Pakistan J. Sci. Ind. Res., **12**,357–364(1970)

PREDICTION OF A CHEMICAL REACTION IN A GAS-FLUIDISED BED

F.D. Toor*

Atomic Energy Centre, Lahore 16

(Received December 16, 1968)

Following some recent investigations of the phenomenon of cloud formation around bubbles in aggregatively fluidised beds, mathematical models have been developed to predict the performance of a fluidised-bed reactor for the two ideal conditions of a perfectly mixed dense phase and plug flow of gas through the dense phase. The theoretical predictions of reactor performance have been compared with the experimental results of a first-order catalytic gas phase reaction, carried out in an 18-inch diameter fluidised-bed reactor in which the size of the catalyst particles, the gas flow rates, the bed height and the reaction rate were widely varied.

Introduction

There is now sufficient theoretical[2–5] and experimental[1,6–8] evidence in the literature to establish the fact that, the bubble rise velocity being greater than the intersticial gas velocity, the bubbles in aggregatively fluidised beds are surrounded by 'clouds'. A number of mathematical models have appeared in the literature which take this phenomenon into account to predict the conversion efficiency of a fluidised bed reactor. The earlier of these models[9–12] which considered that the gas in the bubble contacts only the solid particles present in the surrounding cloud have been shown[13] to be inadequate. In a more recent model, Rowe *et al.*[14,15] have assumed that some interchange of gas also takes place between the cloud surface and the dense phase. However, no experimental data have been included for comparison with the theoretical predictions of the reactor performance.

In the present contribution mathematical models have been derived for the fluidised bed reactors operating under the conditions where the formation of clouds around the bubbles occurs and the theoretical predictions of reactor performance are then compared with the experimental results obtained from an 18-inch diameter fluidised-bed reactor in which a pseudo first order reaction (catalytic decomposition of ozone) is being carried out. Since three different sized catalyst particles were used, along with different gas flow rates, bed heights and reaction rates, this comparison provides a convenient way of testing some of the simplifying assumptions used in the derivation of these and the previous models.[14,15]

Experimental

The details of the experimental procedures employed, the variables studied and the equipment used in the present investigations have been given elsewhere[13,16] along with the presentation of the experimental results and the comparison of the regression lines for the experimental data. Figure 1 shows the line diagram of the experimental set up used.

Mathematical Models

(a) *Basic Assumptions*

(i) All the gas in excess of that required to incipiently fluidise the bed passes through the bed as bubbles[22] which are uniform in size and equally distributed throughout the bed.

$$N.\ V.\ U_a = (U - U_o) \tag{1}$$

(ii) The absolute rise velocity of bubbles, U_a, is a sum of their natural rise velocity, U_b, as given by Davies and Taylor[18] and the upward velocity of the particulate phase between the bubbles.

$$U_a = (U - U_o) + 0.711\,(g.D_c)^{\frac{1}{2}} \tag{2}$$

(iii) The increase in bed height over that at minimum fluidisation is due entirely to the presence of bubbles.

$$N.\ V.\ H = H - H_o \tag{3}$$

(iv) The ratio between the bubble and the cloud volumes as given by Davidson's analysis[2,3] is

$$V_c / V = \frac{3}{\alpha - 1}$$

$$\text{where } \alpha = \frac{U_b\,.\,\varepsilon_o}{U_o}$$

However, Patridge and Rowe[15] have recently shown from the actual measurements of the cloud

