

On Modelling the Convective Mass Transfer over Moving Films Interface for the Reaction-Diffusion Systems of the Second Order

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The paper deals with the methods for approximately analytical and numerical solving the non-self-similar problems of film absorption, accompanied by the partly reversible reaction of a second order. The Peclet number in this case is taken as sufficiently high, and the diffusion boundary layer is very thin. The methods to obtain approximate analytical solutions of the stationary convective diffusion equation for the coupled problem of isothermal film chemisorption at high Peclet numbers have been worked out. The approximate analytical method for solving the following problems: physical absorption of poorly soluble gas and chemisorption with partly reversible reaction of the second order with specially allowance for the kinetics of surface reaction has been submitted. The known Crank-Nicholson method expanded by the iteration procedures has been modified applying to mentioned problems, and preliminary results of computer simulations have been discussed. The obtained results are likely to be of importance to mass transfer modeling and engineering practice in industrial processes and apparatuses design.

1. Introduction

The film absorption processes occur in many industrial chemical and power enterprises (Chen, 1998). It is used for purifying gases from toxic admixtures or for extracting the valuable components (Grossman, 1986). However, the very limited resources to increase the interfacial mass transfer in the film processes still have been found (Cussler, 2009). Among the various causes of those failures (Ouyang et al., 1989), a certain cause, which may be not main but important in our opinion, is the difficulty to solve and to analyze the coupled equations of film motion and mass transfer (Fujita, 1993), especially it is true for the specific peculiarities of the processes at films surfaces (Taitelbaum and Koza, 2000).

The main problem lies in the fact that while solving the coupled problem the surface velocity and the concentrations are initially unknown and must be determined in the process of the solution (Huang and Liu, 2015). Therefore some approximations should be used for these functions, which would be clarified during the numerical process (Bo et al., 2010). However, solving the problem of convective diffusion with boundary conditions at moving films surface, we have to expose the transformation of beforehand unknown function in the boundary conditions (Wassenaar and Segal, 1999).

The basic premise which was used to simplify the approach to creating the model consists in that the chemisorption purification is usually applied in those cases when gases are sparingly soluble, and the process of physical absorption turns out little effective. Therefore, the Peclet number in this case is sufficiently high, and the diffusion boundary layer is very thin. This circumstance gives the opportunity to select such small control parameter as the gradient of surface velocity along the film motion direction. Besides that in the presence of big

or small control parameters there appears the possibility to use effective methods of the asymptotic analysis (Acampora et al, 2015).

The main goal of our paper is to submit both the methods for transforming mathematical model for obtaining both the approximate analytical solutions of the coupled problem of isothermal film chemisorption at high Peclet numbers and appropriate numerical tools for the computer simulation.

The submitted method allows also obtaining the approximate analytical solution of the convective diffusion equation taking into account the phenomenon of changing velocity of the film surface induced by the concentration-dependent surface tension.

2. Theoretical details

This section presents the method for solving the problems of the non-self-similar (Schlichting and Gersten, 2003) film absorption, accompanied by a partially reversible second order chemical reaction at the film surface.

2.1 Master equations and boundary conditions

The simplest scheme of a reversible second-order reaction reads (Gálfi and Ràcz, 1988)



where A (absorbed component) and B (absorbent) are the reagents, E is the reaction product, k_1 and k_2 are the reaction rate constants for direct reverse stages.

The basic system of hydrodynamics and convective diffusion equations in the presence of a chemical source of mass is as follows (Yuste, Acedo, Lindenberg, 2004):

$$\begin{aligned} \frac{\partial C_A}{\partial t} + (\vec{V}, \nabla) C_A &= D_A \Delta C_A - k_1 C_A C_B + k_2 C_E, \\ \frac{\partial C_B}{\partial t} + (\vec{V}, \nabla) C_B &= D_B \Delta C_B - k_1 C_A C_B + k_2 C_B, \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{\partial C_E}{\partial t} + (\vec{V}, \nabla) C_E &= D_E \Delta C_E + k_1 C_A C_B - k_2 C_E \\ \rho_l \frac{\partial \vec{V}}{\partial t} &= -\rho_l g - \nabla P + \mu_l \Delta \vec{V}, \end{aligned} \quad (3)$$

$$\text{div} \vec{V} = 0 \quad (4)$$

Here C_A , C_B , C_E are the concentration of substances; \vec{V} is the liquid velocity; P is the pressure; D_A , D_B , D_E are the diffusion coefficients into the liquid layer; g is the gravitational acceleration; ρ_l is the liquid density; μ_l is the liquid dynamic viscosity.

