

Mathematical Simulation of Multiphase Reactive Chromatography Process

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In order to carry out theoretical analysis and digital simulation for multiphase reactive chromatography, the multiphase and multicomponent reaction chromatography equations are established considering the coupling effect between chemical reaction and multiphase chromatography. The multiphase - multicomponent reaction chromatography equation is solved by using the second order TVD numerical method. The reversible chromatographic process of two-phase four-component is discussed using the second order form with flux limiting factor. The fluctuation image with initial and boundary conditions is analyzed, and the formation mechanism of the wave image is discussed. The results show that after the fluid enters the chromatography, the shock wave will be generated due to the difference of the adsorption property of the component, thus affecting the concentration distribution diagram of the chromatogram.

1. Introduction

Chromatography is a phenomenon of concentration fluctuation. The chromatographic process is a porous medium flow process accompanied by interphase mass exchange. In recent years, reactive chromatography technology coupled with reaction-separation has attracted more and more attention (Oliver et al., 2013). Multiphase reactive chromatography, that is, the chromatography process with multiple flow and chemical reactions, is developed on the basis of adsorption reaction coupling technology.

In the study of chromatography process, mathematical model method is widely used as an important research method (Krause et al., 2015). In this regard, a number of mathematical models with different complexity and many numerical methods have been proposed in the literature (Adelmann et al., 2011). In this respect, there is a difficult point in the study. The nonlinearity of the isotherm will not only cause the concentration shock phenomenon, but also increase the difficulty of theoretical analysis and mathematical simulation (Hyo and Kazuhiko, 2017). Multiphase reactive chromatography is different from multiphase chromatography in the existence of its chemical reaction term, so that the first order partial differential equation of the description process is non-homogeneous, which brings difficulties to theoretical analysis and numerical simulation (Shamsul et al., 2016). In this paper, the mathematical theory and simulation method of multiphase reactive chromatography are studied, and the coupling action of chemical reaction and multiphase chromatography is further considered. An effective mathematical simulation algorithm is developed to solve the numerical simulation problems of concentration shock wave and saturation shock wave.

2. Multiphase and multicomponent reaction chromatography equation

2.1 Mathematical model

Chromatographic process is the propagation process of concentration wave. The fluctuation of solute concentration in chromatographic process is mainly caused by the adsorption and interphase distribution of the solute in the stationary phase (Shamsul et al., 2016), and the understanding for this phenomenon should start with chromatographic equilibrium model. Although the equilibrium model is the simplest chromatographic model, it highlights the most basic characteristics of the chromatographic process.

A multiphase chromatographic process with k immiscible mobile phases, a stationary phase and m component is considered, and the chemical reactions are carried out in the mobile phase and stationary phase of each component. Assuming that the flow of the mobile phase is a flat pushing flow, the distribution of solute between phases is instantaneously balanced. Chromatographic reaction should be operated in isothermal environment. The filling of chromatographic column should be uniform, while the pressure drop and diffusion of column should be ignored (Xinpeng et al., 2016). The conservation equations of each component and mobilephase are established by dimensionless coordinates, and the equations are written in the form of matrix:

$$A_0 \frac{\partial U}{\partial \tau} + B_0 \frac{\partial U}{\partial x} = C_0 \quad (1)$$

In the formula, $U=[S_g, c_{1g}, \dots, c_{mg}]^T_{(m+1)}$ is the space constituted by the dependent variable of composition space. The elements of matrix A_0 and B_0 are as follow:

$$A_0 = \begin{bmatrix} 1 & 0 & \dots & 0 \\ 0 & \sum_j (S_j \frac{dc_{1j}/d\eta}{dc_{1g}/d\eta}) + \varepsilon \frac{Dn_1}{Dc_{1g}} & \dots & \varepsilon \frac{Dn_1}{Dc_{mg}} \\ \dots & \dots & \dots & \dots \\ 0 & \varepsilon \frac{Dn_m}{Dc_{1g}} & \dots & \sum_j (S_j \frac{dc_{mj}/d\eta}{dc_{mg}/d\eta}) + \varepsilon \frac{Dn_m}{Dc_{mg}} \end{bmatrix}$$

$$B_0 = \begin{bmatrix} \partial f_g / \partial S_g & \partial f_g / \partial C_{1g} & \dots & \partial f_g / \partial C_{mg} \\ 0 & \sum_j (f_j \frac{dc_{1j}/d\eta}{dc_{1g}/d\eta}) & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \sum_j (f_j \frac{dc_{mj}/d\eta}{dc_{mg}/d\eta}) \end{bmatrix}$$

$$C_0 = \begin{bmatrix} 0 \\ \sum_{j=1}^k R_{f1j} + \varepsilon R_{s1} \\ \dots \\ \sum_{j=1}^k R_{fmj} + \varepsilon R_{sm} \end{bmatrix}$$

2.2 Multiphase and multicomponent reaction chromatography equation with second order TVD numerical method

The difference between multiphase reaction chromatography and multiphase chromatography is the chemical reaction term. The composition of the first order partial differential equations of the description process is not simple and cannot directly apply the related methods and results of nonlinear chromatography theory. Therefore, the existence and description of the concentration shock wave has become the main difficulty of theoretical research (Thomas, 2017).

