Mathematical Models of Absorption of Poorly Soluble Gas in Co-Current Packed Bed Column under Periodically Changing Conditions

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Original scientific paper
Received: May 3, 2003
Accepted: January 17, 2004

An eight-parameter mathematical model of absorption of poorly soluble gas in co-current column with interfacial mass transfer under transient conditions has been formulated. The model describes the liquid stream by axially dispersed plug flow with stagnant and dynamic zones and the gas stream by axially dispersed model. The result of the model solution has the form of four transfer functions. Additional four models as asymptotic simplification of the basic formulated model considering axial dispersion in both phases, the model with a stagnant zone in the liquid and axial dispersion in the gas phase, the model with stagnant zone in liquid and plug flow in gas and the model with plug flow in both phases, have been formulated and solved. A parametric study of the transfer functions utilizing complex arithmetic feature of the computer has shown that for the selected oxygen-air-water system only two of the derived transfer functions for each model are practically useable.

Keywords:
Trickle bed, co-current down flow, oxygen absorption, transient conditions

Introduction

The real flow of liquid and gas through the layer of particles is a complex phenomenon. From the standpoint of the processes not requiring more than one transfer unit the co-current flow of both fluid phases may be advantageous. The co-current flow arrangement is also effective if there is a strongly exothermic reaction taking place in the system. Principal advantages of the co-current down flow is the possibility of higher gas/liquid loads, absence of the limits of the operation, such as flooding, and usually lower liquid holdup compared to the counter-current flow. Co-current down flow reactors exhibit mostly greater stability of the reaction regime compared to counter-current reactors.

For the design of co-current contactors and/or reactors one usually needs the information about pressure drop[1–6], which is closely related to the rate of energy dissipation in the column. Also needed is the knowledge of mass and heat transfer coefficients,[7–10] that is a function of hydrodynamic conditions and column and packing geometry. Mass transfer efficiency may be strongly affected by axial dispersion[9–12].

Liquid holdup becomes important[3,5,13,14] in situations involving interfacial mass transfer and relatively slow homogeneous reaction in one of the phases. Since liquid holdup affects primarily the residence time of liquid in the column it affects significantly also the selectivity of the reaction if there are several reactions taking place in the system.

The course of the processes in the co-current columns is affected also by the regime of the flow[15,16] which may be continuous, pulsed, trickling or bubble flow regime.

Many authors[13,17–25] dealing with the problem investigated individual parameters characterizing the function under the single-phase flow and in trickle beds[3–5,9,26]. A number of models have been derived describing the flow in co-current columns concentrating on individual specific features. Some of the model abstracts fairly for the physical nature such as the stage wise models. A review of these works may be found in papers.[2,27,28]

Theory

Two-phase flow models

The two-phase co-current gas/liquid flow in packed bed column with interfacial mass transfer poses the problem of inherently large number of parameters of the resulting model. Based on our experience we have chosen five mathematical models with reasonable probability to describe faithfully the physical situation. The choice was made while keeping in mind the real capabilities of evaluating all the parameters involved.

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The model was ultimately formulated for the case of absorption of a poorly soluble gas, namely the oxygen-air –water system. As basic model we have selected an eight parameter model with axial dispersion in, both, the liquid and gas phase and with a stagnant zone in the liquid phase (PDE-AD model). This model is from the mathematical form already fairly complex, yet manageable from the standpoint of working with the resulting formulas. Greater problem poses the number of parameters involved that is probably at the limits of accuracy of the results obtained experimentally. The limiting aspect of the experiments is thus availability of sufficiently fast and accurate sensors.

Bearing this in mind we have solved also simpler models with fewer parameters that appear to be asymptotic cases of the basic model. These simpler models are: The three-parameter plug flow in both phases (PF-PF model), dynamic and stagnant phase in liquid and plug flow in the gas phase six-parameter model (PE-PF model), five-parameter axial dispersion in both phases (AD-AD model), and the model with dynamic and stagnant liquid phase and axial dispersion in the gas phase seven-parameter model (PE-AD model).

Axially dispersed model with stagnant zone liquid and axial dispersion in the gas phase

The model has a total of eight parameters: the gas, dynamic liquid and stagnant liquid holdup: h_G, h_D, h_S, the mass transfer coefficients between gas and dynamic liquid, $k_{LD}a_D$, between gas and static liquid, $k_{LS}a_S$, and between dynamic and static liquid phase zones, $k_q a$, the axial dispersion coefficients in the gas and dynamic liquid phase, E_G and E_D. The mass transfer takes place generally between all phases of the system. However, since we are dealing with a poorly soluble gas its volume mass transfer coefficient is $k_L a$.

The differential mass balances of the absorbed species in the gas, dynamic liquid, and stagnant liquid phase take the following form where we can safely assume (poor solubility) constant mass velocities of both phases in the column:

$$h_G E_G \frac{\partial^2 c_G}{\partial z^2} - v_G \frac{\partial c_G}{\partial z} - k_{LD} a_D \left(\frac{c_G}{k_m} - c_D \right) - \\ - k_{LS} a_S \left(\frac{c_G}{k_m} - c_S \right) = h_G \frac{\partial c_G}{\partial t}, \tag{1}$$

$$h_D E_D \frac{\partial^2 c_D}{\partial z^2} - v_L \frac{\partial c_D}{\partial z} + k_{LD} a_D \left(\frac{c_G}{k_m} - c_D \right) + \\ + k_q a \left(c_S - c_D \right) = h_D \frac{\partial c_D}{\partial t}, \tag{2}$$

$$k_{LS} a_S \left(\frac{c_G}{k_m} - c_S \right) - k_q a \left(c_S - c_D \right) = h_S \frac{\partial c_S}{\partial t} \tag{3}$$

The three holdups appearing in the above expressions are constrained by the available volume. Thus:

$$h_G + h_D + h_S = \varepsilon \tag{4}$$

From the purpose of applying subsequently the Laplace transform it is convenient to define concentrations as deviations from corresponding steady state values:

$$C_i = c_i - c_{si} \qquad i = G, D, S \tag{5}$$

Solution in the frequency domain may be obtained by the following procedure: The differential Equations (1) – (3) are transformed to the Laplace domain which eliminates time as variable. The set thus becomes one of ordinary differential equations. By solving the transformed set one obtains the so called transfer functions defined as the ratios of the Laplace solutions at the point of outlet to that of at the inlet.

Depending on which of the inlet streams is being perturbed and the response of which of the outlet stream we are studying, one can formulate a total of four transfer functions. For the two-phase co-current stream one can get the transfer function defined as the ratio of outlet gas to intlet gas stream, X_{GZ}/X_{G0}, outlet liquid to inlet liquid stream, X_{LZ}/X_{L0}, outlet gas to inlet liquid stream, X_{GZ}/X_{L0}, and outlet liquid to inlet gas stream, X_{LZ}/X_{G0}.

From the transfer functions one can in turn obtain easily the frequency characteristics by replacing the Laplace variable by the product, $i\omega$, where i is the imaginary unit and ω is the angular frequency of the periodic inlet perturbation.

