

# Irreversible and Reversible Reactions in a Liquid Chromatographic Column: Analytical Solutions and Moment Analysis

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## Abstract

Reactive chromatographic processes are investigated theoretically for irreversible  $A \rightarrow B$  and reversible  $A \leftrightarrow B$  reactions. The models consist of two partial differential equations, accounting for each component convection, longitudinal dispersion, adsorption and first order chemical reactions. Analytical and numerical solutions of the models are needed for analyzing and optimizing the processes in the fixed-bed column. Analytical solutions are obtained by means of Laplace transformation. Temporal moments are derived from the Laplace-transformed solutions. For validation, the high resolution upwind finite volume scheme is applied to solve the model equations numerically. Several case studies are carried out and the

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analytical solutions are compared with the numerical ones. The good agreements between solutions verify both the correctness of the analytical solutions and the accuracy of the suggested numerical scheme.

## Introduction

Chromatography is a family of analytical chemistry techniques for the separation of mixtures. Common to all chromatographic techniques is the passing of a sample (the analyte) in the mobile phase past a static retentive medium called the stationary phase. The stationary phase provides resistance to transport via chemical interactions with the components of the sample. Each component in the sample has a characteristic separation rate that can be used to identify it, and thus the composition of the original mixture. It is an effective chemical technique for the separation and purification of life science products such as fine chemicals, pharmaceuticals, food additives and biological products. This technique is useful for the continuous separation of bulk multi-component mixtures and can be implemented for the separation of substances that are not feasibly separable by conventional processes, namely distillation and extraction.<sup>1-3</sup>

In a chromatographic reactor separation and chemical reactions of products take place simultaneously. The process is principally analogous to reactive extraction (or reactive absorption), reactive distillation and sedimentation or electrophoresis when accompanied by reaction. Chromatographic reactors, by virtue of separating products from reactants, can enhance the yield of reactions that in ordinary reactors are limited by equilibrium.<sup>4</sup> Moreover, they have capability to reduce investment, energy, operational cost, size of equipment, pollution and waste. The coupling between chemical reaction and chromatographic separation in a pulse-fed catalytic reactor were investigated by Schweich and Villermaux.<sup>5</sup> General transient models of reactive chromatography with Langmuir adsorption isotherms and mass transfer resistances were studied by Cho et al.<sup>6</sup> This theoretical work was experimentally verified by Petroulas et al.<sup>7</sup> The theoretical model for countercurrent chromatographic reactors was also verified experimentally.<sup>8-12</sup> The authors found

that deviation of experimental results from the theoretical ones was due to the assumption of linear adsorption isotherm. They also showed that these reactors improve the conversion of the product in reversible reactions such as isomerizations. Later on, the system was reviewed with a reversible reaction of the type  $A \leftrightarrow B$  by Carta.<sup>4</sup> The work was extended by Binous and McCoy<sup>13</sup> from two interacting isomers to three-component systems. Several other contributions on chromatographic reactors with different focal points were also published.<sup>1,14–21</sup>

The moment analysis has been used in a number of studies of fixed-bed systems. Schneider and Smith<sup>22</sup> used temporal moments to determine adsorption equilibrium constants, rate constants and intraparticle diffusivities from experimental measurements. Mehta et al.<sup>23</sup> represented the skewness of experimental elution curves by using their higher moments in the Hermite polynomial expansion. Breakthrough curves for fixed-bed adsorbers and reactors were represented with moments of the impulse response.<sup>24</sup> Recently, Javeed et al.<sup>25</sup> used the Laplace transformation to derive analytical solutions of the equilibrium dispersive and lumped kinetic models. Moreover, the authors also derived the first three moments of Laplace transformed solutions for different sets of boundary conditions (BCs).

This paper is focused on the analytical and numerical investigation of irreversible and reversible chromatographic reactions involving two components  $A$  and  $B$ . Analytical solutions are obtained by means of Laplace transformation and temporal moments are derived from the Laplace-transformed solutions.<sup>25,27–29</sup> In the case of no analytical Laplace inversion, the numerical Laplace inversion is used to get back the solution in actual time domain.<sup>30</sup> The high resolution upwind finite volume scheme is applied to solve the models numerically.<sup>17,31</sup> Several case studies are carried out and analytical solutions are compared with the numerical solutions.

The paper is organized as follows. In Section 2, the reactive chromatographic model describing irreversible reaction is analytically solved. In Section 3, the analysis is extended to the reversible reaction case. In Section 4, analytical moments are derived from the Laplace transformed solutions of irreversible and reversible reactions. Section 5, presents numerical test problems to validate analytical and numerical results. Finally, conclusions are drawn in Section 6.

# Chromatographic Reactor: Irreversible Reaction (A→B)

A one-dimensional reactive transport model of linear chromatography is considered. In this process, the component  $A$  (component 1) converts to  $B$  (component 2) through a simple irreversible first order reaction having reaction rate constant  $k$ . Analytical solutions of the model are obtained for different sets of inlet and outlet boundary conditions by means of Laplace transformation. Here, the elegant solution procedure of Quezada et al.<sup>27</sup> is adopted to solve the model equations. Let  $t$  denotes the time coordinate and  $z$  represents the axial coordinate along the column length. Moreover, it is assumed that both components have the same apparent dispersion coefficient  $D = D_1 = D_2$ . This assumptions, which is usually well fulfilled for molecules of similar sizes, simplifies the following mathematical analysis. The governing model equations are expressed as

$$(1 + a_1 F) \frac{\partial c_1}{\partial t} + u \frac{\partial c_1}{\partial z} - D \frac{\partial^2 c_1}{\partial z^2} = -k c_1, \quad (1)$$

$$(1 + a_2 F) \frac{\partial c_2}{\partial t} + u \frac{\partial c_2}{\partial z} - D \frac{\partial^2 c_2}{\partial z^2} = k c_1. \quad (2)$$

For an initially not preloaded fixed-bed holds

$$c_i(0, z) = 0, \quad i = 1, 2. \quad (3)$$

Appropriate boundary conditions at the column inlet and outlet are also needed which will be discussed bellow. In above equations,  $c_1$  and  $c_2$  denote the liquid concentrations for first and second components of the mixture,  $a_1$  and  $a_2$  represent the linear adsorption isotherms (or Henry coefficients),  $u$  is the interstitial velocity, and  $F = (1 - \varepsilon)/\varepsilon$  is a phase ratio based on the external porosity  $\varepsilon \in (0, 1)$ . Moreover,  $k$  is the rate constant of first order chemical reaction.

Normalizing eqs 1 and 2 by taking  $x = \frac{z}{L} \in [0, 1]$  and defining  $Pe = \frac{Lu}{D}$ , we obtain

$$\alpha_1 \frac{\partial c_1}{\partial t} + Pe \frac{\partial c_1}{\partial x} - \frac{\partial^2 c_1}{\partial x^2} = -r_D c_1, \quad (4)$$

$$\alpha_2 \frac{\partial c_2}{\partial t} + Pe \frac{\partial c_2}{\partial x} - \frac{\partial^2 c_2}{\partial x^2} = r_D c_1, \quad (5)$$

and eq 3 becomes

$$c_i(0, x) = 0, \quad i = 1, 2. \quad (6)$$

Here

$$\alpha_i = (1 + a_i F) Pe \frac{L}{u}, \quad r_D = k \frac{L^2}{D}, \quad i = 1, 2. \quad (7)$$

The Laplace transformation is applied to find the analytical solutions of eqs 4 and 5 for the given initial and boundary conditions. Two sets of boundary conditions are considered as discussed below. The derivation of analytical solutions of eqs 1 and 2 in the Laplace domain for irreversible reaction and Dirichlet boundary conditions are presented in the appendix A.

### **Dirichlet Boundary Conditions at the Column Inlet**

In this case, the normalized boundary conditions at the entrance of a not back mixed column of hypothetically infinite length are given as

$$c_i(t, 0) = c_{i,inj}, \quad \frac{\partial c_i}{\partial x}(t, \infty) = 0, \quad i = 1, 2. \quad (8)$$

Here  $c_{i,inj}$  denotes the  $i$ -th injected concentration at the left end of the column (i.e. at  $x = 0$ ).

For the BCs in eq 8, the Laplace domain solution is given as (see Appendix A)

$$\bar{c}_1(s, x) = \frac{c_{1, inj}}{s} M_1, \quad (9)$$

and

$$\bar{c}_2(s, x) = \frac{c_{2, inj}}{s} M_2 - \frac{r_{DC1, inj}}{s[s(\alpha_2 - \alpha_1) - r_D]} (M_2 - M_1), \quad (10)$$

where

$$M_1 = \exp\left(\frac{Pe - \sqrt{Pe^2 + 4(r_D + s\alpha_1)}}{2} x\right), \quad M_2 = \exp\left(\frac{Pe - \sqrt{Pe^2 + 4s\alpha_2}}{2} x\right). \quad (11)$$

The solutions in time domain  $c_i(t, x)$  can be obtained by using the exact formula for the back transformation:

$$c_j(t, x) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{-ts} \bar{c}_j(s, x) ds, \quad j = 1, 2, \quad (12)$$

where,  $\gamma$  is a real constant that exceeds the real part of all the singularities of  $\bar{c}_j(s, x)$ .

