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OPTIMAL FLOWRATE OF A GAS IN SEMI-BATCH GAS-LIQUID REACTORS

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The present work deals with the optimisation of the models for slow and fast kinetic regimes in semi-batch gas-liquid reactors. The control variable is taken to be the inlet gas flowrate, the objective is to minimise the gas consumption when gas is passed continuously through a liquid reactant held within the reactor. The main optimisation techniques used for this purpose were Pontryagin's Maximum Principle and Dynamic Programming. The main conclusion which can be drawn is that savings in gas consumption for slow regimes model are much more significant than for the fast regimes model.

Key words: Optimisation, Gas flow-rate, Gas consumption.

Introduction

The main conventional types of industrial reactor are given by Kuerten and Magnussen [1]. One such type is the stirred tank reactor where gas is bubbled continuously through the liquid. The concentration of liquid reactant falls with time as does the conversion of the gaseous reactant. Such reactors are often described as "semi-batch" because the gas is fed continuously whilst the liquid behaves as in a batch process. This type of reactor was modelled for five different kinetic regimes [2] i.e. pseudo 1st order slow and fast, 2nd order slow, intermediate and instantaneous reactions. These regimes are described by concentration gradients shown in Figs. 1-5. Optimisation studies were made on this model and it was found that the slow regimes gave significant savings in gas consumption when operating with an optimal gas rate policy compared with using a best constant gas rate.

Experimental

Optimisation. Optimisation pervades the field of science, engineering and business. A process can be represented by some equations or perhaps solely by experimental data. There is also a single performance criterion or objective function in mind such as minimum cost. The goal of optimisation is to find the values of the variables in the process that yield the best value of the performance criterion. The ingredients described above - process or model and the performance criterion - comprise the optimisation "problem".

Optimisation of gas-liquid semi-batch stirred tank reactor. Optimisation problems can arise in both the design and operation of the reaction [1]. The most significant variables affecting the type of reactor considered here are gas flow rate, stirrer speed, temperature and pressure. Since the present system has been assumed to be isothermal and isobaric and stirrer speed has also been assumed to be unchanged during the course of the reaction, the objective here is to optimise the conversion or yield of desired product for the type of the reactor described previously. This is possible by considering a variable gas flow rate, so that the possibility exists that the gas consumption required to achieve a given conversion in the liquid phase in a specified time may then be less than that required when operating with a constant gas rate. Hawkins [3] and Gautschi *et al.* [4] proposed the use of an inlet gas flow profile for slow gas-liquid reactions but they did not take into account a variable gas/liquid interfacial area, which is taken account in the current model.

The aim of the present work is to achieve the above described objective. For this purpose, two models have been proposed as follows:-

Fast regimes model. Since the reactions in the pseudo 1st order fast, instantaneous and intermediate regimes occur very rapidly in the film, the gaseous component is never present in the bulk of the liquid. These regimes are generally classified together as fast regimes and have been incorporated into a single model which has then been used to minimise the gas consumption. In mathematical terms the equation relating the concentrations of B in the bulk of the liquid with time is given by:-

$$\frac{dC_B}{dt} = N_{BL}(a_o / \phi) - (b'/a') K C_A C_B \quad \text{...............(1)}$$

With initial conditions $t = O$, $C_A = O$, $C_B = C_{BO}$

In all regimes the molar flux of B from the bulk into the film is then determined by :-

$$N_{BL} = -(b'/a')(N_{Ai} - N_{AL}) \quad \text{........................(2)}$$

$N_{Ai} = 0$ in all cases, where

$N_{Ai} = K_{oG''} P_{Ab}$ (for fast pseudo 1st order reaction)...(3)

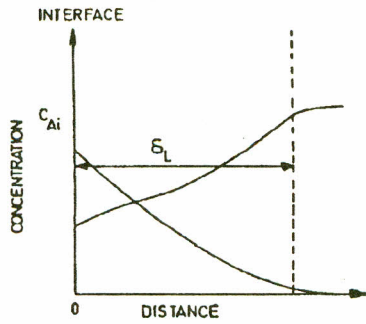Where $K_{oG''}$ is a modified overall mass transfer coefficient

