

Mathematical Model for Gas Phase in Fluidized Bed Catalytic Reactor for Ammoxidation of Propene to Acrylonitrile

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Abstract: A new mathematical model for the gas and solid phases Catalyzed Acrylonitrile (AN) fluidized bed reactor using V-Sb-Al catalyst is presented in this study. This mathematical model accounts for mass and heat transfer between gas and solid phases with chemical reaction that occurs at the surface of the catalyst particles. The proposed mathematical model evaluates the effect of catalyst flow rate and superficial gas velocity on the system. Concentration and temperature profile changes are also estimated. Moreover, the results of the proposed model are compared with experimental data in terms of concentration and temperature reaction. Obtained results shows good agreement with the actual plant data.

Key words: Mathematical model, catalyst, fluidized bed, chemical reaction, solid, phase

INTRODUCTION

Browsing through the literature gives a clear indication that little or almost no published work of a mathematical model that describes the production of Catalyzed Acrylonitrile (AN) can be easily found. In relevant literature, the general classification of AN fluidized bed catalyst reaction models has been considered. Levenspiel (1999) and Dai *et al.* (1993) have studied the mechanism of chemical reaction of production AN. The experimental work, by using different catalyst types, was considered (Hu *et al.*, 2007, Lankhuyzen *et al.*, 1976; Krebs, 1959; Callahan and Milberger, 1966) while in (Li *et al.*, 2002; Xue *et al.*, 1998), the experimental work with optimized operating conditions was adopted. Modeling of fluidized bed for ammoxidation of propane to AN can be found in Fakeekha *et al.* (2000).

In this research, a new mathematical model is proposed. Our model includes gas and solid phases to compare with the mathematical model that was presented in Fakeekha *et al.* (2000). Simulation to evaluate the effect of superficial velocity and catalyst flow rate on reaction temperature and concentration is also presented in this study.

MATERIALS AND METHODS

Descriptive behavior of the new mathematical model for acrylonitrile fluidized bed systems

Fluidized bed system: In this system, the reactant gas is assumed to enter the bottom of the bed and flows up the

reactor in the form of gases phase. As the gases rise, three mechanisms namely; rates of adsorption, desorption and chemical reaction on catalyst surface will be activated between three gases and V-Sb-Al catalyst solid with a chemical reaction which happens on the surface of catalyst particles. The model presented here, accounts for the effects of solid phase on the rate of reaction as shown in Fig. 1. The product then flows up into gases to be separated from the top of the bed. The gases contain very small amounts of catalyst solids. They are not spherical rather, they have an approximately hemispherical top and a pushed-in bottom. Each product of gas has a significant amount of catalyst solids. The assumptions considered while developing the proposed model are listed. In Table 1 however, the differences, in terms of the adopted functions, between our proposed model and those of the model presented in Fakeekha *et al.* (2000) are illustrated. List of assumptions considered for the proposed mathematical model is given below:

Assumptions:

- The fluidized bed comprises two phases: gas and solid phases
- All reactions occur on the catalyst solid phase
- All phases are at minimum fluidizing conditions
- Gas in excess of that required to maintain the minimum fluidizing condition passes through the bed as the gas phase
- There are negligible radial temperature and concentration gradients in the bed due to the agitation produced by the up-flowing gas

