Fluidized-Bed Reactor Model Verification on a Reactor of Industrial Scale

Previous published comparisons between fluidized-bed reactor models and experimental data have almost exclusively been in laboratory and pilot-plant scale equipment. This paper compares data obtained in an industrial phthalic anhydride reactor of 2.13 m dia. using naphthalene as the feedstock with three models, the Kato and Wen bubble-assemblage model, the Kunii and Levenspiel three-phase bubbling-bed model, and Grace's two-phase bubbling-bed model. For the conditions of operation ($U = 0.43$ m/s, $\bar{d}_p = 53$ μm, $H = 7.9$ m, $T = 636$ K), all three models give similar predictions and each gives a good overall prediction of the conversion and selectivity if the reaction kinetics are based on the early study of DeMaria et al. (1961). Hydrodynamic parameters needed for the models are calculated from equations available in the literature. Grid and freeboard effects appear to play relatively minor roles in determining the overall conversion and yields for the reactor in question.

J. E. Johnsson
Department of Chemistry and Chemical Engineering
Engineering Academy of Denmark
2800 Lyngby, Denmark

J. R. Grace
Department of Chemical Engineering
University of British Columbia
Vancouver, Canada V6T 1W5

J. J. Graham
Badger Engineers, Inc.
Cambridge, MA 02142

Introduction

A large number of models have been devised to describe fluidized-bed catalytic reactors operating in the bubbling regime. Testing of these models has generally been carried out via experiments in laboratory-scale equipment with simple first-order reactions, limiting the range of conditions under which the models have been investigated and leaving open the question of how well the models work as tools for scale-up, for complex kinetics, and for simulation of industrial-scale units. In this paper we compare data for an industrial reactor of 2.13 m dia. having an expanded bed depth of 7.9 m with predictions from three representative models, those of Kunii and Levenspiel (1969), Kato and Wen (1969), and Grace (1984). The industrial fluidized-bed reactor was used for the manufacture of phthalic anhydride by catalytic oxidation of naphthalene. Concentrations of an intermediate product, naphthoquinone, as well as that of phthalic anhydride in the product, and the overall conversion of naphthalene have been measured, and these data are compared with values predicted by the models. The bed operated at a superficial gas velocity of 0.43 m/s with a catalyst of 53 μm mean dia., a temperature of 636 K, and a pressure of 266 kPa.

In order to apply the models to the data, measured bed properties and published relationships have been used to calculate bubble diameters, interphase mass transfer rates, and other hydrodynamic parameters. No parameters have been fitted, although we have performed a series of calculations to test the sensitivity of the models to possible variations in a number of factors. Both the kinetic expressions of De Maria et al. (1961) and of Westerman (1980) have been employed. Separate calculations have been carried out to estimate the possible influence of the grid and freeboard regions.

All three of the reactor models investigated give predictions that are in good agreement with yields obtained in the industrial reactor when the models are combined with the kinetic model of De Maria et al. and bubble sizes estimated from hydrodynamic considerations. The differences among the three models are small for the conditions investigated, with the predictions being most sensitive to the kinetic expressions employed and to the estimated bubble sizes. Separate consideration of the grid region does not appear to be needed to simulate the reactor performance for the reactor conditions adopted. Accounting for the freeboard region results in a slight overall improvement in the predictions, but the role of the freeboard appears to be relatively minor for the given reactor, in agreement with the fact that temperature changes were observed to be negligible above the dense bed surface.

Phthalic Anhydride Reactor

There are very few published data showing reaction conversions and yields in fluidized-bed reactors of a size larger than about 0.6 m dia. Although models can be used for complex reactions in commercial-size units (Dutta et al., 1984), data are

Correspondence concerning this paper should be directed to J. R. Grace.

needed to allow discrimination between alternate models and to assist in their improvement.

Phthalic anhydride has been manufactured both from naphthalene and from o-xylene, in both fixed and fluidized beds. The fluid-bed process for making phthalic anhydride by the catalytic oxidation of naphthalene was a successful application of fluidized beds (Graham et al., 1962), but it has now been supplanted in the United States by fixed-bed processes, which can utilize either naphthalene or o-xylene as the feedstock by changing catalysts (Montgomery and Farkas, 1984). The fluidized-bed process is still used in the Far East where naphthalene is the available feedstock. Previously unpublished data on a fluid-bed phthalic anhydride reactor that utilized the Badger process allow us to test the value of representative reactor models on a reactor that is significantly larger than those for which data have been reported previously in the open literature.