* Now at Packages Ltd., Ferozepur Road, Lahore

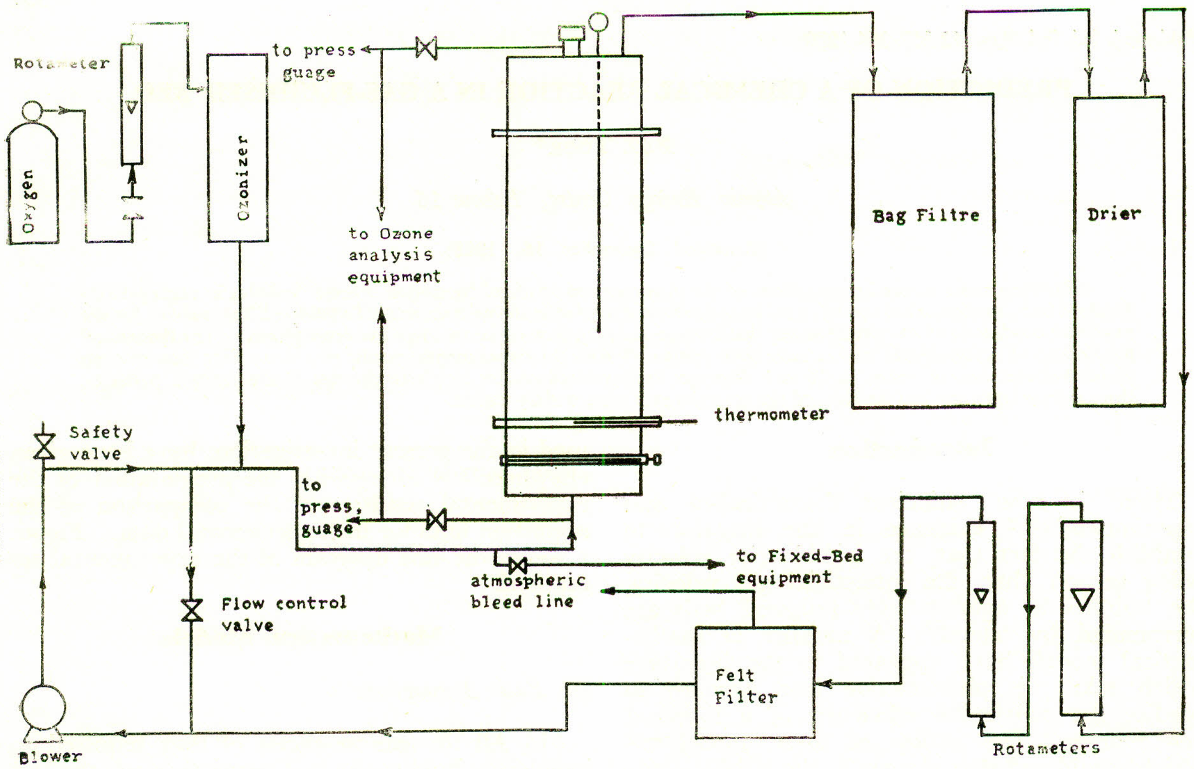

Fig. 1.

volumes around bubbles in two dimensional fluidised beds that the ratio can be more accurately described as:

$$V_c/V=\frac{1.17}{\alpha-1} \tag{4}$$

Equation (4) will be used in the present models.

Also f=fraction of total gas in bubble and cloud that is in cloud

$$=\frac{V_c\varepsilon_o}{V_c\varepsilon_o+V}=\frac{1.17}{\alpha-1+1.17\varepsilon_o} \tag{5}$$

(v) All the gas entering the bed is divided into a bubble/cloud phase and an intersticial phase. The intersticial gas passes only through those parts of the dense phase not occupied by the clouds.

Thus, if Q_b is the gas flow rate through the bubbles $=Q-Q_o$ (6)

Gas flow rate through clouds, using (5)

$$=\frac{f}{1-f}\cdot Q_b \tag{7}$$

Total gas flow rate through bubble and cloud $=Q_{CT}$

$$=\frac{1}{1-f}\cdot Q_b\simeq\left(1+\frac{\varepsilon_o}{\alpha-1}\right)\cdot Q_b \tag{8}$$

Total volume occupied by bubble and cloud gas

$$=Q_b\cdot\frac{H}{U_a}\cdot\left(1+\frac{f}{1-f}\right)$$

$\therefore$ Total volume occupied by bubble and cloud

$$=Q_b\cdot\frac{H}{U_a}\left(1+\frac{f}{(1-f)\varepsilon_o}\right)$$

Area of x-section of bubble and cloud$=A_{CT}$

$$=\frac{Q_b}{U_a}\left(\frac{f}{(1-f)\varepsilon_o}+1\right)\simeq\frac{Q_b}{U_a}\cdot\left(\frac{\alpha}{\alpha-1}\right)$$

Intersticial flow, therefore

$$=Q_i=U_o(A-A_{CT})=U_o\left(A-\frac{Q_b\cdot}{U_a}\frac{(\alpha)}{\alpha-1}\right)$$

$$=Q_o-Q_b\cdot\frac{f}{1-f}\cdots\cdots\ (\alpha-1)=\frac{\varepsilon_o\cdot(1-f)}{f}$$

$$=\frac{1}{1-f}\cdot(Q_o-f\cdot Q)\ldots\ldots\ Q_b=Q-Q_o \qquad (9)$$

Also $Q=Q_{CT}+Q_i$

$$=\left(1+\frac{\varepsilon_o}{\alpha-1}\right)\cdot Q_b+U_o\cdot\left(A-\frac{Q_b}{U_a}\cdot\frac{\alpha}{\alpha-1}\right)$$

but $\dfrac{U_o}{U_a}=\dfrac{\varepsilon_o}{\alpha}$ ....$U_b\simeq U_a$

$$\therefore\ Q=U_oA+Q_b\left(1+\frac{\varepsilon_o}{\alpha-1}-\frac{\varepsilon_o U_a}{U_a(\alpha-1)}\right)=U_oA+Q_b$$

$$\text{or}\quad U=U_o+\frac{Q_b}{A} \qquad (10)$$

Equation 10 further proves assumption (i).

