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Mathematical Modelling and Kinetics of Microchannel Reactor

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Abstract: The coupled nonlinear system of differential equations in 1-butanol dehydration under atmospheric and isothermal conditions are solved analytically for the microchannel reactor. Approximate analytical expressions of concentrations of 1-butanol, 1-butene, water and dibutyl ether are presented by using homotopy analysis method. The homotopy analysis method eliminated the classical perturbation method problem, because of the existence a small parameter in the equation. The analytical results are compared with the numerical solution and experimental results, satisfactory agreement is noted.

Keywords: Mathematical Modelling, Homotopy Analysis Method, 1-Butanol Dehydration, Microchannel Reactor, Channel Electrode, Non Linear Equation

1. Introduction

1-Butanol, is one of the important future bio-compounds for bio-fuel and bio-chemical use. 1-Butanol was produced from renewable sources by Acetone–Butanol–Ethanol (ABE) fermentation process. Recently Khan *et al.* studied the dehydration reactions of different primary and secondary alcohols in microchannel reactors. The basic microchannel reactor design is based on the flow between parallel platelets coated with catalyst. The large aspect ratio of the channel provides extensive surface area in a small volume. Microchannel reactors were developed based on ceramic substrates as well as metal substrates. In both types of reactors, multiple layers coated with catalytic material are bonded, forming a monolithic structure. An added benefit of a layered pattern is the ability to easily scale up or down by adjusting the number of layers. This provides great flexibility in the design if desired production capacity is changed, without the need to redesign the reactor (as it would be the case in a tubular reactor) [1].

Various approaches have been reported in the literature [2-5], to model coated microchannel reactors for gas- phase reactions. In addition to kinetic studies, Spatenka et al [2] and Walter et al [3] developed a two dimensional dynamic model to simulate the coated microchannel reactor. Spatenka developed cylindrical channel by considering axial convection and axial dispersion in an empty space with the external mass transfer coefficient [2]. Walter modelled the cylindrical channel in 2D considering axial convection, dispersion in axial and radial direction for gas-phase [3]. Schmidt developed a steady state model and regarded catalyst layer using a slab geometry [5]. Walter observed that the application of plug flow model to determine kinetics was validated with a dynamic 2D model [3].

However, to the best of our knowledge, there were no analytical results available till date that corresponds to the steady-state concentrations of 1- butanol, 1-butene, water, dibutyl ether for all possible values of the rate constants. Therefore, herein, we employ homotopy analysis method to evaluate the steady-state concentration of 1- butanol, 1-butene, and water and dibutyl ether.

2. Mathematical Formulation of the Problem

The mass balance nonlinear differential equation for reaction scheme for 1-butanol dehydration over γ-alumina are given as follows [1]:

$$\frac{dC_A}{d\tau}=\left(-2r_1-2r_2\right)\rho_b \tag{1}$$

$$\frac{dC_B}{d\tau}=\left(2r_1+2r_3\right)\rho_b \tag{2}$$

$$\frac{dC_C}{d\tau}=\left(2r_1+r_2+r_3\right)\rho_b \tag{3}$$

$$\frac{dC_D}{d\tau}=\left(r_2-r_3\right)\rho_b \tag{4}$$

where C_A, C_B, C_C and C_D are the concentrations of 1-butanol, 1-butene, water and dibutyl ether respectively and ρ_b is bulk density. The initial conditions for Eqs. (1) – (4) are represented as follows:

$$\text{At } \tau=0,\ C_A\left(\tau=0\right)=C_{A_i},\ C_B\left(\tau=0\right)=0,\ C_C\left(\tau=0\right)=0,\ C_D\left(\tau=0\right)=0 \tag{5}$$

The reaction rate r_1, r_2 and r_3 can be represented as follows:

$$r_1=k_1C_A \tag{6}$$

$$r_2=k_1\left(C_A{}^2-\frac{C_CC_D}{K_{eq}}\right) \tag{7}$$

$$r_3=k_3C_D \tag{8}$$

where k_1 and k_3 are rate constants and K_{eq} is equilibrium coefficients. Substituting Eqs. (6) to (8) in the Eqs. (1) to (4), the following nonlinear differential equation can be obtained.

$$\frac{dC_A}{d\tau}+2k_1\rho_bC_A+2k_1\rho_bC_A{}^2-\frac{2k_1\rho_bC_CC_D}{K_{eq}}=0 \tag{9}$$

$$\frac{dC_B}{d\tau}-2k_1\rho_bC_A-2k_3\rho_bC_D=0 \tag{10}$$

$$\frac{dC_C}{d\tau}-2k_1\rho_bC_A-k_1\rho_bC_A{}^2-k_3\rho_bC_D+\frac{k_1\rho_bC_CC_D}{K_{eq}}=0 \tag{11}$$

$$\frac{dC_D}{d\tau}-k_1\rho_bC_A{}^2+k_3\rho_bC_D+\frac{k_1\rho_bC_CC_D}{K_{eq}}=0 \tag{12}$$

3. Analytical Expression of Concentrations Using Asymptotic Methods

In recent years much of the attention is devoted to find the analytical solution for the case of strongly nonlinear differential equations using some asymptotic techniques. The idea behind asymptotic is simple: break the solution into more manageable pieces, each piece helping to produce a better and better approximation. So the first piece describes the system in some idealized state. To this, we may add a second piece representing a small perturbation to the initial state. Each subsequent piece, usually allows for better accuracy, with each piece representing smaller and smaller perturbations. Initially methods like Pade approximation method [6] and variational iteration method [7-8] have been widely used to study the nonlinear problems, later on Liao employed the fundamental ideas of homotopy in topology to propose a general analytic method for solving differential and integral equations, linear and non-linear, namely homotopy analysis method (HAM) [9]. A special case of HAM is homotopy perturbation method (HPM) [10] which was introduced by He, and Elçin Yusufoglu extended it to improved homotopy perturbation method [11], latter Rajendran introduced a new approach to homotopy perturbation method [12]. Adomian decomposition method [13] and modified Adomian decomposition method [14] are frequently used for solving non-linear problems till now. Among these homotopy analysis method is employed to solve the nonlinear ordinary differential equations Eqs. (9) – (12).

4. Analytical Expression of Concentrations Using Homotopy Analysis Method

Liao employed the basic ideas of the homotopy in topology to propose a general analytic method for nonlinear problems, namely the homotopy analysis method [15-19]. In recent years, homotopy analysis method has been used in obtaining approximate solutions of a wide class of non-linear differential equations in [20-23]. The method provides the solution in a rapidly convergent series with components that are elegantly computed. The main advantage of the method is that it can be used directly without using assumptions or transformations.