By applying eq 12 on eqs 9 and 10, we obtain<sup>27-29,32</sup>

$$c_1(t, x) = c_{1, inj} E_1, \quad (13)$$

$$c_2(t, x) = c_{2, inj} E_2 - c_{1, inj} (E_1 - E_2 + F_2 - F_1), \quad (14)$$

where

$$E_i = \frac{e^{\frac{Pex}{2}}}{2} \left[ e^{-a_i b_i} \operatorname{erfc}\left(\frac{a_i t^{-\frac{1}{2}}}{2} - b_i t^{\frac{1}{2}}\right) + e^{a_i b_i} \operatorname{erfc}\left(\frac{a_i t^{-\frac{1}{2}}}{2} + b_i t^{\frac{1}{2}}\right) \right], \quad (15)$$

with

$$a_i = (\alpha_i)^{\frac{1}{2}}x, \quad b_1 = \sqrt{\frac{Pe^2}{4\alpha_1} + \frac{r_D}{\alpha_1}}, \quad b_2 = \sqrt{\frac{Pe^2}{4\alpha_2}}, \quad i = 1, 2. \quad (16)$$

Moreover

$$F_i = \frac{1}{2}e^{\left(\frac{Pex}{2} + \frac{r_D t}{\alpha_2 - \alpha_1}\right)} \left[ e^{-a_i d_i} \operatorname{erfc}\left(\frac{a_i t^{-\frac{1}{2}}}{2} - d_i t^{\frac{1}{2}}\right) + e^{a_i d_i} \operatorname{erfc}\left(\frac{a_i t^{-\frac{1}{2}}}{2} + d_i t^{\frac{1}{2}}\right) \right], \quad (17)$$

with

$$d_1 = \sqrt{\frac{Pe^2}{4\alpha_1} + \frac{\alpha_2 r_D}{\alpha_1(\alpha_2 - \alpha_1)}}, \quad d_2 = \sqrt{\frac{Pe^2}{4\alpha_2} + \frac{r_D}{\alpha_2 - \alpha_1}}. \quad (18)$$

Here, erfc denotes the complementary error function. This completes the derivation of solutions for the boundary conditions given by eq 8.

## Robin (or Danckwerts) Boundary Conditions at the Column Inlet

In this case, back mixing at the inlet of a column of finite length are considered. The boundary conditions have the form<sup>33</sup>

$$c_i(t, 0) = c_{i,inj} + \frac{1}{Pe} \frac{\partial c_i}{\partial x}, \quad \frac{\partial c_i}{\partial x}(1, t) = 0, \quad i = 1, 2. \quad (19)$$

By adopting the procedure of Appendix A, the Laplace domain solutions for the boundary conditions in 19 are given as

$$\bar{c}_1(s, x) = \frac{c_{1,inj}}{s} \frac{\lambda_2 e^{\lambda_2 + \lambda_1 x} - \lambda_1 e^{\lambda_1 + \lambda_2 x}}{\left(1 - \frac{\lambda_1}{Pe}\right) \lambda_2 e^{\lambda_2} - \left(1 - \frac{\lambda_2}{Pe}\right) \lambda_1 e^{\lambda_1}}, \quad \lambda_{1,2} = \frac{Pe \pm \sqrt{Pe^2 + 4(r_D + s\alpha_1)}}{2}, \quad (20)$$

and

$$\begin{aligned} \bar{c}_2(s, x) = & \left( \frac{c_{2,inj}}{s} - \frac{c_{1,inj}}{s} \frac{r_D}{s(\alpha_2 - \alpha_1) - r_D} \right) \left( \frac{\lambda_4 e^{\lambda_4 + \lambda_3 x} - \lambda_3 e^{\lambda_3 + \lambda_4 x}}{\left(1 - \frac{\lambda_3}{Pe}\right) \lambda_4 e^{\lambda_4} - \left(1 - \frac{\lambda_4}{Pe}\right) \lambda_3 e^{\lambda_3}} \right) \\ & + \frac{c_{1,inj}}{s} \left( \frac{r_D}{s(\alpha_2 - \alpha_1) - r_D} \right) \left( \frac{\lambda_2 e^{\lambda_2 + \lambda_1 x} - \lambda_1 e^{\lambda_1 + \lambda_2 x}}{\left(1 - \frac{\lambda_1}{Pe}\right) \lambda_2 e^{\lambda_2} - \left(1 - \frac{\lambda_2}{Pe}\right) \lambda_1 e^{\lambda_1}} \right). \end{aligned} \quad (21)$$

Here,

$$\lambda_{3,4} = \frac{Pe \pm \sqrt{Pe^2 + 4s\alpha_2}}{2}. \quad (22)$$

In this case, no analytical Laplace inversions is possible. Therefore, numerical Laplace inversions will be used to get back the solution in the time domain.<sup>30</sup> In this technique, the exact integrals of back transformation (c.f. eq 12) are approximated by using Fourier series.

## Reversible Reaction $A \leftrightarrow B$

Now, we present a reactive chromatographic model describing reversible reactions. In this case  $A$  (component 1) is injected to the column which converts to  $B$  (component 2) with a reaction rate characterized by the constant  $k_1$ . Because of the reversibility of the reaction,  $B$  is also converted back to  $A$  with reaction of rate constant  $k_2$ . The corresponding model equations are given as

$$(1 + a_1 F) \frac{\partial c_1}{\partial t} + u \frac{\partial c_1}{\partial z} - D \frac{\partial^2 c_1}{\partial z^2} = -k_1 c_1 + k_2 c_2, \quad (23)$$

$$(1 + a_2 F) \frac{\partial c_2}{\partial t} + u \frac{\partial c_2}{\partial z} - D \frac{\partial^2 c_2}{\partial z^2} = k_1 c_1 - k_2 c_2, \quad (24)$$

with initial conditions

$$c_i(0, z) = 0, \quad i = 1, 2. \quad (25)$$



In normalized form the above equations can be rewritten as

$$\begin{aligned}\alpha_1 \frac{\partial c_1}{\partial t} + Pe \frac{\partial c_1}{\partial x} - \frac{\partial^2 c_1}{\partial x^2} &= -r_{D,1}c_1 + r_{D,2}c_2, \\ \alpha_2 \frac{\partial c_2}{\partial t} + Pe \frac{\partial c_2}{\partial x} - \frac{\partial^2 c_2}{\partial x^2} &= r_{D,1}c_1 - r_{D,2}c_2,\end{aligned}\quad (26)$$

where

$$x = \frac{z}{L}, \quad Pe = \frac{Lu}{D}, \quad \alpha_i = (1 + a_i F) \frac{PeL}{u}, \quad r_{D,i} = k_i \frac{L^2}{D}, \quad i = 1, 2. \quad (27)$$

Once again, two different pairs of BCs are considered which are given by eqs 8 and 19. By adopting the same solution procedure of Appendix A, we get the following solutions in the Laplace domain for the considered two types of BCs.

### Dirichlet Boundary Conditions at the Column Inlet

In this first case, again the boundary conditions in eq 8 are taken into account. The solutions in Laplace domain are summarized as

$$\bar{c}_1(s, x) = \frac{\xi_3(r_{D,1}c_{1,inj} - \xi_4 c_{2,inj})}{sr_{D,1}(\xi_3 - \xi_4)} e^{m_2 x} - \frac{\xi_4(r_{D,1}c_{1,inj} - \xi_3 c_{2,inj})}{sr_{D,1}(\xi_3 - \xi_4)} e^{m_4 x}, \quad (28)$$

$$\bar{c}_2(s, x) = \frac{(r_{D,1}c_{1,inj} - \xi_4 c_{2,inj})}{s(\xi_3 - \xi_4)} e^{m_2 x} - \frac{(r_{D,1}c_{1,inj} - \xi_3 c_{2,inj})}{s(\xi_3 - \xi_4)} e^{m_4 x}, \quad (29)$$

where for  $W := r_{D,1} - r_{D,2}$ ,  $R := r_{D,1} + r_{D,2}$ ,  $Q := \alpha_2 - \alpha_1$  and  $G := \alpha_1 + \alpha_2$ ,

$$m_{1,2} = \frac{Pe \pm \sqrt{Pe^2 - 4\xi_1}}{2}, \quad m_{3,4} = \frac{Pe \pm \sqrt{Pe^2 - 4\xi_2}}{2}, \quad (30)$$

and

$$\xi_{1,2} = -\frac{1}{2} \left[ R + sG \mp \sqrt{R^2 + s^2 Q^2 - 2sWQ} \right], \quad (31)$$

$$\xi_{3,4} = -\frac{1}{2} \left[ W - sQ \mp \sqrt{R^2 + s^2 Q^2 - 2sWQ} \right]. \quad (32)$$

Analytical Laplace inversions of the above equations are very difficult to derive. Therefore, numerical Laplace inversions are used again to get back solutions in time domain.<sup>30</sup>

## Robin (or Danckwerts) Boundary Conditions at the Column Inlet

In this case, the BCs in eq 19 are reconsidered. The solutions in the Laplace domain are given as

$$\begin{aligned} \bar{c}_1(s, x) = & \frac{\xi_3(r_{D,1}c_{1,inj} - \xi_4 c_{2,inj})(m_1 e^{m_1+m_2x} - m_2 e^{m_2+m_1x})}{r_{D,1}s(\xi_3 - \xi_4) \left( (1 - \frac{m_2}{Pe})m_1 e^{m_1} - (1 - \frac{m_1}{Pe})m_2 e^{m_2} \right)} \\ & + \frac{\xi_4(\xi_3 c_{2,inj} - r_{D,1}c_{1,inj})(m_3 e^{m_3+m_4x} - m_4 e^{m_4+m_3x})}{r_{D,1}s(\xi_3 - \xi_4) \left( (1 - \frac{m_4}{Pe})m_3 e^{m_3} - (1 - \frac{m_3}{Pe})m_4 e^{m_4} \right)}, \end{aligned} \quad (33)$$

and

$$\begin{aligned} \bar{c}_2(s, x) = & \frac{(r_{D,1}c_{1,inj} - \xi_4 c_{2,inj})(m_1 e^{m_1+m_2x} - m_2 e^{m_2+m_1x})}{s(\xi_3 - \xi_4) \left( (1 - \frac{m_2}{Pe})m_1 e^{m_1} - (1 - \frac{m_1}{Pe})m_2 e^{m_2} \right)} \\ & + \frac{(\xi_3 c_{2,inj} - r_{D,1}c_{1,inj})(m_3 e^{m_3+m_4x} - m_4 e^{m_4+m_3x})}{s(\xi_3 - \xi_4) \left( (1 - \frac{m_4}{Pe})m_3 e^{m_3} - (1 - \frac{m_3}{Pe})m_4 e^{m_4} \right)}, \end{aligned} \quad (34)$$

where  $\xi_i$  and  $m_i$  for  $i = 1, 2, 3, 4$  are given by eqs 31, 32 and 30. Once again, analytical Laplace inversions of the above equations are not possible. Therefore, numerical Laplace inversions are used to determine the time domain solutions.

