Modeling of Falling Film Absorber

Akanksha, K. K. Pant, V.K. Srivastava
Department of Chemical Engineering, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi- 110016,India

Extended Abstract

Interfacial exchange of material between gas and liquid phase plays a very important role in many chemical processes. This transfer forms the basis of distillation, absorption and humidification. In these cases there is a physical transfer of material across the phase boundary controlled by the physical properties of the system.

Falling film gas absorption, in particular, is a typical example wherein the mass transfer takes place with chemical reaction. Often diffusion and reaction occur in the same region, and the two rates phenomena are coupled so closely that they have to be treated simultaneously. It is a very common phenomenon to be encountered in industrial operations specifically in exothermic gas-liquid reactions such as chlorination, sulphonation and nitration etc. in detergent and wetting/dispersing agent industries, polymerization units, fermentation processes and waste disposal systems.

Previous work in the field of mathematical modeling for falling film reactors have been proposed by Johnson and Crynes (1974), Davis et al. (1979), Mann et al. (1977), Gutierrez et al. (1988) and Dabir et al. (1996). Bhattacharya et al. (1988) and Nielsen and Villadsen et al. (1983) studied the gas absorption for chlorination reactions. In all these studies chemical conversion and interfacial temperatures were assumed to be the most important variables as far as product yield and product quality is concerned.

Johnson and Crynes (1974) assumed that the reaction takes place only at the gas-liquid interface and obtained the temperature profiles for the process. Davis *et al.* (1979) propounded another model where they completely described the fluid dynamics of the liquid film determining the film thickness and the velocity profile. Mann *et al.* (1977) extended the film theory solutions by studying the enhancement factor behaviour for the case of pseudo first-order reaction. Gutierrez *et al.* (1988) assumed that all the three phenomena i.e. liquid transfer; gas transfer and reaction rate controls the process and thus obtained the velocity, concentration and temperature profiles using implicit finite difference method. Dabir *et al.* (1996) proposed a model, which was appropriate for both laminar and turbulent films. Nielsen and Villadsen (1983) studied the gas absorption accompanied with a pseudo-first order reaction in a falling film reactor. They mainly discussed the multiplicity aspects of the temperature rise at the gas-liquid interface.The problem of gas absorption with zero and first order reactions with chemical reaction in laminar newtonian falling liquid film for isothermal case was studied by Akanksha and Srivastava (2003). They studied the effect of dimensionless reaction parameter on the concentration of the gas in the newtonian falling film with reaction.

The objective of present study is to develop a mathematical model for the thin film reactor. Therefore attention is restricted to those conditions of simultaneous diffusion and chemical reaction, which can be, regarded as limiting or asymptotic cases. The model reaction

used for the analysis are chlorination of decane and sulphonation of trydecylbenzene. The coupled partial differential equations, which describe the mass and heat transfer in the liquid, are solved by finite difference method using implicit scheme. The concentration and temperature profiles along the radial and axial distances are predicted. The parameters like Arrhenius factor, Thiele modulus and Biot number for mass transfer are optimized using binary coded genetic algorithm technique.

Mathematical Model

Case-I*: First order reaction*

Considering the absorption of a gas into a thin liquid film, gaseous species A undergoes an exothermic reaction with a liquid, phase B. Gas A dissolves and then reacts with liquid according to the following stoichiometry:

$$A(g) \quad + \quad B(l) \longrightarrow \text{Products}$$

The schematic diagram explaining the phenomena of gas absorption in a falling film reactor along with its grid scheme for backward implicit method is shown in Figure 1.