The momentum equation for a gas boundary layer is assumed to obey (Cebeci and Bradshaw, 2012)

$$U_g \frac{\partial U_g}{\partial x} + V_g \frac{\partial U_g}{\partial y} = U_e \frac{dU_e}{dx} + \frac{1}{\rho_g} \frac{\partial \tau}{\partial y}, \quad (5)$$

where (U_g, V_g) are the longitudinal and normal components of the gas velocity, U_e is the velocity at the outer boundary of gas layer; x and y are the longitudinal (along the film motion direction) and normal coordinates accordingly; ρ_g is the gas velocity; τ is the tangential stress in a gas phase (Hihara and Saito, 1993).

The wall conditions are

$$y = 0 \Rightarrow U_l = V_l = 0, \quad \frac{\partial C}{\partial y} = 0. \quad (6)$$

The interfacial boundary conditions at the liquid film surface are the equality of normal mass fluxes of reagents through the interface, the no-slip condition and the balance condition for shear stresses with accounting of the concentrate-induced surface tension gradient along the interface (Brener, 1999):

$$y = h \Rightarrow D_l \frac{\partial C_l}{\partial y} = D_g \frac{\partial C_g}{\partial y}, \mu_l \frac{\partial V_l}{\partial y} - \mu_g \frac{\partial U_g}{\partial y} = \frac{d\sigma}{dC} \frac{dC_s}{dx},$$

$$\frac{\partial C_l}{\partial y} = \frac{\alpha}{D_l} (C_\infty - mC_s).$$
(7)

Here σ is the surface tension; α is the mass transfer coefficient into gas phase; h is the liquid film thickness; $m = H/P_g$, where H is the Henry constant; indices "S" and " ∞ " denote film surface and gas phase far from the interface.

In addition to these conditions, for the gas phase we take quite physically reasonable conditions, consisting in the fact that at the outer edge of the boundary layer the longitudinal component of the velocity is equal to the velocity in the flow core (Chopard et al., 1993), and the tangential stresses are absent (Vijayendran, Ligler, Leckband, 1999).

In this case, you can integrate the equation of gas motion over the boundary layer thickness δ following the known method (Cebeci and Bradshaw, 2012), which will result in the expression

$$\frac{d}{dx} \left(U_S^2 \delta^* \right) + U_S \frac{dU_S}{dx} \int_h^{h+\delta} \frac{U_g}{U_S} dy + \frac{d\delta}{dx} V_e (U_S - V_e) = -\frac{1}{\rho_g} \tau_s$$
(8)

Here

$$\delta^* = \int_h^{h+\delta} \frac{U_g}{U_S} \left(\frac{U_g}{U_S} - 1 \right) dy, \quad \tau_g = \mu_g \frac{\partial U_g}{\partial y}$$
(9)

Expressions (8) and (9) are needed to calculate mass transfer coefficient into gas phase.

2.2 Variables and parameters transformation

For solutions the obtained systems it is necessary to determine the concentration profiles over the film thickness (Kang et al., 2000). In its most general form, the problem is too complex, and effective viable approaches are not offered up today (Bo et al., 2010). At the same time, applying to the most important cases when the Peclet number is large enough, the problem can be simplified (Brener, 1999).

In this limit, the thickness of the diffusion boundary layer in the liquid phase in the vicinity of the free surface is much smaller than the film thickness (Richardson and Kafri, 1999). In this regard, one can replace the value of the fluid velocity in the convective diffusion equation directly by its value at the interface. Then, using the continuity equation, we get after the change of the variable $z = h - y$:

$$U_S \frac{\partial C}{\partial x} - z \frac{dU_S}{dx} \frac{\partial C}{\partial z} = D_l \frac{\partial^2 C}{\partial z^2}$$
(10)

The appropriate boundary conditions read

$$z = 0 \Rightarrow D_l \frac{\partial C}{\partial z} = \alpha (mC - C_\infty); \quad z \rightarrow \infty \Rightarrow \frac{\partial C}{\partial z} \rightarrow 0.$$
(11)

In contrast to the problem which was discussed in some works (Pérez, Picioreanu, van Loosdrecht, 2005), in this case, as the liquid film moves it will be saturated by the absorbed reagent and by the reaction product, and their concentrations will change both over the film thickness and along the film surface (Tomé and de Oliveira, 2015).