Using HAM (refer Appendix A), we can obtain the concentrations of 1- butanol, 1-butene, water and dibutyl ether as follows:

$$\begin{aligned} C_A(\tau) &= C_{A_i} e^{-2k_1\rho_b\tau} \\ &-he^{-2k_1\rho_b\tau}\left\{ C_{A_i}^{\ 2}\left(e^{-2k_1\rho_b\tau}-1\right) + 2m\left[\left(C_{A_i} + \frac{C_{A_i}^{\ 2}}{4}\right)\left(\frac{1-e^{-2k_1\rho_b\tau}}{2k_1\rho_b} - \frac{e^{(2k_1\rho_b - k_3\rho_b)\tau}-1}{2k_1\rho_b - k_3\rho_b}\right)\right.\right. \\ &\left.\left.-C_{A_i}\left(\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right) - \frac{C_{A_i}^{\ 2}}{4}\left(\frac{1-e^{-6k_1\rho_b\tau}}{6k_1\rho_b} + \frac{e^{(-2k_1\rho_b - k_3\rho_b)\tau}-1}{2k_1\rho_b - k_3\rho_b}\right)\right]\right\} \end{aligned} \tag{13}$$

$$C_B(\tau) = C_{A_i}\left(1-e^{-2k_1\rho_b\tau}\right) - \frac{2hk_1k_3\rho_b^{\ 2}C_{A_i}^{\ 2}}{k_3\rho_b - 4k_1\rho_b}\left[\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right] \tag{14}$$

$$\begin{aligned} C_C(\tau) &= C_{A_i}\left(1-e^{-2k_1\rho_b\tau}\right) - \frac{C_{A_i}^{\ 2}}{4}\left(e^{-4k_1\rho_b\tau}-1\right) - \frac{hk_3k_1\rho_b^{\ 2}C_{A_i}^{\ 2}}{k_3\rho_b - 4k_1\rho_b}\left(\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right) \\ &+hm\left[\left(C_{A_i} + \frac{C_{A_i}^{\ 2}}{4}\right)\left(\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right) - C_{A_i}\left(\frac{1-e^{-6k_1\rho_b\tau}}{6k_1\rho_b} + \frac{e^{(-2k_1\rho_b - k_3\rho_b)\tau}-1}{2k_1\rho_b + k_3\rho_b}\right)\right. \\ &\left.-\frac{C_{A_i}^{\ 2}}{4}\left(\frac{1-e^{-8k_1\rho_b\tau}}{8k_1\rho_b} + \frac{e^{(-4k_1\rho_b - k_3\rho_b)\tau}-1}{4k_1\rho_b + k_3\rho_b}\right) - \frac{C_{A_i}^{\ 2}}{4}\left(\frac{1-e^{-8k_1\rho_b\tau}}{8k_1\rho_b} + \frac{e^{(-4k_1\rho_b - k_3\rho_b)\tau}-1}{4k_1\rho_b + k_3\rho_b}\right)\right] \end{aligned} \tag{15}$$

$$\begin{aligned} C_D(\tau) &= \frac{k_3\rho_b C_{A_i}^{\ 2}}{k_3\rho_b - 4k_1\rho_b}\left(e^{-4k_1\rho_b\tau} - e^{-k_3\rho_b\tau}\right) + hme^{-k_3\rho_b\tau}\left\{\left(C_{A_i} + \frac{C_{A_i}^{\ 2}}{4}\right)\left(\tau - \frac{e^{(-4k_1\rho_b + k_3\rho_b)\tau}-1}{k_3\rho_b - 4k_1\rho_b}\right)\right. \\ &\left. C_{A_i}\left(\frac{1-e^{-2k_1\rho_b\tau}}{2k_1\rho_b} - \frac{e^{(k_3\rho_b - 6k_1\rho_b)\tau}-1}{k_3\rho_b - 6k_1\rho_b}\right) - \frac{C_{A_i}^{\ 2}}{4}\left(\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} - \frac{e^{(-8b_1 + k_3\rho_b)\tau}-1}{k_3\rho_b - 8b_1}\right)\right\} \end{aligned} \tag{16}$$

where $m = \dfrac{4k_1^{\ 2}\rho_b^{\ 2}C_{A_i}}{K_{eq}\left(k_3\rho_b - 4k_1\rho_b\right)}$.

5. Discussion

Microchannel reactors are known for their good heat and mass transfer properties enabling nearly isothermal operation of highly exothermic or endothermic reactions. Eqs. (13)-(16) are the new simple analytical solution of the concentration of 1-butanol, 1-butene, water and dibutyl ether C_D. The concentration profile depends upon the rate constants k_1, k_3 and the equilibrium coefficients K_{eq}. At higher temperatures, higher conversion of 1-butanol and high selectivity to 1-butene can be achieved. As the temperate increases the K_{eq} value has decreased. This means the equilibrium has shifted to have more reactants and less products. This would happen if the reaction was exothermic. In exothermic reactions the reverse reaction rate will increase faster than the forward reaction rate when the temperature is increased.

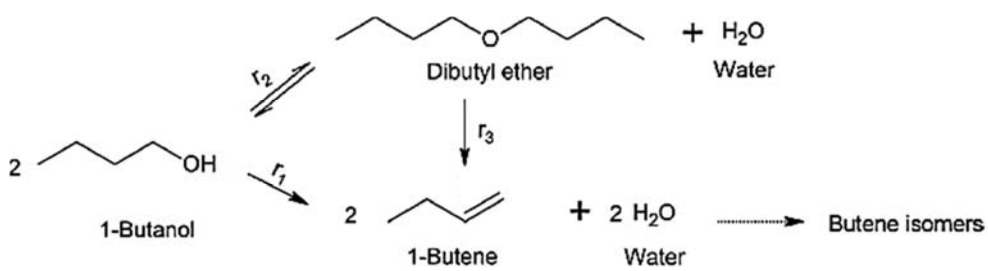

Figure 1. *Reaction scheme for 1-butanol dehydration over γ-alumina [24].*

Figure 2 (a-d) represents the concentration of 1-butanol versus space time over the kinetic parameters. Figure 2a-2b shows that the concentration increases when ρ_b and the rate constants k_1 decreases. Also it is inferred that the over uptake of 1-butanol across time is uniform when the bulk density ρ_b and rate constants k_1 is very small. From Figure 2c-2d, it is observed that for all values of rate constant k_3 and equilibrium coefficient K_{eq} the concentration will remain same. This is because, the K_{eq} is larger than one, this means that the concentration of the products will be higher than the reactants. If the K_{eq} value was less than one the concentration of reactants would be higher than the products.