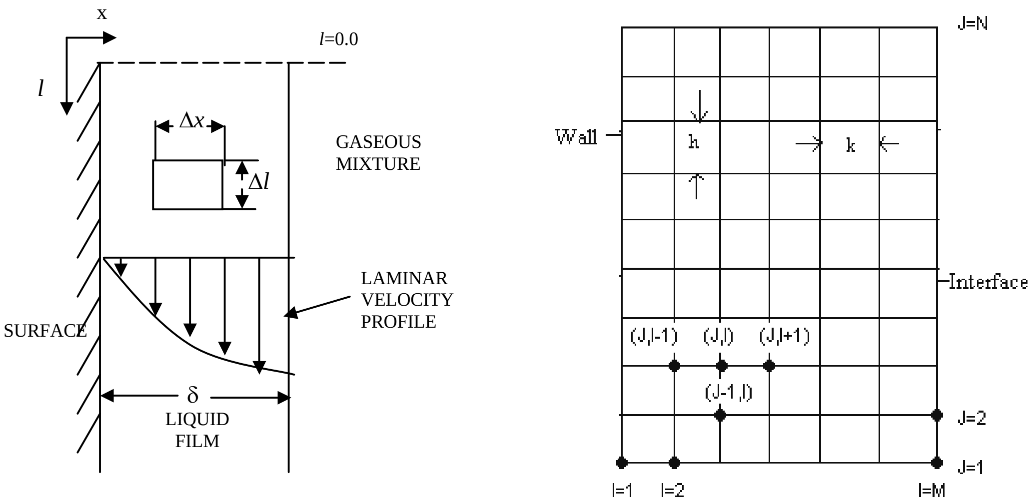

Figure 1. Schematic diagram of falling film reactor and grid scheme

The following assumptions have been made in the analysis of the problem: (i) the liquid reactant B is considered non-volatile and no evaporation in gas phase takes place, (ii) the liquid film is laminar, (iii) the physical properties of liquid and gas such as diffusivity, conductivity, density, and heat capacity are independent of temperature, (iv) steady state, non-isothermal, pseudo-first order irreversible reaction is considered (v) solubility of the gaseous reactant in the liquid film follows Henry's law and (vi) a liquid film of constant thickness is assumed.

The axial velocity is given by

$$v_l(x) = \frac{G\rho}{\mu}\left(\delta x - \frac{x^2}{2}\right) \tag{1}$$

The mass and heat balance equations along with their boundary conditions in the dimensionless form are given as:

Mass balance

For component A

$$\left(1-Y^2\right)\frac{\partial A}{\partial Z}=\frac{\partial^2 A}{\partial Y^2}-\phi^2 A\exp\left(\gamma_R\left(1-\frac{1}{\theta}\right)\right) \qquad (2)$$

[convection] [diffusion] [reaction]

Energy balance

$$Le\left(1-Y^2\right)\frac{\partial \theta}{\partial Z}=\frac{\partial^2 \theta}{\partial Y^2}+\beta_R\phi^2 A\exp\left(\gamma_R\left(1-\frac{1}{\theta}\right)\right) \qquad (3)$$

[convection] [conduction] [reaction]

Initial and Boundary conditions

$$At \quad Z=0,\quad A=0,\qquad \theta=1$$

At the interface, $Y=1,\quad Bi_M\left(A_g-A_sH_o\right)=\frac{\partial A}{\partial Y},\quad Bi_H\left(\theta_g-\theta_s\right)=\frac{\partial \theta}{\partial Y}$

At the wall, $Y=0,\quad \frac{\partial A}{\partial Y}=0,\quad \frac{\partial \theta}{\partial Y}=0$

The following dimensionless variables are defined for non-dimensionalization:

$$Z=\frac{lD}{v_{\max}\delta^2},\quad Y=\frac{x}{\delta},\quad \theta=\frac{T}{T_r},\quad A=\frac{C_A}{C_A(T_r)},\quad \phi=\delta\left(\frac{k(T_r)}{D}\right)^{1/2},\gamma_R=\frac{\Delta E}{RT_r},\quad \beta_R=\frac{(-\Delta H_R)DC_A(T_r)}{k_\lambda T_r},$$

$$Bi_H=\frac{k_l\delta}{D},\quad Bi_H=\frac{h_g\delta}{k_\lambda},\quad Le=\frac{D\rho c_p}{k_\lambda}$$