(vi) It can be shown[13,17] that out of the different assumptions given in the literature[9,11,12,15] for the mechanism of the flow of gas between the bubble and the cloud, the one that considers a complete mixing of the gas in the bubble–cloud system, with the particles contacted by the cloud gas being assumed to be equally distributed between the bubble–cloud system, is the most convenient for use in the development of a mathematical model to predict the performance of a fluidised bed reactor.

If K_c is the rate constant for the first order reaction in the dense phase gas (reactant concentration–volume basis), the reaction rate constant for the gas in the bubble–cloud system is defined as:

$$\bar{K}_c=\frac{V_c\cdot\varepsilon_o\cdot K_c}{V_c\cdot\varepsilon_o+V}=f.K_c \qquad (11)$$

(vii) The increase in bed height over that at minimum fluidisation is due to the presence of bubbles alone.

$$NVH=H-H_o$$

also from continuity of the gas flow and assumption (i) $NVU_a=Q_b/A$

$$\therefore\ (H-H_o)A=\frac{Q_b\cdot H}{U_a}$$

(viii) As there is no mathematical analysis available for the rate of gas exchange between the bubble cloud and the dense phase, one can use the expression of Baird and Davidson.[19] A similar expression has already been used by Partridge and Rowe.[15] Therefore, the rate of gas exchange from the bubble cloud to the dense phase is,

$$Q_E=K_g\,.\,S \qquad (12)$$

where $K_g=0.975D_g^{\frac{1}{2}}.\ (g/D_c)^{\frac{1}{4}}$

$$S=\pi.D_c^2=\pi.D_e^2.\ \left(\frac{\alpha+0.17}{\alpha-1}\right)^{\frac{2}{3}}$$

(ix) The gas in the dense phase is either completely mixed or is in plug flow. Also the batch of catalyst in the reactor is assumed to be perfectly mixed and hence uniform in temperature and activity throughout the dense phase.

With these assumptions we proceed to develop the mathematical models for the performance of a fluidised bed reactor. Consider now that we have N bubbles/unit volume of bed, each spherical and of equivalent diameter D_e, surrounded by a cloud of gas around it (Fig 2).

Let C_B denote the concentration in the bubble–cloud system at any height h in the bed. A material balance on the bubble–cloud system gives:

$$\left(\frac{1}{1-f}\right)V.U_a.\ \frac{dC_B}{dh}+Q_E.(C_B-C_D)+\ddot{V}_{CT}.C_B.\bar{K}_C=0 \qquad (13)$$

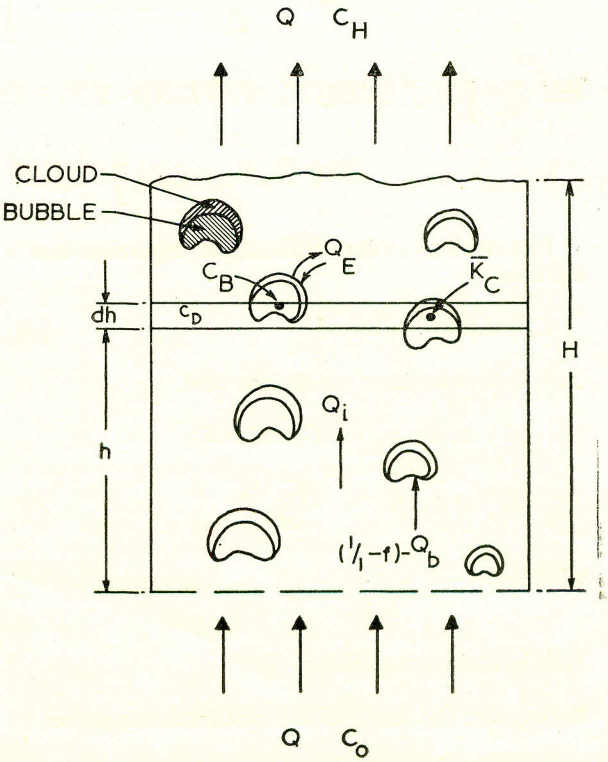

Fig. 2.

where $V_{CT}=V_C.\varepsilon_0+V_B$=total gas volume in the bubble/cloud.