The result of the Laplace transform of the set of differential Equations (1) – (3) with the initial condition:

$$t = 0, \qquad c_S = c_D = c_G = 0 \tag{6}$$

are two ordinary differential and one algebraic equation in the form:

$$h_G E_D \frac{\partial^2 X_G}{\partial z^2} - v_G \frac{\partial X_G}{\partial z} - k_{LD} a_D \left(\frac{X_G}{k_m} - X_D \right) - \\ - k_{LS} a_S \left(\frac{X_G}{k_m} - X_S \right) = h_G s X_G, \tag{7}$$

$$h_D E_D \frac{\partial^2 x_D}{\partial z^2} - v_L \frac{\partial X_D}{\partial z} + k_{LD} a_D \left(\frac{X_G}{k_m} - X_D \right) + \\ + k_q a \left(X_S - X_D \right) = h_D s X_D, \tag{8}$$

$$k_{LS}a_S\left(\frac{X_G}{k_m}-X_S\right)-k_q a\left(X_S-X_D\right)=h_S s X_S \quad (9)$$

This set may be manipulated to yield a single fourth-order differential equation with constant coefficients for X_G in the form:

$$A_1\frac{d^4X_G}{dz^4}+A_2\frac{d^3X_G}{dz^3}+A_3\frac{d^2X_G}{dz^2}+ +A_4\frac{dX_G}{dz}+A_5X_5=0, \quad (10)$$

where

$$A_1=-A_1'A_5'/A_4', \quad (11)$$

$$A_2=-(A_2'A_5'+A_1'A_6')/A_4', \quad (12)$$

$$A_3=-(A_3'A_5'+A_2'A_6'+A_1'A_7')/A_4', \quad (13)$$

$$A_4=-(A_3'A_6'+A_2'A_7')/A_4', \quad (14)$$

$$A_5=(A_4'A_8'-A_3'A_7')/A_4', \quad (15)$$

and where

$$A_1'=h_GE_G \quad (16)$$

$$A_2'=v_G \quad (17)$$

$$A_3'=(k_{LS}a_S)^2/(h_Ss+k_{LS}a_S+k_qa)K_m- -(k_{LD}a_D+k_{LS}a_S)/K_m-h_Gs, \quad (18)$$

$$A_4'=qk_{LS}a_S/(h_Ss+k_{LS}a_S+k_qa)+k_{LD}a_D, \quad (19)$$

$$A_5'=h_DE_D, \quad (20)$$

$$A_6'=v_L \quad (21)$$

$$A_7'=(k_qa)^2/(h_Ss+k_{LS}a_S+k_qa)- -k_qa-h_Ds-k_{LD}a_D, \quad (22)$$

$$A_8'=A_4'/K_m \quad (23)$$

Corresponding characteristic equation:

$$A_1\lambda^4+A_2\lambda^3+A_3\lambda^2+A_4\lambda+A_5=0 \quad (24)$$

is a fourth-order algebraic equation with complex coefficients whose solution may be written in the following form.

$$X_G=k_1\exp(\lambda_1z)+k_2\exp(\lambda_2z)+ +k_3\exp(\lambda_3z)+k_4\exp(\lambda_4z) \quad (25)$$

$$X_{DG}=a_1k_1\exp(\lambda_1z)+a_2k_2\exp(\lambda_2z)+ +a_3k_3\exp(\lambda_3z)+a_4k_4\exp(\lambda_4z) \quad (26)$$

where

$$a_i=B_1\lambda_1+B_2\lambda_2+B_3\lambda_3, \qquad i=1,2,3 \quad (27)$$

$$B_i=-A_i'/A_4', \qquad i=1,2,3 \quad (28)$$

The constants k_1 – k_4 in Equations (25) and (26) may be determined from the Danckwert's boundary conditions expressed for the two phases at the top and bottom of the column as:

$$X_G=X_{G0}+\frac{h_GE_G}{v_G}\frac{dX_G}{dz} \qquad \text{for } z=0 \quad (29)$$

$$X_D=X_{D0}+\frac{h_DE_D}{v_L}\frac{dX_D}{dz} \qquad \text{for } z=0 \quad (30)$$

$$dX_G/dz=0, \qquad \text{for } z=Z \quad (31)$$

$$dX_D/dz=0, \qquad \text{for } z=Z \quad (32)$$

which yield for the four constants the following expressions:

$$k_1=(X_{L0}H_7+X_{G0}H_8)/(H_1H_4-H_2H_3), \quad (33)$$

$$k_2=[a_1\lambda_1\exp(\lambda_1Z)H_5X_{G0}+ +\lambda_1\exp(\lambda_1Z)H_6X_{L0}]/(H_1H_4-H_2H_3), \quad (34)$$

$$k_3=[a_1\lambda_1\exp(\lambda_1Z)H_4X_{G0}- -\lambda_1\exp(\lambda_1Z)H_2X_{L0}]/(H_1H_4-H_2H_3), \quad (35)$$

$$k_4=[-a_3\lambda_1\exp(\lambda_1Z)H_3X_{G0}+ +\lambda_1\exp(\lambda_1Z)H_1X_{L0}]/(H_1H_4-H_2H_3), \quad (36)$$

where

$$H_1=\{a_3\lambda_3\exp(\lambda_3Z)[\lambda_1b_2\exp(\lambda_1Z)- -\lambda_2b_1\exp(\lambda_2Z)]+a_1\lambda_1\exp(\lambda_1Z)[\lambda_2b_3\exp(\lambda_2Z)- -\lambda_3b_2\exp(\lambda_3Z)]+a_2\lambda_2\exp(\lambda_2Z)[\lambda_3b_1\exp(\lambda_3Z)- -\lambda_1b_3\exp(\lambda_1Z)]\}\frac{a_1}{J} \quad (37)$$

$$H_2=\{a_1\lambda_1\exp(\lambda_1Z)[\lambda_2b_4\exp(\lambda_2Z)- -\lambda_4b_2\exp(\lambda_4Z)]+a_2\lambda_2\exp(\lambda_2Z)[\lambda_4b_1\exp(\lambda_4Z)- -\lambda_1b_4\exp(\lambda_1Z)]+a_4\lambda_4\exp(\lambda_4Z)[\lambda_1b_2\exp(\lambda_1Z)- -\lambda_2b_1\exp(\lambda_2Z)]\}\frac{a_1}{J} \quad (38)$$

$$H_3=\{a_1\lambda_1\exp(\lambda_1Z)[a_3d_3\lambda_2\exp(\lambda_2Z)- -a_2d_2\lambda_3\exp(\lambda_3Z)]+a_2\lambda_2\exp(\lambda_2Z)[a_1d_1\lambda_3\exp(\lambda_3Z)- -a_3d_3\lambda_1\exp(\lambda_1Z)]+a_3\lambda_3\exp(\lambda_3Z)[a_2d_2\lambda_1\exp(\lambda_1Z)- -a_1d_1\lambda_2\exp(\lambda_2Z)]\}\frac{1}{J} \quad (39)$$

$$H_4=\{a_1\lambda_1\exp(\lambda_1Z)[a_4d_4\lambda_2\exp(\lambda_2Z)- -a_2d_2\lambda_4\exp(\lambda_4Z)]+a_2\lambda_2\exp(\lambda_2Z)[a_1d_1\lambda_4\exp(\lambda_4Z)-$$

$$-a_4 d_4 \lambda_1 \exp(\lambda_1 Z)] + a_4 \lambda_4 \exp(\lambda_4 Z)[a_2 d_2 \lambda_1 \exp(\lambda_1 Z) -$$

$$-a_1 d_1 \lambda_2 \exp(\lambda_2 Z)]\}\frac{1}{J} \quad (40)$$

$$H_5 = \{a_4 d_4 \lambda_1 \exp(\lambda_1 Z)[a_3 \lambda_3 \exp(\lambda_3 Z) -$$
$$-a_1 \lambda_3 \exp(\lambda_3 Z)] + a_1 d_1 \lambda_3 \exp(\lambda_3 Z)[a_4 \lambda_4 \exp(\lambda_4 Z) -$$
$$-a_3 \lambda_4 \exp(\lambda_4 Z)] + a_3 d_3 \lambda_1 \exp(\lambda_1 Z)[a_1 \lambda_4 \exp(\lambda_4 Z) -$$
$$-a_4 \lambda_4 \exp(\lambda_4 Z)]\}\frac{1}{J} \quad (41)$$

