pde,@pdex4ic,@pdex4bc,x,t);
u1=sol(:,:,1);
```

```
u2=sol(:,:,2);
figure
plot(x,u1(end,:))
title('u1(x,t)')
xlabel('Distance x')
ylabel('u1(x,2) ')
figure
plot(x,u2(end,:))
title('u2(x,t)')
xlabel('Distance x')
ylabel('u2(x,2) ')
function [c,f,s]=pdex4pde(x,t,u,DuDx)
c=[1;1];
f=[1;1].*DuDx;
a=0.001;
b=10;
M=10;
N=0.01;
F= -(a*u(1)*u(2))/(1+(M*u(1))+(N*u(2)));
F1= -(b*u(1)*u(2))/(1+(M*u(1))+(N*u(2)));
s=[F;F1];
function u0=pdex4ic(x);
u0=[1;1];
function [pl,ql,pr,qr]=pdex4bc(xl,ul,xr,ur,t)
pl=[ul(1)-1;0];
ql=[0;1];
pr=[ur(1)-0.1;ur(2)-1];
ql=[0;0];
```

Nomenclature

C_A: Concentration of CO_2 (kmol/m^3)
C_B: Concentration of PGE (kmol/m^3)
D_A: Diffusivity of CO_2 (m^2/s)
D_B: Diffusivity of PGE (m^2/s)
K_1: Reaction equilibrium constant (m^3/ kmol)
k_1: Forward reaction rate constant in reaction eqn. (1a) (m^3/ (kmol s))
k_2: Backward reaction rate constant in reaction eqn. (1a) (1/s)
k_3: Forward reaction rate constant in reaction eqn. (1b) (m^3/ (kmol s))