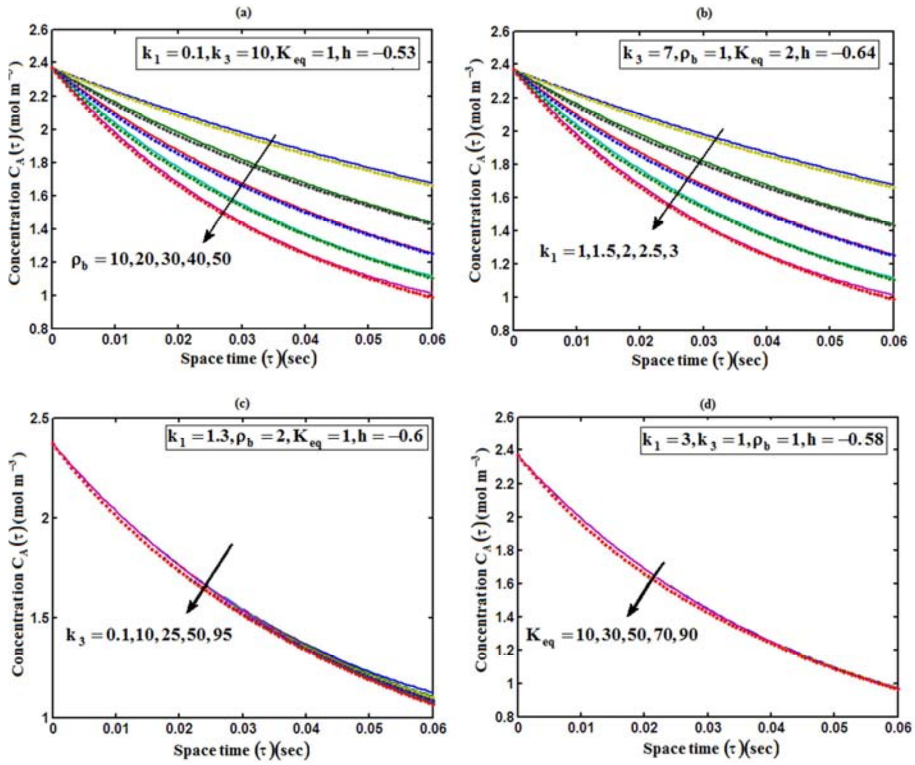

Figure 2. *Plot of the concentration of 1-butanol versus space time using Eqn. (13) for the fixed values of some parameters and various values of* ρ_b, k_1, k_3, K_{eq} . *The key to the graph: solid line represents Eq. (13) and dotted line represents numerical solution.*

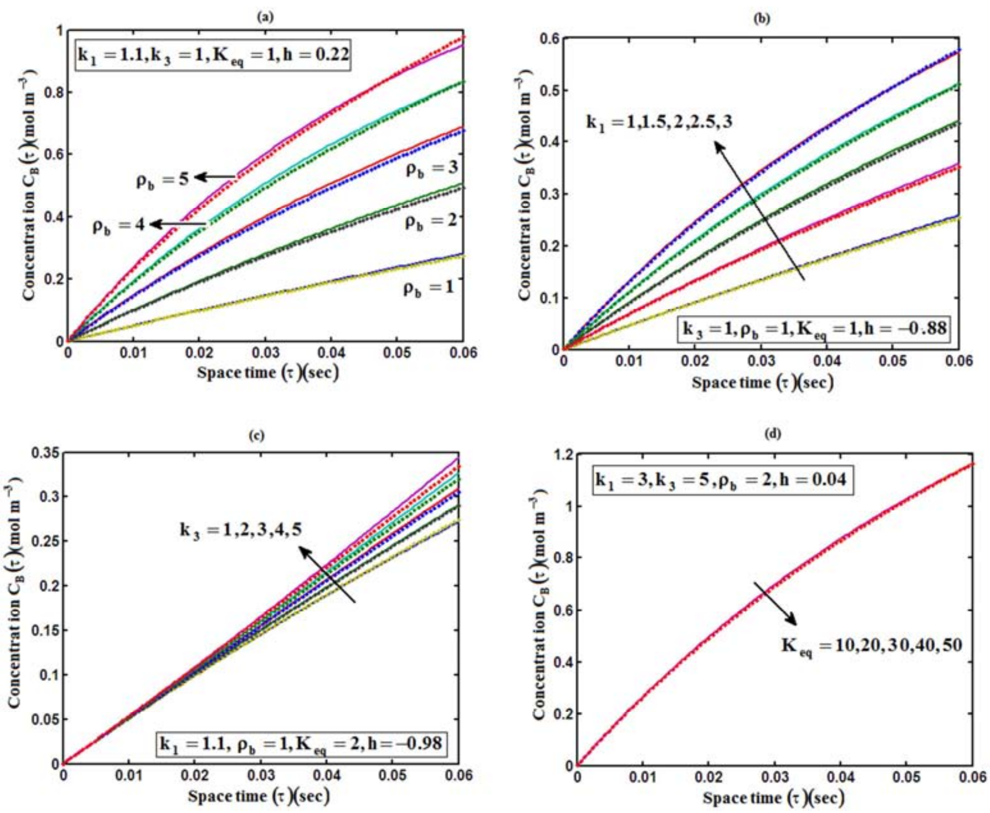

Figure 3. *Plot of the concentration of 1-butanol versus space time using Eqn. (14) for the fixed values of some parameters and various values of* ρ_b, k_1, k_3, K_{eq} . *The key to the graph: solid line represents Eq. (14) and dotted line represents numerical solution.*

Figure 3, shows the influence of kinetic parameters over the concentration of 1-butene. Figure 3a, shows that the concentration of 1-butene versus time for various values of ρ_b and for some fixed values of other parameters. From the figure it is observed that the concentration increases when ρ_b increases. Also for all values of ρ_b the concentration increases from its initial values. Figures 3b-3c, describes that the concentration profile of 1-butene. From the figure it is inferred that concentration increases when k_1 and k_3 increases. From Figure 3d it is observed that the concentration does not significantly various for all values of K_{eq}. This is because of, the rate constant generally depends on the absolute temperature. As the temperate increases the K_{eq} value has decreased. This means the equilibrium has shifted to have more reactants and less products.

Figure 4, shows the concentration of water versus space time for various values of ρ_b, k_1, k_3 and K_{eq}. From the Figure 4a-4d, we observed that for all increasing values of the parameters the concentration also increases. It is understood that the concentration is directly proportional to all the kinetic parameters.