The industrial reactor was a cylindrical vessel of 2.13 m dia. and 13.7 m overall height equipped with vertical tubes occupying approximately 9% of the vessel cross-sectional area for a depth of 7.0 m. The grid was of a dished design with 56 air entry ports. Naphthalene feed was introduced as a liquid spray through three nozzles, each approximately 0.3 m from the wall. Catalyst properties, operating conditions, and corresponding conversion and yield data for the reactor are given in Table 1. The molar flow rates of gas entering and leaving the reactor are seen to be very nearly equal, so that volume changes due to reaction can be neglected. It was not possible to detect naphthalene in the outlet stream; given the detection threshold for the analyzer (~500 ppm), this implies an unconverted naphthalene fraction near 0 and certainly less than 2%.

Table 1. Operating Conditions and Reactor Performance, Industrial Phthalic Anhydride Reactor

Operating temp.	636 K	
Operating press.	266 kPa	
Expanded bed ht.	7.9 m	
Expanded bed dens.	350 kg/m^3	
Superficial gas veloc.	0.43 m/s	
Catalyst properties		
Particle dens.	1,200 kg/m^3	
Bulk dens.	770 kg/m^3	
Size dist.	Size, μm	Mass, %
	0–15	1.5
	0–20	7
	0–44	28
	0–74	44
	0–105	60
	0–148	81
	0–175	90

Mean size = $1/\Sigma\, x_i/d_{pi} = 53\ \mu$m

Molar Balance on Fluid Inlet and Outlet Streams

Component	Mol. Wt.	Flow, kmol/h In	Flow, kmol/h Out
Nitrogen	28.0	192.3	192.3
Argon	39.9	2.2	2.2
Oxygen	32.0	51.7	25.5
Carbon monoxide	28.0	0	2.95
Carbon dioxide	44.0	0	11.58
Water	18.0	3.2	14.94
Naphthalene	128.2	5.21	<0.1
Other feed hydrocarb	129.9	0.08	0
Naphthoquinone	158.2	0	0.068
Phthalic anhydride	148.1	0	4.64
Maleic anhydride	98.1	0	0.168
Total	—	254.7	254.3

Naphthalene unconverted	<2.0%
Conv. to phthalic anhydride	88.94%
Conv. to naphthoquinone	1.31%
Conv. to maleic anhydride	3.22%
Oxidation to CO, CO_2, H_2O	6.5%

Bed Hydrodynamics

Standard correlations and relationships in the literature have been employed to estimate key hydrodynamic quantities required as input to the reactor models to be tested below. Values of these quantities and their sources are listed in Table 2.

Several of the quantities require special comment. The catalyst material falls into group A of Geldart's classification for room-temperature operation as well as for the temperature and pressure of operation (Grace, 1986a). There are limited data available to allow prediction of the hydrodynamic regions of operation. Data of Yerushalmi and Cankurt (1979) for small-scale columns have been correlated by Grace (1982) and suggest a transition velocity for initiation of the turbulent regime of fluidization of the order of 1 m/s; however, this transition velocity appears to decrease with increasing bed diameter, and Avidan (1982) has suggested that the transition may occur for U as low as 0.3 m/s for catalysts of 62 μm mean size in industrial-scale reactors. Although the industrial bed considered here is sufficiently deep for slugging, the bubble sizes derived from bed expansion or from maximum stable size considerations (see below) are much less than the column diameter and also less than the intertube spacing. Therefore slugging seems highly improbable. It seems very likely that the bed operated in the bubbling regime, although turbulent conditions cannot be ruled out as a possibility.

Assuming operation in the bubbling regime, we require values of ϵ_b and ϵ_d, the fraction of bed volume occupied by bubbles and the dense phase voidage, respectively. From the reported bed and particle densities, Table 1, the overall bed voidage is

$$\bar{\epsilon} = 1 - 350/1{,}200 = 0.707 = \epsilon_b + (1 - \epsilon_b)\epsilon_d \qquad (1)$$

Table 2. Derived Properties and Hydrodynamic Quantities

Quantity	Value	Source
Gas dens.	1.56 kg/m^3	—
Gas viscos.	3.2×10^{-5} Ns/m^2	—
Archimedes no.	2.7	—
Min. fluidiz. veloc.	7.7×10^{-4} m/s	Grace (1982)
Static bed voidage	0.36	Bulk and particle dens.
Min. bubbling veloc.	5.0×10^{-3} m/s	Geldart & Abrahamson (1980)
Regime of operation	Bubbling (or turbulent)	See text
Dense phase voidage	0.44–0.55	See text
Bubble volume frac.	0.48–0.35	See text
Bubble dia.	0.045–0.129 m	See text
Corresp. bubble rise veloc.	0.90–1.23 m/s	Eq. 3
Naphthalene diffus.	1.06×10^{-5} m^2/s	*Int. Crit. Tables*

Table 3. Naphthalene Oxidation Reaction Schemes

Reaction Scheme	Ref
NA → NQ → PA → MA, CO, CO_2 NA → PA	De Maria et al. (1961)
NA → PA → MA NA → CO, CO_2	Smith & Carberry (1975)
NA → PA → MA, CO, CO_2	Carberry & White (1969)
NA → NQ → PA NA → CO, CO_2	Westerman (1980)

NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; MA, maleic anhydride.