Formula (1) is the first-order nonlinear hyperbolic partial differential equation, describing the process of general multiphase and multicomponent reactive chromatography. It is very difficult to analyze such a set of equations. The characteristic line method and the coherent analysis theory are all hyperbolic partial differential equations applied to homogeneous order, and the non-homogeneous equations can only be solved by numerical method (Fabian and Berend, 2015).

TVD scheme is kind of monotonicity preserving shock capturing schemes. It can be used to eliminate the nonphysical numerical oscillations of the scheme by modifying the inverse dissipation term of the high-order flux in a low order scheme, such as the numerical flux of first-order upwind scheme (Jingming et al., 2015). The TVD difference scheme has high resolution for discontinuous solutions, while maintaining the higher order accuracy of the smooth solution region (Bertrand et al., 2012). For the formula (1), the second-order TVD scheme can be constructed as the formula (2):

$$U_j^{n+1} = U_j^n - \lambda (\hat{f}_{j+\frac{1}{2}} - \hat{f}_{j-\frac{1}{2}}) + \Delta \tau A_0^{-1} \cdot C_0(U_j^n) \quad (2)$$

In the formula, $\lambda = \Delta \tau / \Delta x$. n and j are the numbers along the x and τ directions. \hat{f} is the numerical flux.

3. Four component reversible reaction two mobile phase chromatography process

In this section, a specific chromatographic process containing two mobile phases and four reaction components is taken as an example. The following assumptions need to be added:

The first mobile phase is used as the reference phase, that is, $g=1$. The distribution relation of solute between two phases of liquid can be expressed as linear (Bernd and Alexei, 2014).

Reactants are added in step mode. The reversible reaction occurs not only on the surface of the stationary phase, but also in the mobile phase. $A_1 + A_2 \leftrightarrow A_3 + A_4$.

The splitting rate f_j and the phase saturation S_j of j phase are both constants (Rebecca et al., 2013).

Adsorption follows the Langmuir isotherm and reaches the adsorption equilibrium instantaneously (Lena et al., 2016).

For the adsorption model of solute on stationary phase, the extended Langmuir isotherm is used to represent the adsorption of various solutes on the stationary phase. Its form is as follows:

$$n_i = \frac{K_i N_i c_{i1}}{1 + \sum_{i=1}^4 (K_i c_{i1})} \quad i = 1, 2, 3, 4 \quad (3)$$

N_i represents the maximum adsorption concentration of solute i on the stationary phase, and K_i is a constant related to solute adsorption heat. Each parameter is taken as the following: $f_1=0.7$, $S_1=0.6$, $N_1=N_2=1.0$, $N_3=0.1$, $N_4=0.1$, $K_1=1.0$, $K_2=1.5$, $K_3=0.8$, $K_4=0.4$, $k_1=2.5$, $k_2=1.8$, $k_3=1.3$, $k_4=0.5$, $\varepsilon=4$, $kr_{11}=1$, $kr_{21}=0.5$, $kr_{12}=3$, $kr_{22}=0.1$, $kr_{1s}=8$, $kr_{2s}=0.4$.

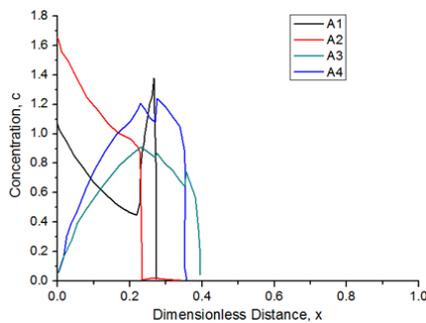


Figure 1: Concentration distribution of four component reaction chromatography $\tau=0.5$

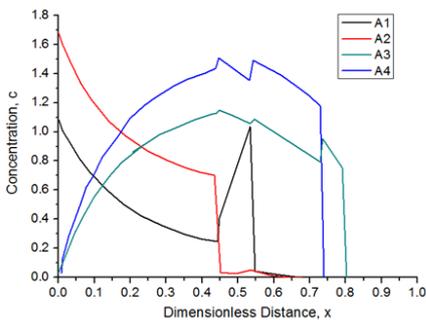


Figure 2: Concentration distribution of four component reaction chromatography $\tau=1$

The concentration distribution of the components at different time is shown in figure 1, figure2, figure3, figure 4, figure 5 and figure 6. As shown in the figures, there are four shocks that divide the coordinate space into five intervals, from left to right, respectively, fourth, third, second, first and zeroth interval. The shock wave (the first shock) in the figure contains only component A3, and the second shock wave contains two weak adsorption components A3 and A4. Both third and fourth shock waves contain four components. Interval 1 contains only components A1. Interval 2 contains four components, but mainly contains weak adsorption components A3 and A4. Interval 3 contains four components, but the content of strongest adsorption component A2 is rare. Interval 4 is also contains four components. The concentration of A1 and A2 concentrations have a downward

trend, while A3 and A4 have an upward trend. It is worth noting that in the process of interval 1 developing with time, the change of A3 evolves from higher left to lower left.