Optimization

The above-mentioned set of equations are highly sensitive to parameters like Thiele modulus and Lewis numbers. Oscillations were obtained for a very narrow range of parameters. To minimize such oscillations, parameters (ϕ,γ and Bi_M) were optimized using Genetic Algorithm (GA) technique. GA is a computerized search and optimization algorithm based on the mechanics of natural genetics and natural selection. It is used for combinatorial optimization problem in diverse fields and particularly in chemical engineering. The objective function is defined as

Minimize $f\left(\varphi,\gamma_R,Bi_M\right)=X_{A,cal}-X_{A.s}$,

in the interval

$$0.35\le\phi\le 0.6,$$

$$30.0\le\gamma_R\le 40.0,$$

$$1.0\le Bi_M\le 7.0$$

This above range is fixed based on the sensitivity analysis. The fitness function used is

$$F(x)=\frac{1}{\left(1+f\left(\varphi,\gamma_R,Bi_M\right)\right)}$$

In order to solve this problem using genetic algorithms, binary coding has been chosen to represent variables ϕ, γ_R, and $Bi_{M.}$. In the present analysis, 5-bits are chosen for each variables which present an accuracy of $\left(x_i^{(U)}-x_i^{(L)}\right)/2^{l_i}$ or 0.0021, 0.3125 and 0.1875 for parameters ϕ, γ_R, and $Bi_{M.}$ respectively, thereby making the total string length equal to 15. The crossover and mutation probabilities assigned are 0.8 and 0.2, respectively. The population size taken is 50. The random population created using Knuth's random number generator with a random seed equal to 0.123. The generation counter is initialized with t=0 to a maximum value of t_{max}=50.

Case II: *Instantaneous reaction*

The above model is extended for the case of absorption with an instantaneous reaction for varying film thickness. Here mass and heat balance is made in both liquid and gas phase. The film is considered to be fully laminar and the gas to be fully turbulent. The physical properties of liquid such as diffusivity, density, and viscosity are considered to be temperature dependent.

Gas Phase

Mass Transfer

$$\frac{d\left(w_G Y_A\right)}{dz}=-k_l\,p_A \tag{4}$$

which on integration gives

$$p_A = p_o \exp\left(-\frac{k_l P}{w_G}z\right) \tag{5}$$

using the inlet condition $p_A(o)=p_o$.

The fractional conversion of A down the reactor length can be defined as

$$X_A = 1-\exp\left(-\frac{k_l P}{w_G}z\right) \tag{6}$$

Heat Transfer

The heat balance on the gas phase is given as

$$\frac{d(w_G c_G T_g)}{dz}=h_g\left(T_{y=\delta}-T_g\right) \tag{7}$$

The velocity profile as a function of radial distance is given as

$$v_z=\frac{\rho\,G}{\mu}\left(\delta y-\frac{y^2}{2}\right)+J\,\frac{\tau_G y}{\mu} \tag{8}$$

For co-current systems J is +1 and for counter current systems J is –1. Film thickness, δ can be calculated by trial and error procedure from the following equation:

$$\Gamma=\frac{\rho G}{3\mu}\delta^3+\frac{\tau_G\delta^2}{2\mu} \tag{9}$$

Liquid Phase

Heat balance

Heat transfer in the liquid phase is determined by means of the microscopic heat balance as:

$$v_Z \frac{\partial T}{\partial z} = \alpha\left(\frac{\partial^2 T}{\partial y^2}\right) \tag{10}$$

Boundary Conditions:

At Z=0 $T=T_o$ (inlet liquid temperature)

For Y=0, at the wall $T=T_w$ (wall temperature)