If either ϵ_d or ϵ_b is known, the other can be calculated from Eq. 1. For such a fine catalyst, the dense phase expands beyond the voidage corresponding to minimum fluidization, ϵ_{mf}. For the catalyst here, the static bed voidage, determined from particle and bulk densities, is 0.36, and it seems unlikely that ϵ_{mf} would be so low for such a fine material. Correlations proposed by Abrahamson and Geldart (1980) and Chen et al. (1984) can be used to estimate ϵ_d providing that ϵ_{mf} is known. The corresponding ϵ_d values are 0.42 and 0.47, respectively, for $\epsilon_{mf} = 0.36$, and are 0.47 and 0.55, respectively, for the more realistic value of $\epsilon_{mf} = 0.42$. We consider the most likely range of ϵ_d to extend from 0.44 to 0.55. The corresponding range of ϵ_b is 0.48 to 0.35. The bubble volume fraction, ϵ_b, is also linked to the mean bubble diameter, d_b, by the relationship

$$\epsilon_b = Y(U - U_{mf})/v_b \tag{2}$$

where v_b is the bubble velocity given by

$$v_b = 0.711\sqrt{gd_b} + (U - U_{mf}) \tag{3}$$

(Davidson and Harrison, 1963) and Y can be taken as close to unity for the deep bed employed here (Peters and Grace, 1987). Hence values of d_b can be derived for each ϵ_b. These values range from 0.04 m to 0.13 m for the ϵ_b range specified above. It may be noted that this d_b range exceeds the maximum stable bubble diameter, 0.02 m, calculated using a procedure suggested by Geldart (Grace, 1982). This procedure is at best approximate and appears to have originated only for systems operated at atmospheric temperature and pressure. In addition, such a small bubble size would lead to the unrealistic ϵ_b and ϵ_d values of 0.57 and 0.33, respectively, from Eq. 1 to 3.

Kinetics of Catalytic Oxidation of Naphthalene to Phthalic Anhydride

The oxidation of naphthalene is rather complex and involves several byproducts and intermediates. An extensive review has been prepared by Wainwright and Foster (1979).

Most researchers have chosen to simplify the complex reaction scheme. Reaction sequences commonly adopted are shown in Table 3. In the data that are available from the industrial phthalic anhydride reactor in this study, naphthoquinone has been found in the product stream. Therefore the simple series reaction pathways in Table 3 cannot be used, and we require one of the more complex schemes. In this work we have attempted to use the reaction kinetics of both De Maria et al. (1961) and Westerman (1980). Although the latter is a more rigorous kinetic study, we have had to reply primarily on the earlier study since the catalyst formulation in the industrial reactor appears to have been much closer to that employed in the De Maria et al. study, and since maleic anhydride was recorded in the reactor outlet stream (but is not included in the Westerman kinetic model). Nevertheless, some comparison with the Westerman model is reported below.

The data of De Maria et al. are rather difficult to interpret. Reaction orders appear in Table 4. At low naphthalene concentrations the order of the naphthalene oxidation with respect to naphthalene is unity, but decreases as the concentration increases. It is suggested that first-order kinetics can be used for naphthalene feed concentrations of about 1% or less. For the industrial reactor, naphthalene constitutes 2 mol % of the feed, but most of the reaction takes place in the dense phase where the concentration is considerably lower, so these reactions are taken to be first order.

An intrinsic rate constant was given by De Maria et al. only for k_4, the other rate constants reported being derived from laboratory fluidized-bed experiments. The reactors were assumed to behave as integral reactors, probably assuming plug flow. After converting so that the rate constants are based on particle volume, the rate constants at the reactor temperature are estimated as shown in Table 4 from the data for catalyst A employed by De

Table 4. Reaction Kinetics Derived from De Maria et al. (1961)

Reaction	Reaction Order: Organic Species	Reaction Order: Oxygen	Assumed True Kinetics	Assumed Pseudo-first-order Rate Constants
1. NA → NQ	0.5 to 1	~1	$-\frac{1}{V_p}\frac{dN_{NA}}{dt} = k_1 C_{NA} C_{O_2}$	$K_1 = k_1 C_{O_2} = 1.8\ s^{-1}$
2. NA → PA	0.5 to 1	~1	$-\frac{1}{V_p}\frac{dN_{NA}}{dt} = k_2 C_{NA} C_{O_2}$	$K_2 = k_2 C_{O_2} = 1.8\ s^{-1}$
3. NQ → PA	~1	—	$-\frac{1}{V_p}\frac{dN_{NQ}}{dt} = k_3 C_{NQ}$	$K_3 = k_3 = 4.6\ s^{-1}$
4. PA → OP	~1	~0.8	$-\frac{1}{V_p}\frac{dN_{PA}}{dt} = k_4 C_{PA} C_{O_2}^{0.8}$	$K_4 = k_4 C_{O_2}^{0.8} = 0.023\ s^{-1}$

NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products of PA (primarily maleic anhydride, CO, and CO_2).