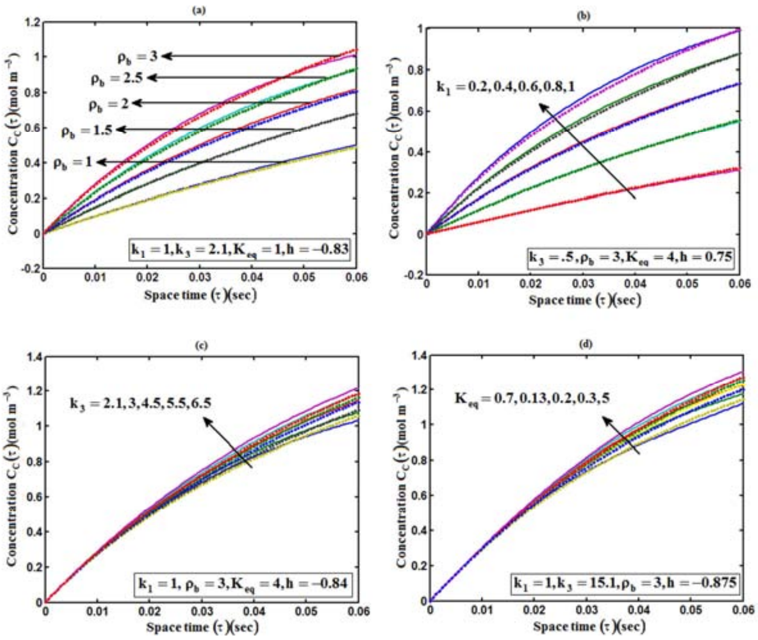

Figure 4. *Plot of the concentration of 1-butanol versus space time using Eqn. (15) for the fixed values of some parameters and various values of* ρ_b, k_1, k_3, K_{eq}. *The key to the graph: solid line represents Eq. (15) and dotted line represents numerical solution.*

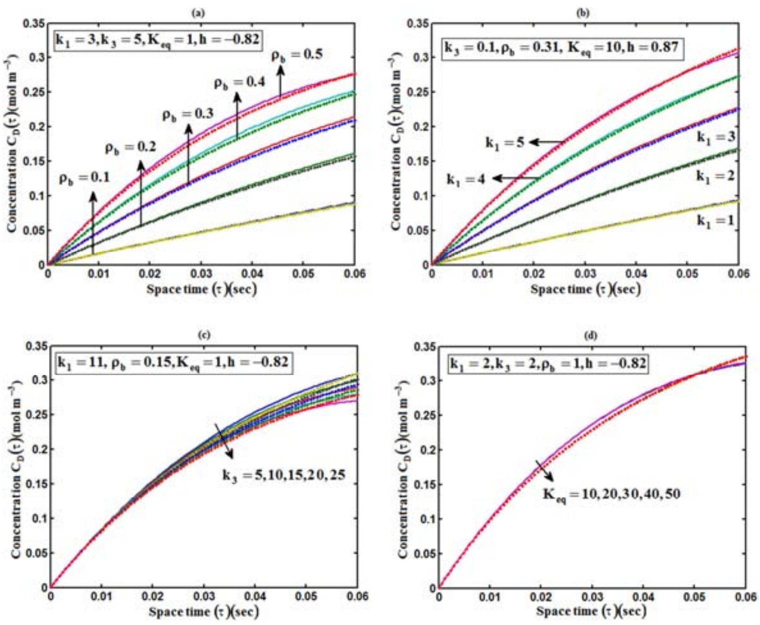

Figure 5. *Plot of the concentration of 1-butanol versus space time using Eqn. (16) for the fixed values of some parameters and various values of* ρ_b, k_1, k_3, K_{eq}. *The key to the graph: solid line represents Eq. (16) and dotted line represents numerical solution.*

Figure 5, describes the concentration profile of 1-butene over the kinetic parameters. Figure 5a - 5b, shows that the concentration increases for all the increasing values of ρ_b increases and k_1. From Figure 5c-5d, it is inferred that the concentration increases when k_3 decreases and K_{eq} decreases.

Figure 6, shows that the comparison of our analytical expressions of concentration of 1-butanol, 1-butene, and water and dibutyl ether with experimental results [1]. Satisfactory agreement is noted.

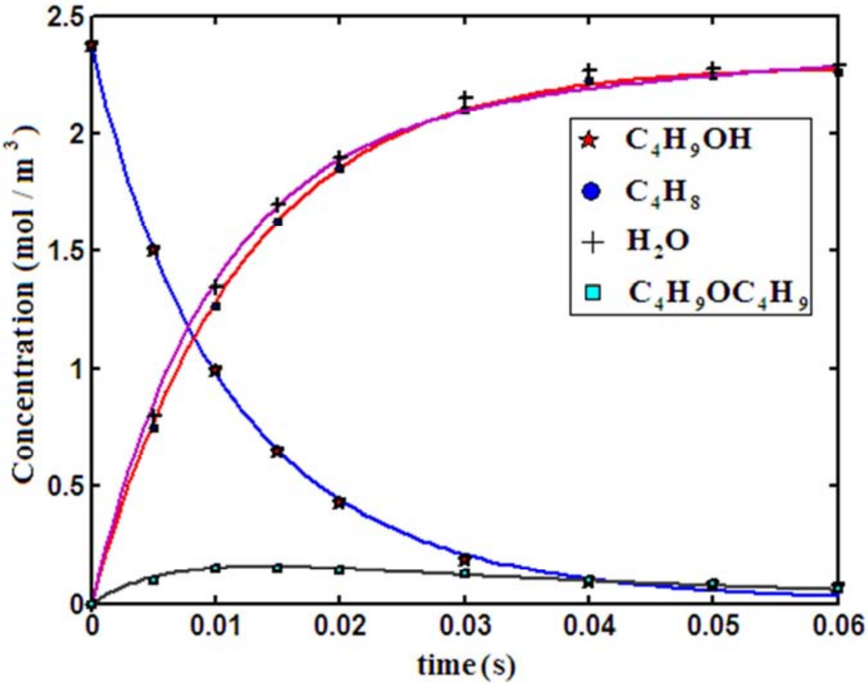

Figure 6. *Comparison of analytical result of concentration of 1-butanol, 1-butene, and water and dibutyl ether with experimental results (13-16).*