(b) *Plug Flow*

Consider first that the gas in the dense phase is in plug flow. A material balance on an infinitesimal strip of height dh and total bed cross-section gives:

$$Q_i.C_D+NAQ_EC_B\mathrm{d}h=Q_i(C_D+\mathrm{d}C_D)+NAC_DQ_E\,\mathrm{d}h$$
$$+K_C[1-N(V_C+V)]\varepsilon_0.C_D.A.\mathrm{d}h$$

or $$Q_i.\frac{\mathrm{d}C_D}{\mathrm{d}h}+NA(C_D-C_B).\,Q_E$$
$$+K_C[1-N(V_C+V)]\varepsilon_0C_D\,A=0 \qquad (14)$$

Eliminating C_D from within (13) and (14) and using assumption (vii) gives a second order differential equation of the form

$$\frac{\mathrm{d}^2C_B}{\mathrm{d}h^2}+Y.\frac{\mathrm{d}C_B}{\mathrm{d}h}+Z.C_B=0 \qquad (15)$$

where $$Y=\left[\frac{(1-f)\,(V_C.\bar{K}_C+Q_E)}{U_a.V}+\frac{NAQ_E+K_CA[1-N(V_C+V)]\varepsilon_0}{Q_i}\right]$$

and $$Z=\Big[(1-f)\{NAQ_E.V_{CT}.\bar{K}_C+K_CA[1-N(V_C+V)]$$
$$\times\varepsilon_0\,(\bar{K}_CV_{CT}+Q_E)\}\Big]\div Q_iU_aV$$

The second order differential equation has a solution

$$C_B=a.e^{m_1H}+b.e^{m_2H} \qquad (16)$$

The two boundary conditions are:

(i) at $h=0$ $\quad C_D=C_B=C_0$

(ii) at $h=0$ $\quad \dfrac{\mathrm{d}C_B}{\mathrm{d}h}=C_0.L$

where $L=-\dfrac{V_{CT}.\bar{K}_C.(1-f)}{V.U_a}$ ....from equation (13)

and boundary condition (i)

m_1, m_2 are the roots of the quadratic equation

$$m^2+m.Y+Z=0$$

The constants a, b as evaluated by the two boundary conditions are:

$$a=-C_0.\left[\frac{L-m_2}{m_2-m_1}\right]$$

$$b=C_0.\left[\frac{L-m_1}{m_2-m_1}\right]$$

Equation (16) then gives the fraction of reactant unconverted in the bubble–cloud system at height H as:

$$\Phi(B)_H=(C_B/C_0)_{h=H}=\left[\frac{L-m_1}{m_2-m_1}\right].e^{m_2}$$
$$-\left[\frac{L-m_2}{m_2-m_1}\right].e^{m_1H} \qquad (17)$$

Concentration in the dense phase at height H is obtained from (13) whereby:

$$\Phi(D)_H=(C_D/C_0)_{h=H}=\left[1+\frac{V_{CT}}{Q_E}.\bar{K}_C.\right]\Phi(B)_H$$
$$+\frac{1}{1-f}\,\frac{V.U_a}{Q_E}.\frac{\mathrm{d}}{\mathrm{d}h}.\{\Phi(B)_H\} \qquad (18)$$

A material balance at the bed outlet gives:

$$\Phi(K)=\frac{Q_i}{Q}.\Phi(D)_H+\frac{Q_{CT}}{Q}.\Phi(B)_H \qquad (19)$$

Where $\Phi(K)$=fraction of reactant gas unconverted at the bed outlet.

(c) *Perfect Mixing*

With the assumption of a perfectly mixed dense phase we can take a material balance over the total bed volume. Equation (13) still applies, whereby:

$$\int_{C_0}^{C_B}\frac{\mathrm{d}C_B}{Q_E.C_D-C_B.(Q_E+V_{CT}.\bar{K}_C)}=\int_0^h\frac{1-f}{U_a.V}.\mathrm{d}h$$

or $$C_B=\frac{Q_E.C_D}{Q_E+V_{CT}.\bar{K}C}+\left[.C_0-\frac{Q_E}{Q_E+V_{CT}.\bar{K}_C}.C_D\right].$$

$$\times \exp\left[-\left(\frac{Q_E+V_{CT}.\bar{K}_C}{U_a.V}\quad(1-f)_h\right)\right] \qquad (20)$$