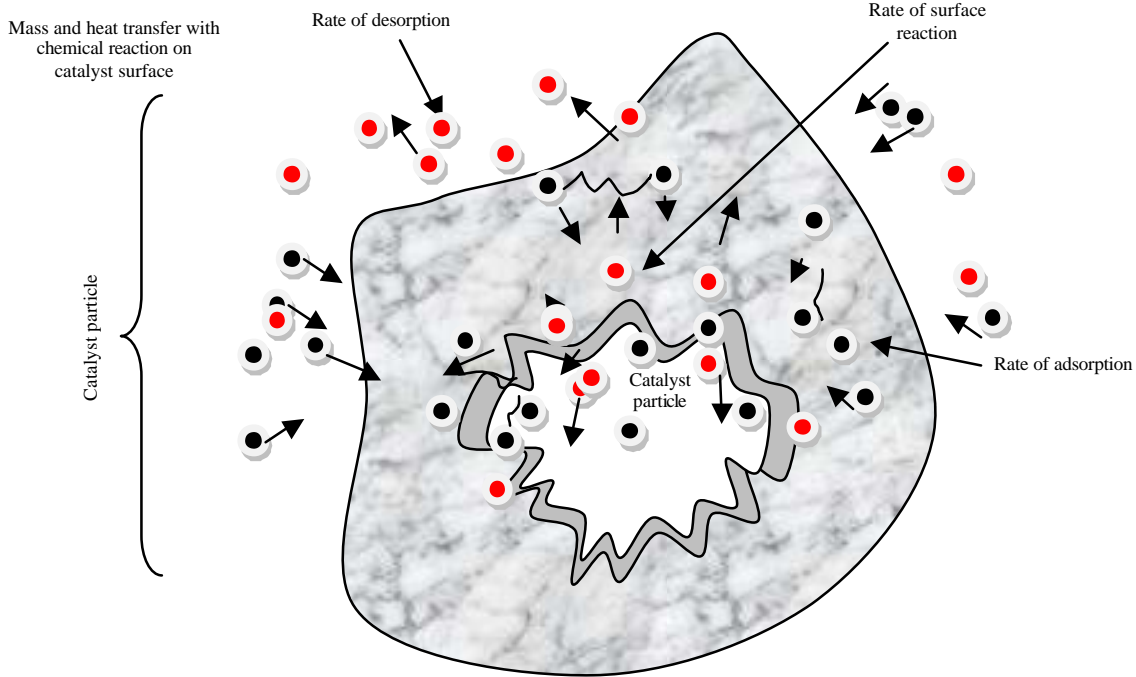


Fig. 1: Mechanism of chemical reaction

Table 1: A comparison in terms of adopted functions between the proposed mathematical model and the model by Fakeeha *et al.* (2000)

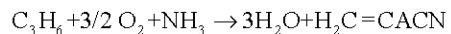
Functions <i>et al.</i> (2000)	The proposed mathematical model	Mathematical model of Fakeeha <i>et al.</i> (2000)
Mass transfer from gas to the solid	Mass transfer from gas to the solid with chemical reaction	Not applicable for catalyst solid phase
Rate of reaction	Rate of reaction for catalysis and gases phases	Activation reaction not depending on the types of catalysts
Energy transfer	Considered with solid phase	Not considered
Rate of adsorption	Considered	Ignored
Rate of desorption	Considered	Ignored

- The gas phase is composed of oxygen, ammonia and propene
- The dynamics of reactions are represented by the rate of reaction at the surface of porous catalysts

Reaction kinetics: The rate of reaction in catalyst involves three parts of mechanisms; adsorption of reactants into the catalyst surface, reaction of reactants compounds to form products compounds and desorption of products compounds from the surface. The rate of chemical reaction is different from the other models that do not consider what happens inside the layers of catalysts particles. Based on that, it is important to know the effects of porous catalyst that is used in fluidized-bed heterogeneous catalyst in this process in order to specify the mathematical model formulation. Most solid catalysts are supplied as cylinders or spherical particles with length and diameter in the range of 10-60 μm . The catalysts particles are actually porous, with microspores ranging in diameter from a few angstroms to few microns. The internal surface area, accessible through the pores is enormous, ranging from ten to hundreds of square

meters per gram. It is this internal area that accounts for most of the catalytic activity. Regardless of the specific geometry used to contact the gas and the solid, all these schemes require a complex set of mass transfer and reaction steps. These steps included in the reaction involve diffusion of gases from the bulk of ethane, carbon monoxide and hydrogen to the surface of porous catalyst, diffusion of products compounds from the catalysts interior to the external surface and mass transfer of products compounds away from the surface to the bulk fluid. All these steps can influence the overall reaction and mathematical model design for the fluidized bed process as shown in Fig. 2.