Maria et al., catalyst B having been shown to give predictions that diverge widely from the model predictions (Johnsson, 1986). There is little information available for comparison with these constants. Smith and Carberry (1975) employ rate constants that are significantly lower than those given above. On the other hand, Ross and Calderbank (1971) give a value equivalent to $k_1 + k_3$, which is within about 20% of the corresponding value from above. In view of the uncertainty, we employ the De Maria et al. constants given above, but report some studies below where the absolute (but not the relative) values of k_1, k_2, k_3, and k_4 are varied in order to test the sensitivity of the model predictions to the kinetic rate constants.

Because of the small sizes of the catalyst particles employed in the phthalic anhydride reactor, the catalyst effectiveness factor was assumed to be unity in all of the reactor simulations.

Bubbling-Bed Models: Predictions and Comparison with Measured Results

The fluidized bed can be considered to consist of a grid region, a bubbling bed, and the freeboard. It is shown below that the grid and freeboard zones have relatively little influence for the reactor in question. Accordingly, this section compares experimental predictions with predictions derived from models where the entire bed is taken to be in the bubbling regime.

There are many models available for predicting the performance of bubbling fluidized-bed reactors. For reviews see Grace (1971, 1986b,c) and Yates (1983). While most of the models were originally devised for simple first-order kinetics, several models have been extended to apply to more complex reaction schemes (El Nashaie and Yates, 1972; Shaw et al., 1974; Irani et al., 1980; Jaffres et al., 1984; Grace, 1986b).

It is beyond the scope of this paper to compare the industrial data with all available models. Table 5 lists the major features of four bubbling-bed models that are representative of those in the literature. For the phthalic anhydride reactor being treated in this paper, $U \gg U_{mf}$ so that there is little reason to choose a model that allows for emulsion or dense phase flow of gas. The Orcutt et al. (1962) model has also not been very successful in predicting performance for smaller reactors (Chavarie and Grace, 1975; Shaw et al. 1974). The bubble-assemblage model of Kato and Wen (1969) and Yoshida and Wen (1970) was found to give the best results of models tested by Shaw et al. for hydrogenolysis of n-butane (a complex reaction), by Stergiou and Laguerie (1984), and by Jaffres et al. (1984). The Kunii and Levenspiel (1969) model is widely used and was the most successful of the early models tested by Chavarie and Grace (1975). The two-phase bubbling-bed model of Grace (1984) also gives excellent agreement with the Chavarie and Grace data, is simpler to apply than the Kunii and Levenspiel model, and gives a better description of interphase mass transfer, a key feature in modeling fluid-bed reactors. Hence we restrict our attention to the last three models listed in Table 5. In applying

Table 5. Features of Four Fluidized-Bed Reactor Models

Orcutt et al. (1962)	Kunii & Levenspiel (1969)	Kato & Wen (1969)	Grace (1984)
		Phases	
Two 1. Bubble 2. Dense	Three 1. Bubble 2. Cloud + wake 3. Emulsion	Two 1. Bubble + cloud (or cloud + wake) 2. Emulsion	Two 1. Bubble 2. Dense
		Particles Associated with Bubbles	
Bubbles empty of particles	Particles in bubbles	Bubbles empty of particles	Particles in bubbles
		Gas Flow in Bubble Phase	
$(U - U_{mf})A$, plug flow (mixed in each bubble)	UA (in simple model), plug flow (mixed in bubble, mixed in cloud + wake)	UA, perfectly mixed in each compartment*	UA, plug flow (mixed in each bubble)
		Gas Flow in Dense or Emulsion Phase	
$U_{mf}A$, (a) mixed flow or (b) plug flow	None	None, perfectly mixed in each compartment*	None
		Interphase** Mass Transfer	
B–D; Davidson & Harrison (1963), diffusion + throughflow	B–C; Davidson & Harrison (1963), diffusion + throughflow C–E; Kunii & Levenspiel (1969), diffusion	C–E; Kobayashi et al. (1966), diffusion	B–D; Sit & Grace (1981), diffusion + throughflow
		Bubble Size	
Constant	Constant	Varies with height	Constant
		Reaction Takes Place in	
Dense phase exclusively	All three phases	Emulsion + cloud phases, or cloud + wake phases	Both phases

*Tanks in series model.
**Phase: B, bubble; D, dense; C, cloud; E, emulsion.