Therefore, any transformations should take into account the longitudinal coordinate, in addition to the self-transverse coordinate (Wassenaar and Segal, 1999).

The suitable transformations are (Brener, 1999)

$$z \rightarrow \xi = z \sqrt{U_S^2 / D_l \int_0^x U_S dt}, \quad x \rightarrow X = \int_{\varepsilon}^x \left(U_S / \int_0^t U_S dq \right) dt \quad (12)$$

Now, after the change of variables the convective diffusion equation reduces to the form with constant coefficients.

$$\begin{aligned} \frac{\partial C_A}{\partial X} - \frac{1}{2} \xi \frac{\partial C_A}{\partial \xi} &= n_1 \frac{\partial^2 C_A}{\partial \xi^2} - \bar{k}_1 C_A C_B + \bar{k}_2 C_E, \\ \frac{\partial C_B}{\partial X} - \frac{1}{2} \xi \frac{\partial C_B}{\partial \xi} &= \frac{\partial^2 C_B}{\partial \xi^2} - \bar{k}_1 C_A C_B + \bar{k}_2 C_E, \\ \frac{\partial C_E}{\partial X} - \frac{1}{2} \xi \frac{\partial C_E}{\partial \xi} &= \frac{\partial^2 C_E}{\partial \xi^2} n_2 + \bar{k}_1 C_A C_B - \bar{k}_2 C_E \end{aligned} \quad (13)$$

Here $n_1 = D_A/D_B$, $n_2 = D_E/D_B$.

The appropriate boundary conditions are

$$\xi \rightarrow \infty \Rightarrow \frac{\partial C}{\partial \xi} = 0, \quad \xi = 0 \Rightarrow \frac{\partial C}{\partial \xi} \sqrt{D_l \int_0^x \left(\frac{U}{U_S} \right)^2 dt} = \frac{\alpha}{D_l} (1 - m C_S) \quad (14)$$

In many cases, the chemisorption process is carried out under conditions of supersaturation of the solution by the active absorbent, as by this the most effective absorption of the target component can be achieved. Thus in the considered case the most quickly changing concentration is C_A , but the gradient of concentration C_B is small, and its concentration is close to the one at the surface (Bo et al., 2010).

Therefore, taking the concentration of the absorbent close to the surface concentration, we can write the approximate equality.

$$\frac{\partial}{\partial \xi} (C_A C_B) \approx \frac{\partial}{\partial \xi} [C_A (C_{BS} + \Delta C_B)] \approx C_{BS} \left(1 + \frac{\Delta C_B}{C_{BS}} \right) \frac{\partial C_A}{\partial \xi} \quad (15)$$

Now there appears a small parameter $\varepsilon = \frac{\Delta C_B}{C_{BS}}$, and it opens the opportunity to linearize the master equations

(Giga et al., 2010).

For this small parameter it can be given a simple sense of the relationship between the characteristic time of the conversion and the residence time of the reaction mixture in the absorber. From this it follows the main limitation for the mentioned approximation. Namely, the described asymptotic approach is admissible only under the weak reversibility of the reaction, i.e., as an engineering evaluation of the parameter, we suggest using the ratio between rate constants of inverse and direct reactions

$$\varepsilon = k_2/k_1. \quad (16)$$

In the future, we propose on the base of these ideas to develop a method for analysing the described model with the help of the Laplace transform and asymptotic tools. It may be relevant to many industrial processes.

In the next section the numerical scheme for investigating non-linear problem Eqs(13), (14) and some preliminary results of computer simulation are submitted.