Kinetic reaction: The kinetic reaction includes three mechanisms namely; rate of adsorption, surface reaction and desorption:



Let us substitute with letters for simplicity:

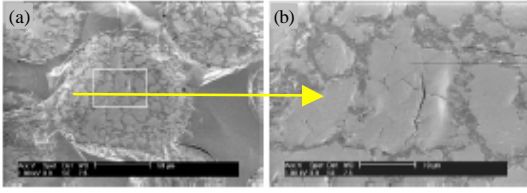
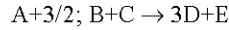
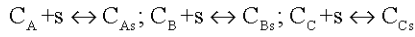


Fig. 2: Mass transfer diffusion on the surface and inside layers of catalyst with a chemical reaction happens at the surface of the catalyst layers of the particles Wolf *et al.* (2005)



For rate of adsorption:

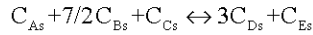


$$r_{ad1} = k_{1ad} + \left[P_A C_v - \frac{C_{As}}{k_{ad1}^*} \right] \quad (1)$$

$$r_{ad2} = k_{2ad} + \left[P_B C_v - \frac{C_{Bs}}{k_{ad2}^*} \right] \quad (2)$$

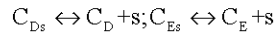
$$r_{ad3} = k_{3ad} + \left[P_C C_v - \frac{C_{Cs}}{k_{ad3}^*} \right] \quad (3)$$

For rate of surface reaction:



$$r_s = k_s + \left[C_{As} C_{Bs}^{3/2} C_{Cs} - \frac{C_{ds}^3 C_{Es}}{k_s^*} \right] \quad (4)$$

For rate of desorption:



$$r_{d1} = k_D + \left[C_{Ds} - \frac{P_D C_v}{k_D^*} \right] \quad (5)$$

$$r_{d2} = k_E + \left[C_{Es} - \frac{P_E C_v}{k_E^*} \right] \quad (6)$$

By assuming that the rate of surface of reaction controls all reactions, i.e., $r_{ad1} = r_{ad2} = r_{ad3} = r_{d1} = r_{d2} = 0$. Applying this assumptions, Eq. 1-6 will be:

$$C_{As} = P_A C_v k_{ad1}^* \quad (7)$$

$$C_{Bs} = P_B C_v k_{ad2}^* \quad (8)$$

$$C_{Cs} = P_C C_v k_{ad3}^* \quad (9)$$

$$C_{Ds} = \frac{P_D C_v}{k_D^*} \quad (10)$$

$$C_{Es} = \frac{P_E C_v}{k_E^*} \quad (11)$$

Substituting Eq. 9-11 in Eq. 4, we have:

$$r_s = k_s^* \left[P_A C_v k_{ad1}^* (P_B C_v k_{ad2}^*)^{3.5} (P_C C_v k_{ad3}^*)^3 - \left(\frac{P_D C_v}{k_D^*} \right)^3 \left(\frac{P_E C_v}{k_E^*} \right)^7 \right] \quad (12)$$

$$C_T = C_{As} + C_{Bs} + C_{Cs} + C_{Ds} + C_{Es} + C_v \quad (13)$$

$$C_T = C_v \left[P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*} \right] \quad (14)$$

$$C_v = \frac{C_T}{P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*}}$$

Substituting Eq. 12 in 4, we have:

$$r_s = k_s^* \left[\frac{P_A C_T k_{ad1}^*}{P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*}} \left[\frac{P_B C_T k_{ad2}^*}{P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*}} \right]^{3.5} \frac{P_C k_{ad3}^*}{P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*}} \left[\frac{P_D}{(P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*}) k_D^*} \right]^3 \right] \quad (15)$$

$$\left[\frac{P_E}{(P_A k_{ad1}^* + P_B k_{ad2}^* + P_C k_{ad3}^* + \frac{P_D}{k_D^*} + \frac{P_E}{k_E^*}) k_s^*} \right]$$

Equation 15 represents the overall chemical reactions and it will be adopted in the mathematical model.