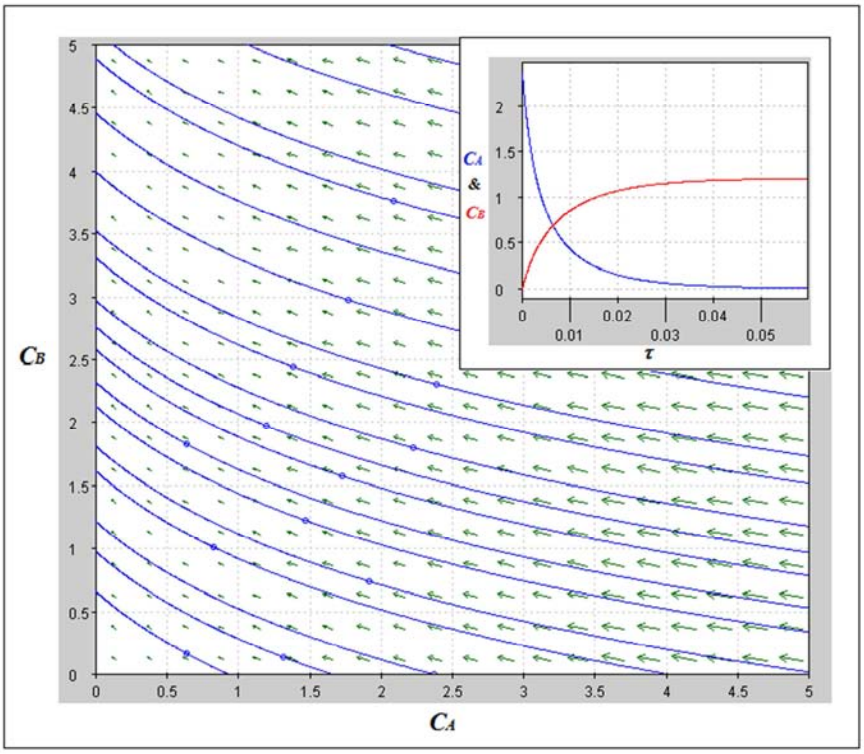

Figure 7. *Phase plane with parametric plot of the absolute values of C_A versus C_B. The curves correspond to trajectories with the parameters rate constants k_1, k_3 and different initial conditions.*

In Figure 7, we introduce a graphical approach for the system of nonlinear differential equations (13-16) based on phase plane analysis. This approach has the advantage of incorporating the nonlinear dynamics of the system while being graphically described. Phase trajectories will be plotted with different representative initial conditions for the concentration of C_A and C_B which is obtained by the relation between the concentration C_A and C_B. The effect of initial conditions on model time domain response is given in Figure 5. In particular time domain the phase plane analysis shows the concentration of C_A is increases and C_B decreases at high values of kinetic parameters k_1, k_3.

The kinetic constants are also determined from the rate equation (6) to (8). Plot of r_1 versus C_A and r_3 versus C_D gives the slope (= k_1, k_3 .). The rate equation (7) can be rewritten as follows:

$$\frac{r_2}{C_A{}^2} = k_1 - \left(\frac{C_C C_D}{C_A{}^2}\right) \cdot \frac{k_1}{K_{eq}} \tag{17}$$

Now the plot of $r_2 / C_A{}^2$ versus $C_C C_D / C_A{}^2$, gives the intercept k_1 and slope $\left(-k_1 / K_{eq}\right)$. From the slope and intercept, we can obtain the rate constants k_3 and equilibrium coefficient K_{eq} (figure 8).

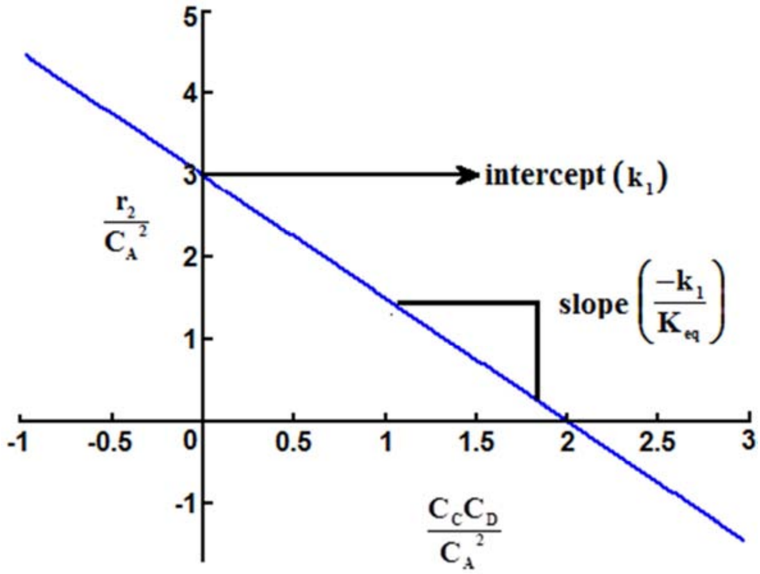

Figure 8. *Plot of r_2 / C_A^2 versus $C_C C_D / C_A^2$ using Eq. (17) for the fixed values $k_1 = 3, K_{eq} = 2$.*

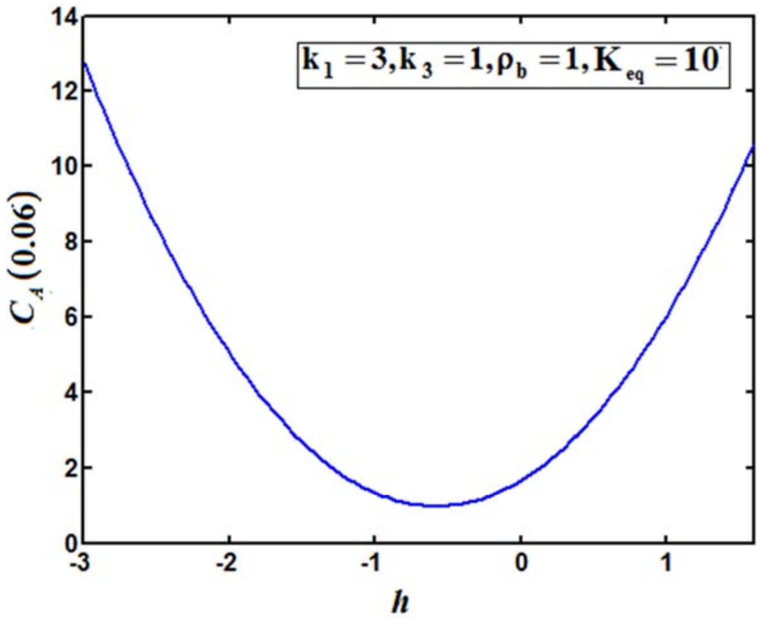

Figure 9. *The h curve to indicate the convergence region for $C_A(0.06)$.*

6. Conclusions

The system of nonlinear equations in microchannel reactor are solved using the homotopy analysis method (HAM). Analytical expression for the concentration of 1-butanol, 1-butene, and water and dibutyl ether production are derived in terms of the kinetic parameters. We have compared the analytical results with numerical and experimental results. The graphical procedure for the evaluation kinetic parameters are also reported.