3. Numerical scheme and computer experiment

As coefficients of the model system remain to be constant the known Crank - Nicholson method (Musabekova et al., 2012) added by the iteration procedures can be used with sufficient efficiency. The numerical algorithm has been realized by the software of PTC Mathcad 15.0. The used code is shown in Figure 1. Figure 2 depicts certain preliminary results of the computer simulation based on model – see Eqs.(13) and (14).

```

A(dx, dy, m, n) :=
  for j ∈ 0..m
  for i ∈ 0..n
    Uaj,i ← A0
    Ubj,i ← B0
    Uej,i ← E0
    Fj,i ← dy·[a·(a·b - m·as) - k1s·as]
  E1 ← 1
  for v ∈ 1..1
  for j ∈ 1..m
  for i ∈ 1..n-1
    y ← y0 + i·dy
    A ← dx
    Bi ← dy2 - 0.5·dy·dx·y + 2dx
    Ci ← dx - 0.5·dx·dy·y
    Dj ← k2·dx·dy2·Uej-1,i-1 + 0.5·y·dy·dx·(Uaj-1,i - Uaj-1,i-1) + dy2·Uaj-1,i
    Dj-1,i ← dx·(Uaj-1,i+1 - 2Uaj-1,i + Uaj-1,i-1) - dx·dy2·k1·Uaj-1,i-1·Ubj-1,i-1 + Dj
    Ei+1 ←  $\frac{A}{B_i - C_i \cdot E_i}$ 
    Fj-1,i+1 ←  $\frac{D_{j-1,i} + C_i \cdot F_{j-1,i}}{B_i - C_i \cdot E_i}$ 
  Uaj,n ←  $\frac{F_{j-1,n-1}}{1 - E_{n-1}}$ 
  for i ∈ n..1
    Uaj,i-1 ← Ei-1·Uaj,i + Fj-1,i-1
  Ua

```

Calculating initial concentrations

Calculating coefficients with tridiagonal matrix algorithm

Calculating concentrations to the right of the interface border

Figure 1: Mathcad code for the computer simulation

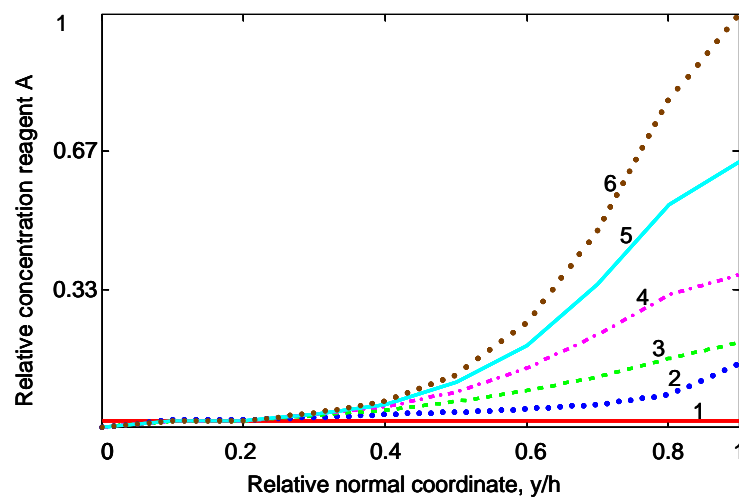


Figure 2: Concentration of absorbed reagent over the film thickness for $k_2/k_1 = 0.1$: $X=0.02$ (1); $X=0.1$ (2); $X=0.2$ (3); $X=0.4$ (4); $X=0.5$ (5); $X=0.6$ (6)

4. Conclusions

It can be concluded that using special coordinate transformation (12), we can offer a method for solving the problem of non-self-similar film absorption, accompanied by a second-order reversible chemical reaction. Namely, the complex system of convective diffusion equations can be reduced to the form with constant coefficients (13) and boundary conditions (14). Moreover, at low reversibility of the chemical reaction and slow change of surface features along the longitudinal coordinate the model system can be reduced to the linear form. It opens up the possibility of an asymptotic analysis under the boundary conditions of sufficiently general

form implemented in practical terms. In general case system (13), (14) can be solved numerically using the modified Crank-Nicholson method with subsequent calculating the surface parameters in iteration process. The results of preliminary calculations show that the noticeable effect of the concentration-dependent capillary stresses at the film surface occurs only on very short, initial areas near the starting point of absorption (Figure 2). This effect manifests itself in the growth rate of the surface of the film along the longitudinal coordinates and the more rapid growth of the surface concentration.

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