Dynamic behaviour of a semibatch non-isothermal gas-liquid reactor

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A dynamic model to predict transient temperature profiles of a nonisothermal semibatch gas-liquid reactor was developed. The enhancement factor for non-isothermal gas absorption was calculated by extending the model of Bhattacharya et al. (AICheJ (1987) 33 1507) to incorporate the effect of finite gas film resistance. For a particular combination of values of heat of reaction, heat transfer and activation energy parameters, transient temperature profiles of the semibatch reactor were found to be highly parameter sensitive. In the reactor model, gas phase dynamics were taken into account and heat generated in the reactor was assumed to be removed by a coolant flowing through a cooling coil.

Keywords: temperature profiles; gas-liquid reactor; modelling

Nomenclature

\[\begin{align*}
A & : \text{External heat transfer area} \\
a & : \text{Interfacial area per unit volume of reactor} \\
C_A & : \text{Concentration of reactant A in bulk} \\
C_A^* & : \text{Concentration of reactant A at the gas-liquid interface} \\
C_B & : \text{Concentration of reactant B in the bulk} \\
C_p & : \text{Specific heat} \\
D & : \text{Diffusivity} \\
E & : \text{Activation energy} \\
-\Delta H_A & : \text{Heat of solution} \\
-\Delta H_R & : \text{Heat of reaction} \\
h_g & : \text{Gas side heat transfer coefficient} \\
h_l & : \text{Liquid side heat transfer coefficient} \\
k & : \text{Second-order reaction rate constant} \\
k_l & : \text{Liquid side mass transfer coefficient} \\
l & : \text{Liquid hold-up} \\
q_x & : \text{Volumetric flow rate of gas} \\
t & : \text{Time} \\
T & : \text{Reactor liquid temperature} \\
T^* & : \text{Temperature at the gas-liquid interface} \\
T_x & : \text{Gas temperature} \\
\delta & : \text{Distance coordinate in the film} \\
U & : \text{Overall heat transfer coefficient from reactor to coolant side} \\
V & : \text{Volume of reactor.} \\
\delta & : \text{Thickness of the concentration boundary layer} \\
\rho & : \text{Density}
\end{align*}\]

Greek symbols

\[\begin{align*}
\delta & : \text{Thickness of the concentration boundary layer} \\
\rho & : \text{Density}
\end{align*}\]

Subscripts

\[\begin{align*}
0 & : \text{Initial} \\
i & : \text{Interface} \\
f & : \text{Feed} \\
L & : \text{Liquid} \\
g & : \text{Gas} \\
A,B & : \text{Reacting species}
\end{align*}\]

Introduction

Absorption of a gas into a liquid is normally accompanied by heat evolution in the liquid due to heat of solution and also heat of reaction if the absorption process is accompanied by a chemical reaction. A rise in temperature at the gas-liquid interface lowers the solubility. However, if the absorption is accompanied by a chemical reaction, a rise in the temperature of the gas-liquid film causes an increase in the value of reaction rate constant and hence rate of reaction, thus resulting in an enhancement of mass transfer. Film and bulk liquid temperatures may not be identical as the extent of heat transfer from the liquid film to the bulk will determine the difference between the interface and bulk temperatures. Modelling of heat effects in a gas absorption process is important as temperature affects solubility, values of equilibrium and reaction rate constants, and many other parameters like surface tension, density, viscosity, diffusivity, etc., which in turn can influence heat and mass transfer coefficients as well as interfacial area. If heat of reaction is large, reactor stability may have to be investigated.

Shah critically reviewed the theoretical and experimental studies made by different authors. Danckwerts investigated heat effects on absorption accompanied by a first order reaction by using penetration theory, but made
an assumption that even the temperature-sensitive reaction rate constant is not affected by a rise in temperature. Shah solved the penetration model for the non-isothermal case numerically and he took into account the variation of diffusivity, solubility and the first-order rate constant. Mann and Moyes applied the film model to account for heat effects by assuming the film to be at a uniform temperature equal to the interface temperature. Bhattacharya et al. extended the model of Mann and Moyes to cover depletions and instantaneous reaction regimes. Whether the model is based on film theory or penetration theory, the model becomes complicated if solvent evaporation, volume change due to absorption, Dufour and Soret effects, as well as Marangoni and Raleigh effects need also to be taken into account. In the present work, the dynamic behaviour and parametric sensitivity of a semibatch reactor are investigated by applying the film model of Bhattacharya et al. and accounting for gas film resistance, heat transfer to gas, and gas phase dynamics. The following assumptions are made in the development of the reactor model:

1. gas phase is completely backmixed;
2. interfacial area, \( k_{\text{i}} \), and gas phase hold-up are constant;
3. liquid phase is completely backmixed;
4. two-film theory is applicable;
5. no evaporation of solvent or any other species from the liquid phase;
6. physical properties like density, specific heat, thermal conductivity of both the phases are constant;
7. volume change due to absorption, Dufour and Soret effects are negligible;
8. reaction is irreversible, second order and of the type \( A + B \rightarrow \text{products} \);
9. the thickness of the thermal boundary layer is large compared to that of the concentration boundary layer such that the latter is at a uniform temperature equal to the gas-liquid interface temperature;
10. solubility and rate constant vary with respect to temperature according to the equations

\[
C_A(T^*) = C_A(T) \exp \left[ \frac{-\Delta H_c}{R} \left( \frac{1}{T^*} - \frac{1}{T} \right) \right] \tag{1}
\]

\[
k(T^*) = k(T) \exp \left[ -E/R \left( 1/T^* - 1/T \right) \right] \tag{2}
\]

With the help of these assumptions, the following equations can be written.

Mole balances:

\[
-D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x \to 0} = (l - a\delta)k_{\text{A}}C_B \tag{3}
\]

\[
\frac{(l - a\delta)}{b} \frac{dC_B}{dt} = q \left[ -D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x \to 0} \right] - \left( -D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x = \delta} \right) + k_{\text{A}}C_B(l - a\delta) \tag{4}
\]

\[
-D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x = \delta} = k_{\text{l}} \frac{M_{l}^{1/2}}{\tanh M_{l}^{1/2}} \left[ C_A(T^*) - \frac{C_A}{\cosh M_{l}^{1/2}} \right] \tag{5}
\]

\[
D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x = \delta} = k_{\text{l}} \frac{M_{l}^{1/2}}{\tanh M_{l}^{1/2}} \left[ C_A(T^*) - \frac{C_A}{\cosh M_{l}^{1/2}} \right] \tag{6}
\]

\[
M_{l}^{1/2} = (k(T^*)D_{\text{A}}C_B)^{1/2} \tag{7}
\]

\[
C_B^{*} = 1 + \frac{D_{\text{B}}b}{D_{\text{A}}C_B} \left[ C_A(T^*) - C_A \right] - \frac{D_{\text{B}}bC_A(T_0)E_1}{D_{\text{A}}C_B} \tag{8}
\]

where

\[
E_1 = \frac{-D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x = 0}}{k_{\text{l}} C_A(T_0)} \tag{9}
\]

Energy balances:

\[
(-\Delta H_c) \left[ -D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x \to 0} \right] + (-\Delta H_R) \left[ -D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x \to 0} \right] - \left( -D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x = \delta} \right) = h_{l}(T^* - T) + h_{v}(T^* - T_0) \tag{10}
\]

\[
\rho_{V_R}C_{ps}(1 - l) \frac{dT_{s}}{dt} = q_s \rho_{V_s}C_{ps}(T_{ps} - T_0) \tag{11}
\]

\[
V_R \rho_{C_p}(l - a\delta)dt/dt = h_{l}aV_R(T^* - T) \tag{12}
\]

When gas film resistance to mass transfer is not negligible, these additional equations need to be solved:

\[
-D_{\text{A}} \frac{dC_A}{dx} \bigg|_{x \to 0} = k_{\text{g}}(\rho_{A} - H_{2}C_{A}) \tag{13}
\]

\[
\frac{dn_{B}}{dt} = -k_{\text{g}}aV_R(\rho_{A} - H_{2}C_{A}) + \frac{q_{g}}{R_{c}T_{s}} \tag{14}
\]

If we assume the ideal gas law to be valid, then the following equation can be written:

\[
n_{B} = V_B(l - l) \frac{\rho_{B}}{R_{c}T_{s}} \tag{15}
\]