Fig. 1. Fast reaction.
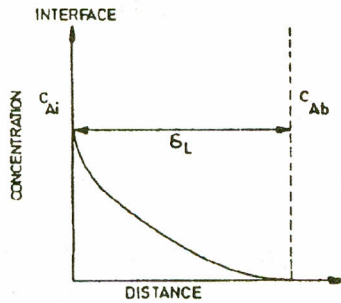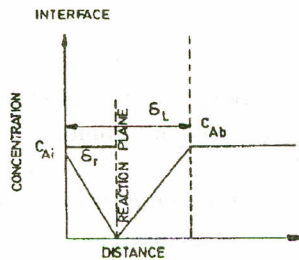

Fig. 4. Slow reaction
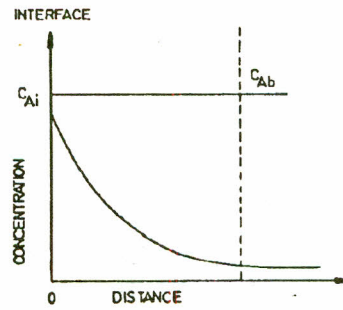

Fig. 2. Fast pseudo 1st order reaction.

Fig. 5. Very slow reaction.

Fig. 3. Instantaneous reaction
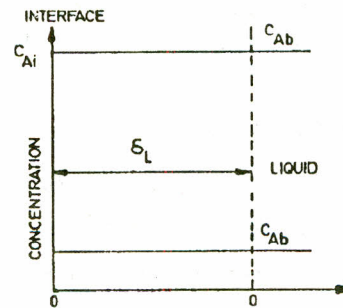
C_{Ai} = Concentration of A at the interface of the liquid (Kmol m⁻³). C_{Ab} = Concentration of A in the bulk of the liquid (Kmol m⁻³). δ_l= Film thickness (m). δ_r= Thickness from reaction plant (m).

given by:

$$1/K_{oG'} = (1/K_G) + H' / (K D_A C_B)^{0.5} \quad \dots\dots\dots\dots(4)$$

$$N_{Ai} = K_L \; E \; C_{Ai} \quad \text{(for intermediate reaction)} \dots\dots(5)$$

$$N_{Ai} = K_G (P_{Ab} - H' C_{Ai}) \quad \dots\dots\dots\dots\dots(6)$$

$$N_{Ai} = K_{oG} [P_{Ab} + H'(a'/b') (D_B/D_A) C_{Bb}] \text{ (For instantaneous reaction)} \dots\dots\dots\dots\dots(7)$$

For $C_{Bb} < (K_G/K_L)(b'/a') (D_A/D_B) P_{Ab}$

and

$$N_{Ai} = K_G P_{Ab} \text{ For } C_{Bb} > (K_G/K_L) (b'/a') (D_A/D_B) P_{Ab} \dots(8)$$

When the reaction plane is at the gas/liquid interface.

In this model, equation (1) has been integrated numerically using the NAG subroutine DO2EBF which uses the Runge-Kutta-Merson integration method with a global error estimate and a check of stiffness. Dynamic programming has been applied here to decompose the main optimisation problem into a sequence of subproblems. For the present system,

since $N_{Ai} = 0.0$ there is only one state variable i.e. C_B which is to be considered during the optimisation process, hence the application of dynamic programming in this case is appropriate. The whole process has been broken down into stages of time and each individual stage has been optimised by the golden section search technique. Because every stage in a serial structure influences other stages, the last stage is optimised first for the possible input flowrate of a gas it receives. Once the last stage is optimised, the last two stages are grouped together and optimised for possible input flowrate of a gas to the next to last stage. The procedure continues until the entire structure is included in the optimisation.