Table 6. Principal Cases for which Outlet Concentrations were Predicted by Reactor Models (Base Case Values Underlined)

1	2	Case 3	4	5
		Reactor Model		
Grace (1984)	Grace (1984)	Grace (1984)	Kunii & Levenspiel (1969)	Kato & Wen (1969)
		Chemical Kinetics		
De Maria et al. (1961)	De Maria et al. (1961)	Westerman (1980)	De Maria et al. (1961)	De Maria et al. (1961)
		Method of Solution		
Analytical	Numerical	Numerical	Numerical	Numerical
		Parameters Varied and Range of Values		
A. Bubble dia. d_b = 0.04–0.13 m (0.09 m) B. $\mathcal{D}$ of organics, 6.9 to 10.6 × 10^{-6} m^2/s C. Kinetic const., as in Table 4, and with each K_i augmented 40% D. Solids in bubble phase, ϕ_b = 0 and 0.0035	A. O_2 conc. constant throughout bed, or allowed to vary	—	A. Wake frac. f_w = 0.2 and 0.4 B. Eff. dense phase diffus. $\mathcal{D}_e = \mathcal{D}$ and $\epsilon_d \mathcal{D}$	A. Dilute phase solids, cloud only, or cloud + wake included with dilute phase

these models we have endeavored to restrict ourselves to the assumptions of the reactor models themselves. In order to use the models we require also the kinetic models and hydrodynamic relationships discussed above.

Five base cases have been taken and are listed in Table 6. The equations solved in each case are listed in a report by Johnsson (1986) that is available from the authors. Key assumptions appear in Table 5. In all cases we ignore changes in gas volume due to reaction and to hydrostatic pressure gradients. The molecular diffusivity of napthoquinone and phthalic anhydride have been taken as equal to that for naphthalene. Parametric studies have been carried out to investigate the influences of several factors that are subject to uncertainty. The parameters varied, the range of variation and base case values are indicated in Table 6. The base case values are believed to be the best available, or the most consistent with the intentions of the originators of the reactor models, so they are used except where otherwise specified. Some comparisons between predictions and the outlet concentrations, C', expressed in dimensionless form by dividing by the inlet naphthalene concentration, follow.

(a) *Reactor Model Comparison.* Table 7 gives a comparison between predictions from the three reactor models, all with the De Maria et al. kinetics assumed and for a bubble size of 0.09 m. The final column is a pseudoconcentration of unwanted byproducts (maleic anhydride, CO, CO_2, etc.) formed with different stoichiometric constants by oxidation of the desired phthalic anhydride. All three models are seen to give quite good predictions. The Kato and Wen model gives the best predictions of phthalic anhydride (PA) but the poorest prediction of naphthoquinone (NQ) intermediate. The Kunii-Levenspiel model, by contrast, gives the best prediction of the amount of NQ but is most in error in its predictions of the PA yield and the amount of unconverted naphthalene. The Grace model is generally between the other two models.

Table 7. Comparison of Three Reactor Models with Data from Industrial Unit

Model*	Outlet Conc./Inlet NA Conc. × 100% NA	NQ	PA	OP
Kunii & Levenspiel (1969)	2.13	0.95	86.2	10.7
Kato & Wen (1969)	0.14	0.11	88.8	10.9
Grace (1984)	1.28	0.55	87.5	10.7
Measured	~0(<2)	1.31	88.9	~9.8

*All with kinetics of De Maria et al. (1961) as in Table 5, and with d_b = 0.09 m.

NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products.

(b) *Influence of Bubble Diameter.* The influence of bubble diameter (with simultaneous changes in ϵ_b and ϵ_d to satisfy Eq. 1 to 3) is illustrated in Table 8. Increasing the bubble size is seen to lead to improved prediction of concentration of the intermediate product NQ, but at the expense of less accurate predictions of PA and NQ concentrations. The predicted naphthalene (NA) and NQ concentrations are quite sensitive to the bubble sizes adopted.

(c) *Effect of Organics Molecular Diffusivity.* The base value of $\mathcal{D}$ was obtained from the *International Critical Tables* value for naphthalene at 0°C and 1 atm (101.3 kPa) and adjusted assuming $\mathcal{D} \propto T^2 p^{-1}$. If $\mathcal{D}$ is instead assumed proportional to $T^{1.5} p^{-1}$, a lower value of $\mathcal{D}$ results. As shown in Table 9, the decrease in $\mathcal{D}$ results in a somewhat improved prediction of NQ but worse predictions for NA and PA. The influence of this variable is seen to be rather small.