Hence

\[
\frac{dn_B}{dt} = \frac{V_B(l - l)}{R_{c}T_{s}} \left[ \frac{d\rho_{A}}{dt} \frac{\rho_{A}}{T_{s}} \frac{dT_{s}}{dt} \right] \tag{16}
\]
Substituting Equation (14) in Equation (16), Equation (16) can be rewritten as
\[
\frac{dp_A}{dt} = -k_\alpha \rho A \rho T \left( \rho_A - H_A C_A^* \right) + \frac{q_g T_k}{V_k(1 - T)} + \frac{p_A}{T} \frac{dT_k}{dt}
\]
\[
\left[ \frac{p_A}{T} + \frac{p}{T} \frac{dT_k}{dt} \right] \frac{dn_A}{dt} + \frac{p_A}{T} \frac{dT}{dt}
\]
Equation (17):
\[
\frac{dp_A}{d\theta} = -G_{d} \rho T \left( \rho_A - C_A^* \exp[-G_d(1/T^* - 1)] \right)
\]
\[
+ \frac{T_k}{G_d} \left( 1 - \frac{G_{d}}{G_{d} + \rho_A} \right) \frac{dT}{d\theta}
\]
(29)

The Equations (3)–(17) can be rewritten in dimensionless form as shown in Equations (18)–(29) given below:

Equation (3):
\[
G_1 \phi_s = \exp[-G_d(1/T^* - 1)] C_A^* C_B^*
\]
(18)

Equation (4):
\[
-\frac{dC_A}{d\theta} = G_2 (\phi_0 - \phi_s) + (G_2 / G_d) \exp[-G_d(1/T^* - 1)] C_A C_B^*
\]
(19)

Equation (5):
\[
\phi_0 = \frac{-D_{\text{in}}}{k_1 C_1(T_0)} \left| \frac{dC_A}{dx} \right|_{x = 0} = E_1
\]
\[
= \frac{M_{12}}{\tanh M_{12}} \left[ C_A^* - \frac{C_A}{\cosh M_{12}} \right]
\]
(20)

Equation (6):
\[
\phi_A = \frac{-D_{\text{in}}}{k_1 C_1(T_0)} \left| \frac{dC_A}{dx} \right|_{x = s} = E_1
\]
\[
= \frac{M_{12}}{\tanh M_{12}} \left[ \frac{-C_A}{\cosh M_{12}} - C_A^* \right]
\]
(21)

Equation (7):
\[
M_{12}^2 = C_B^* M_{10}^2 \exp[-G_d(1/T^* - 1)]
\]
(22)

Equation (8):
\[
\frac{C_A}{C_B} = (1/sq)(C_A^* - C_A) - (1/sq)\phi_0
\]
(23)

Equation (9):
\[
E_1 = \left. -\frac{dC_A}{dx} \right|_{x = 0} = \phi_0
\]
(24)

Equation (10):
\[
G_2 \phi_0 + G_2 (\phi_0 - \phi_A) = G_d (T^* - T) + G_1 (T^* - T_k)
\]
(25)

Equation (11):
\[
G_0 \frac{dT}{d\theta} = T_k - T_s + G_0 (T^* - T_k)
\]
(26)

Equation (12):
\[
G_0 \frac{dT}{d\theta} = G_0 (T^* - T) - G_0 (T - T_s)
\]
\[
+ (G_0 / G_d) \exp[-G_d(1/T - 1)] C_A C_B^*
\]
(27)

Equation (13):
\[
\phi_A = \frac{k_{\text{in}}}{k_1 C_1(T_0)} \left[ p_A - \frac{H_A}{H_A/\cosh M_{12}} C_A^* \right]
\]
(31)

Equations (20) and (31) can be solved for \( C_A^* \) to give
\[
C_A^* = \left\{ \frac{k_{\text{in}}}{k_1 C_1(T_0)} \phi_A + \left( \frac{M_{12}^2}{\sinh M_{12}} \right) \right\} \times
\]

By solving for \( C_A^* \) from Equations (18) and (21),
\[
C_A^* = \frac{M_{12}^2 G_1 C_A^*}{M_{12}^2 G_1 C_A^*} \]
\[ \left\{ \frac{k_A H_A(T^* - 1)}{k_L} + \frac{M^{1/2}}{\tanh M^{1/2}} \right\}^{-1} \]  

where \( H_A = H_{ab} \exp[-G_A(1/T^* - 1)] \) \( \) (32)