For Y=δ, at the interface $k_\lambda \frac{\partial T}{\partial y} = q_{Gen} - h_g\left(T_{Y=\delta} - T_g\right)$

where, $q_{Gen} = (-\Delta H_R)k_l p_o \exp\left(-\frac{k_l P}{w_G} z\right)$

Numerical Scheme

The above-mentioned second order partial differential equations of mass and energy balances are solved using backward implicit numerical scheme. Discretization of the partial derivatives is done by backward, forward or central differencing schemes depending on the boundary conditions, which on transformation can be written into matrix form of type

[A]x [B]= [C]

where A is the coeffcient matrix of order (M x M), B is the variable matrix of order (M x 1) and C is the constant matrix of order (M x 1). The matrix equation thus obtained is solved using Srivastava routine [10], wherein tridiagonal banded matrix (TDM) (M x M) is converted into TDM (M x 3) form, thus saving a lot of computer processing time and storage memory.

Results and discussion

Case I:*First order reaction*

Dimensionless parameters defined in the above equations were calculated using the data available in literature [Bhattacharya et al.,1988] for chlorination of n-decane. Results are given in the form of concentration and temperature profiles developed for both radial and axial distances (Figs. 2-5). Final values for the parameters ϕ, γ_R and Bi_M obtained after optimization are 0.598, 39.355 and 7.0 respectively.

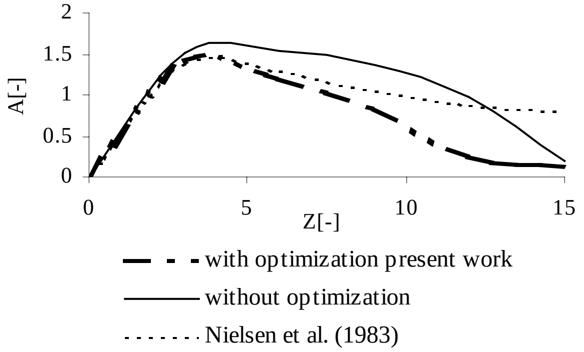

Figure 2. Variation of concentration of A with axial distance

The predicted values are compared with the Nielsen et al. [1983] work. It should be noted that no optimization technique was used by them. The difference in the concentration and temperature profile of two could be because of the sensitivity of the model parameters, which were not optimized before.The concentration of species of A increases first and then passes through maxima. The shape of the curve is due to the coupling of absorption and chemical reaction. Similar trends were reported by Nielsen et al. [1983].

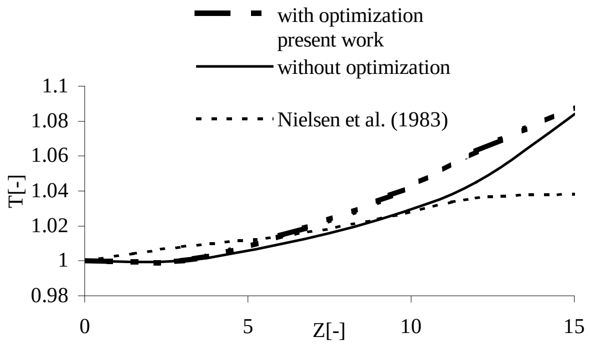

Figure 3. Variation of liquid temperature with axial distance

The temperature increases with axial distance due to the exothermicity of the reaction. Although concentration of A has a significant effect in radial direction (Figure 4) but negligible change has been observed for the variation of temperature (Figure 5) which is because of small thickness of the liquid film, resulting in not much exothermic effects occurring in radial direction.

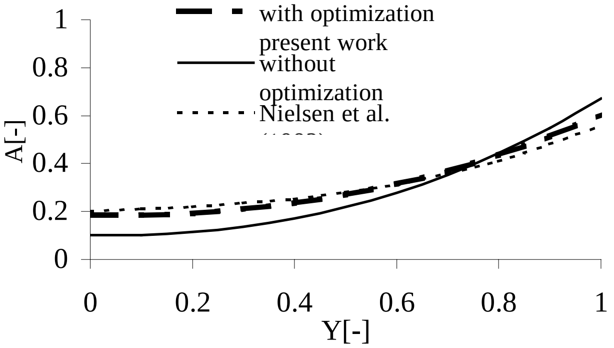

Figure 4. Variation of concentration of A with radial for distance Z=12[-]