## Moments Analysis

Moment analysis is an effective method for deducing important information about the retention equilibrium and mass transfer kinetics in the column.<sup>3,25,34,35</sup> The Laplace transformation can be

used as a basic tool to obtain moments. The numerical inverse Laplace transformation provides optimum solution, but this solution is not helpful to study the behavior of chromatographic profiles in the column. The retention equilibrium-constant and parameters of mass transfer kinetics in a column are related to the moments in Laplace domain. Analytical moments are derived from the solutions in Laplace domain by using the moment generating property for continuous breakthrough curves.<sup>25</sup> In this case,  $\bar{c}_i$  are multiplied with  $s$  to transform the step responses to closed pulse responses that allow calculation of finite moments.

The zeroth moments are defined as

$$\mu_0^{(i)} = \lim_{s \rightarrow 0} (s\bar{c}_i(s, x = 1)), \quad i = 1, 2 \quad (35)$$

and the  $n$ -th moments are given as

$$\mu_n^{(i)} = (-1)^n \frac{1}{\mu_0^{(i)}} \lim_{s \rightarrow 0} \frac{d^n (s\bar{c}_i(s, x = 1))}{ds^n}, \quad n = 1, 2, 3, \dots \quad (36)$$

Next, we define temporal moments to obtain moments from analytical and numerical solutions in the actual time domain. The normalized  $n$ -th temporal moments of the band profiles at the exit of chromatographic column of length  $x = 1$  are defined as

$$\mu_n^{(i)} = \frac{\int_0^\infty \dot{c}_i(t, x = 1) t^n dt}{\int_0^\infty c_i(t, x = 1) dt}, \quad \text{where } \dot{c} = \frac{dc}{dt} \quad n = 0, 1, 2, \dots, \quad i = 1, 2. \quad (37)$$

While, the  $n$ -th central moments are expressed as

$$\mu_n'^{(i)} = \frac{\int_0^\infty \dot{c}_i(t, x = 1) (t - \mu_1^{(i)})^n dt}{\int_0^\infty c(t, x = 1) dt}, \quad n = 0, 1, 2, \dots, \quad i = 1, 2. \quad (38)$$

The formulas given above use derivatives to approximate the moments and transform the step response to pulse response which is the requirement of finite results of numerical integration. These moments will be used to compare analytical and numerical moments.

Complete derivations of the moments up to the third moments are presented in the appendix B, using the availability of solutions in Laplace domain and the moment generating property of this transformation for continuous boundary conditions. Moreover, it is assumed that  $c_{2,inj} = 0$ , i.e. only component A is injected to the column.

## Numerical Test Problems

Analytical results of the previous sections are validated by considering selected test problems. For this, analytical solutions are compared with the numerical solutions of high resolution flux-limiting finite volume scheme (FVS).<sup>31,36</sup>

In all test problems, it is assumed that  $c_{2,inj} = 0$ , i.e. only component A is injected to the column.

### Problem 1: Irreversible Reaction

In this test problem, analytical and numerical results of model equations given by eqs 1 and 2 are compared for Dirichlet and Danckwerts inlet BCs (c.f. eqs 8 and 19). All parameters of the problems are given in Table 1. The values of  $k$ ,  $k_1$  and  $k_2$  were selected to ensure that significant degrees of conversion can be achieved within available residence times which is compatible to the adsorption properties and allow for separating the components A and B.<sup>37,38</sup> It has been proven experimentally that such a careful match in a chromatographic reactor leads to improved performance compared to the conventional fixed bed reactor.<sup>39,40</sup>

Figure 1 (left) shows the comparison of solutions for Dirichlet inlet BCs on a column of infinite length with outflow BCs at the outlet (c.f. eq 8). In this case, three types of solutions are compared, such as analytical solutions obtained by analytical Laplace inversions, solutions obtained through numerical Laplace inversions, and solutions obtained from the finite volume scheme. Good agreements of the solution profiles validate the accuracy of numerical Laplace inversion and FVS. From the results it is clear that the first component with larger value of adsorption coefficient  $a_1$  elutes at

later time from the column compared to the second component with smaller value of  $a_2$ . Because of only a forward reaction, the concentration  $c_1$  of component 1 is decreasing and  $c_2$  of component 2 is increasing.

The right plot in Figure 1 (right) depicts the comparison of solutions for Danckwerts inlet BCs on a column of finite length with outflow BCs at the right end (c.f. eq 19). In this case, two kinds of solutions are compared, such as analytical solutions obtained through numerical Laplace inversion and solutions obtained from the FVS. Good agreements of the results validate again the accuracy of numerical Laplace inversion and the FVS. Moreover, the behaviors of concentration profiles are exactly the same as observed in the case of Dirichlet BCs.

Figure 2 illustrates the effect of boundary conditions on the solution. Here, we take the interstitial velocity  $u = 0.6 \text{ cm}/\text{min}$ . It can be observed that more accurate Danckwerts boundary conditions are needed for chromatographic model equations when the Peclet number is relatively small, e.g.  $Pe < 60$  (or  $D > 0.01 \text{ cm}^2/\text{min}$ ) in this case. For such values, there are visible differences between the results obtained by using Dirichlet and Danckwerts boundary conditions. On the basis of these results, we can conclude in agreement with previous findings, e.g in Danckwerts,<sup>33</sup> that the implementation of Dirichlet boundary conditions is not sufficient for larger dispersion coefficients. However, for large values of Peclet number ( $Pe \geq 60$ ) or smaller axial dispersion coefficients ( $D \leq 0.01 \text{ cm}^2/\text{min}$ ), typically encountered in chromatographic columns well packed with small particles, there is not much difference between the solutions of Dirichlet and Danckwerts boundary conditions.

### **Discussion on the Analytically and Numerically Determined Moments**

Now we present an analysis of analytically and numerically determined temporal moments for considered BCs. It is an effective strategy to deduce important information about retention time and mass transfer kinetics in the chromatographic column. The complete derivation of moments for considered BCs are given in the Appendix B. Some analytical expressions for  $\mu_2^{(i)}$  and  $\mu_3^{(i)}$  were very lengthy. Therefore, only plots of these central moments are presented in such situations.

The numerical moments are obtained from the FVS by using the moment formulas given in eqs 37 and 38 for the zeroth, first, second central, and third central moments, respectively. The trapezoidal rule is applied to numerically approximate the integral terms appearing in these equations. Here, derivatives of the concentration profiles are used to approximate the moments, transforming the step response to a pulse response which is a requirement for finite results of the numerical integration.

A quantitative comparison of the zeroth, first, second and third analytical and numerical moments over different flow rates was made. The zeroth absolute moments represent the total masses of the solutes (area under  $c_i$  versus  $t$ ). The first moments  $\mu_1^{(i)}$  denote the retention times (mean of the concentration pulses). The values of the equilibrium constants  $a_i$  can be estimated from the slopes of a straight lines,  $\mu_1^{(i)}$  over  $1/u$  for constant column length and porosity. The second central moments  $\mu_2'^{(i)}$  are a measure of the spread of the concentration profiles about the location of the center of masses (i.e. the variance of the elution curves) and provide suitable information about the mass transfer processes in the column. The third central moments  $\mu_3'^{(i)}$  represent the skewness of the concentration distributions (i.e. they evaluate front asymmetries).

Figure 3 shows the comparison of moments corresponding to Danckwerts boundary conditions. Due to the determined dependencies the zeroth, first, second, and third moments are plotted versus  $u$ ,  $1/u$ ,  $1/u^3$ , and  $1/u^5$ . The expected linear trends were found. A good agreement of the results verifies the correctness of analytical moments and also the high precision of our numerical results.

## **Problem 2: Reversible Reaction**

This part focuses on the comparison of analytical and numerical results for the two-component linear reactive equilibrium dispersive model with Dirichlet and Danckwerts inlet boundary conditions (c.f. eqs 23, 24, 8 and 19). The reaction is reversible. All parameters of the problems are given in Table 1.

Figure 4 (left) shows the comparison of analytical and numerical solutions for Dirichlet continuous inlet boundary conditions. Similarly, Figure 4 (right) shows the solutions for Danckwerts

BCs. Here, two solutions are compared, such as the analytical solution obtained through numerical Laplace inversion and solution obtained from the FVS. The expressions of the third analytical moments for Dirichlet and Danckwerts BCs are very long and complicated. Therefore, third moments were only calculated from the numerical Laplace inversion solution and the numerical solutions of FVS. Good agreements of the solution profiles validate the accuracy of numerical Laplace inversion and the FVS. From the results it is clear that the component with larger value of adsorption coefficient  $a_i$  elutes at later time from the column compared to the component with smaller value of  $a_i$ . Because of the reversibility of the reaction, heights of concentrations are changing for both components. The concentration of first component with larger value of decay rate constant  $k_1$  is decaying while concentration of component 2 is increasing due to smaller value of decay rate constant  $k_2$ .