Substituting Equation (30) for \( C_A \) in Equation (32), and solving for \( \tilde{C}_A^* \) gives

\[ \frac{\tilde{C}_A^*}{Y_A - \bar{p}_A} = \frac{Y_A - Y_A Y_I}{Y_A} \]  

where \( Y_A = k_A H_A / k_L \) \( \) (35)

\[ Y_I = M^{1/2} / \sinh M^{1/2} \]  

\[ Y_A = M^{1/2} G_A / M^{1/2} G, \cosh M^{1/2} + (k/k_b) \tilde{C}_A \sinh M^{1/2} \] \( \) (36, 37, 38)

Substituting Equation (20) for \( \phi_0 \) in Equation (23), the equation for \( \tilde{C}_B^* \) becomes

\[ \tilde{C}_B^* = \tilde{C}_B^* + \frac{\tilde{C}_A^*}{s} - \frac{M^{1/2}}{\tanh M^{1/2}} \]  

\[ \frac{M^{1/2}}{\cosh M^{1/2}} \{ \tilde{C}_A^* - \tilde{C}_A \} \]  

\[ + \tilde{C}_A \] \( \) (39)

The differential Equations (19), (26), (27) and (29) can be solved for \( \tilde{C}_B^*, \tilde{T}_*^*, \tilde{P}_*^*, \text{ and } \bar{p}_A^* \), respectively. Equations (34) and (30) can be solved for \( \tilde{C}_A^* \) and \( \tilde{C}_B^* \), respectively. However, the values of \( \tilde{T}_*^* \) and \( \tilde{C}_B^* \) need to be solved by using the Equations (25) and (39), respectively, so that the values of derivatives involved in the differential equations can be found. The procedure for solution of \( \tilde{T}_*^* \) and \( \tilde{C}_B^* \) is iterative. Firstly, a set of values of \( M^{1/2}, \tilde{C}_A, \tilde{C}_B \) are calculated by using the Equations (22), (32) and (30), (20) and (21), respectively. Finally, the correctness of the assumed values of \( \tilde{T}_*^* \) and \( \tilde{C}_B^* \) is checked by using Equations (25) and (39), respectively. Equations (25) and (39) can be used to generate new trial values of \( \tilde{T}_*^* \) and \( \tilde{C}_B^* \) until convergence is achieved. When the value of \( M^{1/2} \) > 10, the value of \( \tilde{C}_B^* \) will become negligible small and hence can be taken as zero. If the computed value of \( \tilde{C}_B^* \) turns out to be less than \( \tilde{C}_B^* \) (i.e. \( \sqrt{M^{1/2}} \) > 8) the equation for the instantaneous reaction regime can be used instead of the equation for the fast-instantaneous reaction regime. The equation for \( \phi_0 \) corresponding to the instantaneous reaction regime can be shown to be given as

\[ \phi_0 = \tilde{C}_A^* + \frac{s}{s} \tilde{C}_B^* \]

Applying the flux balance at the gas-liquid interface gives

\[ \phi_0 = k_A(p_A - H_A C_A^*) / k_L \tilde{C}_B^* = \frac{[s \tilde{C}_B^* + \tilde{C}_A^*]}{\tilde{C}_B^*} \]

Solving this equation for \( C_A^* \) gives

\[ C_A^* = \frac{Y_A \bar{p}_A - \tilde{C}_B^*}{1 + Y_A H_A / H_{ab}} \]  

where \( H_A / H_{ab} = \exp[-G_A(1/T^* - 1)] \). \( \) (32)

If \( Y_A \tilde{C}_A^* < \tilde{C}_B^* \), then \( \tilde{C}_A^* = 0 \) and therefore \( \phi_0 = Y_A \bar{p}_A \)

If \( Y_A \tilde{C}_A^* > \tilde{C}_B^* \)

\[ \phi_0 = Y_A \tilde{p}_A + (H_A / H_{ab}) \tilde{C}_B^* \]  

\[ 1 + Y_A (H_A / H_{ab}) \]