$$H_6 = \{a_3 \lambda_3 \exp(\lambda_3 Z)[\lambda_4 b_1 \exp(\lambda_4 Z) -$$
$$-\lambda_1 b_4 \exp(\lambda_1 Z)] + a_1 \lambda_1 \exp(\lambda_1 Z)[\lambda_3 b_4 \exp(\lambda_3 Z) -$$
$$-\lambda_4 b_3 \exp(\lambda_4 Z)] + a_4 \lambda_4 \exp(\lambda_4 Z)[\lambda_1 b_3 \exp(\lambda_1 Z) -$$
$$-\lambda_3 b_1 \exp(\lambda_3 Z)]\}\frac{a_1}{J} \quad (42)$$

$$H_7 = \{a_3 \lambda_3 \exp(\lambda_3 Z)[\lambda_2 b_4 \exp(\lambda_2 Z) -$$
$$-\lambda_4 b_2 \exp(\lambda_4 Z)] - a_4 \lambda_4 \exp(\lambda_4 Z)[\lambda_2 b_3 \exp(\lambda_2 Z) -$$
$$-\lambda_3 b_2 \exp(\lambda_3 Z)] - a_2 \lambda_2 \exp(\lambda_2 Z)[\lambda_3 b_4 \exp(\lambda_3 Z) -$$
$$-\lambda_4 b_3 \exp(\lambda_4 Z)]\}\frac{a_1 \lambda_1 \exp(\lambda_1 Z)}{J} \quad (43)$$

$$H_8 = \{a_2 d_2 \lambda_3 \exp(\lambda_3 Z)[a_4 \lambda_4 \exp(\lambda_4 Z) -$$
$$-a_3 \lambda_4 \exp(\lambda_4 Z)] + a_3 d_3 \lambda_2 \exp(\lambda_2 Z)[a_4 \lambda_4 \exp(\lambda_4 Z) -$$
$$-a_2 \lambda_4 \exp(\lambda_4 Z)] + a_4 d_4 \lambda_2 \exp(\lambda_2 Z)[a_2 \lambda_3 \exp(\lambda_3 Z) -$$
$$-a_3 \lambda_3 \exp(\lambda_3 Z)]\}\frac{a_1 \lambda_1 \exp(\lambda_1 Z)}{J} \quad (44)$$

In Equations (37) – (44) we have:

$$J = a_1 \lambda_2 \exp(\lambda_2 Z) - a_2 \lambda_2 \exp(\lambda_2 Z), \quad (45)$$

$$b_i = 1 - (h_G E_G / v_G)\lambda_i, \quad i = 1, 2, 3, 4 \quad (46)$$

$$d_i = 1 - (h_D E_D / v_L)\lambda_i, \quad i = 1, 2, 3, 4 \quad (47)$$

Substituting for $k_1 - k_4$ in Equations (25) and (26) and putting $z = Z$ one can finally obtain the following four transfer functions for the outlet concentrations in both flowing phases:

On putting $X_{L0} = 0$ we get:

$$\frac{X_{GZ}}{X_{G0}} = \frac{\exp(\lambda_1 Z)[H_8 + a_1 \lambda_1 H_5 \exp(\lambda_2 Z) +}{H_1 H_4 - H_2 H_3}$$
$$\frac{+a_1 \lambda_1 H_4 \exp(\lambda_3 Z) - a_1 \lambda_1 H_3 \exp(\lambda_4 Z)]}{H_1 H_4 - H_2 H_3} \quad (48)$$

$$\frac{X_{LZ}}{X_{G0}} = \frac{a_1 \exp(\lambda_1 Z)[H_8 + a_2 \lambda_1 H_5 \exp(\lambda_2 Z) +}{H_1 H_4 - H_2 H_3}$$
$$\frac{+a_3 \lambda_1 H_4 \exp(\lambda_3 Z) - a_4 \lambda_1 H_3 \exp(\lambda_4 Z)]}{H_1 H_4 - H_2 H_3} \quad (49)$$

and on putting $X_{G0} = 0$ we get

$$\frac{X_{LZ}}{X_{L0}} = \frac{\exp(\lambda_1 Z)[a_1 H_7 + a_2 \lambda_1 H_6 \exp(\lambda_2 Z) +}{H_1 H_4 - H_2 H_3}$$
$$\frac{-a_3 \lambda_1 H_2 \exp(\lambda_3 Z) + a_4 \lambda_1 H_1 \exp(\lambda_4 Z)]}{H_1 H_4 - H_2 H_3} \quad (50)$$

$$\frac{X_{GZ}}{X_{L0}} = \frac{\exp(\lambda_1 Z)[H_7 + \lambda_1 H_6 \exp(\lambda_2 Z) +}{H_1 H_4 - H_2 H_3}$$
$$\frac{-\lambda_1 H_2 \exp(\lambda_3 Z) + \lambda_1 H_1 \exp(\lambda_4 Z)]}{H_1 H_4 - H_2 H_3} \quad (51)$$

Axial dispersion model AD-AD

The limiting case of the PDE-AD model is the model with axial dispersion in both phases and no stagnant zone in liquid ($h_S = 0$). This reduces the number of parameters from eight to five: The gas and liquid holdups, h_G and h_L, axial dispersion coefficients in gas and liquid phase, E_G and E_L and the volume gas/liquid mass transfer coefficient $k_L a$. The balance equations then take the form:

$$h_G E_G \frac{\partial^2 c_G}{\partial z^2} - v_G \frac{\partial c_G}{\partial z} - k_L a \left(\frac{c_G}{K_m} - c_L \right) = h_G \frac{\partial c_G}{\partial t}, \quad (52)$$

$$h_L E_L \frac{\partial^2 c_L}{\partial z^2} - v_L \frac{\partial c_L}{\partial z} + k_L a \left(\frac{c_G}{K_m} - c_L \right) = h_L \frac{\partial c_L}{\partial t}, \quad (53)$$

The concentrations are again given as deviations from corresponding steady states. The method of solution of Equations (52) and (53) is the same as for the PDE-AD model and it is given in the APPENDIX 1. The Danckwert's boundary conditions determining the constants $k_1 - k_4$ take now the form:

$$X_G = X_{G0} + \frac{h_G E_G}{v_G} \frac{dX_G}{dz}, \quad \text{for } z = 0 \quad (54)$$

$$X_L = X_{L0} + \frac{h_L E_L}{v_L} \frac{dX_L}{dz}, \quad \text{for } z = 0 \quad (55)$$

$$\frac{dX_L}{dz} = 0, \quad \frac{dX_G}{dz} = 0. \quad \text{for } z = Z \quad (56)$$

The obtained transfer functions then have the same form as in Equations (48) – (51) but the constants $B_1 - B_3$ and $d_1 - d_4$ are defined differently as given in APPENDIX 1

Model with stagnant zone in the liquid phase and axial dispersion in the gas phase (PE-AD)

Another way of simplifying the basic PDE-AD model is to drop axial dispersion in the dynamic part of liquid phase, $E_D = 0$. This reduces the number of parameters to seven and the remaining parameters are identical with those of the basic model.