(d) *Influence of Kinetic Rate Constants.* As discussed above, the kinetic rate constants obtained from the study of De Maria et al. are subject to some uncertainty. It is not possible to estimate the extent of mass transfer disguise in the De Maria data because the experimental conditions were not specified. To illustrate what the effect of error might be, Table 9 (case 1C) gives results for a case where K_1, K_2, K_3, and K_4 in Table 4 are all arbitrarily augmented by 40%. (A more valid approach would be to apply different factors to the four constants, but there is no information available to allow us to estimate the correction fac-

Table 8. Influence of Bubble Diameter for Case 1, Table 6*

	Values						
	Predicted						Meas.
d_b, m	0.043	0.060	0.075	0.090	0.11	0.126	—
ϵ_b	0.48	0.44	0.41	0.39	0.37	0.35	—
ϵ_d	0.44	0.48	0.50	0.52	0.54	0.55	—
	Concentration, %						
C'_{NA}	0.01	0.12	0.49	1.28	3.23	5.47	~0(<2)
C'_{NQ}	0.02	0.10	0.28	0.55	0.99	1.35	1.31
C'_{PA}	89.1	89.0	88.5	87.5	85.1	82.6	88.9
C'_{OP}	10.8	10.8	10.7	10.7	10.6	10.6	~9.8

*Grace (1984) model with Table 4 kinetic constants.
NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products.

tors.) Comparing predictions for this case with case 1 and with the measured values, we see that the increase in K_i values results in worse predictions for both NQ and PA concentrations. The effect of variations in the kinetic rate constants is seen to be quite significant.

(e) *Influence of Solids in Bubble Phase.* Case 1D in Table 9 can be compared with the corresponding base predictions, case 1, to see the effect of the fraction of bubble volume occupied by solids. Letting $\phi_b \rightarrow 0$ results in somewhat worse predictions for NA, NQ, and PA, although the change is very small in each case.

(f) *Influence of Variable Oxygen Concentration.* De Maria et al. do not provide information on the concentration of oxygen in their kinetic experiments. It seems probable that they used a feed of ~1% naphthalene in air in an integral reactor with high conversion. This means that the oxygen concentration would have changed from about 20.5 to 15 mol %, and a mean concentration of 17.75 mol % has been assumed in evaluating K_1 to K_4. To obtain the values shown for case 2A in Table 9, the rate constants at each bed level have been corrected using the actual predicted O_2 concentration at that level. Since the oxygen concentration changes slowly with height and the molecular diffusivity of oxygen is much larger than that of naphthalene, differences in oxygen concentration between the bubble and dense phases at a given level have been neglected in this calculation. Comparing column 2A with column 1D, we find that the NA concentration is worse, while the NQ and PA predictions are improved somewhat by this modification.

(g) *Alternative Kinetic Scheme.* Predictions of the same reactor model combined with the chemical kinetics reported by Westerman (1980) appear under case 3 in Table 9. Westerman must have used a more active catalyst with improved selectivity toward PA. The predicted conversion to PA is too high and the amount of oxidation products much too low compared with the industrial reactor. For this reason the Westerman kinetic results have not been used further in this study. Clearly catalyst *A*

Table 9. Influence of Various Parameters Subject to Uncertainity on Predictions from Grace (1984) Model

	Case						
	1	1B	1C	1D	2A	3	Exp.
	Molecular Diffusivity of Organic Species, $\mathcal{D} \times 10^6$, m^2/s						
	10.6	6.9	10.6	10.6	10.6	10.6	—
	Bed Solids Fraction Assigned to Bubble Phase, ϕ_b						
	0.0035	0.0035	0.0035	0.0	0.0	0.0	—
	Oxygen Concentration						
	Constant	Constant	Constant	Constant	Varies	Constant	—
	Kinetics						
	De Maria et al. (1961)	De Maria et al. (1961)	Modified De Maria et al.	De Maria et al. (1961)	De Maria et al. (1961)	Westerman (1980)	—
	Pseudofirst-order Reaction Rate Constants, K_1–K_4						
	Table 4	Table 4	Table 4 values × 1.4	Table 4	Table 4	N.A.	—
	Concentration, %						
C'_{NA}	1.28	2.22	0.88	1.64	2.27	0.57	~0(<2)
C'_{NQ}	0.55	0.79	0.36	0.53	0.56	0.04	1.31
C'_{PA}	87.5	86.3	84.0	87.1	89.4	98.6	88.0
C'_{OP}	10.7	10.6	14.8	10.7	7.8	0.8	~9.8

NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products

investigated by De Maria et al. was much closed to the catalyst employed in the industrial phthalic anhydride reactor.

(h) *Influence of Wake Fraction, Kunii-Levenspiel Model.* The wake fraction is estimated to be approximately 0.4 from results summarized in Kunii and Levenspiel (1969) and Grace (1982). However, this could be in error by as much as a factor of 2. In Table 10 predictions for $f_w = 0.2$ are compared with those for $f_w = 0.4$ and with the measured concentrations. The decrease in wake fraction is seen to make predictions worse for NA and PA while improving the NQ prediction. The naphthalene concentration is most sensitive to changes of this parameter.