Slow regimes model. In mathematical terms the equations relating the concentrations of 'A' and 'B' in the bulk of the liquid with time for slow reactions in dimensionless form are represented as:-

$$\frac{dF_A}{dT} = D a DK_{OG} (X - F_A) - DK F_A F_B \quad \dots\dots\dots(9)$$

$$\frac{dF_B}{dT} = -Z \; DK \; F_A \; F_B \qquad \text{..................(10)}$$

The dimensionless form of the equation for the gas phase mass balance is given as:-

$$U \left[(X_F - X) / (X_T - X) \right] = Da \; DK_{OG} (X - F_A) \quad \text{........(11)}$$

As system is isothermal and isobaric stirring speed is unchanged during the course of the reaction. The operating variable is therefore only the flow of the gas i.e. U. Differentiating Eq. [11] w.r.t. 'T' substituting the value of dF_A/dT, Da, $(X - F_A)$, F_A in the resulting equation and rearranging dX/dT is expressed as:-

$$\frac{dX}{dT} = \{[U(X_F{-}X)/(X_T{-}X)] - DK \; F_B \{ \; X - [U(X_F{-}X)/$$
$$[DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]]\} + (X_F{-}X)$$
$$(dU/dT) / [DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]\} /$$
$$\{1 + [U(3X_T{-}X_F{-}2X) / [3DK_{OG}(X_T{-}X_F)^{0.667}$$
$$(X_T{-}X)^{1.333}]]\} \qquad \text{..................(12)}$$

The total gas consumption for the above reaction is calculated by integrating the following equation:-

$$\frac{dS}{dT} = U \qquad \text{..................(13)}$$

The state equation for the said reaction are, therefore, represented by equation (10), (12) and (13).

Adjoint equations. The derivation of the adjoints for this system according to Pontryagin's Maximum Principle is as follows:-

Hamiltonian function H is generally defined as:

$$\left(H = \sum_{i=1}^{n} \lambda_i \; f_i \right)$$

where λ_i and f_i are adjoints and state functions respectively, and from the state equations (10), (12) and (13), therefore, the Hamiltonian function H is expressed as:-

$$H = \lambda_x \{\{[U(X_F{-}X)/(X_T{-}X)] - DK \; F_B \{ \; X - [U(X_F{-}X)/$$
$$[DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]]\} + [(X_F{-}X)(dU/dT)/$$
$$[DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X^{0.333}]]\} /$$
$$\{1 + [U(3X_T{-}X_F{-}2X) / [3DK_{OG}(X_T{-}X_F)^{0.667}$$
$$(X_T - X)^{1.333}]]\}\}\}$$
$$+ \lambda_s U - Z \; DK \; F_B \; F_A \; \lambda_B$$

Where $F_A = X - \{ [U(X_F{-}X)] / [DK_{OG}(X_T{-}X_F)^{0.667}$
$$(X_T - X)^{0.333}]\} \qquad \text{..................(14)}$$

Differentiating H w.r.t. U in equation (14).

$$\frac{\partial H}{\partial U} = \{[(X_F{-}X)/(X_T{-}X)] + [DK \; F_B(3X_F X_T{-}$$

$$4XX_F + X^2] / [3DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{1.333}]$$
$$- [3(3X_T{-}X_F{-}2X)(X_F{-}X)(dU/dT)] /$$
$$[(X_T{-}X_F)^{0.667}(X_T{-}X)^{1.333}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]$$
$$\lambda_x / [1 + [U(3X_T{-}X_F{-}2X)] / [3DK_{OG}(X_T{-}X_F)^{0.667}$$
$$(X_T{-}X)^{1.333}]]^2] + \{ [Z\lambda_B \; DK \; F_B(X_F{-}X)] /$$
$$[(DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]\} + 1.0 \quad \text{.......(15)}$$

B.C's: (i) $t = 0$; X is unknown, and $F_B = F_{BO}$
          (ii) $t = T$; $F_B = F_{BR}$: $\lambda_X = o$; $\lambda_s = 1$

From equation (14) H is differentiated w.r.t. X to get

$$\frac{d\lambda_X}{dt} = -\frac{\partial H}{\partial X} \qquad \text{..................(16)}$$

From equation (14) H is differentiated w.r.t. F_B to give $d\lambda_B/dt$:

$$d\lambda_B/dt = -\partial H/\partial F_B = DK \{ X - [U(X_F{-}X)] /$$
$$[DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]\}$$
$$\{ \lambda_X / \{ 1 + [U(3X_T{-}X_F - 2X) / [3DK_{OG}$$
$$(X_T{-}X_F)^{+0.667}(X_T{-}X)^{1.333}]]\} + Z\lambda_B \}\text{........(17)}$$

The equation (10), (12), (13), (14), (15), (16) and (17) can then be solved by hill climbing in function space using routine DO2YAF.