Fluidized-bed reactor modeling: The estimation of the reactor model parameters are given in following equation From Fig. 1, it can be seen that the main reaction process in the fluidized bed reactor occurs in catalyst solid phase. Estimation of the reactor model parameters for mathematical model system is given as:

$$\begin{aligned} \epsilon_{mf} &= 0.586 \Psi^{-0.72} \left(\frac{\mu^2}{\rho_g \eta d_p^3} \right)^{0.029} \left(\frac{\rho_g}{\rho_c} \right)^{0.021} \\ \Psi &= 1.6 \text{ for } D_{bed} > 1m \\ \eta &= g(\rho_c - \rho_g) \\ u_{mf} &= \frac{(\Psi d_p)^2}{150\mu} \eta \frac{\epsilon_{mf}^3}{1 - \epsilon_{mf}} \\ d_{bm} &= 0.652 [A_c (u_0 - u_{mf})]^{0.4} \frac{d_{bm} - d_b}{d_{bm} - d_{b0}} = e^{-0.3h/D_t} \\ u_b &= u_0 - u_{mf} + (0.71)(gd_p)^{1/2} \\ K_{bc} &= 4.5 \left(\frac{u_{mf}}{d_p} \right) + 5.85 \left(\frac{D^{1/2} g^{1/4}}{d_p^{5/4}} \right) \\ K_{ce} &= 6.77 \left(\frac{D_g \epsilon_{mf} u_b}{d_p^3} \right)^{1/2} \\ W_s &= p_c Ah(1 - \epsilon_{mf}) \end{aligned}$$

Mass transfer with chemical reaction from gas phase to the catalyst phase and production acrylonitrile: Mass transfer from bulk gas phase to the catalyst phase with chemical reaction happens in this step as seen in Fig. 3 and this assumption is not the same as compared to the other mathematical model:

Mass balance on catalyst solid phase: In the material balance on the clouds and wakes in section Δz , it is more appropriate to base all terms on the bubble volume. The material balance for the clouds and wakes is given as:

$$\begin{aligned} \text{Accumulation} &= \text{By flow-out by flow+} \\ &\quad \text{By mass transport-} \\ &\quad \text{out by mass transport+generation} \end{aligned}$$

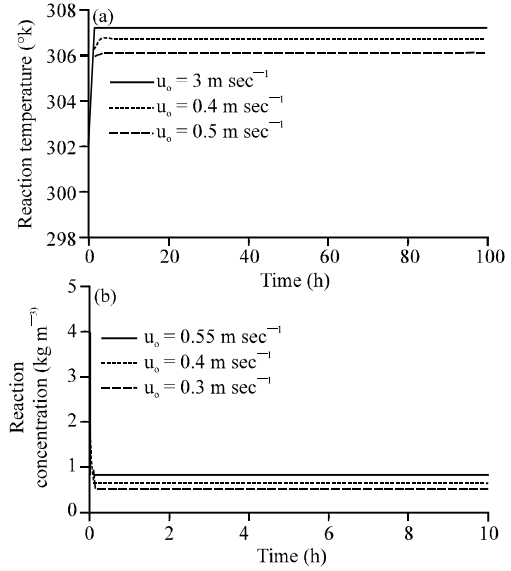


Fig. 3: Effects of superficial velocity in the gas and solid phases with variable time for: a) reaction temperature and b) reaction concentration

$$\begin{aligned} A_1 H \epsilon_{mf} \frac{dC_{Ae}}{dt} &= [C_{Ac} - C_{Ao}] \\ A_1 H \epsilon_{mf} + \frac{-D_{EC} A_1 dC_{Ae}}{dr} + r_{as} W_s & \end{aligned} \quad (16)$$

To simplify the solution consider the following equality:

$$\begin{aligned} A_1 H \epsilon_{mf} \frac{dC_{Ae}}{dt} &= [C_{Ac} - C_{Ao}] \\ A_1 H \epsilon_{mf} + \frac{-D_{E,C} A_1 dC_{Ae}}{dr} + r_{as} W_s & \end{aligned} \quad (17)$$