Where C_B represents the concentratinion in the bubble-cloud at height h. A material balance on the whole bed yields

$$NAQ_E\int_0^H C_B.dh+Q_i.C_O=Q_i.C_D+NNQ_EC_DH+K_C.C_D$$

$$\times\{1-N(V_C+V)\}AH\varepsilon_0 \qquad (21)$$

Evaluating the term $\int_0^H C_B.dh$ using equation (20), inserting the resulting values in (21) and rearranging, one gets:

$$\Phi(D)_H=\left[\frac{C_D}{C_O}\right]_{h=H}$$

$$=(J-Q_i)\div\left[J\left[\frac{Q_E}{Q_E+V_{CT}.\bar{K}_C}\right]-Q_i+NQ_EAH\right.$$

$$\left.\times\left[\frac{Q_E}{Q_E+V_{CT}.\bar{K}_C}-1\right]-K_C\left[1-N(V_C+V)\right]AH\varepsilon_0\right]$$

$$\text{where } J=NQ_EA\left[\frac{U_a.V}{(Q_E+V_{CT}.\bar{K}_C)(1-f)}.\right.$$

$$\times\left[\exp\left(-\frac{Q_E+V_{CT}.\bar{K}_C}{U_a.V}.(1-f)\,H\right)-1\right]$$

and $\Phi(B)H=(C_B/C_O)_{h=H}$ and can be evaluated by putting $h=H$ in equation 20 and, as before

$$\Phi(K)=\frac{Q_i}{Q}.\ \Phi(D)_H+\frac{Q_{CT}}{Q}.\ \Phi(B)_H \qquad (22)$$

Equations 19 and 22 were solved for experimental sets of values of U, U_O, H, H_O, D_e, ε_O and D_g, using a KDF9 computer to get the predicted conversions. The values of D_e, the average equivalent diameter of a spherical cap bubble, were obtained from the bubble frequency measurements, as explained elsewhere.[13,16] Some of the resulting graphs are shown in Figs. 3 to 10 where they are compared with the statistical 'best fit' lines through the experimental data. The complete results are tabulated elsewhere.[13]

Discussion

It is evident from Figs. 3 to 10 that the theoretical results are not always in agreement with the experimental data, the deviations of the theoretical predictions from the experimental results generally increasing with an increase in the particle size and a decrease in the bed height. This is a result of the uncertainty in some of the assumptions used in the derivation of these and the previous models,[14,15] which will be briefly discussed now.

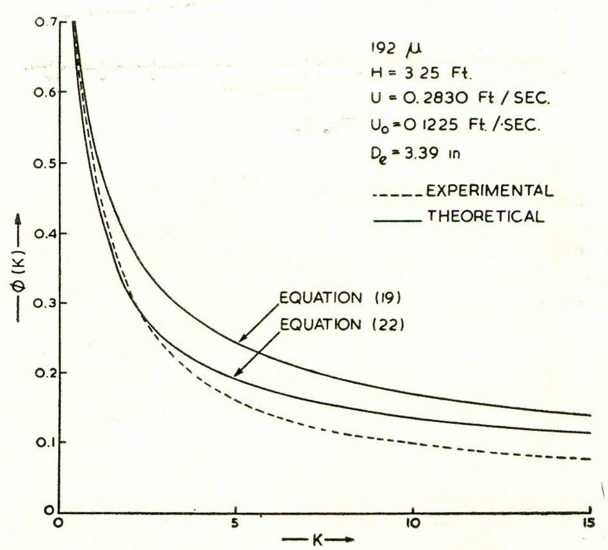

Fig. 3.

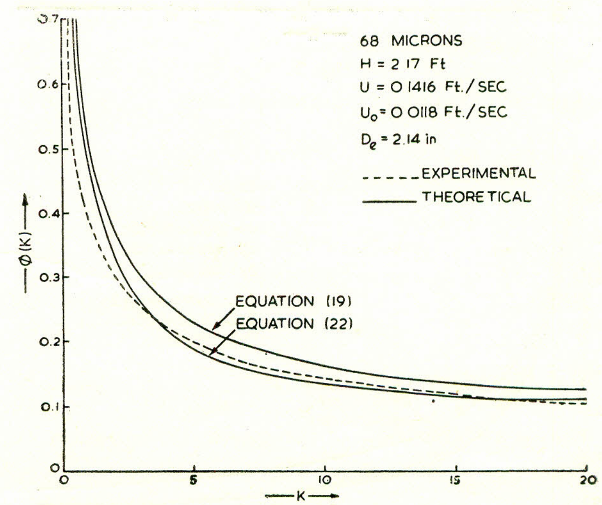

Fig. 4.

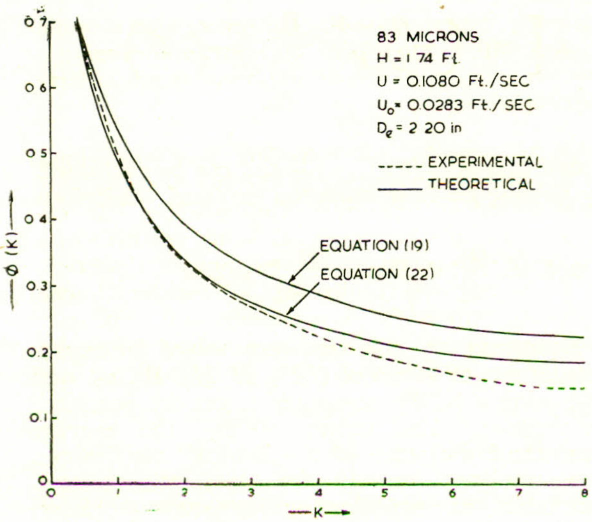

Fig. 5.