### **Discussion on the Analytically and Numerically Determined Moments**

A quantitative comparison of the zeroth, first, second and third analytical and numerical moments over different flow rates was made. Figure 5 shows the moments for Danckwerts BCs. A good agreement of the results with each other verify the high precision of our numerical results and reveal the expected linear trends.

### **Effects of reaction rate constants on the solution**

The effects of the reaction rate constants on breakthrough profiles was investigated for reversible reactions using Danckwerts BCs and choosing again  $c_{1,inj} = 1$  and  $c_{2,inj} = 0$ . Figure 6 presents the concentration profiles for the flow rate given in Table 1. Moreover, we considered  $k_1 = 0.4 \text{ min}^{-1}$  and varied values of  $k_2$ . As expected due to thermodynamic considerations, it was found that the trends of the steady state concentrations correlate with the ratios  $k_1/k_2$ . For  $k_1/k_2 = 0.1$ , the values of concentrations at steady state are  $c_1 = 0.9 \text{ g/l}$  and  $c_2 = 0.1 \text{ g/l}$  and for  $k_1/k_2 = 10$  they are  $c_1 = 0.67 \text{ g/l}$  and  $c_2 = 0.33 \text{ g/l}$ , satisfying always  $c_1 + c_2 = 1 \text{ g/l}$ .

# Conclusion

In this article, reactive chromatographic models were analyzed for linear adsorption isotherms incorporating irreversible and reversible reactions. Both Dirichlet and Danckwerts inlet boundary conditions were considered. The Laplace transformation was employed as a basic tool to transform the linear sub-models of PDEs to linear ODEs which could be solved analytically in the Laplace domain. In the case of no analytical Laplace inversion, the numerical Laplace inversion technique produced reliable results to get back the solution in actual time domain. Moment analysis of the models was carried out analytically and numerically up to third order orders under linear conditions. The second order flux-limiting finite volume was used to generate the concentration profiles and the numerical moments. Good agreement between analytical and numerical results ensured correctness of the analytical results and accuracy of the proposed numerical scheme.

Work is in progress to utilize the analytically determined moments for parameter estimation.

## Appendix A

### Analytical solution of eqs 1 and 2

In the matrix notation, eqs 4 and 5 are expressed as

$$\begin{bmatrix} \alpha_1 & 0 \\ 0 & \alpha_2 \end{bmatrix} \frac{\partial}{\partial t} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} + Pe \frac{\partial}{\partial x} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} - \frac{\partial^2}{\partial x^2} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix} = \begin{bmatrix} -r_D & 0 \\ r_D & 0 \end{bmatrix} \begin{Bmatrix} c_1 \\ c_2 \end{Bmatrix}, \quad (\text{A-1})$$

where parenthesis [ ] stands for a square matrix and { } represents column matrix. By applying the Laplace transformation in time domain, the above equation gives<sup>27</sup>

$$s \begin{bmatrix} \alpha_1 & 0 \\ 0 & \alpha_2 \end{bmatrix} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix} + Pe \frac{d}{dx} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix} - \frac{d^2}{dx^2} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix} = \begin{bmatrix} -r_D & 0 \\ r_D & 0 \end{bmatrix} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix}, \quad (\text{A-2})$$



where in the Laplace domain,  $\bar{c}_1$  and  $\bar{c}_2$  are the concentrations of mixture components in the liquid phase. By rearranging eq A-2, we obtain

$$Pe \frac{d}{dx} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix} - \frac{d^2}{dx^2} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix} = \begin{bmatrix} -r_D - s\alpha_1 & 0 \\ r_D & -s\alpha_2 \end{bmatrix} \begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix}. \quad (\text{A-3})$$

Thus, a combined reaction coefficient matrix  $[B]$  on the right hand side of eq A-3 becomes

$$B = \begin{bmatrix} -r_D - s\alpha_1 & 0 \\ r_D & -s\alpha_2 \end{bmatrix}. \quad (\text{A-4})$$

Next, we compute the linear transformation matrix  $[A]$ . Note that, the columns of  $[A]$  should be the eigenvectors of the combined reaction coefficient matrix  $[B]$ . The eigenvalues and eigenvectors of  $[B]$  are given as:

$$\lambda' = -r_D - s\alpha_1, \quad x_1 = \begin{bmatrix} A_{11} \\ \frac{r_D A_{11}}{s(\alpha_2 - \alpha_1) - r_D} \end{bmatrix} \quad \text{and} \quad \lambda'' = -s\alpha_2, \quad x_2 = \begin{bmatrix} 0 \\ A_{22} \end{bmatrix}. \quad (\text{A-5})$$

Here,  $\lambda'$  and  $\lambda''$  are the eigenvalues and  $A_{11}$  and  $A_{22}$  are the arbitrary constants. For simplicity, we take the values of  $A_{11}$  and  $A_{22}$  equal to one. Then, using eq A-5, the diagonal matrix  $\tilde{k}$  and the transformation matrix  $[A]$  can be written as

$$\tilde{k} = \begin{bmatrix} -r_D - s\alpha_1 & 0 \\ 0 & -s\alpha_2 \end{bmatrix}, \quad A = \begin{bmatrix} 1 & 0 \\ \frac{r_D}{s(\alpha_2 - \alpha_1) - r_D} & 1 \end{bmatrix}. \quad (\text{A-6})$$

The matrix  $[A]$  can be used for the following linear transformation

$$\begin{Bmatrix} \bar{c}_1 \\ \bar{c}_2 \end{Bmatrix} = \begin{bmatrix} 1 & 0 \\ \frac{r_D}{s(\alpha_2 - \alpha_1) - r_D} & 1 \end{bmatrix} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix}. \quad (\text{A-7})$$

By applying the above linear transformation on eq A-3 we get

$$Pe \frac{d}{dx} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix} - \frac{d^2}{dx^2} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix} = \begin{bmatrix} -r_D - s\alpha_1 & 0 \\ 0 & -s\alpha_2 \end{bmatrix} \begin{Bmatrix} b_1 \\ b_2 \end{Bmatrix}. \quad (\text{A-8})$$

One can see that eq A-8 represents the two independent, steady state, advection-dispersion equations with decay term of first order. Next is to find the explicit solutions of these two independent ordinary differential equations (ODEs)

$$\frac{d^2 b_1}{dx^2} - Pe \frac{db_1}{dx} - (r_D + s\alpha_1)b_1 = 0, \quad (\text{A-9})$$

$$\frac{d^2 b_2}{dx^2} - Pe \frac{db_2}{dx} - s\alpha_2 b_2 = 0. \quad (\text{A-10})$$

The solutions of ODEs in eqs A-9 and A-10 are given as

$$b_1(s, x) = A_1 e^{\lambda_1 x} + B_1 e^{\lambda_2 x}, \quad \lambda_{1,2} = \frac{Pe \pm \sqrt{Pe^2 + 4(r_D + s\alpha_1)}}{2}, \quad (\text{A-11})$$

and

$$b_2(s, x) = A_2 e^{\lambda_3 x} + B_2 e^{\lambda_4 x}, \quad \lambda_{3,4} = \frac{Pe \pm \sqrt{Pe^2 + 4s\alpha_2}}{2}. \quad (\text{A-12})$$

Here,  $A_1, B_1, A_2$  and  $B_2$  are constants of integration which can be obtained by using suitable BCs at the column inlet and outlet. In this study, we consider two sets of BCs given in eqs 8 and 19. If  $r_D = 0$ , eqs A-11 and A-12 reduce to the well known non-reactive chromatographic model equations discussed in Javeed et al.<sup>25</sup>

## Dirichlet Boundary Conditions at the Column Inlet

In the Laplace domain, the boundary conditions in eq 8 can be expressed as

$$\bar{c}_i(s, 0) = \frac{c_{i,inj}}{s}, \quad \frac{d\bar{c}_i}{dx}(s, \infty) = 0 \quad i = 1, 2. \quad (\text{A-13})$$

Using the transformation given in eq A-7, we have

$$\bar{c}_1(s, x) = b_1(s, x), \quad (\text{A-14})$$

which gives

$$\bar{c}_1(s, 0) = b_1(s, 0) = \frac{c_{1,inj}}{s}, \quad \frac{db_1}{\partial x}(s, \infty) = 0. \quad (\text{A-15})$$

Similarly

$$b_2(s, x) = \bar{c}_2(s, x) - \frac{r_D b_1(s, x)}{[s(\alpha_2 - \alpha_1) - r_D]}, \quad (\text{A-16})$$

so that

$$b_2(s, 0) = \bar{c}_2(s, 0) - \frac{r_D b_1(s, 0)}{[s(\alpha_2 - \alpha_1) - r_D]}, \quad \frac{db_2}{dx}(s, \infty) = 0. \quad (\text{A-17})$$

After applying the boundary conditions in eqs A-15 and A-17 on eq A-11, the values of  $A_1$  and  $B_1$  become

$$A_1 = 0, \quad B_1 = \frac{c_{1,inj}}{s}. \quad (\text{A-18})$$

Thus, eq A-11 takes the following simple form

$$b_1(s, x) = \frac{c_{1,inj}}{s} e^{\lambda_2 x}. \quad (\text{A-19})$$

Using the relation in eq A-14, we get the solution in Laplace domain as

$$\bar{c}_1(s, x) = \frac{c_{1, inj}}{s} M_2. \quad (\text{A-20})$$

Similarly, using eq A-17 in eq A-12, we get the values of  $A_2$  and  $B_2$  as

$$A_2 = 0, \quad B_2 = \frac{c_{2, inj}}{s} - \frac{r_D c_{1, inj}}{s[s(\alpha_2 - \alpha_1) - r_D]}. \quad (\text{A-21})$$