Where:

D_{EC} = The diffusivity of gases molecules towards catalysts particles ($m^2 \text{ sec}^{-1}$)

$G1$ = The gas rate of the gases ($kg \text{ m}^{-2} \text{ sec}^{-1}$)

So Eq. 16 will be:

$$\begin{aligned} A_1 H \epsilon_{mf} \frac{dC_{Ae}}{dt} &= [C_{Ao} - C_{Ae}] A_1 H \epsilon_{mf} + \\ &\quad G1(C_{Ao} - C_{Ae}) - \\ &\quad Q_o C_{Ae} \epsilon_{mf} + r_a W_s \end{aligned} \quad (18)$$

Energy balance: Energy balance occurs from bulk flow gas phase to the solid phase. So, we will find the variation of reaction temperature with the time is not the same assumptions as of Choi and Ray (1985), McAuley *et al.* (1990) and Hatzantonis and Kiparissides (1998) and is given by:

$$A_1 \left\{ (1 - \epsilon_{mf}) \rho_s C_{ps} + \epsilon_{mf} C_e C_{pg} \right\} \frac{dT_r}{dt} + A_1 H (T_r - T_{ref})$$

$$\epsilon_{mf} C_{pg} \frac{dc_e}{dt} = -G C_e C_{pg} (T_e - T_f) + A_B H_{be} \int (T_b - T_e) dz +$$

$$(-\Delta H_r) R_{as} - Q_o \epsilon_{mf} C_e C_{pg} (T_r - T_{fs}) - \pi D H (1 - \delta^*) h_w (T_r - T_w) \quad (19)$$

RESULTS AND DISCUSSION

Model solution and analysis: The previously described process model shown in equations (1-19) incorporating the parameter values of were solved in MATLAB by Ibrahim (2010) using the Differential Algebraic Equation solver (DAE) with the modified fourth order Runge kutta method variable step size. Physical constants and operating parameters for the mathematical model system are as illustrated in Algorithm 1.

Physical constants and operating parameters for the mathematical model system:

- $C_{pg} = 0.414 \times 10^3 \text{ j kg}^{-1} \text{ k}$
- $C_{ps} = 1.91 \times 10^3 \text{ j kg}^{-1} \text{ k}$
- $D = 2.5$
- $D_g = 0.06 \text{ m}^2 \text{ sec}^{-1}$
- $E_a = 3.76 \times 10^4 \text{ j mol}^{-1}$
- $H = 6 \text{ m}$
- $-\Delta H_r = 3.829 \times 10^6 \text{ j kg}^{-1}$
- $u_o = 0.97 \times 10^3 \text{ kg m}^{-3}$
- $p_g = 1.0136 \text{ kg m}^{-3}$
- $\mu = 1.16 \times 10^{-5} \text{ kg m}^{-1} \text{ sec}^{-1}$
- $q_c = 1.39 \times 10^{-4} \text{ g sec}^{-1}$
- $T_{ref} = 300 \text{ k}$
- $T_f/T_{ref} = 1$
- $T_w/T_{ref} = 1$
- $C_{propene} = 28.57 \%$
- $C_{oxygen} = 42.86 \%$
- $C_{amonia} = 28.57 \%$

The process was simulated for the effects of superficial velocity on temperature reaction in the model with variable time and effects of superficial velocity and catalyst flow rate in the gas and solid phases with variable time on reaction temperature and concentration of reactants. In the following studies the simulation results are described for the different phases of the system.