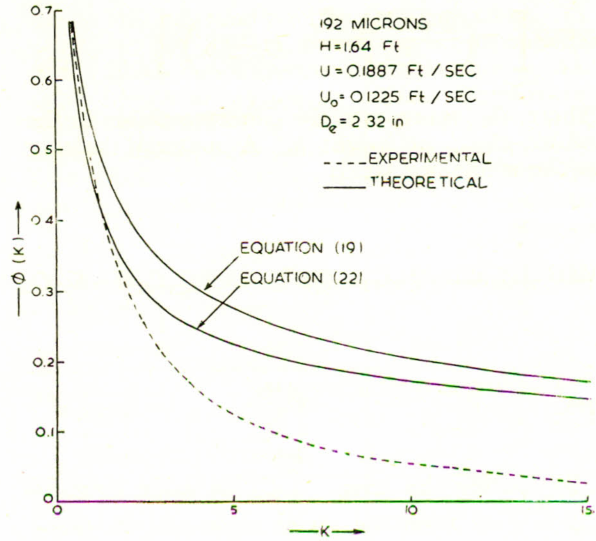

Fig. 6.

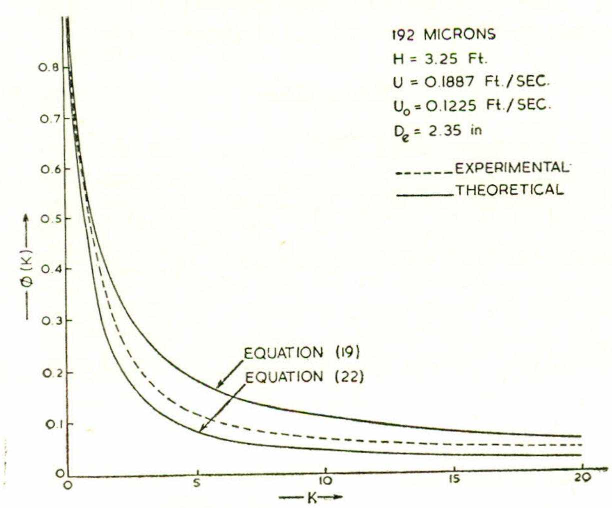

Fig. 7.

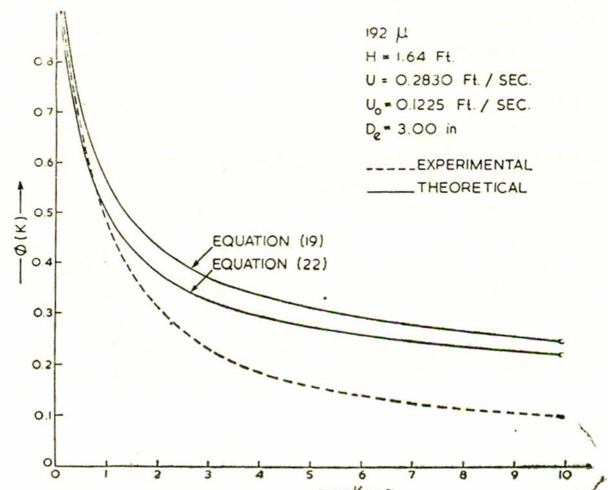

Fig. 8.

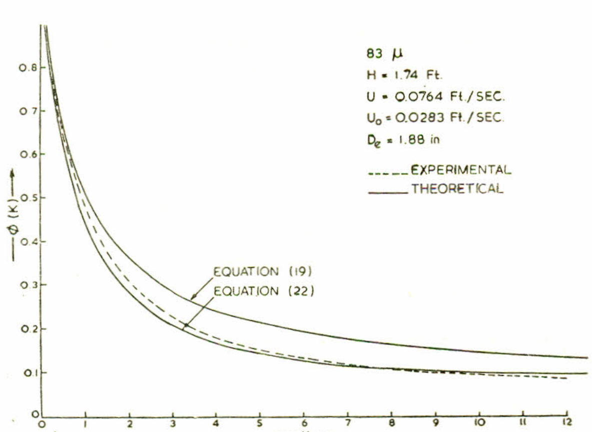

Fig. 9.