Thus, eq A-12 together with the values of  $A_2$  and  $B_2$  becomes

$$b_2(s, x) = \left( \frac{c_{2, inj}}{s} - \frac{r_D c_{1, inj}}{s[s(\alpha_2 - \alpha_1) - r_D]} \right) e^{\lambda_4 x}. \quad (\text{A-22})$$

After using eq A-16 in eq A-22 we obtain

$$\bar{c}_2(s, x) = \frac{c_{2, inj}}{s} M_2 - \frac{r_D c_{1, inj}}{s[s(\alpha_2 - \alpha_1) - r_D]} (M_2 - M_1), \quad (\text{A-23})$$

where according to eqs A-11 and A-12

$$M_1 = \exp\left(\frac{Pe - \sqrt{Pe^2 + 4(r_D + s\alpha_1)}}{2} x\right), \quad M_2 = \exp\left(\frac{Pe - \sqrt{Pe^2 + 4s\alpha_2}}{2} x\right). \quad (\text{A-24})$$

## Appendix B

### Analytical moments of the elution profiles

Analytical moments are presented for Dirichlet and Danckwerts boundary conditions. Here,  $c_{2, inj} = 0$  is taken into account, i.e. only component A is injected to the column.

## Irreversible Reaction with Dirichlet inlet BCs

Here, eqs 35 and 36 are used to obtain moments  $\mu_n^{(i)}$  of eqs A-20 and A-23 obtained for the Dirichlet boundary conditions in eq 8 for  $i = 1, 2$  and  $n = 0, 1, 2, 3$ . Let us define

$$\gamma := \sqrt{Pe^2 + 4r_D}, \quad \beta_{1,2} := Pe \mp \gamma, \quad Q := \alpha_2 - \alpha_1. \quad (\text{A-25})$$

By using eq 35, the zeroth moments are given as

$$\mu_0^{(1)} = c_{1,inj} e^{\frac{\beta_1}{2}}, \quad \mu_0^{(2)} = c_{1,inj} \left[ 1 - e^{\frac{\beta_1}{2}} \right]. \quad (\text{A-26})$$

From eq A-26, it follows that  $\mu_0^{(1)} + \mu_0^{(2)} = c_{1,inj}$ , because  $c_{2,inj} = 0$ .

The first moments are calculated by employing eq 36 for  $n = 1$

$$\mu_1^{(1)} = Pe \frac{L}{u\gamma} (1 + aF), \quad \mu_1^{(2)} = \frac{Pe \left( \gamma Q - r_D \alpha_1 \right) e^{\frac{\beta_1}{2}} - \gamma \left( QPe - r_D \alpha_2 \right)}{r_D Pe \gamma \left( 1 - e^{\frac{\beta_1}{2}} \right)}, \quad (\text{A-27})$$

The second moments are expressed as

$$\mu_2^{(1)} = \frac{L^2 Pe^2}{u^2 \gamma^3} (1 + aF)^2 (\gamma + 2), \quad (\text{A-28})$$

$$\mu_2^{(2)} = \frac{1}{1 - e^{\frac{\beta_1}{2}}} \left[ e^{\frac{\beta_1}{2}} \left( -\frac{2Q^2}{r_D^2} + \frac{2\alpha_1 Q}{r_D \gamma} - \frac{2\alpha_1^2}{\gamma^3} - \frac{\alpha_1^2}{\gamma^2} \right) + \frac{2Q^2}{r_D^2} - \frac{2\alpha_2 Q}{r_D Pe} + \frac{2\alpha_2^2}{Pe^3} + \frac{\alpha_2^2}{Pe^2} \right]. \quad (\text{A-29})$$

The second central moments can be calculated from above moments using the relations

$$\mu_2^{(i)} = \mu_2^{(i)} - \left( \mu_1^{(i)} \right)^2, \quad i = 1, 2. \quad (\text{A-30})$$

Thus, the second central moments are given as

$$\mu_2^{(1)} = \frac{2L^2 Pe^2 (1 + a_1 F)^2}{u^2 \gamma^3}, \quad (\text{A-31})$$

$$\begin{aligned} \mu_2^{(2)} = & \frac{1}{1 - e^{\frac{\beta_1}{2}}} \left[ e^{\frac{\beta_1}{2}} \left( -\frac{2Q^2}{r_D^2} + \frac{2\alpha_1 Q}{r_D \gamma} - \frac{2\alpha_1^2}{\gamma^3} - \frac{\alpha_1^2}{\gamma^2} \right) + \frac{2Q^2}{r_D^2} - \frac{2\alpha_2 Q}{r_D Pe} + \frac{2\alpha_2^2}{Pe^3} + \frac{\alpha_2^2}{Pe^2} \right] \\ & - \left[ \frac{Pe (\gamma Q - r_D D \alpha_1) e^{\frac{\beta_1}{2}} - \gamma (Q Pe - r_D \alpha_2)}{r_D Pe \gamma (1 - e^{\frac{\beta_1}{2}})} \right]^2. \end{aligned} \quad (\text{A-32})$$

The third moments are given as

$$\mu_3^{(1)} = \frac{L^3 Pe^3 (1 + a_1 F)^3}{u^3 \gamma^5} (\gamma^2 + 6\gamma + 12). \quad (\text{A-33})$$

$$\begin{aligned} \mu_3^{(2)} = & \frac{-1}{1 - e^{\frac{\beta_1}{2}}} \left[ e^{\frac{\beta_1}{2}} \left\{ -\frac{6Q^3}{r_D^3} + \frac{6\alpha_1 Q^2}{r_D^2 \gamma} - \frac{6\alpha_1^2 Q}{r_D \gamma^3} - \frac{3Q\alpha_1^2}{r_D \gamma^2} + \frac{12\alpha_1^3}{\gamma^5} + \frac{6\alpha_1^3}{\gamma^4} + \frac{\alpha_1^3}{\gamma^3} \right\} \right. \\ & \left. + \frac{6Q^3}{r_D^3} - \frac{6Q^2 \alpha_2}{r_D^2 Pe} + \frac{6Q\alpha_2^2}{r_D Pe^3} + \frac{3Q\alpha_2^2}{r_D Pe^2} - \frac{12\alpha_2^3}{Pe^5} - \frac{6\alpha_2^3}{Pe^4} - \frac{\alpha_2^3}{Pe^3} \right]. \end{aligned} \quad (\text{A-34})$$

Finally, the third central moments can be deduced from the relations

$$\mu_3^{(i)} = \mu_3^{(i)} - 3\mu_1^{(i)} \mu_2^{(i)} + 2 \left( \mu_1^{(i)} \right)^3, \quad i = 1, 2. \quad (\text{A-35})$$

## Irreversible Reaction with Danckwerts BCs

Here, the moments of solutions in eqs 20 and 21, obtained for the Robin boundary conditions given in eq 19, are derived.

The zeroth moments are given as

$$\mu_0^{(1)} = c_{1,inj} \frac{4\gamma Pe e^{Pe}}{\beta_1^2 e^{\frac{\beta_1}{2}} - \beta_2^2 e^{\frac{\beta_2}{2}}}, \quad \mu_0^{(2)} = c_{1,inj} \left[ 1 - \frac{4\gamma Pe e^{Pe}}{\beta_1^2 e^{\frac{\beta_1}{2}} - \beta_2^2 e^{\frac{\beta_2}{2}}} \right]. \quad (\text{A-36})$$

From eq A-36, it follows that  $\mu_0^{(1)} + \mu_0^{(2)} = c_{1,inj}$ , as  $c_{2,inj} = 0$  is considered.

The first moments have the forms

$$\mu_1^{(1)} = \frac{2\alpha_1}{\gamma^2(\beta_1^2 e^{\frac{\beta_1}{2}} - \beta_2^2 e^{\frac{\beta_2}{2}})} \left[ \gamma(2r_D + Pe^2) \left( e^{\frac{\beta_1}{2}} + e^{\frac{\beta_2}{2}} \right) + (4r_D(1 + Pe) + Pe^3) \left( e^{\frac{\beta_1}{2}} - e^{\frac{\beta_2}{2}} \right) \right]. \quad (\text{A-37})$$

$$\begin{aligned} \mu_1^{(2)} = & \left[ (\gamma Pe^4 + 6\gamma^3 Pe^2 + \gamma^5 - 64Per_D^2 - 8Pe^5 - 48r_D Pe^3)(QPe - r_D \alpha_2) e^{\beta_2} \right. \\ & + (-2(\gamma Pe^4 + \gamma^3(4r_D - Pe^2))(QPe - r_D \alpha_2) e^{\frac{\beta_1}{2}} - 4Pe^2 e^{Pe} (-Pe^2 r_D \alpha_1 \gamma - 2QPe^4 + 2r_D \alpha_1 Pe^3 \\ & - 12Pe^2 Qr_D + 2(\gamma^3 Q + 4\alpha_1 r_D^2) Pe - ((16Q - 8\alpha_1)r_D + \alpha_1 \gamma^3)r_D) e^{\frac{\beta_2}{2}} + \left. \left( (QPe - r_D \alpha_2) \right. \right. \\ & \left. \left. (\gamma^5 + \gamma Pe^4 + 48r_D Pe^3 + 6\gamma^3 Pe^2 + 64Per_D^2 + 8Pe^5) e^{\frac{\beta_1}{2}} - 4Pe^2 (-Pe^2 r_D \alpha_1 \gamma + 2QPe^4 \right. \right. \\ & \left. \left. - 2r_D \alpha_1 Pe^3 + 12Pe^2 Qr_D + 2(\gamma^3 Q - 4\alpha_1 r_D^2) Pe - ((8\alpha_1 - 16Q)r_D + \alpha_1 \gamma^3)r_D \exp(Pe) \right) e^{\frac{\beta_1}{2}} \right] \\ & / \left[ -r_D Pe \gamma (\beta_1^2 e^{\frac{\beta_1}{2}} - \beta_2^2 e^{\frac{\beta_2}{2}} - 4\gamma Pe e^{Pe}) (\beta_1^2 e^{\frac{\beta_1}{2}} - \beta_2^2 e^{\frac{\beta_2}{2}}) \right], \quad (\text{A-38}) \end{aligned}$$

The expressions on analytical second central moments were very lengthy. Therefore, only plots of analytical  $\mu_2^{(i)}$  are presented. Moreover, plots of third central moments  $\mu_3^{(i)}$  are only obtained from the solutions of numerical Laplace inversion and FVS (c.f. Figure 3 and Figure 5).