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Appendix A

Basic idea of homotopy analysis method

In order to show the basic idea of HAM, we consider a linear or nonlinear equation in a general form:

$$N[u(x;t)] = 0; \tag{A1}$$

where N is a nonlinear operator $u(x;t)$ is an unknown function, x and t are independent variables. Let $u_0(x;t)$ denote an initial approximation of the solution of equation, h a nonzero auxiliary parameter, $H(x,t)$ a nonzero auxiliary function and L an auxiliary linear operator. For simplicity, we ignore all boundary or initial conditions, which can be treated in the similar way. By means of the HAM, we first construct the so-called zero-th order deformation equation.

$$(1-p)L[\phi(x;t;p) - u_0(x;t)] = phH(x;t)N[\phi(x;t;p)]; \tag{A2}$$

where $p \in [0,1]$ is the embedding parameter, $h \neq 0$ is an auxiliary parameter, L is an auxiliary linear operator, $\phi(x;t;p)$ is an unknown function, $u_0(x;t)$ is an initial guess of $u(x;t)$ and $H(x,t)$ denotes a nonzero auxiliary function. It is obvious that when the embedding parameter $p = 0$ and $p = 1$, it holds

$$\phi(x;t;0) = u_0(x;t); \quad \phi(x;t;1) = u(x;t); \tag{A3}$$

respectively. Thus as p increases from 0 to 1, $\phi(x;t;p)$ varies from the initial uses $\varphi(x;t;0)$ to the equation $\varphi(x;t;1)$ of equation. Expanding $\phi(x;t;p)$ in Taylors series with respect to p, we have

$$\phi(x,t;p) = u_0(t) + \sum_{m=1}^{+\infty} u_m(t)\, p^m, \tag{A4}$$

$$\text{Where } u_m(t) = \left[\frac{1}{m!}\frac{\partial^m m\phi(x;t;p)}{\partial p^m}\right]_{p=0} \tag{A5}$$

The convergence of the series (A4) depends upon the auxiliary parameter h. If it is convergent at $p = 1$, one has

$$u(x;t) = u_0(x;t) + \sum_{m=1}^{+\infty} u_m(x;t); \tag{A6}$$

This must be one of the solutions of the original nonlinear equation. Define the vectors

$$\vec{u} = \{u_{0,}(x,t), u_1(x,t)_{,} \ldots . u_n(x,t)\} \tag{A7}$$

Differentiating the zero-order deformation Eq. (A1) m-times with respect to p and then dividing them by $m!$ and finally setting $p = 0$, we get the following mth-order deformation equation.

$$L[u_m(x,t) - \chi_m u_{m-1}(x,t)] = hH(x,t)\Re_m\left(\vec{u}_{m-1}\right) \tag{A8}$$

$$\text{where } \Re_m\left(\vec{u}_{m-1}\right) = \frac{1}{(m-1)!}\frac{\partial^{m-1} m\phi(x;t;p)}{\partial p^{m-1}} \tag{A9}$$

and

$$\chi_m = \begin{cases} 0, & m \le 1, \\ 1, & m > 1 \end{cases}$$

Operating the inverse operation of L^{-1} on the both sides of Eq. (A5), we have

$$u_m(t) = \chi_m u_{m-1}(x,t) + hl^{-1}\left[H(t)\Re_m\left(\vec{u}_{m-1}\right)\right] \tag{A10}$$

In this way, it is easy to obtain $u_1(x;t); u_2(x;t); \ldots$. One after another, finally, we get an exact solution of the original equation.

$$u(t) = \sum_{m=1}^{+\infty} u_m(t) \tag{A11}$$

For the convergence of the above method we refer the reader to Liao [15]. If Eq. (A1) admits unique solution, then this method will produce the unique solution. If Eq. (A1) does not possess a unique solution, the HAM will give a solution among many other possible solutions.

Appendix B

Solution of the non-Linear equations using Homotopy analysis method

In this appendix, we derive the general solution of non-linear reaction Eq. (9), (10), (11), (12) using Homotopy analysis method.

To find the solution of Eq. (9), first the homotopy is constructed as follows:

$$(1-p)\left(\frac{dC_A}{d\tau}+2k_1\rho_b C_A\right)=ph\left(\frac{dC_A}{d\tau}+2k_1\rho_b C_A+2k_1\rho_b C_A{}^2-2\frac{k_1\rho_b}{K_{eq}}C_C C_D\right) \tag{B1}$$

the approximate solution of Eq. (B1) is:

$$C_A=C_{A_0}p^0+C_{A_1}p^1+C_{A_2}p^2+\ldots \tag{B2}$$

Substituting Eq. (B2) in Eq. (B1) results in:

$$(1-p)\begin{pmatrix}\dfrac{d\left(C_{A0}+C_{A1}p+C_{A2}p^2\right)}{d\tau}+\\ 2k_1\rho_b\left(C_{A0}+C_{A1}p+C_{A2}p^2\right)\end{pmatrix}=ph\begin{pmatrix}\dfrac{d\left(C_{A0}+C_{A1}p+C_{A2}p^2\right)}{d\tau}+2k_1\rho_b\left(C_{A0}+C_{A1}p+C_{A2}p^2\right)\\ +2k_1\rho_b\left(C_{A0}+C_{A1}p+C_{A2}p^2\right)\\ -2\dfrac{k_1\rho_b}{K_{eq}}\left(C_{C0}+C_{C1}p+C_{C2}p^2\right)\left(C_{D0}+C_{D1}p+C_{D2}p^2\right)\end{pmatrix}$$

Comparing the coefficients of like powers of p, we have

$$p^0:\frac{dC_{A_0}}{d\tau}+2k_1\rho_b C_{A_0}=0 \tag{B3}$$

$$p^1:\frac{dC_{A_1}}{d\tau}+2k_1\rho_b C_{A_1}-\left(\frac{dC_{A_0}}{d\tau}+2k_1\rho_b C_{A_0}\right)-h\left(\frac{dC_{A_0}}{d\tau}+2k_1\rho_b C_{A_0}+2k_1\rho_b C_{A_0}-2\frac{k_1\rho_b}{K_{eq}}C_{C_0}C_{D_0}\right)=0 \tag{B4}$$

Solving Eqs. (B3) and (B4) and using the initial condition (5), we have:

$$C_{A_0}(\tau)=C_{A_i}e^{-2k_1\rho_b\tau} \tag{B5}$$

$$C_{A_1}(\tau)=-h\left\{\begin{matrix}C_{A_i}{}^2\left(e^{-2k_1\rho_b\tau}-1\right)+2m\left(C_{A_i}+\dfrac{C_{A_i}{}^2}{4}\right)\left[\dfrac{1-e^{-2k_1\rho_b\tau}}{2k_1\rho_b}-\dfrac{e^{(2k_1\rho_b-k_3\rho_b)\tau}-1}{2k_1\rho_b-k_3\rho_b}\right]\\ -C_{A_i}\left[\dfrac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b}+\dfrac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right]-\dfrac{C_{A_i}{}^2}{4}\left[\dfrac{1-e^{-6k_1\rho_b\tau}}{6k_1\rho_b}+\dfrac{e^{(-2k_1\rho_b-k_3\rho_b)\tau}-1}{2k_1\rho_b+k_3\rho_b}\right]\end{matrix}\right\} \tag{B6}$$

where $m=\dfrac{4k_1{}^2\rho_b{}^2C_{A_i}}{Keq\left(k_3\rho_b-4k_1\rho_b\right)}$.