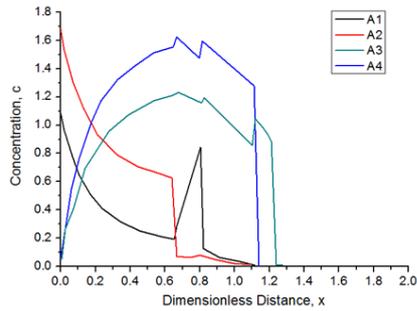


Figure 3: Concentration distribution of four component reaction chromatography $\tau=1.5$

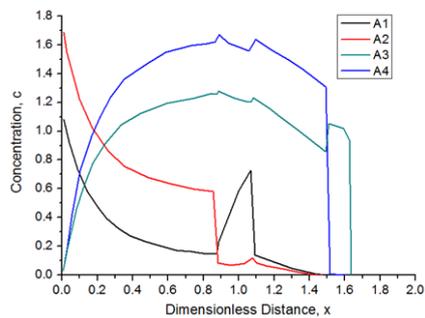


Figure 4: Concentration distribution of four component reaction chromatography $\tau=2$

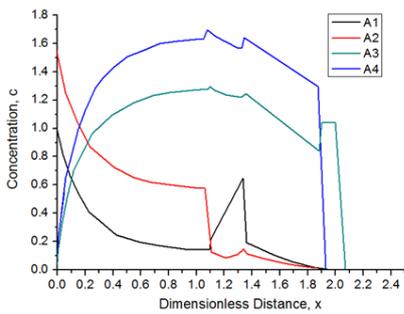


Figure 5: Concentration distribution of four component reaction chromatography $\tau=2.5$

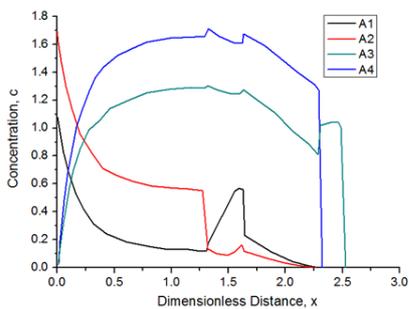


Figure 6: Concentration distribution of four component reaction chromatography $\tau=3$

The reason for the above characteristics is that after the fluid enters the chromatography, four shock waves are generated due to the differences in the adsorption properties of the components A1, A2, A3 and A4. In the early stage of reaction (interval 4), because the concentration of A1 and A2 is much higher than the concentration of A3 and A4, the rate of positive reaction is faster than reverse reaction. At this time, A3 and A4 are continuously generated, while A1 and A2 are constantly consumed Nan et al., (2017). Due to the strong adsorption effect, the component A2 forms a discontinuity at the fourth shock wave, and the concentration almost decreases to 0. At the same time, A1, A3 and A4 cross the fourth shock wave due to their weak adsorption properties, which are enriched in the range 3. At this time, the reaction speed is higher than the positive reaction speed (Rong-Zhu et al., 2016). The components A1 and A2 are continuously generated, while the concentrations of A3 and A4 begin to decrease. Due to the adsorption effect, the concentration of A1 decreased rapidly after forming third shock wave, and the mainly remains components A3 and A4 in interval 2. At this point, the reverse reaction dominates. Although a small amount of A1 and A2 are generated, it is difficult to continuously penetrate the second shock due to their strong adsorption effect (Pedro, 2014). Because the concentration of A4 is reduced to 0 after the second shock wave is formed, interval 1 contains only component A3. This interval is equivalent to a single component of two mobile phases without reaction. The change of A3 in interval 1 is due to the reverse reaction on the second shock surface (Boon et al., 2016), while the A3 and A4 are consumed constantly. The concentration of A3 on the right side of the second shock wave decreases continuously, and finally the waveform of the lower left is formed (William et al., 2017). According to the concentration distribution under dimensionless time, multiphase reactive chromatography seems to be no different from single phase reactive chromatography. But in fact, if the j phase splitting rate and the j phase saturation are not constants in this case, the difference of multiphase system relative to the single phase system will be reflected.

4. Conclusion

Chromatography process involves many important practical applications. Chromatography technology has been developed rapidly in the past forty years, and has become a very important analytical technology and industrial separation technology. In the adsorption reactor or chromatographic reactor, the simultaneous action of reaction and adsorption strengthens the concentration transient behavior within the bed layer. For the multiphase reaction system, the second order scheme with flux limiting factor is used to solve multiphase and multicomponent reaction chromatography equation. A concrete reaction chromatography process containing two mobile phases and four components is taken as an example. The fluctuation image with initial and boundary conditions is analyzed, and the formation mechanism of the wave image is discussed. The results show that after the fluid enters the chromatography, the shock wave will be generated due to the difference of the adsorption property of the component, thus affecting the concentration distribution diagram of the chromatogram.

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