r_A: Reaction rate of CO_2 in consecutive reaction model (kmol/m^3s)
S_t: Surface area of catalyst (m^2)
z: Distance (m)
z_L: Film thickness (m)
a: Normalized concentration of CO_2 (Dimensionless)
b: Normalized concentration of PGE (Dimensionless)
α_1, α_2, β_1, β_2 and k: Normalized parameters (Dimensionless)
β: Flux of CO_2 (Dimensionless)

Subscripts

A: CO_2
B: PGE
L: Bulk solution
o: Feed or solvent

Figure Captions

Figure 1. Normalized concentration of CO_2 for various values of parameters is plotted using eqn. (10) when $\alpha_1 = 0.1,\ \beta_1 = 0.5,\ \beta_2 = 0.7$ The key to the graph (stacked line) represents the eqn. (10) and (dotted line) represents the numerical simulation.

Figure 2. Normalized concentration of CO_2 for various values of parameters is plotted using eqn. (10) when $k = 0.1,\ \alpha_1 = 0.5,\ \beta_2 = 0.001$ The key to the graph (stacked line) represents the eqn. (10) and (dotted line) represents the numerical simulation.

Figure 3. Normalized concentration of PGE for various values of parameters is plotted using eqn. (11). The key to the graph (stacked line) represents the eqn. (11) and (dotted line) represents the numerical simulation.

Figure 4. Diagrammatic representation of the normalized flux for various values of β_1

Figure 5. Diagrammatic representation of the normalized flux for various values of α_1

Figure 6. Diagrammatic representation of the normalized flux for various values of C_{B_o}

Figure 7. Diagrammatic representation of the normalized flux for various values of C_{A_i}

Figure 1

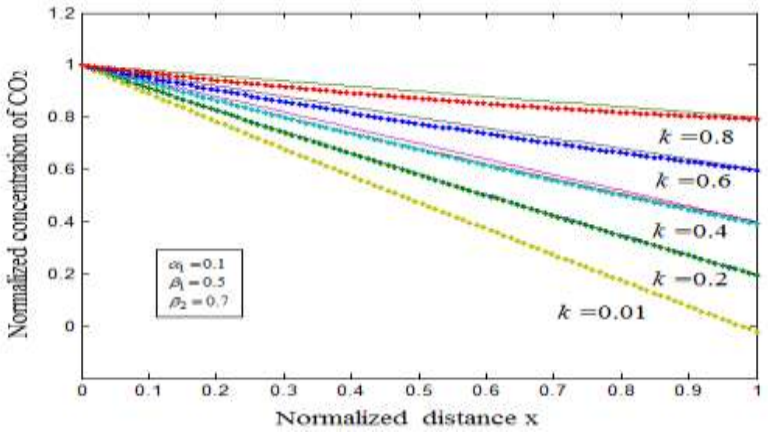


Figure 2

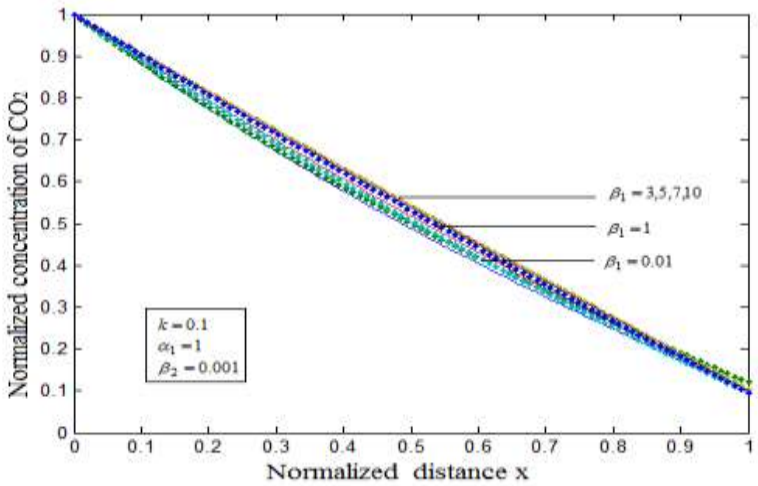


Figure 3

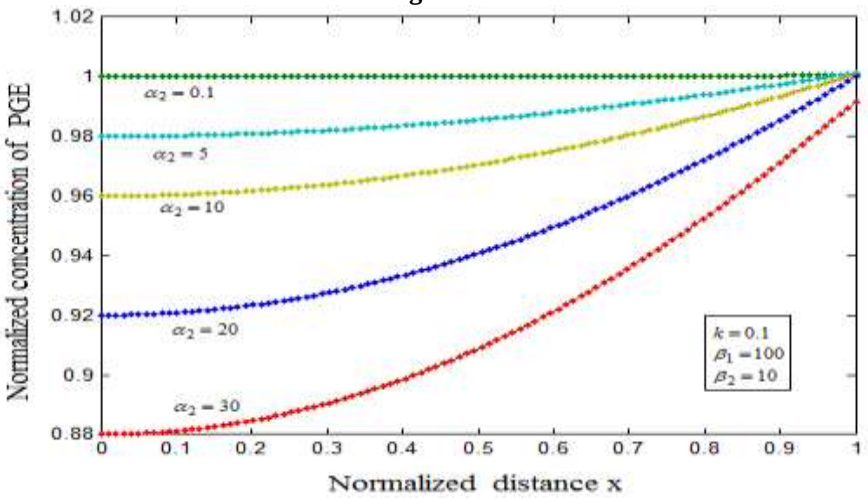


Figure 4

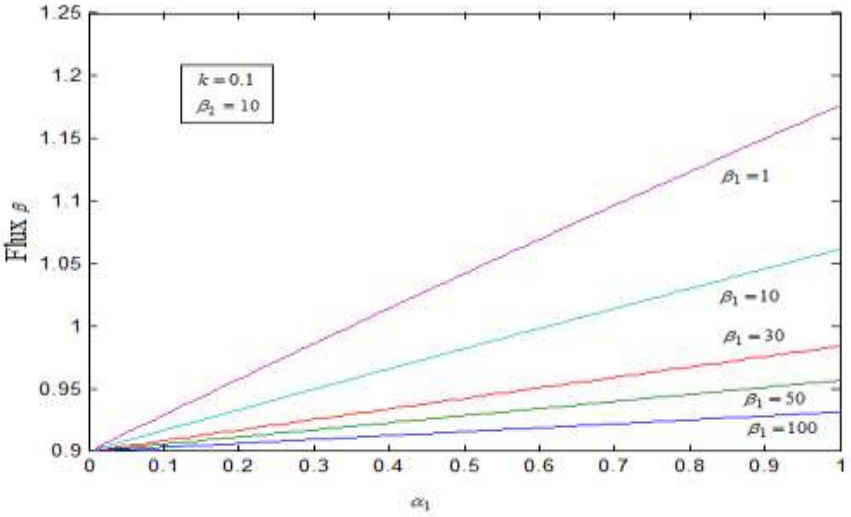


Figure 5

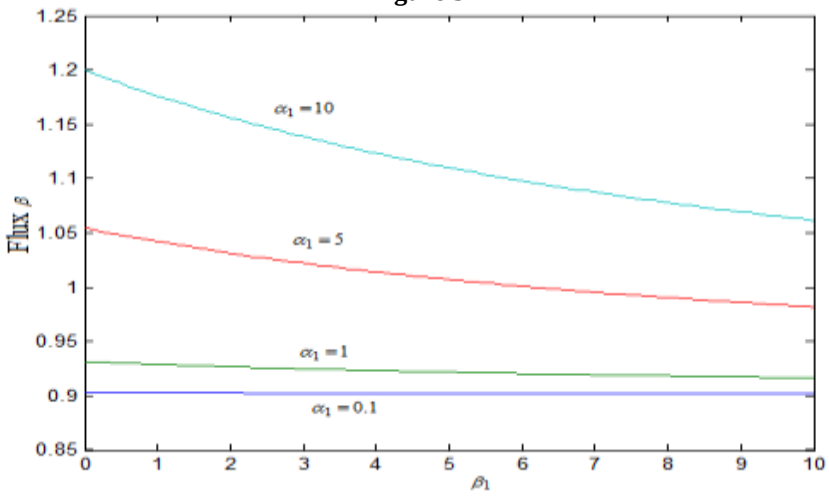


Figure 6

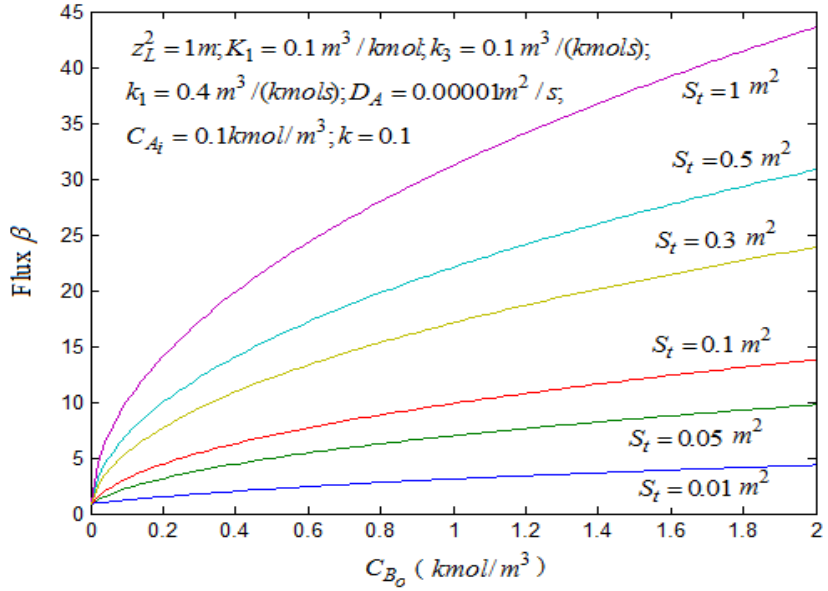
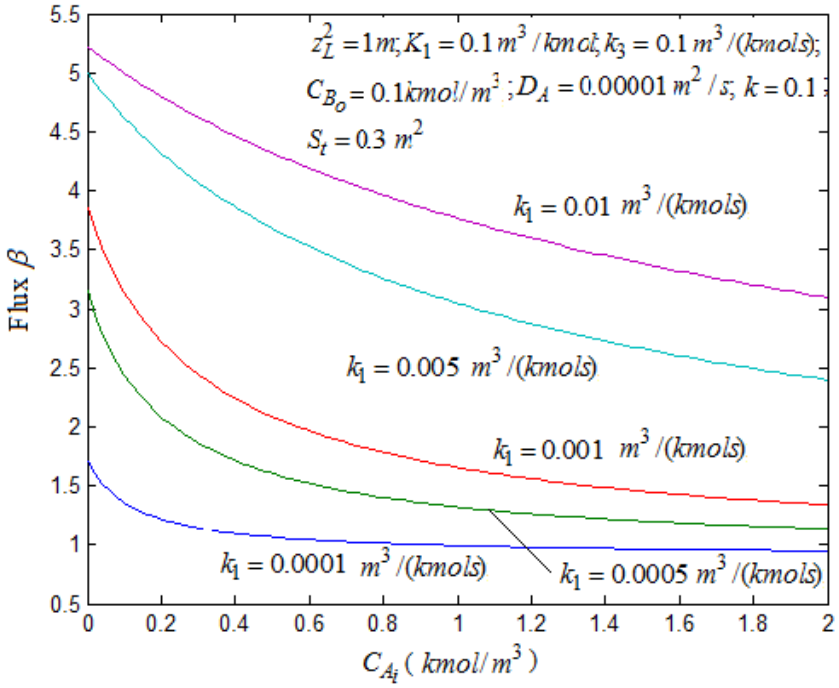


Figure 7



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