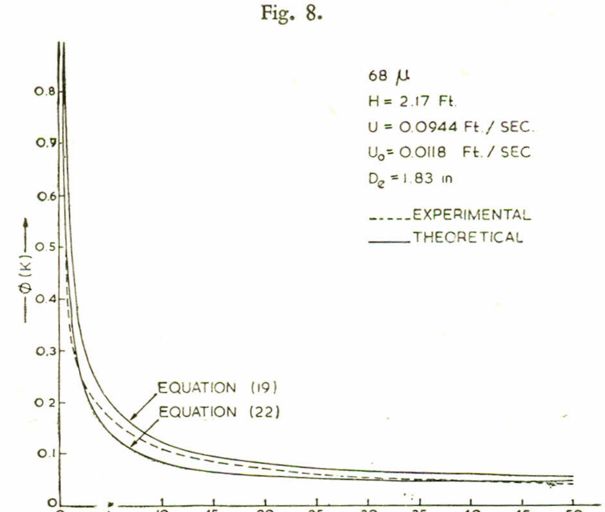

Fig. 10.

(1) So far the information about the rate of gas exchange from the cloud surface to the dense phase is limited and contradictory. Davies and Richardson[20] have recently measured this parameter experimentally and Table 1 below presents a comparison of their experimental results with the theoretical predictions of Baird and Davidson,[19] i.e. equation 12, and Partridge and Rowe.[15]

D_e(in)	Davies and Richardson U_x (in/sec)	Baird and Davidson Kg (in/sec)	Partridge and Rowe h_M (in/sec)
2.08	0.835	0.498	0.304
2.52	0.807	0.476	0.288
2.80	0.905	0.462	0.278
3.07	0.921	0.445	0.272

It is clear from the above table that the theoretical predictions of the rate of gas exchange between the cloud and the dense phase are about half of those observed experimentally and this explains the lower predicted conversions by equations 19 and 22. The agreement is good for tall beds because of an increased residence time of the bubble–cloud system in the bed, when the gas contained in the bubble–cloud system is nearly completely purged during its passage through the bed and only a fraction of the bubble–cloud gas passes unreacted.

Rowe *et al.* [21] concluded from their gas tracing experiments that the interphase gas exchange takes place by a phenomenon of cloud shedding. Whereas this phenomenon is well marked for small values of α (a large cloud volume), the gas just seeps out of the bottom of the bubble for $\alpha \geqslant 10$, and the particle wake behind the bubble is never clear. However, there is as yet no quantitative information available for this.

(2) The assumption about the mode of gas flow between the bubble and the cloud is purely theoretical and holds good only when the cloud surrounding the bubble is very small, because under these conditions the extent of reaction in the bubble–cloud system is small and can be represented by assuming that the cloud and bubble are perfectly mixed. This assumption may not be true for large particle sizes where the cloud volume is comparable to the bubble volume.

(3) It is assumed that the 'two-phase postulate' of Tooney and Johnstone holds good for all particle sizes used. This, however, is not always true,[20,23,24] as with small particles (i.e. less than 100 μ) a uniform expansion of bed takes place. This would result in a better conversion efficiency experimentally. However, the relation between the particle size and the minimum gas flow rate for spontaneous bubbling is not clearly understood so far.

(4) Assumption (v) considers that the cloud gas flow is a contribution of the gas flow through dense phase at minimum fluidisation. The residence time of the cloud gas being smaller than that of the dense phase gas, on increased particle size i.e. large cloud volume, would result in a lower conversion efficiency theoretically and this may explain a lower predicted conversion efficiency with larger particle sizes than with small particle sizes.

(5) Equations 19 and 22 consider only idealized conditions and do not take into account the experimentally observed phenomenon[25] of bubble splitting, particle raining through bubbles, the disappearance of bubbles in dense phase etc. All of these phenomenon are insufficiently known so far, and they give rise to improved gas–solid contact and better theoretical conversion efficiencies.

Conclusions

In view of the oversimplifications of the theory leading to the development of these mathematical models, the agreement between theory and experimental results is remarkable. However, it becomes clear that the present knowledge of aggregatively fluidised bed reactors is insufficient to permit the development of true and representative models of fluidised bed reactors, the chief limitation being the estimate of the rate of interphase gas exchange.

Acknowledgement.—The author wishes to acknowledge the continuous help and guidance of his supervisor, Professor P.H. Calderbank, D.Sc., Department of Chemical Engineering, University of Edinburgh, during the course of these studies. Thanks are also due to the trustees of Saigol Foundation, Lahore, for providing the financial assistance to carry out these studies.