Proceeding like this we can get an approximate solution of Eq. (9). According to the HAM, it can be concluded that

$$C_A(\tau)\approx C_{A_0}(\tau)+C_{A_1}(\tau) \tag{B7}$$

After putting Eqs. (B5) and (B6) in (B7), the final results can be described as Eq. (13) in the text. To find the solution of Eq. (10), first the homotopy is constructed as follow:

$$(1-p)\left[\frac{dC_B}{d\tau}-2k_1\rho_b C_{A_i}e^{-2b_1\tau}\right]=ph\left[\frac{dC_B}{d\tau}-2k_1\rho_b C_A-2k_3\rho_b C_D\right] \tag{B8}$$

The approximate solution of Eq. (B13) is:

$$C_B = C_{B_0} p^0 + C_{B_1} p^1 + C_{B_2} p^2 + \dots \tag{B9}$$

Substituting Eq. (B9) in Eq. (B8) results in:

$$(1-p)\begin{bmatrix} \dfrac{d\left(C_{B_0} + C_{B_1} p + C_{B_2} p^2\right)}{d\tau} \\ -2k_1\rho_b C_{A_i} e^{-2\mathbf{b}_1\tau} \end{bmatrix} = ph\begin{bmatrix} \dfrac{d\left(C_{B_0} + C_{B_1} p + C_{B_2} p^2\right)}{d\tau} - 2k_1\rho_b\left(C_{A_0} + C_{A_1} p + C_{A_2} p^2\right) \\ -2k_3\rho_b\left(C_{D_0} + C_{D_1} p + C_{D_2} p^2\right) \end{bmatrix}$$

Comparing the coefficients of like powers of p, we have

$$p^0 : \frac{dC_{B_0}}{d\tau} = 2k_1\rho_b C_{A_i} e^{-2k_1\rho_b\tau} \tag{B10}$$

$$p^1 : \frac{dC_{B_1}}{d\tau} - \left(\frac{dC_{B_0}}{d\tau} + 2k_1\rho_b C_{A_i} e^{-2k_1\rho_b\tau}\right) - h\left(\frac{dC_{B_0}}{d\tau} - 2k_1\rho_b C_{A_0} - 2k_3\rho_b C_{D_0}\right) = 0 \tag{B11}$$

Solving Eqs. (B10) and (B11) and using the initial condition (5), we have:

$$C_{B_0} = C_{A_i}\left(1 - e^{-2k_1\rho_b\tau}\right) \tag{B12}$$

$$C_{B_1}(\tau) = -\frac{2hk_1k_3{}^2\rho_b{}^3C_{A_i}{}^2}{k_3\rho_b - 4k_1\rho_b}\left[\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_{31}\rho_b\tau} - 1}{k_3\rho_b}\right] \tag{B13}$$

Proceeding like this we can get an approximate solution equals to the exact solution. According to the HAM, it can be concluded that

$$C_B(\tau) \approx C_{B_0}(\tau) + C_{B_1}(\tau) \tag{B14}$$

After putting Eqs. (B12) and (B13) in (B14), the final results can be described as Eq. (14) in the text. To find the solution of Eq. (11), first the homotopy is constructed as follow:

$$(1-p)\left[\frac{dC_C}{d\tau} - 2k_1\rho_b C_{A_i} e^{-2k_1\rho_b t} - k_1\rho_b C_{A_i}{}^2 e^{-4k_1\rho_b t}\right] = ph\left[\frac{dC_C}{d\tau} - 2k_1\rho_b C_A - k_1\rho_b C_A{}^2 + \frac{k_1\rho_b}{K_{eq}} C_C C_D - k_3\rho_b C_D\right] \tag{B15}$$

The approximate solution of Eq. (B15) is:

$$C_C = C_{C_0} p^0 + C_{C_1} p^1 + C_{C_2} p^2 + \dots \tag{B16}$$

Substituting Eq. (B16) in Eq. (B15) results in:

$$(1-p)\begin{bmatrix} \dfrac{d\left(C_{C_0} + C_{C_1} P + C_{C_2} P^2\right)}{d\tau} \\ -2k_1\rho_b C_{A_i} e^{-2k_1\rho_b t} \\ -k_1\rho_b C_{A_i}{}^2 e^{-4k_1\rho_b t} \end{bmatrix} = ph\begin{bmatrix} \dfrac{d\left(C_{C_0} + C_{C_1} P + C_{C_2} P^2\right)}{d\tau} - 2k_1\rho_b\left(C_{A_0} + C_{A_1} P + C_{A_2} P^2\right) \\ -k_1\rho_b\left(C_{A_0} + C_{A_1} P + C_{A_2} P^2\right)^2 \\ +\dfrac{k_1\rho_b}{K_{eq}}\left(C_{C_0} + C_{C_1} P + C_{C_2} P^2\right)\left(C_{D_0} + C_{D_1} P + C_{D_2} P^2\right) \\ -k_3\rho_b\left(C_{D_0} + C_{D_1} P + C_{D_2} P^2\right) \end{bmatrix}$$

Comparing the coefficients of like powers of p, we have

$$p^0 : \frac{dC_{C_0}}{d\tau} = 2k_1\rho_b C_{A_i} e^{-2k_1\rho_b\tau} + k_1\rho_b C_{A_i}{}^2 e^{-4k_1\rho_b\tau} \tag{B17}$$

$$p^1 := \frac{dC_{C_1}}{d\tau} + 2k_1\rho_b C_{A_i} e^{-2k_1\rho_b\tau} + k_1\rho_b {C_{A_i}}^2 e^{-4k_1\rho_b\tau} - h\begin{bmatrix} \frac{dC_{C_0}}{d\tau} + 2k_1\rho_b C_{A_0} + k_1\rho_b {C_{A_0}}^2 \\ + \frac{k_1\rho_b}{K_{eq}} C_{C_0} C_{D_0} - k_3\rho_b C_{D_0} \end{bmatrix} \tag{B18}$$