The balance equations then take the form:

$$E_{\rm G} h_{\rm G} \frac{\partial^2 c_{\rm G}}{\partial z^2} - v_{\rm G} \frac{\partial c_{\rm G}}{\partial z} - k_{\rm LD} a_{\rm D} \left(\frac{c_{\rm G}}{K_m} - c_{\rm D} \right) -$$

$$- k_{\rm LS} a_{\rm S} \left(\frac{c_{\rm G}}{K_m} - c_{\rm S} \right) = h_{\rm G} \frac{\partial c_{\rm G}}{\partial t}, \qquad (57)$$

$$- v_{\rm L} \frac{\partial c_{\rm D}}{\partial z} + k_{\rm LD} a_{\rm D} \left(\frac{c_{\rm G}}{K_m} - c_{\rm D} \right) +$$

$$+ k_{\rm q} a (c_{\rm S} - c_{\rm D}) = h_{\rm D} \frac{\partial c_{\rm D}}{\partial t}, \qquad (58)$$

$$k_{\rm LS} a_{\rm S} \left(\frac{c_{\rm G}}{K_m} - c_{\rm S} \right) - k_{\rm q} a (c_{\rm S} - c_{\rm D}) = h_{\rm S} \frac{\partial c_{\rm S}}{\partial t}. \qquad (59)$$

Just as with the previous models the concentrations are deviations from the steady state values. Solution of Equations (57) – (59) and the derivation of the transfer functions are given in the APPENDIX 2.

Plug flow model PF-PF

The simplest of the models describing the dynamics of the flow in co-current packed bed column with interfacial mass transfer is the plug flow model in both fluid phases PF-PF. From the basic PDE-AD model it can be arrived at by putting the stagnant liquid holdup and the dispersion coefficients in the gas and liquid phases all equal to zero. The obtained model contains only three parameters. Namely, gas and liquid holdups, $h_{\rm G}$, $h_{\rm L}$ and the volume gas/liquid mass transfer coefficient, $k_{\rm L}a$. The two holdups are again constrained by the condition in Equation (4).

The balance equations take the form:

$$- v_{\rm L} \frac{\partial c_{\rm L}}{\partial z} - k_{\rm L} a \left(\frac{c_{\rm G}}{K_m} - c_{\rm L} \right) = h_{\rm L} \frac{\partial c_{\rm L}}{\partial t}, \qquad (60)$$

$$- v_{\rm G} \frac{\partial c_{\rm G}}{\partial z} - k_{\rm L} a \left(\frac{c_{\rm G}}{K_m} - c_{\rm L} \right) = h_{\rm G} \frac{\partial c_{\rm G}}{\partial t}. \qquad (61)$$

Further processing is given in APPENDIX 3.

Model with stagnant zone in liquid and plug stream in gas phase PE-PF

The PE-PF model is a further simplification of the PE-AD model when we drop axial dispersion in the gas phase. The model carries six parameters: The holdups of gas, $h_{\rm G}$, dynamic and stagnant liquid, $h_{\rm D}$, $h_{\rm S}$ and the mass transfer coefficients between gas, and dynamic liquid, $k_{\rm LD}a_{\rm D}$, between gas and stagnant liquid, $k_{\rm LS}a_{\rm S}$ and between the dynamic and stagnant liquid, $k_{\rm q}a$. The holdups are again constrained by Equation (4).

The balance equations take the form:

$$- v_{\rm G} \frac{\partial c_{\rm G}}{\partial z} - k_{\rm LS} a_{\rm S} \left(\frac{c_{\rm G}}{K_m} - c_{\rm S} \right) -$$

$$- k_{\rm LD} a_{\rm D} \left(\frac{c_{\rm G}}{K_m} - c_{\rm D} \right) = h_{\rm G} \frac{\partial c_{\rm G}}{\partial t}, \qquad (62)$$

$$- v_{\rm L} \frac{\partial c_{\rm D}}{\partial z} + k_{\rm LD} a_{\rm D} \left(\frac{c_{\rm G}}{K_m} - c_{\rm D} \right) +$$

$$+ k_{\rm q} a \left(c_{\rm S} - c_{\rm D} \right) = h_{\rm D} \frac{\partial c_{\rm D}}{\partial t}, \qquad (63)$$

$$k_{\rm LS} a_{\rm S} \left(\frac{c_{\rm G}}{K_m} - c_{\rm S} \right) - k_{\rm q} a \left(c_{\rm S} - c_{\rm D} \right) = h_{\rm S} \frac{\partial c_{\rm S}}{\partial t}. \qquad (64)$$

Further course of solution of Equations (62) – (64) is given in APPENDIX 4.

Results and discussion

Response of the column to periodically changing conditions

Four transfer functions have been derived for all models discussed. The form of the solution in the frequency domain, after substituting the Laplace variable by $i\omega$, is called frequency characteristic. The frequency characteristic represents actually a solution of the original differential equations in quasi-steady state. This is the part of the solution for a periodically variable input after the transients from the initial state have faded out.

The dependence of the transfer functions on frequency is often presented in the form of Bode diagrams, which is a dependence of the amplitude ratio and the phase lag on frequency. Bode diagram thus illustrate the deformation of the input signal after passing through the system, in our case the co-current packed bed column.

For a given periodic input at the inlet of one of the phases one can, after separating the real and the imaginary part using the computer complex arithmetic feature, calculate the amplitude ratio, P and the phase lag, ϕ from:

$$P = \sqrt{R^2 + I^2} \qquad (65)$$

$$\phi = \operatorname{arctg}(I/R), \qquad -\frac{\pi}{2} \le \phi \le \frac{\pi}{2} \qquad (66)$$

where R is the real and I is the imaginary part of the transfer function.

Expressions for the transfer function in the frequency domain are transcendental functions. Therefore explicit separation of the real and the imaginary part is impossible. Separation can be achieved only numerically for specific values of parameters.

Nevertheless, for parameter evaluation one can use directly the frequency characteristics of the transfer functions, because the real and imaginary part of the transfer function have comparable magnitudes, and their weight in the optimization is approximately the same. In contrast, the amplitude ratio and phase lag may be different by as much as an order of magnitude with correspondingly variable sensitivity to parameters to these parts of the objective function.

Amplitude and phase lag in the parameter domain

Numeric testing of usability of transfer function for parameter estimation

In the preceding parts we have derived four possible transfer functions. Their utilization in experiments requires introduction of a periodic concentration disturbance at the inlet of either gas or liquid phase and its monitoring in both outlet streams. By periodic disturbance we mean periodically variable (with angular velocity ω) concentration of a species that may be transferred across the interface between the flowing phases.

First, however, we need to test the transfer functions for anticipated conditions of our experiment from the standpoint of suitability for parameter evaluation.

The test calculations were carried out for the model of physical absorption of oxygen in water. Henry constant puts oxygen among poorly soluble gases in water, i.e. the conditions for which the above models have been derived. Additional inputs characterized a 2 meter long packed column, its voidage being ε = 0.4. For 0.01 m diameter glass sphere packing this gives the specific area of 360 m^2 m^{-3}. Tested mass flow rates of gas and liquid, v_G and v_L fall approximately into the middle of the range of operating conditions. Liquid holdup for the purposes of testing was divided equally between the dynamic and the stagnant zone. The volume mass transfer coefficient was evaluated from the correlation of *Onda* et.al.[31].

$$Sh = 0.0097\ Re^{0.67} Sc^{0.5} Ga^{0.33} \tag{67}$$

Same values of the volume mass transfer coefficient were adopted for the dynamic and the stagnant liquid. The coefficient of mass transfer between the dynamic and the stagnant zone, $k_q a$, was taken from the work of *Moravec.*[32]

Table 1 – *Values of model quantities and phase superficial velocities used for testing.*

v_G, ms^{-1}	0.2	0.05	0.1	0.2	0.3	0.35	
v_L, ms^{-1}	0.004	0.001	0.004	0.005	0.01		
E_G, m^2s^{-1}	0.02	0.001	0.02	0.05	0.1	0.5	
E_D, m^2s^{-1}	0.02	0.01	0.02	0.1	0.5		
H_G, –	0.3	0.2	0.25	0.3			
H_D, –	0.05	0.025	0.05	0.1			
H_S, –	0.05	0.075	0.05	0.0			
$k_{LD}a_D$, s^{-1}	0.05	0.001	0.01	0.05	0.1		
$k_{LS}a_S$, s^{-1}	0.05	0.001	0.01	0.02	0.05	0.1	0.5
$k_q a$, s^{-1}	0.04	0.001	0.005	0.04			

The basic set of input data tested is given in the first column of Table 1. The equilibrium constant, K_m, was taken equal to 30. More values of model parameters used in the tests of parametric sensitivity is shown in additional columns of Table 1.