Pseudo 1st order slow reaction. The state equations for this reaction are given as:-

$$\frac{dF_A}{dT} = Da \{[DK_{OG}Ha/Cosh(\beta l)] [X + (DH F_A/Cosh (\beta l)]$$
$$- (K_L \; Hat_F F_A \; (a_i / \phi))\} - DK \; F_A \; F_B \quad \text{...............(19)}$$

$$\frac{dF_B}{dT} = -ZDa \{[DK_{OG} \; Ha \; [X{-}F_A/Cosh (\beta l)]] -$$
$$\{[(DK_{OG}Ha/Cosh (\beta l)] - [X + (DH F_A/Cosh (\beta l))]\}$$
$$- [K_{LL} \; Ha \; F_A / \phi] \} - ZDK \; F_A \; F_B \quad \text{...............(20)}$$

F_A, F_B and S for the above reaction, which are similar to the 2nd order slow reaction quantities are calculated by integrating the equations (19), (20) and (21) whereas the gas phase mass balance for this reaction is given by:-

$$U(X_F{-}X) / [Ha \; DK_{OG}(X_T{-}X_F)^{0.667}(X_T{-}X)^{0.333}]$$
$$= X - [F_A / Cosh (\beta l)]\text{............................ (21)}$$

Gas profile. It is calculated from equation (21) by successive substitution. The results obtained from the method of Hill Climbing in function space [1] for 2nd order slow reaction show that the control variable is only a single gas rate, therefore, the derivation of the adjoint equations for the pseudo

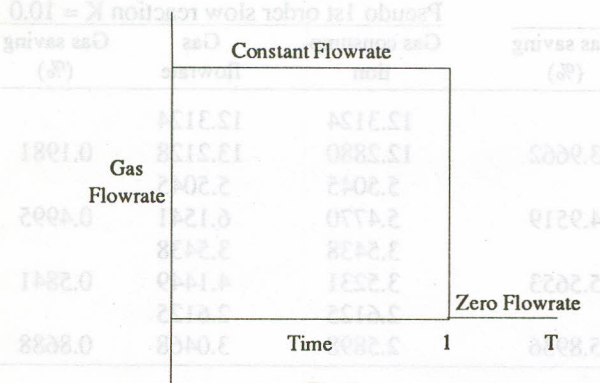1st order slow reaction is unnecessary. A gas profile (Fig. 6) of this form suggests that in this case:-

Fig. 6.

(i) This is the shape of the optimal path.

(ii) The flowrate of the gas remains constant until a particular liquid conversion is reached and then the gas flowrate becomes zero until the specified time T is obtained. During this latter time, the reaction behaves essentially as a batch reactor and the dimensionless expression for F_B in terms of F_A is given as:-

$$F_B = F_{B1} + F_A + F_{A1} \quad\quad\quad\quad\quad (22)$$

where

$$F_A = F_{Al} (1 - Z) \quad \text{and}$$

$$Z = F_{B1} [1 - e^{-kt(F_{B1} - F_{A1})}] /$$
$$[F_{B1} - F_{Al} e^{-kt(F_{B1} - F_{Al})}] \quad\quad\quad (23)$$

where subscript 1 refers to the beginning of the zero gas flowrate section. As the control variable is now a single constant gas rate, a single variable search i.e. golden section search technique [5] was used to achieve this objective. The NAG routines DO2YAF [6] and DO2EBF [7] were used to integrate the system for these reactions.

Results and Discussion

Tables 1 to 4 show typical results and also indicate the effects of the specified conversion, the inlet gas concentration, the reaction rate constant and the Henry's law constant on the improvements in gas consumption when operating with an optimal gas feedrate to compared with a constant feed-rate. Savings in gas consumption were most predominant when the required conversion of liquid reactant 'B' exceeded a value of 95%, lower conversions giving rather more limited differences (Table 1). Table 2 shows that higher inlet gas concentrations favour the use of an optimal policy. An increase in the reaction rate constant causes an overall reduction in the mass transfer resistance by lowering the bulk concentration of the absorbed gases. This effect is illustrated in Table 3. An increase in the Henry's law constant has the opposite effect by reducing the driving force (P_{Ab} - H C_{Ab}) which in turn increases the resistance to mass transfer. There is some scope for improvement when operating with an optimal gas rate as shown in Table 4, but much more as in the case of a 2nd order slow reaction, than for a pseudo-first order slow reaction.