## Reversible Reaction with Dirichlet BCs

Here, the moments of solutions in eqs 28 and 29, obtained for the Dirichlet boundary conditions in eq 8, are derived. Let us define

$$Q := \alpha_2 - \alpha_1, \quad R := r_{D,1} + r_{D,2}, \quad W := r_{D,1} - r_{D,2}, \quad G := \alpha_1 + \alpha_2, \quad (\text{A-39})$$

and

$$\beta_{3,4} := Pe \mp \sqrt{Pe^2 + 4R}, \quad Y := 2r_{D,1} + 3W, \quad Z := 2r_{D,1} + W, \quad \delta := \sqrt{Pe^2 + 4R}. \quad (\text{A-40})$$

Then, the zeroth moments are given as

$$\mu_0^{(1)} = \frac{1}{R} [r_{D,2} + r_{D,1}e^{\beta_3}], \quad \mu_0^{(2)} = \frac{r_{D,1}}{R} [1 - e^{\beta_3}]. \quad (\text{A-41})$$

The first moments are expressed as

$$\mu_1^{(1)} = \frac{r_{D,2}\delta[GR^2 + Q(W - 2Pe)R - 2WQPe] + r_{D,1}Pe[4r_{D,2}Q\delta - WRQ + GR^2]e^{\frac{\beta_3}{2}}}{2\delta\nu R^2 (r_{D,1}e^{\frac{\beta_3}{2}} + r_{D,2})}. \quad (\text{A-42})$$

$$\mu_1^{(2)} = \frac{-\delta[GR^2 + WQR - 2WQPe] + Pe[-2\delta QW - WRQ + GR^2]e^{\frac{\beta_3}{2}}}{2\delta\nu R^2 (e^{\frac{\beta_3}{2}} - 1)}. \quad (\text{A-43})$$

The second moments are given as

$$\begin{aligned} \mu_2^{(1)} = & \frac{4}{\delta^7 R^4 Pe^3 (r_{D,1}e^{\frac{\beta_3}{2}} + r_{D,2})} \left[ -\frac{1}{8} \left\{ G^2(2 + Pe)R^4 + 2Q((Q - 2G)Pe^2 + GWPe + 2GW)R^3 \right. \right. \\ & - 4Q((Q + G)Pe^2 - \frac{1}{4}WQPe - \frac{1}{2}WQ)WR^2 - 6WQ^2Pe^2(-2Pe + W)R \\ & \left. \left. + 12Q^2W^2Pe^3 \right\} \frac{\delta^7}{4} (-R + W)e^{\delta/2} + Pe^3 e^{Pe/2} \left\{ \left( \frac{1}{32}R^4G^2 - \frac{1}{16}WR^3QG \right. \right. \right. \\ & \left. \left. \left. + \frac{1}{32}WQ^2(-48 + W)R^2 + \frac{3}{2}Q^2(W - \frac{1}{4}Pe^2)WR + \frac{3}{8}Q^2W^2Pe^2 \right) \delta^5 \right. \right. \\ & \left. \left. + \left( (G^2 + 8QG - 4Q^2)R^3 - \left( 10 * \left( \left( \frac{Q}{10} - \frac{G}{5} \right) Pe^2 + W \left( \frac{4}{5}Q + G \right) \right) \right) QR^2 \right. \right. \right. \\ & \left. \left. \left. - 2WQ \left( (Q + G)Pe^2 - \frac{13}{2}WQ \right) R + 3Q^2W^2Pe^2 \right) \frac{\delta^4}{16} R \right\} (R + W) \right]. \quad (\text{A-44}) \end{aligned}$$



$$\begin{aligned}
\mu_2^{(2)} = & \frac{8}{\delta^7 R^4 Pe^3 (e^{\frac{\beta_3}{2}} - 1) e^{\delta/2}} \left[ -\frac{\delta^7 e^{\frac{\delta}{2}}}{32} \left\{ G^2(2 + Pe)R^4 + 2Q(QPe^2 + GWPe + 2GW)R^3 \right. \right. \\
& + (-4GWQPe^2 - 4Q^2Pe^3 + W^2Q^2Pe + 2W^2Q^2)R^2 - 6W^2Q^2Pe^2R + 12W^2Q^2Pe^3 \left. \left. \right\} \right. \\
& + \left\{ \left[ \frac{1}{32}R^4G^2 - \frac{1}{16}Q(8Q + GW)R^3 + \left( \frac{1}{32}W^2Q^2 - \frac{1}{8}Q^2v^2 \right)R^2 + \frac{3}{2}W^2Q^2R \right. \right. \\
& + \left. \left. \frac{3}{8}W^2Q^2Pe^2 \right] \delta^5 + \frac{\delta^4}{4} \left( (-4Q^2 + G^2)R^3 + (-Q^2Pe^2 - 10GWQ)R^2 \right. \right. \\
& \left. \left. + (13W^2Q^2 - 2GWQPe^2)R + 3W^2Q^2Pe^2 \right) R \right\} Pe^3 e^{\frac{Pe}{2}} \right]. \tag{A-45}
\end{aligned}$$

eq A-30 can be used to obtain the second central moments from the above equations. Moreover, expressions of  $\mu_3^{(i)}$  were very lengthy. Therefore, plots of third central moments are obtained from the solutions of numerical Laplace inversion and FVS.

## Reversible Reaction with Danckwerts BCs

In this case, the moments of solutions in eqs 33 and 34, obtained for the Robin boundary conditions in eq 19, are derived. The zeroth moments are given as

$$\mu_0^{(1)} = \frac{r_{D,2}(\beta_3Pe + 2R)e^{\frac{\beta_3}{2}} - r_{D,2}(\beta_4Pe + 2R)e^{\frac{\beta_4}{2}} - 2r_{D,1}\delta Pe e^{Pe}}{R \left[ (\beta_3Pe + 2R)e^{\frac{\beta_3}{2}} - (\beta_4Pe + 2R)e^{\frac{\beta_4}{2}} \right]}, \tag{A-46}$$

$$\mu_0^{(2)} = \frac{r_{D,1} \left[ (\beta_3Pe + 2R)e^{\frac{\beta_3}{2}} - (\beta_4Pe + 2R)e^{\frac{\beta_4}{2}} + 2\delta Pe e^{Pe} \right]}{R \left[ (\beta_3Pe + 2R)e^{\frac{\beta_3}{2}} - (\beta_4Pe + 2R)e^{\frac{\beta_4}{2}} \right]}. \tag{A-47}$$

The first moments are expressed as

$$\begin{aligned}
\mu_1^{(1)} = & \left[ -r_{D,1}Pe^2 \left\{ \left( -\frac{1}{2}R^3G + \left(\frac{1}{2}WQ - 2PeQ - \frac{1}{4}Pe^2G\right)R^2 + \frac{1}{4}Qv(-2Pe^2 + WPe + 8W)R \right. \right. \\
& + \left. \left. \frac{1}{2}WPe^3Q \right) \delta \left( e^{\frac{2Pe+\beta_3}{2}} + e^{\frac{2Pe+\beta_4}{2}} \right) + \left[ (G + PeG + 4Q)R^3 + (-PeWQ + \frac{1}{4}Pe^3G - 5WQ \right. \right. \\
& + \left. \left. 3Pe^2Q)R^2 + \frac{1}{4}QPe^2(-2Pe^2 + WPe + 12W)R - \frac{1}{2}WQPe^4 \right] \left( e^{\frac{2Pe+\beta_3}{2}} - e^{\frac{2Pe+\beta_4}{2}} \right) \right\} \\
& + 2r_2(R^2G + Q(W - 2Pe)R - 2PeWQ) \left\{ \left( -\frac{Pe^4}{8} - \frac{RPe^2}{2} - \frac{R^2}{4} \right) \delta \left( e^{\beta_3} + e^{\beta_4} \right) \right. \\
& + \left. Pe \left( \frac{Pe^2}{2} + R \right) \left( \frac{Pe^2}{4} + R \right) \left( e^{\beta_3} - e^{\beta_4} \right) + \frac{1}{2}R^2\delta e^{Pe} \right\} / \left[ \delta Pe \left( r_{D,2} \frac{Pe\beta_3 + 2R}{2} e^{\frac{\beta_3}{2}} \right. \right. \\
& \left. \left. - r_{D,2} \frac{Pe\beta_4 + 2R}{2} e^{\frac{\beta_4}{2}} - r_{D,1} \delta e^{Pe} Pe \right) \left( \frac{Pe\beta_3 + 2R}{2} e^{\beta_3} - \frac{Pe\beta_4 + 2R}{2} e^{\beta_4} \right) R^2 \right]. \tag{A-48}
\end{aligned}$$