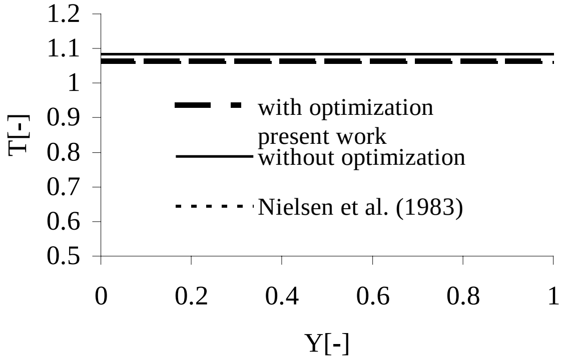

Figure 5. Variation of temperature with radial distance for Z=15[-]

Case II: *Instantaneous reaction*

Parameters defined were calculated using the data available in literature [Davis et al.,1979] for sulphonation of trydecylbenzene. Conversion, interfacial temperature and gas temperatures are plotted in Figure 6. The maxima of interfacial temperature and the mixed mean liquid temperature increases within a short distance from the inlet. This increase is due to the high exothermicity of the reaction. Similar trends were reported by Johnson and Crynes [1974] and Davis et al. [1979] model. However the difference in the curves is due to the fact that Davis et al. predicted a piecewise continuous axial temperature profile as a result of the step changes in film thickness incorporated in the model whereas Johnson and Crynes used a constant film thickness in their model.