The effect of superficial gas velocity and catalyst flow rate on the temperature and concentration in the gas phase with respect to time are shown in Fig. 3 and 4, respectively. By examining these two figures, it can be seen that the temperature of reaction and gases concentration in the gas phase depend on the values of superficial gas velocity and catalyst flow rate. The reaction temperature has an inverse relationship with the increase in superficial gas velocity. The change in reactants concentration has an inverse relationship with the increase in superficial gas velocity because the mass and heat transfer have inverse relationships with the increase of the superficial velocity. The reactants concentration is therefore reduced. This reduction leads

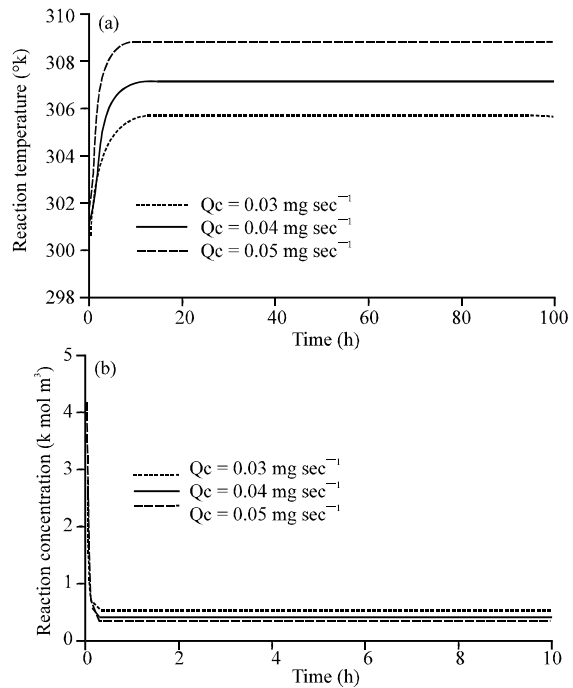


Fig. 4: Effect of variation in catalyst flow rate in the gas and solid phases for: a) reaction temperature and b) reaction concentration

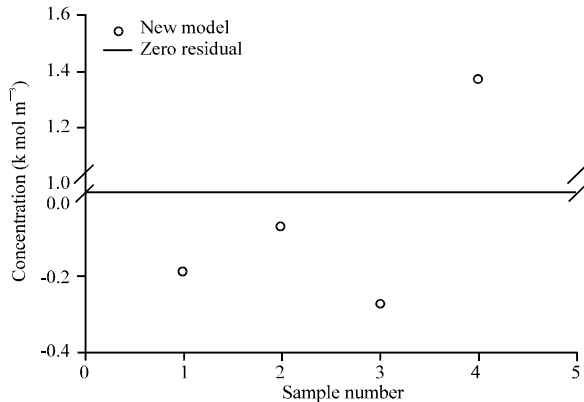


Fig. 5: Actual plant versus new model predicted concentration values

to a decrease in the rate of reaction and temperature. On the other hand, the reaction temperature is proportionally increases with the catalyst flow rate because there is an increase of the rate of reaction that leads to the increase in reaction temperature.

Model validation study: The accuracy of the steady state behavior of our proposed mathematical model can be seen by making a comparison with the published actual plant data presented in (Hu *et al.*, 2007). Figure 5 and 6 illustrate

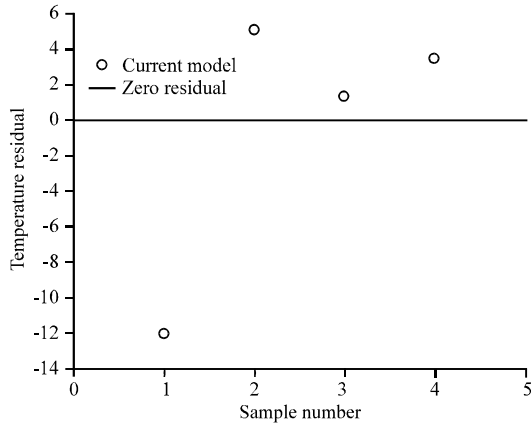


Fig. 6: Actual versus model predicted reaction temperature

the concentration and reaction temperature of AN, respectively. The condition related to four different samples of (Hu *et al.*, 2007) are compared in the two figures. In Fig. 5 and 6, for instance, the first sample differs only about 0.2 (kmol m⁻³) of concentration with respect to the actual plant. Values for other samples can be compared the same way. Data illustrated in both figures are showing a good agreement between the results obtained from our model and the actual plant results.