$$\begin{aligned}
\mu_1^{(2)} = & -2 \left[ -\frac{1}{2}Pe^2 \left\{ \left( \frac{1}{2}Pe^3WQ - \frac{1}{4}R(GR - WQ)Pe^2 + 2PeWQR - \frac{1}{2}R^2(GR - WQ) \right) \right. \right. \\
& \delta \left( e^{\frac{2Pe+\beta_3}{2}} + e^{\frac{2Pe+\beta_4}{2}} \right) + \left( -\frac{1}{2}WQPe^4 + \frac{1}{4}R(GR - WQ)Pe^3 - 3Pe^2RWQ \right. \\
& + \left. \left. (R^3G - R^2WQ)Pe - 5R^2WQ + R^3G \right) \left( e^{\frac{2Pe+\beta_3}{2}} - e^{\frac{2Pe+\beta_4}{2}} \right) \right\} + \left( R^2G + RWQ \right. \\
& \left. - 2PeWQ \right) \left\{ \left( -\frac{1}{2}Pe^2R - \frac{1}{8}Pe^4 - \frac{1}{4}R^2 \right) \delta \left( e^{\beta_3} + e^{\beta_4} \right) + \left( \frac{1}{4}Pe^2 + R \right) Pe \right. \\
& \left. \left( \frac{1}{2}Pe^2 + R \right) \exp \delta \left( e^{\beta_3} + e^{\beta_4} \right) + \frac{1}{2}R^2\delta e^{Pe} \right\} / \left[ \delta Pe \left( \frac{Pe\beta_3 + 2R}{2} e^{\frac{\beta_3}{2}} - \frac{Pe\beta_4 + 2R}{2} e^{\frac{\beta_4}{2}} \right) \right. \\
& \left. R^2 \left( \frac{Pe\beta_3 + 2R}{2} e^{\frac{\beta_3}{2}} - \frac{Pe\beta_4 + 2R}{2} e^{\frac{\beta_4}{2}} + \delta e^{Pe} Pe \right) \right]. \tag{A-49}
\end{aligned}$$

Due to lengthy expressions of analytical  $\mu_2^{(i)}$  and  $\mu_2^{\prime(i)}$ , only plots of analytical  $\mu_2^{\prime(i)}$  are presented. Moreover, the plots of  $\mu_3^{\prime(i)}$  are obtained from the solutions of numerical Laplace inversion and FVS.

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Table 1: Parameters for linear reaction case.

| Parameters                                      | values                                |
|---|---------------------------------------|
| Column length                                   | $L = 1.0 \text{ cm}$                  |
| Porosity  | $\varepsilon = 0.4$                   |
| Interstitial velocity                           | $u = 1 \text{ cm/min}$                |
| Dispersion coefficient of first component       | $D_1 = 0.005 \text{ cm}^2/\text{min}$ |
| Dispersion coefficient of second component      | $D_2 = 0.005 \text{ cm}^2/\text{min}$ |
| Initial concentrations                          | $c_{i,init} = 0 \text{ g/l}$          |
| Concentration at inlet for component 1          | $c_{1,inj} = 1.0 \text{ g/l}$         |
| Concentration at inlet for component 2          | $c_{2,inj} = 0.0 \text{ g/l}$         |
| Adsorption equilibrium constant for component 1 | $a_1 = 1.8$                           |
| Adsorption equilibrium constant for component 2 | $a_2 = 1.0$                           |
| Irreversible reaction rate constant             | $k = 0.4 \text{ min}^{-1}$            |
| Reversible reaction rate constant (component 1) | $k_1 = 0.4 \text{ min}^{-1}$          |
| Reversible reaction rate constant (component 2) | $k_2 = 0.2 \text{ min}^{-1}$          |

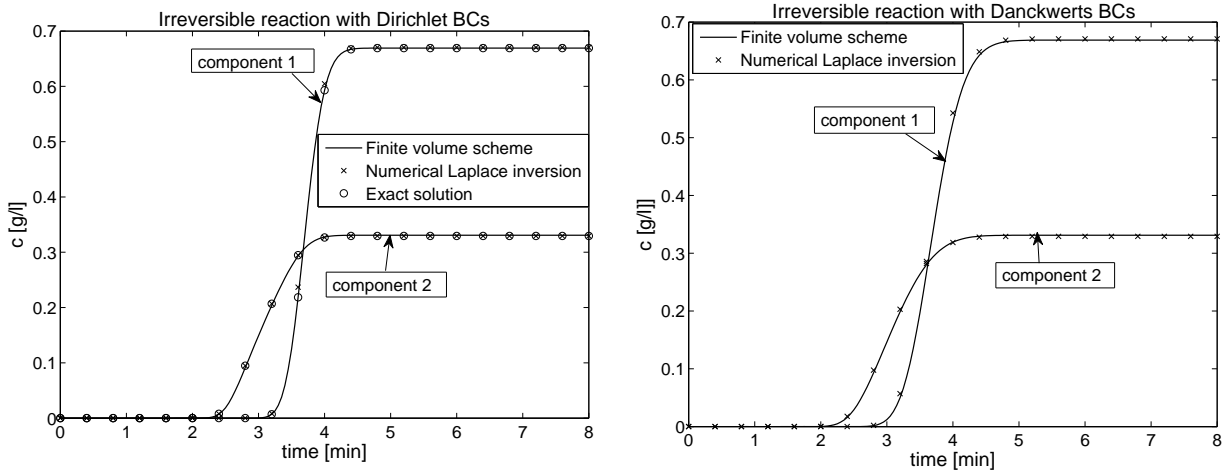


Figure 1: Problem 1: Irreversible reaction, left: solutions for Dirichlet BCs at  $x = 1$ , right: solution for Danckwerts BCs at  $x = 1$ . All other parameters are given in Table 1.

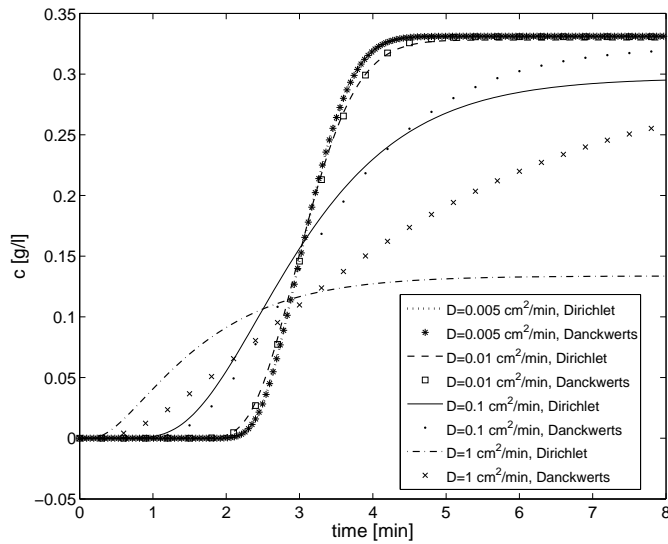


Figure 2: Problem 1: Irreversible reaction, effect of BCs on the breakthrough curves at the column outlet i.e  $x = 1$  for component 2 considering different values of dispersion coefficients  $D$  and  $u = 0.6 \text{ cm/min}$ . Other parameters can be found in Table 1.