It may be noted that the dimensionless parameters \( G_A, G_A, G_A, \text{ and } G_A \) are identical to the dimensionless variables \( G_A, G_A, G_A, \text{ and } G_A \) respectively, of Bhattacharya \textit{et al.} The significance of the various dimensionless parameters is obvious. \( G_A \) is the ratio of reaction time to physical saturation time. \( G_A \) is the ratio of hold-up of total liquid to hold-up of liquid less the hold-up of film liquid. The parameters \( G_A \) and \( G_A \) signify the ratios of heat transferred to liquid bulk and bulk gas to the rate of heat liberated in the mass transfer controlled regime, respectively. The parameter \( G_A \) is the dimensionless residence time of gas. The parameter \( G_A(G_A + 1) \) is a measure of the time constant of the gas phase energy balance. \( G_A \) is a measure of the time required to bring the bulk to the interface temperature. \( G_A \) is a measure of the efficiency of heat removal by the cooling system relative to the heat supplied to the bulk from the interface. \( G_A \) is a measure of the mass transfer rate for the gas phase. \( G_A \) is a measure of the time required to consume the liquid phase reactant in the mass transfer controlled regime. \( Y_A \) is the ratio of the liquid film resistance to the gas film resistance for physical mass transfer. If multiple steady states exist for \( T^* \), then the value of \( T^* \) that will be attained at a given time will depend on the initial temperature of the concentration boundary layer. If we assume that the concentration boundary layer is initially heated to a temperature much higher than that of the bulk, then a different temperature profile will be obtained from the start when compared to a temperature profile that will be obtained if the concentration boundary layer were assumed to be initially at a temperature level equal to that of the bulk.

\[ \text{Figure 1 shows two significantly different profiles (curves 3 and 5) obtained by using two different starting trial values for } T^*, \text{ namely } T^* = 1.5T \text{ for curve 3 and } T^* = T \text{ for curve 3. It may be noted that for the reaction runs shown in Figure 1, the values of the dimensionless parameters } G_A, G_A, G_A, \text{ and } G_A \text{ are chosen the same as the values chosen by Bhattacharya } \textit{et al.} \text{ for the run shown in Figure 6 of their paper, in which they predicted multiplicity. However, physically it is rather difficult to realise a situation where it is possible to heat the film alone leaving the liquid bulk at its original temperature. In all the runs shown in Figure 1, the dimensionless interfacial temperature is initially and finally close to bulk temperature. But, during the transient period, especially when the bulk temperature starts increasing rapidly, the interfacial temperature is very much higher than the bulk temperature. In Figure 1 the large effect on temperature profiles due to a small variation in the heat-removal parameter } G_A \text{ can also be seen by comparing curves 1 and 3. The plots of } T \text{ versus } \theta (\text{curves 2 and 3}) \text{ shown in Figure 1 exhibit a high parametric sensitivity of } T_{\text{Hmax}} \text{ with respect to the parameter } G_A. \text{ In Figure 1, the effect of a small perturbation in the initial temperature of the bulk liquid } T(\theta = 0) \text{ can be seen by comparing curves 3 and 4, which indicates again a high parametric sensitivity with respect to } T_{\text{H}}. \text{ Figure 2 shows the variation of fluxes at the gas-liquid and film-bulk interfaces as a function of time. From Figure 2 it can be seen that there is a sharp transition in regime from slow to fast for curve 1, when compared with curve 3, which is due to a small decrease in the liquid side heat transfer coefficient parameter, } G_A. \text{ A similar effect of a small increase in } T_0 \text{ can be seen when curves 3 and 4 are compared. When curves 2 and 3 are compared, the effect of a small decrease in the heat removal parameter, } G_A, \text{ is to cause a substantial rise in the peak value of interfacial} \]
Figure 1  Interface and liquid bulk temperature as a function of time

Figure 2  Dimensionless interface and film-bulk fluxes as a function of θ
flux although the regime transition is smooth.

The semibatch reactor model presented above can be easily extended to continuous-flow mixed reactors, packed and plate columns. Extension of the film model to the non-isothermal case for reversible and complex reactions is also straightforward. If the physical and transport properties are functions of temperature, their variation can be accounted for by evaluating the various dimensionless parameters as a function of composition and temperature.

Conclusions

For certain values of dimensionless heat of reaction, activation energy, and heat removal parameters, a semibatch gas-liquid reactor is found to give rise to multiplicity and high parametric sensitivity.

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