The effect of individual model parameters was investigated so that the amplitude ratio and phase lag were computed for a number of values of the selected parameter while the others were kept constant.

This method of investigation, actually a test of parameter sensitivity, is virtually impossible to realize experimentally but for the assessment of the effect on amplitude ratio and phase lag it is very convenient.

The results of these tests have shown that the liquid-inlet-to-liquid-outlet transfer function, X_{LZ}/X_{L0}, is practically unusable. This is the consequence of the oxygen concentration in the outlet liquid stream being too low due to almost total desorption and as such undetectable by current technical means. This transfer function could be of use possibly in extremely short columns. Such measurements, however, would be of little value due to the end-effects.

We have arrived at similar conclusion concerning the outlet-gas-to-inlet-liquid transfer function, X_{GZ}/X_{L0}. This function for poorly soluble gas is also unusable because the low solubility of oxygen causes that the inlet liquid stream does not carry enough oxygen into the column to bring about measurable changes of oxygen concentration in the outlet gas stream. The found amplitude ratios were smaller, or at zero frequency equal the v_L/v_G ratio which amounts to 0.02 for the basic data set. Using the water-air-oxygen system and an oxygen electrode as a detector this value is still about 30 times lower (insufficient sensitivity).

As suitable for parameter estimation thus appear the two remaining transfer functions: Outlet-gas-to-inlet-gas, X_{GZ}/X_{G0} and the outlet liquid-to-inlet gas, X_{LZ}/Z_{G0}, transfer function. The transfer function X_{GZ}/X_{G0} in the investigated range of input data appears particularly sensitive to gas phase related parameters (axial dispersion coefficient, E_G, gas superficial velocity, v_G and gas holdup, h_G) even though it is generally a function of all parameters involved.

The distinct sensitivity of X_{GZ}/X_{G0} to gas-related-parameters may be explained simply so that in view of the low solubility of oxygen in water the interfacial mass transfer causes relatively minor changes of oxygen concentration in gas. From the viewpoint of the gas phase oxygen thus plays a role of a "tracer". The X_{GZ}/X_{G0} transfer function is therefore characteristic of the gas phase dynamics.

For illustration the dependences of the amplitude ratio and phase lag are shown graphically in the form of Bode plots in Figures 1–3 for selected combinations of the flow rates, gas holdup, and axial dispersion coefficient in the gas phase.

The amplitude ratio of the X_{LZ}/X_{G0} transfer function is always less than 0.033; this value being given by the equilibrium constant k_m = 30. It would therefore appear that the measurement of oxygen concentration would be little sensitive. However, with the aid of polarographic oxygen electrode as a detector, the output of the electrode is proportional to the partial pressure of oxygen in the given phase, not its concentration. The output signals in the gas as well as liquid phase will range between zero and unity and as such will be well measurable. In the gas phase, though the measured value must be scaled by the equilibrium constant k_m.

The transfer function X_{LZ}/X_{G0} is influenced primarily by the parameters related to the liquid phase: Axial dispersion coefficient in liquid, E_D, dynamic and stagnant liquid holdups, h_D and h_S, the flow rate of liquid, Q_L, the mass transfer coefficient, $k_q a$ and the volume mass transfer coefficients $k_{LD}a_D$ and $k_{LS}a_S$, see Figures 4–7. Unfortunately, the effect of $k_q a$ and E_D is rather weak, see Figures (4) and (5), but evaluation of the remaining parameters should proceed smoothly.

From the dependences of the phase lag on frequency, it follows that the changes due to the variation of model parameters are rather small. Our ability to utilize this transfer function will therefore rest more with the amplitude ratio.

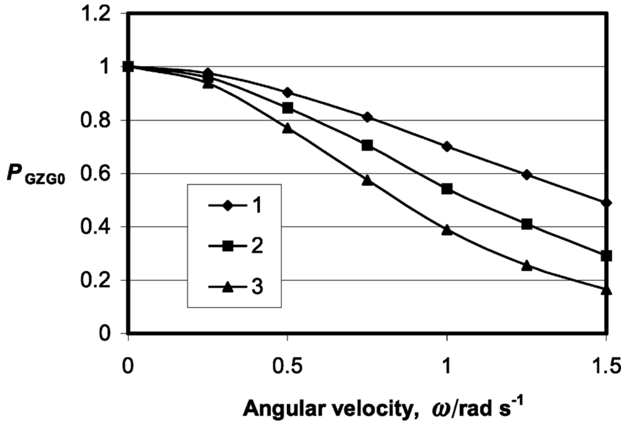


Fig. 1 – *Dependence of the amplitude ratio P_{GZG0} on ω for three values of gas holdup h_G and gas velocity v_G = 0.1 m s^{-1}: 1) h_G = 0.2; 2) h_G = 0.25; 3) h_G = 0.3*

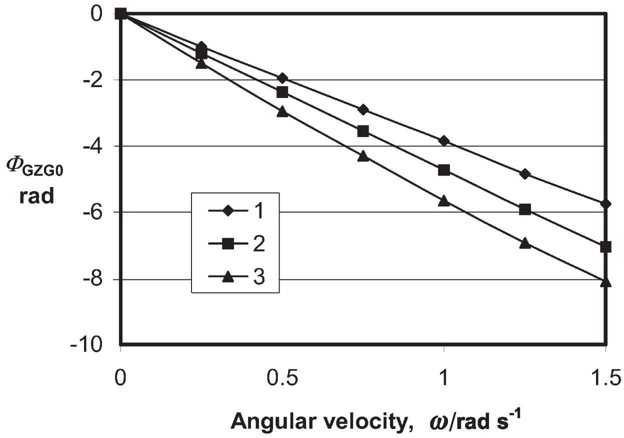


Fig. 2 – *Dependence of the phase lag Φ_{GZG0} on ω for three values of gas holdup h_G and superficial gas velocity v_G = 0.1 m s^{-1}: 1) h_G = 0.2; 2) h_G = 0.25; 3) h_G = 0.3*