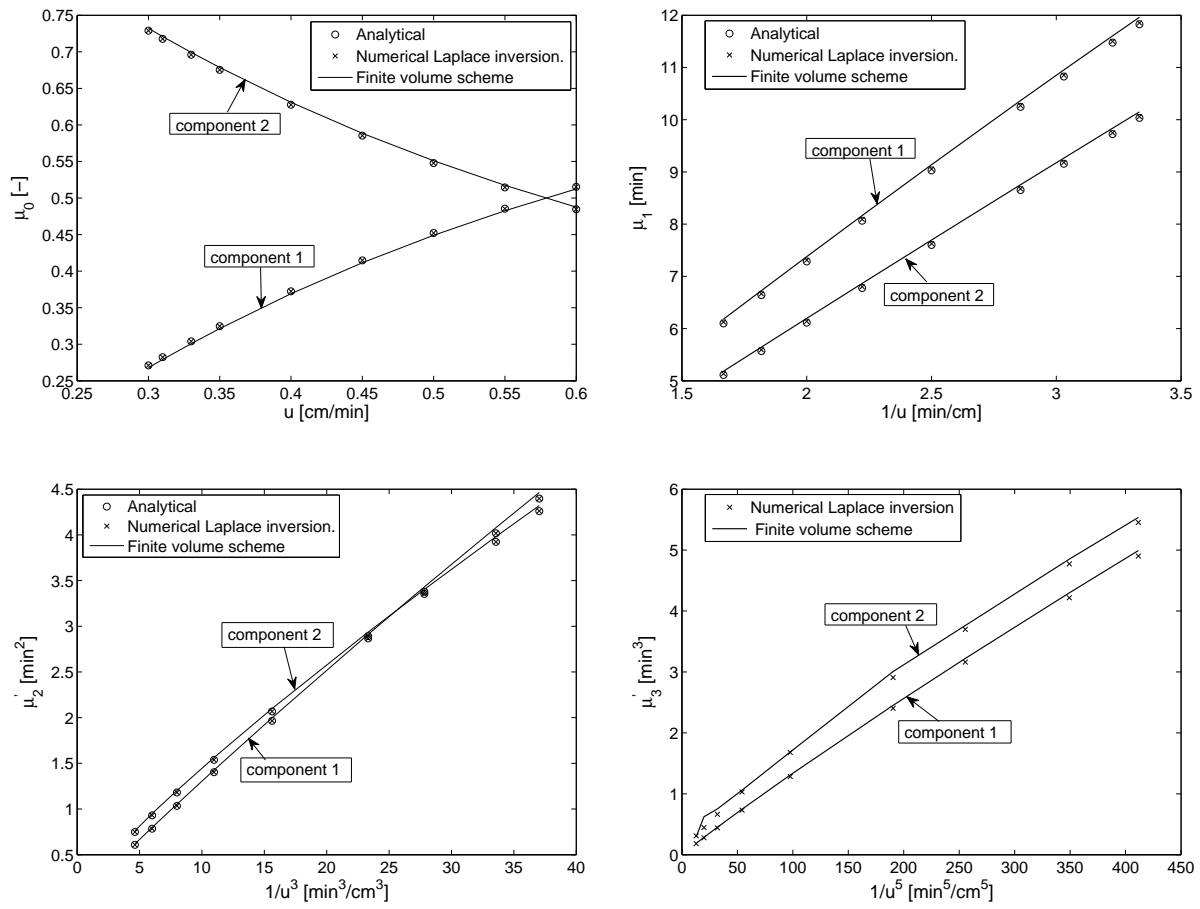


Figure 3: Problem 1: Moments of irreversible reaction with Danckwerts BCs considering different values of  $u$ . Other parameters are presented in Table 1.

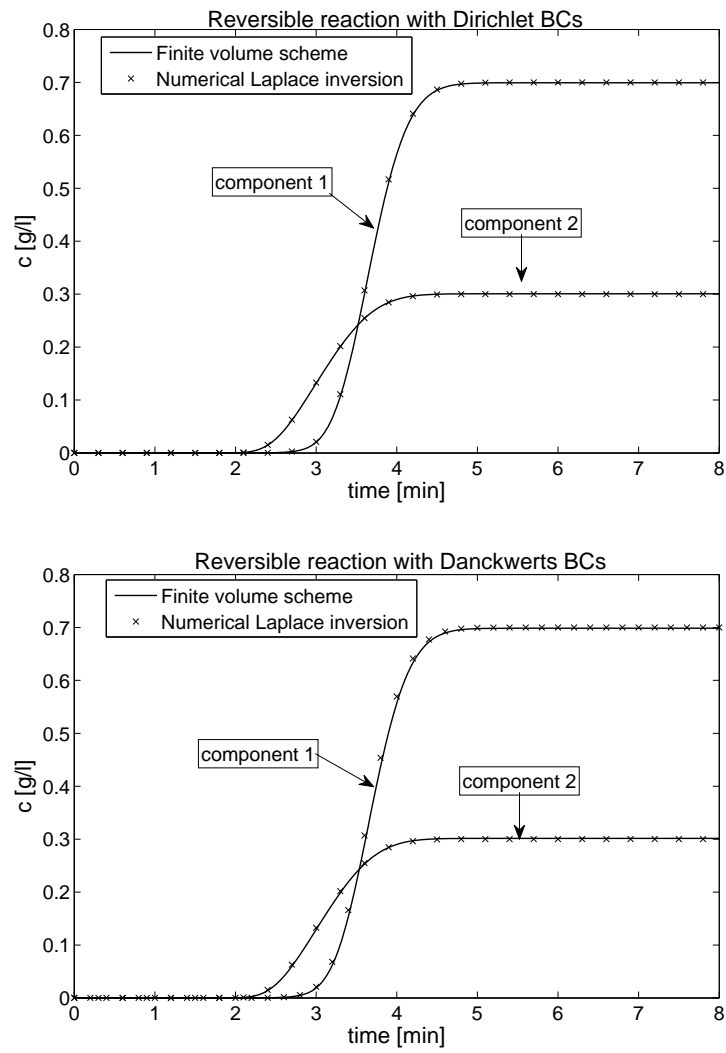


Figure 4: Problem 2: Reversible reaction, top: solution for Dirichlet BCs at the column outlet i.e  $x = 1$ , bottom: solution for Danckwerts BCs at  $x = 1$ . Parameters can be found in Table 1.

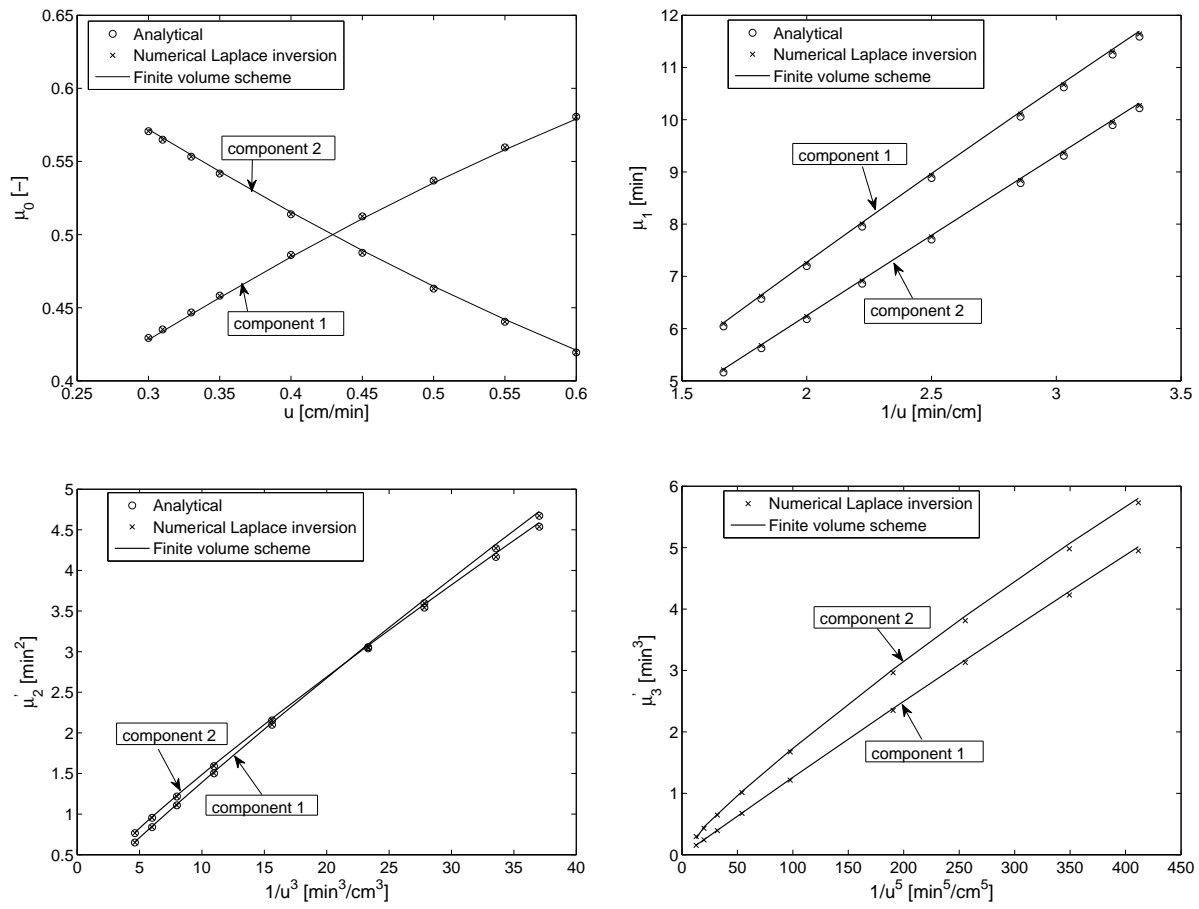


Figure 5: Problem 2: Moments of reversible reaction with Danckwerts BCs considering different values of  $u$ . All other parameters are given in Table 1.

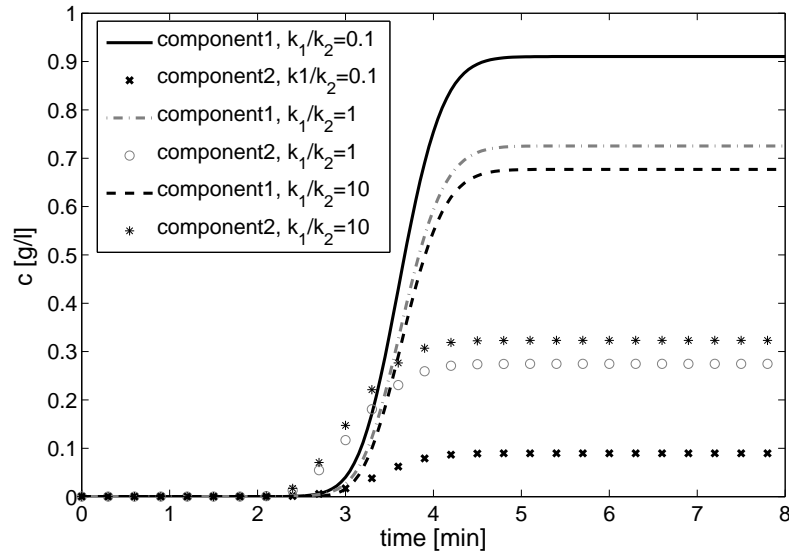


Figure 6: Breakthrough curves at the column outlet,  $x = 1$  using Danckwerts BCs. Effects of reaction rate constants on reversible reaction keeping  $k_1 = 0.4 \text{ min}^{-1}$  fixed. Other parameters can be found in Table 1.

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