Solving Eqs. (B17) and (B18) and using the initial condition (5), we have:

$$C_{C_0} = C_{Ai}\left(1 - e^{-2k_1\rho_b\tau}\right) + \frac{{C_{Ai}}^2}{4}\left(1 - e^{-4k_1\rho_b\tau}\right) \tag{B19}$$

$$C_{C_1}\left(\tau\right) = -\frac{hk_3k_1{\rho_b}^2{C_{A_i}}^2}{k_3\rho_b - 4k_1\rho_b}\left[\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right] + hm\begin{bmatrix} \left(C_{A_i} + \frac{{C_{A_i}}^2}{4}\right)\left(\frac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b} + \frac{e^{-k_3\rho_b\tau}-1}{k_3\rho_b}\right) \\ -C_{A_i}\left(\frac{1-e^{-6k_1\rho_b\tau}}{6k_1\rho_b} + \frac{e^{(-2k_1\rho_b - k_3\rho_b)\tau}-1}{2k_1\rho_b + k_3\rho_b}\right) \\ -\frac{{C_{A_i}}^2}{4}\left(\frac{1-e^{-8k_1\rho_b\tau}}{8k_1\rho_b} + \frac{e^{(-4k_1\rho_b - k_3\rho_b)\tau}-1}{4k_1\rho_b + k_3\rho_b}\right) \end{bmatrix} \tag{B20}$$

Proceeding like this we can get an approximate solution equals to the exact solution. According to the HAM, it can be concluded that

$$C_C\left(\tau\right) \approx C_{C_0}\left(\tau\right) + C_{C_1}\left(\tau\right) \tag{B21}$$

After putting Eqs. (B19) and (B20) in (B21), the final results can be described as Eq. (15) in the text. To find the solution of Eq. (12), first the homotopy is constructed as follow:

$$\left(1-p\right)\left[\frac{dC_D}{d\tau} + k_3\rho_b C_D - k_1\rho_b {C_{A_i}}^2 e^{-4k_1\rho_b\tau}\right] = ph\left[\frac{dC_D}{d\tau} - k_1\rho_b {C_A}^2 + \frac{k_1\rho_b}{K_{eq}} C_C C_D + k_3\rho_b C_D\right] \tag{B22}$$

The approximate solution of Eq. (B22) is

$$c_D = c_{D_0} p^0 + c_{D_1} p^1 + c_{D_2} p^2 + ... \tag{B23}$$

Substituting Eq. (B23) in Eq. (B22) results in:

$$(1-p)\begin{bmatrix} \frac{d\left(C_{D0} + C_{D1}p + +C_{D2}p^2\right)}{d\tau} \\ + b_3\left(C_{D0} + C_{D1}p + +C_{D2}p^2\right) \\ -b_1 {C_{A_i}}^2 e^{-4b_1\tau} \end{bmatrix} = ph\begin{bmatrix} \frac{d\left(C_{D0} + C_{D1}p + +C_{D2}p^2\right)}{d\tau} - b_1\left(C_{A0} + C_{A1}p + C_{A2}p^2\right)^2 \\ + b_1k\left(C_{C0} + C_{C1}p + +C_{C2}p^2\right)\left(C_{D0} + C_{D1}p + +C_{D2}p^2\right) \\ + b_3\left(C_{D0} + C_{D1}p + +C_{D2}p^2\right) \end{bmatrix}$$

Comparing the coefficients of like powers of p, we have

$$p^0 : \frac{dC_{D_0}}{d\tau} + k_3\rho_b C_{D_0} = k_1\rho_b {C_{A_i}}^2 e^{-4k_1\rho_b\tau} \tag{B24}$$

$$p^1 : \frac{dC_{D_1}}{d\tau} + k_3\rho_b C_{D_1} + k_1\rho_b {C_{A_i}}^2 e^{-4k_1\rho_b\tau} - h\left[\frac{dC_{D_0}}{d\tau} - k_1\rho_b C_{A_0} + \frac{k_1\rho_b}{K_{eq}} C_{C_0} C_{D_0} + k_3\rho_b C_{D_0}\right] = 0 \tag{B25}$$

Solving Eqs. (B24) and (B25) and using the initial condition (5), we have:

$$C_{D_0} = \frac{k_1\rho_b {C_{A_i}}^2}{k_3\rho_b - 4k_1\rho_b}\left[e^{-4k_1\rho_b\tau} - e^{-k_3\rho_b\tau}\right] \tag{B26}$$

$$C_{D_1} = he^{-k_3\rho_b\tau}\left\{\begin{array}{l} m\left(C_{A_i}+\dfrac{C_{A_i}{}^2}{4}\right)\left(\tau-\dfrac{e^{(-4k_1\rho+k_3\rho_b)\tau}-1}{k_3\rho_b-4k_1\rho}\right)-C_{A_i}\left[\dfrac{1-e^{-2k_1\rho_b\tau}}{2k_1\rho_b}-\dfrac{e^{(k_3\rho_b-6k_1\rho_b)\tau}-1}{k_3\rho_b-6k_1\rho_b}\right] \\ -\dfrac{C_{A_i}{}^2}{4}\left[\dfrac{1-e^{-4k_1\rho_b\tau}}{4k_1\rho_b}-\dfrac{e^{(-8k_1\rho_b+k_3\rho_b)\tau}-1}{k_3\rho_b-8k_1\rho_b}\right] \end{array}\right\} \quad \text{(B27)}$$

Proceeding like this we can get an approximate solution equals to the exact solution. According to the HAM, it can be concluded that

$$C_D(\tau) \approx C_{D_0}(\tau) + C_{D_1}(\tau) \quad \text{(B28)}$$

After putting Eqs. (B26) and (B27) in (B28), the final results can be described as Eq. (16) in the text.

Appendix C

Determining the Validity Region of h

The analytical solution represented by (13), (14), (15) and (16) contains the auxiliary parameter h, which gives the convergence region and rate of approximation for homotopy analysis method. The analytical solution should converge. It should be noted that the auxiliary parameter h controls the convergence and accuracy of the solution series. In order to define region such that the solution series is independent of h, a multiple of h curves are plotted. The region where the distribution of C_A, C_B, C_C and C_D versus h is a horizontal line is known as the convergence region for the corresponding function. The common region among concentrations is known as the overall convergence region. To study the influence of h on the convergence of solution, the h curves of $C_A(0.06)$ are plotted in Figure 9. This figure clearly indicates that the valid region of h is about (−0.5 to 0.6). Similarly we can find the value of the convergence-control parameter h for different values of constant parameters.

Appendix D

Nomenclature

C_A : Concentration for 1-butanol ($mol\, m^{-3}$)

C_B : Concentration for 1-butene ($mol\, m^{-3}$)

C_C : Concentration for water ($mol\, m^{-3}$)

C_D : Concentration for dibutyl ether ($mol\, m^{-3}$)

τ : Space time

k_1, k_3 : Reaction rate constant ($m^3 mol^{-1} s^{-1}$)

ρ_b : Bulk density ($kg\, m^{-3}$)

K_{eq} : Equilibrium coefficients (*None*)

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