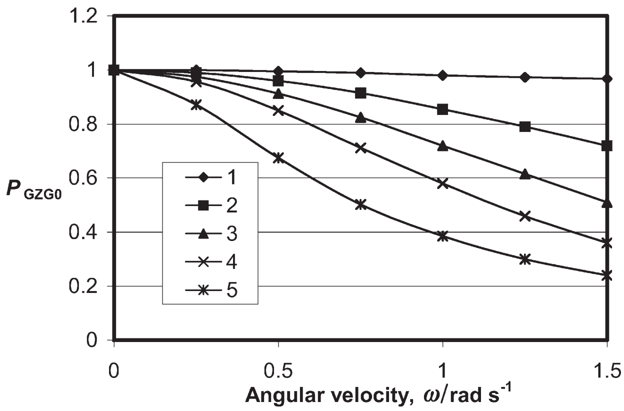
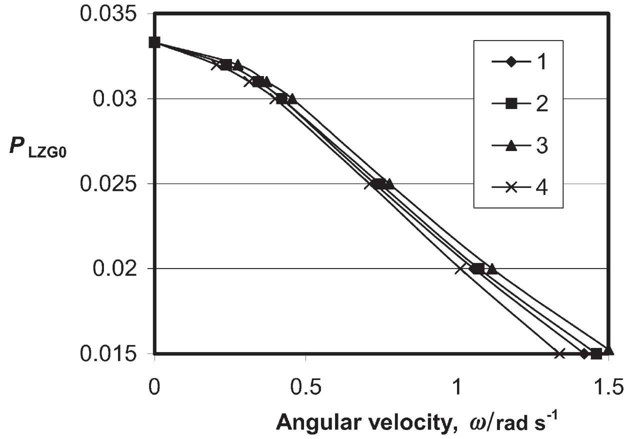
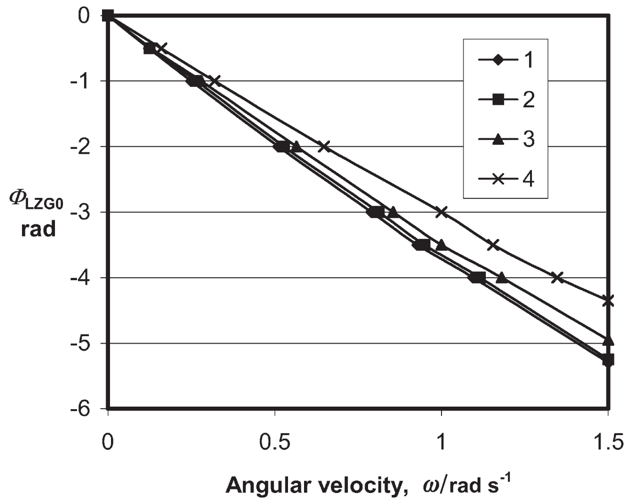


Fig. 3 – *Dependence of the amplitude ratio P_{GZG0} on ω for five values of axial dispersion E_G / m^2 s^{-1} and superficial gas velocity v_G = 0.2 m s^{-1}: 1) E_G = 0.001; 2) E_G = 0.02; 3) E_G = 0.05; 4) E_G = 0.1; 5) E_G = 0.5*

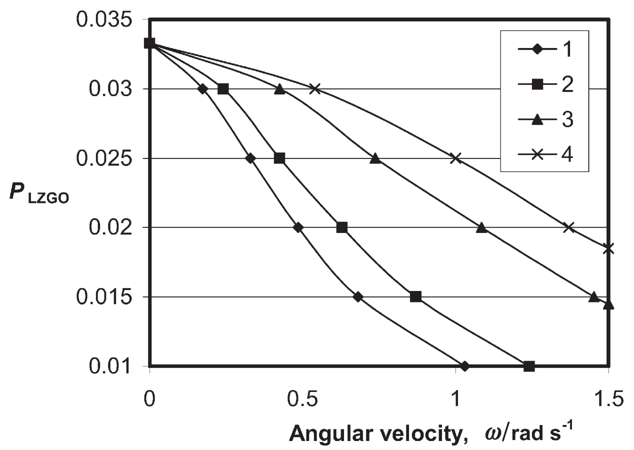
These conclusions hold generally for all four studied models. For the PDE-AD and PE-AD models we have to expect problems primarily with the quantity $k_q a$.



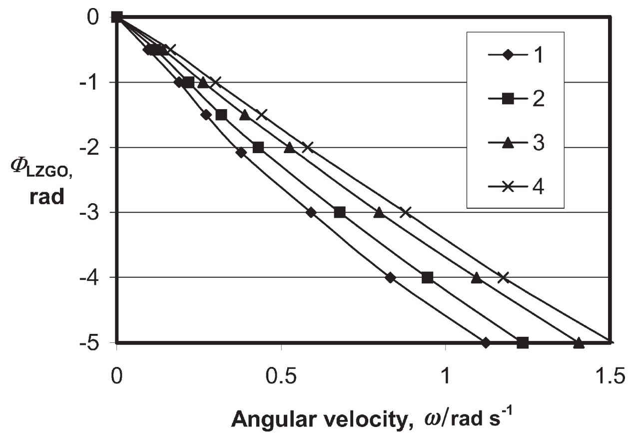
F i g . 4 – *Dependence of the amplitude ratio P_{LZG0} on ω for values of axial dispersion E_D / m^2 s^{-1} and superficial liquid velocity L = 0.001 m s^{-1}: 1) E_D = 0.01; 2) E_D = 0.02; 3) E_D = 0.1; 4) E_D = 0,5*



F i g . 5 – *Dependence of the phase lag Φ_{LZG0} on ω for four values of axial dispersion E_D / m^2 s^{-1} and superficial liquid velocity L = 0.001 m s^{-1}: 1) E_D = 0.01; 2) E_D = 0.02; 3) E_D = 0.1; 4) E_D = 0.5*



F i g . 6 – *Dependence of the amplitude ratio P_{LZG0} on ω for four values of volume mass transfer coefficient $k_{LD}a_D$ and for superficial liquid velocity L = 0.001 m s^{-1}: 1) $k_{LD}a_D$ = 0.001; 2) $k_{LD}a_D$ = 0.01; 3) $k_{LD}a_D$ = 0.05; 4) $k_{LD}a_D$ = 0.1*



F i g . 7 – *Dependence of the phase lag Φ_{LZG0} on ω for four values of volume mass transfer coefficient $k_{LD}a_D$ and for superficial liquid velocity L = 0.001 m s^{-1}: 1) $k_{LD}a_D$ = 0.001; 2) $k_{LD}a_D$ = 0.01; 3) $k_{LD}a_D$ = 0.05; 4) $k_{LD}a_D$ = 0.1*

Mathematical model of oxygen electrode

For the work on the dynamics of the flow in packed bed columns it is important to know the dynamics of the employed probe – in our case the polarographic oxygen electrode. This knowledge is indispensable and affects the accuracy of the measurement.

Utilizing the results and experience of the work,[29, 30] the oxygen electrode was described by the two-zone model assuming that the controlling resistance to oxygen transfer is that within the membrane of the electrode. The model has been described in detail in[32].

Currently the oxygen electrodes of the polarographic type are being displaced by the potentiometric ones extensively employed in biotechnological research[9] and industry. However, the dynamics of the potentiometric electrode is substantially slower and as such for the purposes of our research ill suited.

Conclusions

Parametric study of an eight-parameter model of co-current transient absorption of oxygen in a packed bed column and its four asymptotic cases has shown that from the four possible transfer functions only two are fully useable for the investigation of the given system.

These are: The gas outlet to gas inlet transfer function, X_{GZ}/X_{G0}, and the liquid outlet to gas inlet transfer function, X_{LZ}/X_{G0}, in the investigate range of parameters pertaining to the system. The X_{GZ}/X_{G0} function is more sensitive to gas phase-related parameters, while the X_{LZ}/X_{G0} function is affected primarily by the parameters relating to the liquid phase.

For the most complex eight parameter PDE-AD model, as well as the PE-AD model it appears that the obtained transfer functions are rather little sensitive to the mass transfer coefficient between the stagnant and dynamic zone of liquid, $k_q a$. Also the evaluation of the dispersion coefficient, E_D, could experience difficulties.

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support of the project by the Grant Agency of the Czech Republic under the grant number 104/03/1558.