References

1. P.F. Wace and S. J. Burnett, Trans. I. Ch. E. (London), **39**, 169 (1961).
2. J.F. Davidson, Discussion, Symp. on Fluidisation, Trans. I. Ch. E. (London), **39**, 230, (1961).
3. J.F. Davidson and D. Harrison, *Fluidised Particles* (Cambridge University Press, 1963).

4. R. Jackson, Trans. I. Ch. E. (London), **41,** 22 (1963).
5. J.D. Murray, National Science Foundation Grant E.P. 2226, Report No. 1. Harvard University, October 1963.
6. P.N. Rowe, Chem. Eng. Prog. Symp. Series, **58,** 42(1962).
7. J.W. de Kock, Ph.D. Thesis, University of Cambridge, (1961).
8. P.N. Rowe, B.A. Partridge, E. Lyall and G.M. Arden, Nature, **195,** 278(1962).
9. P.N. Rowe, Chem. Eng. Prog., **60,** 75(1964).
10. D.L. Pyle and P.L. Rose, Chem. Eng. Sci., **20,** 25(1965).
11. P.L. Rose, Ph.D. Thesis, University of Cambridge (1965).
12. F.H. Lancaster, Ph.D. Thesis, University of Edinburgh (1965).
13. F.D. Toor, Ph.D. Thesis, University of Edinburgh (1967).
14. P.N. Rowe, B.A. Partridge and J.G. Yates, Proceedings International Symposium on Fluidisation, Holland (1967), pp. 711.
15. B.A. Partridge, and P.N. Rowe, Trans. I. Ch. E. (London), **44,** T335 (1966).
16. P.H. Calderbank, F.D. Toor and F.H. Lancaster, Proceedings International Symposium on Fluidisation, Holland (1967), pp. 652.
17. F.D. Toor, and P.H. Calderbank, *Ibid.*, p. 373.
18. R.M. Davies and Sir Geoffery Taylor, Proc. Roy. Soc., **A-200,** 375 (1950).
19. M.H.I. Baird and J.F. Davidson, Chem. Eng. Sci., **17,** 87(1962).
20. L. Davies and J.F. Richardson, Trans. I. Ch. E. (London), **44,** T293(1966).
21. P.N. Rowe, B.A. Partridge and E. Lyall, Chem. Eng. Sci., **19,** 973(1964).
22. R.D. Toomey and H.F. Johnstone, Chem. Eng. Prog., **48,** 220(1952).
23. J.F. Richardson and L. Davies, Nature, **199,** 898(1963).
24. D.L. Pyle and D. Harrison, Chem. Eng. Sci., **22,** 1199(1967).
25. P.N. Rowe and B.A. Partridge, Chem. Eng. Sci., **18,** 511 (1963).

Nomenclature

a, b	Arbitrary constants of equation (16)
A	Area of cross-section of bed
A_{CT}	Area of cross section of bubble and cloud
C_B	Concentration in the bubble–cloud system at any height h
C_D	Concentration in the dense phase
C_H	Reactant concentration at bed exit
C_O	Inlet reactant concentration
D_C	Diameter of cloud
D_e	Equivalent diameter of a spherical cap bubble
D_g	Gas phase diffusion coefficient
f	Fraction of total gas in bubble and cloud that is in cloud
g	Acceleration of gravity
H	Total bed height
H_O	Bed height at minimum fluidisation
h_M	Mass transfer coefficient—reference 15
J,L	Constants
K_C	Rate constant for the first order reaction (concentration–volume basis)
$\bar{K}_C$	Rate constant for the bubble-cloud gas.
K	Diamensionless rate constant= $(K_C H_O \varepsilon_o/U)$
K_g	Mass transfer coefficient—reference 19
m_1, m_2	Roots of quadratic equation
N	No. of bubbles/unit volume of bed
Q	Total gas flow rate
Q_b	Bubble gas flow rate
Q_E	Total gas flow rate from the bubble–cloud to the dense phase
Q_o	Gas flow rate at minimum fluidisation
Q_i	Intersticial gas flow rate
Q_{CT}	Total gas flow rate through bubble and cloud
S	Surface area of the cloud
U	Superficial gas velocity
U_a	Absolute rise velocity of bubble
U_b	Natural rise velocity of bubble
U_o	Gas velocity at minimum fluidisation
V	Volume of bubble
V_C	Volume of cloud
V_{CT}	Total gas volume in the bubble–cloud.
Y,Z	Constants of equation 15
α	$=\dfrac{U_b \cdot \varepsilon_o}{U_o}$
ε_o	Voidage at minimum fluidisation
$\Phi(B)_H$	Fraction of reactant unconverted in the bubble–cloud system at bed exit.
$\Phi(D)_H$	Fraction of reactant unconverted in the dense phase at bed exit
$\Phi(K)$	Overall fraction of reactant unconverted at the bed exit.