(i) *Influence of Dense Phase Effective Diffusivity.* Kunii and Levenspiel state that $\mathcal{D}_e$ can take values from $\epsilon_d\mathcal{D}$ to $\mathcal{D}$. Comparison of cases 4 and 4B in Table 10 show that changing $\mathcal{D}_e$ over this range has a relatively small influence and that the effect is again to make agreement worse with the measured NA and PA concentrations while giving some improvement in the NQ prediction.

(j) *Solids Included with Bubble Phase, Kato-Wen Model.* In their original model, Kato and Wen (1969) included particles in the clouds with the bubble phase. In a later paper (Yoshida and Wen, 1970), the wake was also included with the dilute phase. Comparison of cases 5 and 5A in Table 10 shows that this modification causes a significant drop in the predicted NA and NQ concentrations. Agreement with the measured data appears to be somewhat better for the original model, which included only the cloud with the bubble phase.

(k) *Turbulent Regime Model.* In all of the cases considered above, the bed was assumed to operate in the bubbling bed regime. While this appears to be the most likely regime of operation, there is some possibility, as discussed earlier, that the bed may have operated in the turbulent regime of fluidization. Models for fluidized beds operating in the turbulent regime are not well developed. Van Swaaij (1978) and Wen (1979) have proposed that a single-phase plug flow model may be appropriate, while Avidan (1982) suggested that considerable axial dispersion exists. All three agree that interphase mass transfer resistances should be negligible. A comparison between the two limiting cases of single-phase plug flow and CSTR models with the bubbling-bed model (case 1) and experimental data appears in Table 11. The single-phase plug flow model does an excellent job in predicting the PA concentration, but greatly underpredicts the NQ concentration, whereas the single-phase perfectly mixed model overpredicts the NA and NQ concentrations while underpredicting the yield of phthalic anhydride. The bubbling-bed model generally gives better predictions than either of these limiting turbulent regime models.

Table 10. Influence of Various Parameters Subject to Uncertainty on Predictions from Kunii and Levenspiel (1969) and Kato and Wen (1969) Models

	Case*					
	4	4A	4B	5	5A	Exp.
	Wake Volume per Unit Bubble Volume, f_w					
	0.4	0.2	0.4	n.a.	0.4	—
	Effective Dense Phase Diffusivity, $\mathcal{D}_e$					
	$\mathcal{D}$	$\mathcal{D}$	$\epsilon_d\mathcal{D}$	n.a.	n.a.	—
			Bubble Phase Solids			
	None	None	None	Cloud only	Cloud + wake	—
	Concentration, %					
C'_{NA}	2.13	3.57	2.48	0.14	0.002	~0(<2)
C'_{NQ}	0.95	1.38	1.17	0.11	0.003	1.31
C'_{PA}	86.2	84.4	85.7	88.8	89.0	88.9
C'_{OP}	10.7	10.7	10.7	10.9	11.0	~9.8

*See Table 6 for other details on cases

Kinetics of De Maria et al. (1961); $d_b = 0.09$ m; $\mathcal{D} = 10.6 \times 10^{-6}$ m^2/s

n.a., not applicable

NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products

Grid Region Influence

The grid region can play a major role in determining the performance of fluidized-bed reactors when there are fast reactions and rapid mass transfer from grid jets to the dense phase (Grace and de Lasa, 1978). In the present case, the grid jet penetration predicted by the correlation of Merry (1975) is about 10% of the total bed height and the reaction is relatively slow. The fact that air and naphthalene were injected separately is bound to lessen the effect of the grid further. To see what the maximum effect might be, Table 12 compares predictions from the Grace (1984) model for the bed itself with two cases where the bottom 10% of the bed has a much higher volumetric interphase mass transfer rate, 10 and 100 times that in the bubbling region. As shown in Table 12, the influence of this major increase in mass transfer in the lower part of the unit is predicted to be very small. Overall, the inclusion of the jet region is helpful in reconciling predicted and measured NA and PA values, while leading to somewhat poorer agreement for the NQ values. Similar findings are obtained with the Kunii and Levenspiel (1969) model when allowance is made for enhanced interphase mass transfer in the lowest 10% of the bed (Johnsson, 1986).

Freeboard Influence

The freeboard region can also have a strong influence on fluid-bed reactors for some cases, especially for shallow beds with high gas velocities and large quantities of unreacted gases leaving the dense bed surface (de Lasa and Grace, 1979). In order to estimate the influence of the freeboard on the models, a simplified form of the Chen and Wen (1982) freeboard model has been used to estimate a vertical profile of solids holdup in the freeboard and this, combined with assumed plug flow of gas, has led to predicted reaction rates above the bed. Details are provided by Johnsson (1986). Results are presented in Table 12 with the Grace model used to describe the bubbling-bed region.