CONCLUSION

A modified dynamic two-phase structure model was developed in this research. This model takes into account the presence of particles participating in the reaction with gas and catalyst phases which depend on superficial velocity and catalyst feed. In addition, heat and mass transfer between the two phases. The solid phase was considered in the mass and heat transfer calculations. From its observed accuracy, we can conveniently use this model as a predictive tool to study the effects of operating, kinetic and hydrodynamics parameters on the reactor performance as well as acrylonitrile properties. The model developed here will also be used in model-based prediction control to control the reactor which is part of our future research.

NOMENCLATURE

- A_1 = Cross-sectional area of the bed (cm²)
- A_b = Cross sectional area of bubble phase (m²)
- C_d^k = Concentration of deactivated catalyst active sites, (mol cm⁻³)
- C_{pg} = Specific heat capacity of gaseous stream (cal/g/k)
- C_{PM} = Specific heat of "I" monomer (cal/mol/k)
- C_{PS} = Specific heat capacity of catalyst (cal/g/k)
- C_{AS} = Adsorbed surface concentration of A in kmol Kg⁻¹ catalyst
- $C_{B,S}$ = Product desorption of B in kmol kg⁻¹ catalyst
- C_b = Product concentration kmol kg⁻¹ catalyst

- C_v = Vacant molar concentration sites kmol kg⁻¹ catalyst
- C_{cat} = Mass fraction of catalyst in the solid phase
- C_{AB} = Concentration of monomer gas in bubble phase (kg m⁻³)
- C_{AC} = Concentration of monomer gas in cloud phase (kg m⁻³)
- C_{se} = Concentration of emulsion phase (kg m⁻³)
- d_{bm} = Maximum stable bubble size (cm)
- d_p = Particle diameter (cm)
- d_b = Bubble diameter (cm)
- D_g = Gas self-diffusion coefficient (cm² s⁻¹)
- D_n^k = Concentration of "dead" copolymer chains (mol cm⁻³)
- D_{bed} = Bed diameter (m)
- h = Random bed height (m)
- H = Total bed height (cm)
- H_{mf} = Bed height at minimum fluidization conditions (m)
- E_a = Activative energy (J mol⁻¹)
- $[H_2]$ = Hydrogen concentration mol m⁻³
- K_g = Gas thermal conductivity (J/m/s/k)
- K^h = Rate constant of chain transfer to hydrogen 1 (sec⁻¹)
- P_A = Partial pressure of monomer in gas phase
- u_{mf} = Minimum fluidization velocity (m sec⁻¹)
- u_o = Superficial gas velocity (m s⁻¹)
- u_b = Bubble gas velocity (m s⁻¹)
- Q_0 = Volumetric product removal rate (m³ sec⁻¹)
- V = Volume (m³)
- T = Temperature (k)
- T_b = Temperature in the bubble phase (k)
- T_{ref} = Reference temperature (k)
- T_e = Reaction temperature (k)
- T_w = Wall temperature (k)
- T_{fs} = Temperature of inlet catalyst (k)
- T_f = Temperature of the feed gas (k)
- r = Radius (m)
- Z = Bed height (m)
- W_s = Weight of catalyst (kg)
- ρ_g = Gas density (kg⁻³m)
- Ψ = Shaping factor
- q_c = Mass velocity of catalyst (gm sec⁻¹)
- δ^* = Fraction of fluidized-bed consisting of bubbles
- μ_g = Viscosity of gas (g/cm/s)
- π = Constant ratio
- ε = Void fraction of the bed at minimum fluidized velocity
- δ_b = Bubble phase volume fraction
- ρ_s = Solid density (kg m⁻³)
- ΔH_{rn} = Heat of reaction (kj kg⁻¹)
- I_k = Objective function
- ξ = Suitable large number
- η = Driving force

Letters

- B = Bubble phase
- cat = Catalyst property
- e = Emulsion phase
- k = Type of catalyst active site
- mf = Minimum fluidization conditions
- n = Compartment number
- ref = Reference value

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