List of symbols

a – specific interfacial surface, m^{-1}
c – concentration, kmol m^{-3}
d_p – diameter of filler element, m
v_G – superficial velocity of gas, m s^{-1}, m^3 s^{-1} m^2
E – axial dispersion coefficient, m^2 s^{-1}
h – hold up
I – imaginary part of the transfer function
k_L – mass transfer coefficient, m s^{-1}
k_{LD}, k_{LS} – mass transfer coefficient between dynamic (D) or static (S) liquid hold up and gas phase, m s^{-1}
v_L – superficial liquid velocity m s^{-1}
k_m – Henry constant, dimensionless
P – amplitude ratio
Pe_D – Peclet criterion for the dynamic liquid phase, $v_L d_p / h_o E_D$
Pe_G – Peclet criterion for the gas phase, $v_G d_p / h_6 E_G$
$k_q a$ – mass transfer coefficient between dynamic and static liquid, s^{-1}
Q_L – liquid flow rate, m^3 s^{-1}
s – Laplace variable
R – real part of transfer function
X – Laplace transform of concentration x
t – time, s
z – axial coordinate, m
Z – depth of packed section, m
Φ – phase angle, rad
ε – void fraction
ω – angular velocity (frequency), rad s^{-1}

Subscripts

D – dynamic liquid
G – gas
L – total liquid
S – static liquid

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APPENDIX 1

Axially dispersed flow model AD-AD

Constants A_1 – A_5 take the form:

$$A_1 = -\frac{h_G E_G h_L E_L}{k_L a} \quad (1\text{–}1)$$

$$A_2 = \frac{v_G h_L E_L + v_L h_G E_G}{k_L a} \quad (1\text{–}2)$$

$$A_3 = \frac{h_L E_L h_G s + h_G E_G h_L s}{k_L a} + h_G E_G + \frac{h_L E_L}{K_m} \quad (1\text{–}3)$$

$$A_4 = -\left(\frac{v_G h_L s + v_L h_G s}{k_L a} + \frac{v_L}{K_m} + v_G\right) \quad (1\text{–}4)$$

$$A_5 = -\left(\frac{h_L s\, h_G s}{k_L a} + \frac{h_L s}{K_m} + h_G s\right) \quad (1\text{–}5)$$

constants B_1, B_2 and B_3 take here the form:

$$B_1 = -\frac{h_G E_G}{k_L a} \quad (1\text{–}6)$$

$$B_2 = \frac{v_G}{k_L a} \quad (1\text{–}7)$$

$$B_3 = \frac{h_G s}{k_L a} + \frac{1}{K_m} \quad (1\text{–}8)$$

also the constants d_1 through d_4 take a different form:

$$d_i = 1 - \frac{h_L E_L}{v_L}\lambda_1 \qquad i = 1, 2, 3, 4 \quad (1\text{–}9)$$

APPENDIX 2

Model with stagnant zone in liquid and axial dispersion in gas phase (PE-AD)

Ordinary 3-rd order differential equation with constant coefficients:

$$A_1 \frac{d^3 X_G}{dz^3} + A_2 \frac{d^2 X_G}{dz^2} + A_3 \frac{dX_G}{dz} A_4 X_G = 0, \quad (2\text{–}1)$$

where the constants A_1 through A_4 are given by:

$$A_1 = -\frac{A_1' A_4'}{A_7'}, \quad (2\text{–}2)$$

$$A_2 = \frac{A_1' A_5' + A_2' A_4'}{A_7'}, \quad (2\text{–}3)$$

$$A_3 = -\frac{A_1' A_6' + A_2' A_5'}{A_7'}, \quad (2\text{–}4)$$

$$A_4 = \frac{A_3' A_7' - A_2' A_6'}{A_7'}, \quad (2\text{–}5)$$

where

$$A_1' = -v_L, \quad (2\text{–}6)$$

$$A_2' = \frac{(v_q a)^2}{h_S s + q + k_{LS} a_S} - k_{LD} a_D - v_q a - h_D s, \quad (2\text{–}7)$$

$$A_3' = \frac{k_q a k_{LS} a_S / (h_S s + k_q a + k_{LS} a_S) + k_{LD} a_D}{K_m}, \quad (2\text{–}8)$$

$$A_4' = E_G h_G, \qquad A_5' = -v_G, \quad (2\text{–}9,\ 2\text{–}10)$$

$$A_6' = \frac{k_{LS} a_S k_{LD} a_D / (h_S s + k_q a + k_{LS} a_S) - k_{LD} a_D - k_{LS} a_S - h_S s K_m}{K_m}, \quad (2\text{–}11)$$

$$A_7' = K_m A_3'. \quad (2\text{–}12)$$

The characteristic equation that has the form:

$$A_1 \lambda^3 + A_2 \lambda^2 + A_3 \lambda + A_4 = 0 \quad (2\text{–}13)$$

and may be solved similarly as equation (24)

By solving equation (2–1) we obtain expressions for X_G and X_D in the form:

$$X_G = k_1 \exp(\lambda_1 z) + k_2 \exp(\lambda_2 z) + k_3 \exp(\lambda_3 z), \quad (2\text{–}14)$$

$$X_D = a_1 k_1 \exp(\lambda_1 z) + a_2 k_2 \exp(\lambda_2 z) + a_3 k_3 \exp(\lambda_3 z), \quad (2\text{–}15)$$

where

$$a_i = B_1 \lambda_i^2 + B_2 \lambda_i + B_3, \quad i = 1,2,3, \quad (2\text{–}16)$$

and

$$B_1 = -(A_4' / A_7'), \quad (2\text{–}17)$$

$$B_2 = (A_5' / A_7'), \quad (2\text{–}18)$$

$$B_3 = (A_6' / A_7'). \quad (2\text{–}19)$$

Constants k_1 through k_4 were determined from the following boundary conditions:

$$z = 0 \qquad X_G = X_{G0} + \frac{h_G E_G}{v_G}\frac{dX_G}{dz}, \qquad X_D = X_{D0}, \quad (2\text{–}20)$$

$$z = Z \ \frac{dX_G}{dz} = 0, \quad (2\text{–}21)$$

and take the following form:

$$k_1 = \{X_{D0}[b_3 \lambda_2 \exp(\lambda_2 Z) - b_2 \lambda_3 \exp(\lambda_3 Z)] + {}$$
$$+ X_{G0}[a_2 \lambda_3 \exp(\lambda_3 Z) - a_3 \lambda_2 \exp(\lambda_2 Z)]\} / CJ \quad (2\text{–}22)$$

$$k_2 = \{X_{G0}[a_3 \lambda_1 \exp(\lambda_1 Z) - a_1 \lambda_3 \exp(\lambda_3 Z)] - {}$$
$$- X_{D0}[b_3 \lambda_1 \exp(\lambda_1 Z) - b_1 \lambda_3 \exp(\lambda_3 Z)]\} / CJ \quad (2\text{–}23)$$

$$k_3 = \lambda_1 \exp(\lambda_1 Z)\ \{X_{D0}[b_2 \lambda_1 \exp(\lambda_1 Z) - b_1 \lambda_2 \exp(\lambda_2 Z)] - {}$$
$$- X_{G0}[a_2 \lambda_1 \exp(\lambda_1 Z) - a_1 \lambda_2 \exp(\lambda_2 Z)]\} / CJ \quad (2\text{–}24)$$

where

$$CJ = \lambda_1 \exp(\lambda_1 Z)(a_3 b_2 - a_2 b_3) + \lambda_2 \exp(\lambda_2 Z)(a_1 b_3 - a_3 b_1) + {}$$
$$+ \lambda_3 \exp(\lambda_3 Z)(a_2 b_1 - a_1 b_2) \quad (2\text{–}25)$$

and

$$b_i = 1 - \lambda_i (h_G E_G / v_G), \qquad i = 1, 2, 3 \quad (2\text{–}26)$$

Substituting for k_1, k_2 and k_3 in equations (2–14) and (2–15) and putting $z = Z$ we obtain expressions for four transfer functions as:

$$X_{GZ} / X_{G0} = \{\exp(\lambda_1 Z)[a_2 \lambda_3 \exp(\lambda_3 Z) - a_3 \lambda_2 \exp(\lambda_2 Z)] + {}$$
$$+ \exp(\lambda_2 Z)[a_3 \lambda_1 \exp(\lambda_1 Z) - a_1 \lambda_3 \exp(\lambda_3 Z)] - \quad (2\text{–}27)$$
$$- \exp(\lambda_3 Z)[a_2 \lambda_1 \exp(\lambda_1 Z) - a_1 \lambda_2 \exp(\lambda_2 Z)]\} / CJ$$

and

$$X_{LZ}/X_{G0} = \{a_1 \exp(\lambda_1 Z)[a_2\lambda_3 \exp(\lambda_3 Z) - a_3\lambda_2 \exp(\lambda_2 Z)] + a_2 \exp(\lambda_2 Z)[a_3\lambda_1 \exp(\lambda_1 Z) - a_1\lambda_3 \exp(\lambda_3 Z)] - a_3 \exp(\lambda_3 Z)[a_2\lambda_1 \exp(\lambda_1 Z) - a_1\lambda_2 \exp(\lambda_2 Z)]\}/C\,J \quad (2\text{–}28)$$

and

$$X_{GZ}/X_{L0} = \{\exp(\lambda_1 Z)[b_3\lambda_2 \exp(\lambda_2 Z) - b_2\lambda_3 \exp(\lambda_3 Z)] - \exp(\lambda_2 Z)[b_3\lambda_1 \exp(\lambda_1 Z) - b_1\lambda_3 \exp(\lambda_3 Z)] + \exp(\lambda_3 Z)[b_2\lambda_1 \exp(\lambda_1 Z) - b_1\lambda_2 \exp(\lambda_2 Z)]\}/C\,J \quad (2\text{–}29)$$

and

$$X_{LZ}/X_{L0} = \{a_1 \exp(\lambda_1 Z)[b_3\lambda_2 \exp(\lambda_2 Z) - b_2\lambda_3 \exp(\lambda_3 Z)] - a_2 \exp(\lambda_2 Z)[b_3\lambda_1 \exp(\lambda_1 Z) - b_1\lambda_3 \exp(\lambda_3 Z)] + a_3 \exp(\lambda_3 Z)[b_2\lambda_1 \exp(\lambda_1 Z) - b_1\lambda_2 \exp(\lambda_2 Z)]\}/C\,J \quad (2\text{–}30)$$

APENDIX 3

Plug flow model (PF-PF)

On performing the Laplace transform and eliminating the concentration c_L a single ordinary second-order differential equation with constant coefficients results in the form:

$$A_1 \frac{d^2 X_G}{dz^2} + A_2 \frac{dX_G}{dz} + A_3 X_G = 0, \quad (3\text{–}1)$$

where

$$A_1 = v_L v_G / k_L a, \quad (3\text{–}2)$$

$$A_2 = \frac{v_G h_G s + v_G h_L s}{k_L a} + \frac{v_L}{K_m} + v_G, \quad (3\text{–}3)$$

$$A_2 = \frac{h_L s\, h_G s}{k_L a} + \frac{h_L s}{K_m} + h_G s. \quad (3\text{–}4)$$

Corresponding characteristic equation now has the form as:

$$A_1\lambda^2 + A_2\lambda + A_3 = 0. \quad (3\text{–}5)$$

which is a quadratic equation whose roots are given by:

$$\lambda_{1,2} = \frac{-A_2 \pm (A_2^2 - 4A_1A_3)^{0.5}}{2A_1}. \quad (3\text{–}6)$$

The solution then may be written in the form:

$$X_G = k_1 \exp(\lambda_1 z) - k_2 \exp(\lambda_2 z), \quad (3\text{–}7)$$

$$X_L = k_1 a_1 \exp(\lambda_1 z) - k_2 a_2 \exp(\lambda_2 z), \quad (3\text{–}8)$$

where

$$a_i = B_1\lambda_1 + B_2, \qquad i = 1,2,. \quad (3\text{–}9)$$

and

$$B_1 = v_G / k_L a, \quad (3\text{–}10)$$

$$B_2 = h_G s / k_L a + 1/K_m. \quad (3\text{–}11)$$

The constant k_1 and k_2 are determined from the boundary conditions:

$$z = 0, \qquad X_L = X_{L0} \quad (3\text{–}12)$$

$$X_G = X_{G0} \quad (3\text{–}13)$$

which have the form:

$$k_1 = (a_2 X_{G0} - X_{L0})/(a_2 - a_1), \quad (3\text{–}14)$$

$$k_2 = (X_{L0} - a_1 X_{G0})/(a_2 - a_1). \quad (3\text{–}15)$$

The transfer functions of the plug flow model for $z = Z$ are then given as follows:

$$X_{GZ}/X_{G0} = [a_2 \exp(\lambda_1 Z) - a_1 \exp(\lambda_2 Z)]/(a_2 - a_1), \quad (3\text{–}16)$$

$$X_{LZ}/X_{G0} = a_1[a_2 \exp(\lambda_1 Z) - a_1 \exp(\lambda_2 Z)]/(a_2 - a_1), \quad (3\text{–}17)$$

and as:

$$X_{GZ}/X_{L0} = [\exp(\lambda_2 Z) - \exp(\lambda_1 Z)]/(a_2 - a_1), \quad (3\text{–}18)$$

$$X_{LZ}/X_{L0} = [a_2 \exp(\lambda_2 Z) - a_1 \exp(\lambda_1 Z)]/(a_2 - a_1). \quad (3\text{–}19)$$

APPENDIX 4

The model with the stagnant zone in liquid and plug flow in gas (PE-PF).

The constants A_1 through A_3 are given by:

$$A_1 = -A_1' A_4' / A_6', \quad (4\text{–}1)$$

$$A_2 = (A_1' A_3' + A_2' A_4') / A_6', \quad (4\text{–}2)$$

$$A_3 = (A_6' A_3' - A_5' A_2') / A_6', \quad (4\text{–}3)$$

where

$$A_1' = -v_L, \quad (4\text{–}5)$$

$$A_2' = \frac{(k_q a)^2}{h_S s + k_{LS} a_S + k_q a} - k_{LD} a_D - k_q a - h_D s, \quad (4\text{–}6)$$

$$A_3' = \frac{k_{LD} a_D + k_q a\, k_{LS} a_S / (h_S s + k_{LS} a_S + k_q a)}{m}, \quad (4\text{–}7)$$

$$A_4' = -v_G, \quad (4\text{–}8)$$

$$A_5' = \frac{(k_{LS} a_S)^2 / (h_S s + k_{LS} a_S + k_q a) - k_{LS} a_S - k_{LD} a_D - h_G s K_m}{K_m}, \quad (4\text{–}9)$$

$$A_6' = k_{LD} a_D + \frac{k_{LS} a_S k_q a}{h_S s + k_{LS} a_S + k_q a}, \quad (4\text{–}10)$$

The characteristic equations has the form:

$$A_1\lambda^2 + A_2\lambda + A_3 = 0. \quad (4\text{–}11)$$

Its solution is the same as in APPENDIX 3 except that the constants B_1 and B_2 have now the form:

$$B_1 = -\frac{A_4'}{A_6'}, \quad (4\text{–}12)$$

$$B_2 = -\frac{A_5'}{A_6'}, \quad (4\text{–}13)$$

And the constants k_1 and k_2 are evaluated from the boundary conditions:

$$z = Z, \qquad X_D = X_{D0} \quad \text{and} \quad X_G = X_{G0} \quad (4\text{–}14)$$

Expression for the constants k_1 and k_2 are the same as the those for the PF-PF model and are given by equations (3–14) and (3–15). The same is true also about the transfer functions which are given by equations (3–16) through (3–19).