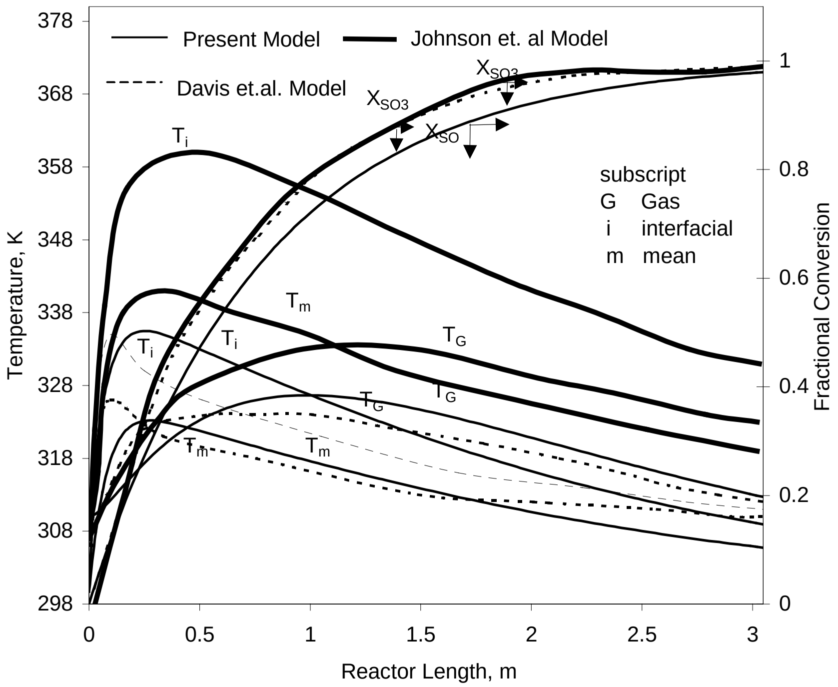

Figure 6. Temperature and conversion profiles down the reactor length

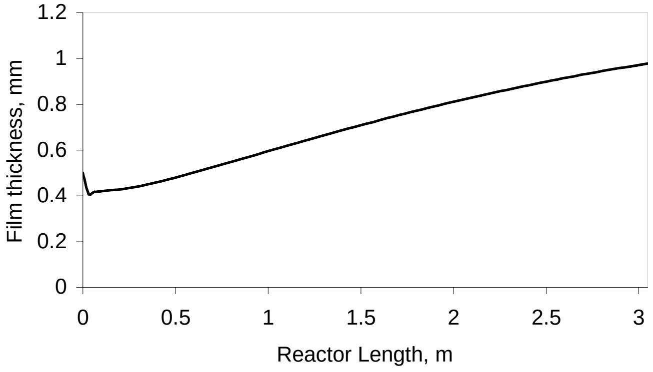

Figure 7. Film thickness v/s reactor length

Figure 7 shows the variation of film thickness as a function of reactor length. It can be observed that the film thickness increases substantially over the length of the reactor due to the significant increase in liquid viscosity.

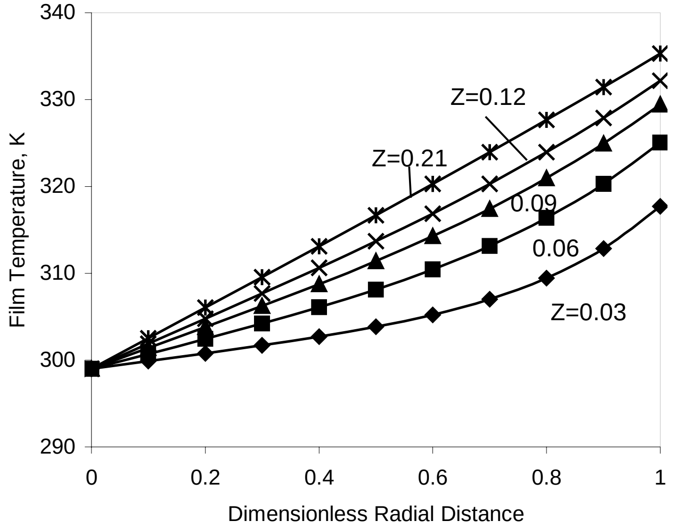

Figure 8a. Transverse temperature profiles downstream of peak interfacial temperature

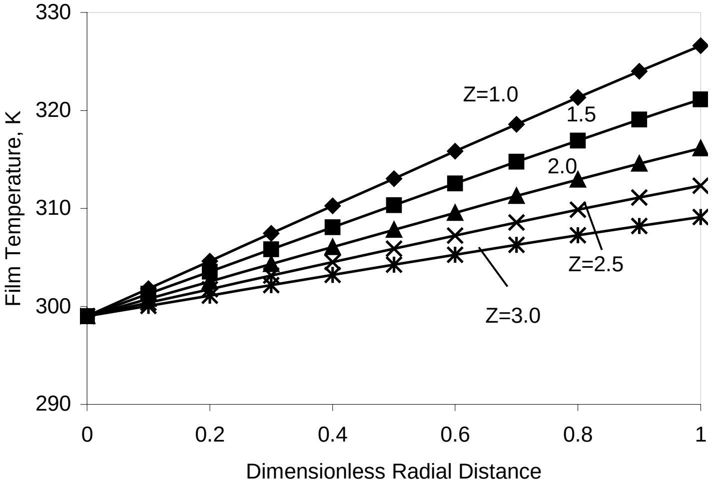

Figure 8b. Transverse temperature profiles upstream of peak interfacial temperature

Transverse temperature profiles in the liquid film are shown in Figures 8a and 8b. It can be seen that except near the reactor inlet, the temperature profiles are nearly linear. In contrast to the first order reaction (Case I), there was a significant increase in liquid film temperature from reactor wall to free surface. The temperature rise increased significantly down the reactor along with the film thickness.