Conclusion

(i). It was found in general that in fast regimes the results obtained for both the optimum and the best constant flowrates of a gas were almost the same.

(ii). The results of hill climbing in function space for the slow regimes indicate that a single constant gas rate followed by a period of zero gas addition is the best operating policy. In such cases a single variable search technique can be used to optimise the process.

(iii). The slow regimes give significant savings in gas consumption when operating with an optimal gas rate policy compared with using a best constant gas rate. The savings are only worthwhile if the conversion of liquid reactant exceeds a

TABLE 1. EFFECT OF DESIRED CONVERSION ON GAS CONSUMPTION. (GAS CONCENTRATION = 20%, H' = 1.0, C_{BO} = 0.1).

		2nd order slow reaction K = 1.0			Pseudo 1st order slow reaction K = 10.0		
	Desired conversion of B (%)	Gas consumption	Gas flowrate	Gas saving (%)	Gas consumption	Gas flowrate	Gas saving (%)
Constant		5.0280	5.0280		4.8901	4.8901	
Optimum	90.00	5.0027	6.1761	0.5031	4.8930	5.0976	Nil
Constant		5.4231	5.4231		5.2009	5.2009	
Optimum	95.00	5.2841	6.0737	2.5631	5.2723	6.3521	Nil
Constant		5.6274	5.6274		5.3366	5.3366	
Optimum	97.00	5.4209	6.1010	3.6695	5.3609	6.0919	Nil
Constant		5.9411	5.9411		5.5045	5.5045	
Optimum	99.00	5.6469	6.9715	4.9519	5.4770	6.1541	0.4995
Constant		6.3677	6.3677		5.6721	5.6721	
Optimum	99.90	5.8929	7.8571	7.4563	5.5470	6.3759	2.2055

TABLE 2. EFFECT OF GAS CONCENTRATION ON GAS CONSUMPTION. (DESIRED CONVERSION OF B = 99%; H' = 1.0, C_{BO} = 0.1).

	2nd order slow reaction K = 1.0				Pseudo 1st order slow reaction K = 10.0		
	Gas concentration	Gas consumption	Gas flowrate	Gas saving (%)	Gas consumption	Gas flowrate	Gas saving (%)
Constant		13.4585	13.4585		12.3124	12.3124	
Optimum	10	12.9247	14.3606	3.9662	12.2880	13.2128	0.1981
Constant		5.9411	5.9411		5.5045	5.5045	
Optimum	20	5.6469	6.9715	4.9519	5.4770	6.1541	0.4995
Constant		3.8111	3.8111		3.5438	3.5438	
Optimum	30	3.5990	4.4432	5.5653	3.5231	4.1449	0.5841
Constant		2.8047	2.8047		2.6125	2.6125	
Optimum	40	2.6394	3.3839	5.8936	2.5898	3.0468	0.8688

TABLE 3. EFFECT OF K ON GAS CONSUMPTION. (GAS CONCENTRATION = 20%; H' = 1.0; DESIRED CONVERSION = 99%; C_{BO} = 0.1).

	2nd order slow reaction					Pseudo 1st order slow reaction		
	K	Gas consumption	Gas flowrate	Gas saving (%)	K	Gas consumption	Gas flowrate	Gas saving (%)
Constant		7.0597	7.0597			5.5698	5.5698	
Optimum	0.2	6.2414	8.7908	11.5911	5.0	5.4788	6.1559	1.6338
Constant		6.2672	6.2672			5.5342	5.5342	
Optimum	0.5	5.8013	7.4375	7.4339	7.0	5.4780	6.1551	1.0115
Constant		6.0290	6.0290			5.5045	5.5045	
Optimum	0.8	5.6888	7.2010	5.6427	10.0	5.4770	6.1541	0.4995
Constant		5.9411	5.9411			5.4784	5.4784	
Optimum	1.0	5.6414	6.7160	5.0445	15.0	5.4760	6.1529	0.0365
Constant		5.8789	5.8789			5.4640	5.4640	
Optimum	1.2	5.6129	6.6035	4.5246	20.0	5.4754	6.1521	Nil

TABLE 4. EFFECT OF H ON GAS CONSUMPTION. (DESIRED CONVERSION = 99%; GAS CONCENTRATION = 20%; C_{BO} = 0.1).