Conclusion

Diffusion-convection-reaction model is developed considering momentum; mass and heat transfer effects into account. The resultant equations are solved using finite difference backward implicit scheme. Results are given in the form of concentration and temperature profiles development for both radial and axial distances. The results indicated an increase in the axial temperature of the liquid film for a shorter distance from the reactor top for a varying film thickness model and the predicted conversion was in close agreement with the experimental results. Moreover the final parameters of the model for a first order reaction are optimized using binary coded genetic algorithm technique. The model is simple and is also time effective. The developed model is simple and may be helpful to scale up a thin film reactor to predict the performance of nonisothermal gas-liquid reactions.

Nomenclature

A = $C_A/C_A(T_r)$, dimensionless concentration of gaseous reactant A,[-]
A_g,A_s = A in bulk gas, in liquid at the interface,[-]
Bi_H = Biot number for heat transfer, $h_g\,\delta / k_\lambda$, [-]
Bi_M = Biot number for mass transfer, $k_l\,\delta / D$,[-]
b = stoichiometric coefficient of B,[-]
C_A = concentration of dissolved gas,[kmol .m^{-3}]
$C_A(T_r)$ = reference gas phase concentration,[kmol .m^{-3}]
c_G = molar heat capacity of gas, [J.kgmoles^{-1}.K^{-1}]
$C_p\rho$ = heat capacity of liquid, [J.m^{-3} ·K^{-1}]
D_A = diffusivity of A,[m^2 .s^{-1}]
G = acceleration due to gravity,[m.s^{-2}]
h_g = heat transfer coefficient in gas phase,[J.s^{-1}. m $^{-2}$. K^{-1}]
H_o = Henry's constant, 0.093,[-]
k = first order rate constant at temperature T_r,[m^3. kmol $^{-1}$.s^{-1}]
k_l = liquid phase mass transfer coefficient,[m. s^{-1}]
k_λ = thermal conductivity of liquid,[J.s^{-1} . m^{-1} . K^{-1}]
l = axial coordinate,[m]
Le = $D\rho c_p/ k_\lambda$, Lewis number,[-]
P = total pressure, [atm]
p_A = partial pressure of gaseous reactant A in bulk , [atm]
p_o = initial pressure of A at z=0, [atm]
q_{gen} = heat generated due to reaction, [J.kgmoles^{-1}]
R = gas constant,[J. kmol $^{-1}$. K^{-1}]
T = temperature of liquid, [K]
T_g = temperature of bulk gas, [K]
T_o = temperature of liquid at z=0, [K]
T_r = reference temperature,[K]
T_w = wall temperature, [K]
v = axial velocity in liquid film,[m.s^{-1}]
w_G = molar flow rate of gas per unit wetted perimeter, [kgmoles.s^{-1}.m^{-1}]
x = radial coordinate,[m]
X_A = conversion of reactant A,[-]
$X_{A,cal}$, $X_{A,s}$ = conversion of A obtained after optimization and set value of conversion respectively,[-]
Y = x/δ, dimensionless coordinate through film from reactor wall,[-]
Y_A = mole fraction of A in gaseous mixture, [-]
y = radial distance, [m]

Z = $lD/v_{max}\delta^2$, dimensionless axial distance,[-]
z = axial distance, [m]
α = thermal conductivity, [$m^2.s^{-1}$]
β = $(-\Delta H_R)D_A\ C_A(T_r)/\ k_\lambda\ T_r$,[-]
δ = liquid film thickness, [m]
ΔE = activation energy, [$J.kmol^{-1}$]
$-\Delta H_R$ = heat of reaction, [$J.\ kmol^{-1}$]
Γ = volumetric flow rate of the liquid per unit wetted perimeter, [$m^2.s^{-1}$]
γ_R = $\Delta E/RT_r$, [-]
μ = liquid viscosity,[$kg.m^{-1}.s^{-1}$]
ϕ = $\delta\,(k(T_r)/D_A)^{1/2}$,[-]
ρ = liquid density,[kg/m^3]
τ_G = interfacial shear stress, [$N.m^{-2}$]
θ = T/T_r, dimensionless temperature,[-]
$\theta_g\ \theta_s$ = θ in bulk gas phase, in liquid at interface,[-]

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