	2nd order slow reaction K = 1.0				Pseudo 1st order slow reaction K = 10.0		
	H	Gas consumption	Gas flowrate	Gas saving (%)	Gas consumption	Gas flowrate	Gas saving (%)
Constant		5.9411	5.9411		5.4784	5.4784	
Optimum	1.0	5.6414	6.7160	5.0445	5.4760	6.1529	0.0365
Constant		5.6563	5.6563		5.2593	5.2593	
Optimum	2.0	5.3308	6.6635	5.7546	5.2301	6.3782	0.5552
Constant		5.5678	5.5678		5.1828	5.1828	
Optimum	3.0	5.2299	6.8815	6.0688	5.1459	6.5138	0.7170
Constant		5.5246	5.5246		5.1453	5.1453	
Optimum	4.0	5.1756	7.0952	6.3171	5.0970	6.3713	0.9387
Constant		5.4991	5.4991		5.1232	5.1232	
Optimum	5.0	5.1495	6.8660	6.3574	5.0665	6.1786	1.1067

value of around 95%.

iv. The higher the inlet gas concentration and the higher the Henry's law constant, the greater are improvements in using an optimal gas policy.

v. Saving in gas consumption using an optimal gas rate policy become smaller as the reaction rate increases and the regimes pass from the slower regimes to the faster ones.

NOTATIONS

a', b'	-	Stoichiometric coefficients.
ao	-	Interfacial area per unit volume (m^{-1})
A	-	Gaseous component
B	-	Liquid component
C_A	-	Liquid phase concentration of A (Kmol m^{-3})
C_{Ai}	-	Liquid phase concentration of A at the interface (Kmol m^{-3})
C_B	-	Liquid phase concentration of B (Kmol m^{-3})

C_{BO} - Initial concentration of B (Kmol m^{-3})
D_A - Liquid phase diffusivity of A (m^2 s^{-1})
D_B - Liquid phase diffusivity of B (m^2 s^{-1})
H' - Henry's law constant PA/CA (bar m^3 Kmol^{-1})
K - Second order reaction rate constant (m^3 Kmol^{-1} s^{-1})
K_G - Gas phase mass transfer coefficient (Kmol m^2 s^{-1} bar)
K_L - Liquid phase mass transfer coefficient (m s^{-1})
K_{OG} - Overall gas phase mass transfer coefficient(Kmol m^{-2}s^{-1} bar^1)
K_{OG} - Overall gas phase mass transfer coefficient for fast pseudo 1st order reaction (Kmol m^2 s^{-1})
N_{Ai} - Molar flux of A at the interface (Kmol m^2 s^{-1})
N_{AL} - Molar flux of A (Kmol m^2 s^{-1})
N_{BL} - Molar flux of B into the bulk of the liquid (Kmol m-2 s-1)
P_{Ab} - Partial pressure of A into the bulk of the gas (bar)
t - Time (sec)
t_F - Total time (sec)
V - Reactor volume (m^3)

DIMENSIONLESS QUANTITIES

Da - Interfacial area ao/ai
DK - Second order reaction rate constant
DK_{OG} - Overall mass transfer coefficient
E - Enhancement factor
F_A - Liquid phase concentration of A
F_{AI} - Liquid phase concentration of A at the interface
F_B - Liquid phase concentration of B = C_B/C_{BO}
F_{BO} - Initial concentration of B
F_{BR} - Specified concentration of B
Ha - Hatta number
H - Hamiltonian function
K_{LL} - Liquid phase mass transfer coefficient
S - Gas consumption
T - Final value of time t/t_F

U - Flowrate of gas
Z - Stoichiometric ratio of the coefficient of A and B

GREEK LETTERS

δL - Liquid film thickness (m)
δr - Thickness from reaction plane (m)
ϕ - Fractional liquid holdup
$\lambda_B, \lambda_s, \lambda_x$ -Adjoint variables
Kinetic parameter = $(KC_BD_A)^{0.5}/K_L$

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