Table 11. Limiting Predictions for Turbulent Bed Compared with Bubbling Bed Model and Experimental Results

		Limiting Turbulent Bed Models		
Com. %	Bubbling-Bed Model (case 1)	Single-phase Plug Flow	Single-phase Perfectly Mixed	Exp.
C'_{NA}	1.64	3×10^{-7}	4.9	~0(<2)
C'_{NQ}	0.53	6×10^{-7}	1.8	1.31
C'_{PA}	87.1	89.0	82.9	88.9
C'_{OP}	10.7	11.0	10.4	~9.8

NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products.

Table 12. Influence of Grid and Freeboard Regions Compared with Bubbling Bed Alone*

	Bubbling Bed Only	Grid + Bubbling Region	Grid + Bubbling Region	Bubbling Bed Only	Bed + Freeboard	Exp.
ϕ_b	0.0	0.0	0.0	0.0035	0.0035	—
$k_j a_j$, s^{-1}	N.A.	7.27	72.7	N.A.	N.A.	—
C'_{NA}, %	1.64	0.73	0.49	1.28	0.68	~0(2)
C'_{NQ}, %	0.53	0.43	0.38	—	—	—
C'_{PA}, %	87.1	88.2	88.4	87.5	87.8	88.9
C'_{OP}, %	10.7	10.7	10.7	10.7	11.1	~9.8

*As predicted by Grace (1984) model with $d_b = 0.09$ m
NA, naphthalene; NQ, naphthoquinone; PA, phthalic anhydride; OP, oxidation products

Similar predictions were obtained with the bed represented by the Kunii and Levenspiel model.

Table 12 indicates that the freeboard, like the grid, has only a small influence for the reactor under investigation. The direction of the influence is again to improve the NA and PA predictions slightly while making the NQ predictions slightly worse. The predicted temperature rise in the freeboard is 15–20°C without any allowance for heat losses from the walls or recycle of heat to the bed surface by returning particles. This is felt to be consistent with the failure to observe any temperature rise in the industrial unit.

Discussion

Comparison between the fluidized-bed reactor models and the industrial data is less conclusive than we would have liked because results are available only for a single set of operating conditions, because the kinetics of the particular catalyst used where subject to some uncertainty, because hydrodynamic properties such as bubble size have had to be estimated, and because only outlet concentrations were measured rather than concentration profiles. Nevertheless, the bubbling-bed models have been found to give good predictions for the overall conversion and product distribution in the 2.13 m reactor when kinetic data from De Maria et al. (1961) are employed and bubble size is estimated from measured overall bed density and probable dense phase voidages. Predictions are shown to be rather insensitive to most other factors, such as the fraction of particles assigned to the bubble phase or the effective dense phase diffusivity for the conditions studied. For the particular conditions of the phthalic anhydride reactor, it was found also that grid jets and the freeboard do not have major influences, although their inclusion does give a small overall improvement in the predictions of the Grace (1984) and Kunii and Levenspiel (1969) models.

Botton et al. (1984) found that bubble models can correctly describe interphase mass transfer in pilot plants and industrial-scale equipment. The results of the present study are clearly also encouraging in showing that such models can give good agreement with measured yields for a complex reaction scheme in a commercial reactor. However, further results are needed in large-scale equipment to provide additional evidence of the worth of these models.

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Notation

A = cross-sectional area of column
C = molar concentration
C' = outlet concentration/inlet naphthalene concentration
$\mathcal{D}$ = molecular diffusivity of organic species
$\mathcal{D}_e$ = effective dense phase diffusivity
d_b = bubble diameter
$\bar{d}_p$ = mean particle diameter
f_w = wake volume per unit bubble volume
g = acceleration due to gravity
H = expanded bed depth
K_1–K_4 = pseudofirst-order reaction rate constants
k_1–k_4 = reaction rate constants, Table 4, based on particle volume
N = number of moles
NA = naphthalene
NQ = naphthoquinone
OP = oxidation products other than NQ and PA
PA = phthalic anhydride
p = pressure
T = temperature
t = time
U = superficial gas velocity
U_{mf} = minimum fluidization velocity
V_p = total particle volume
v_b = bubble velocity
Y = visible bubble flow rate/$(U - U_{mf})A$

Greek letters

$\bar{\epsilon}$ = overall bed voidage
ϵ_b = fraction of bed volume occupied by bubbles
ϵ_d = dense phase void fraction
ϵ_{mf} = bed voidage at minimum fluidization
ϕ_b = fraction of bed solids assigned to bubble phase

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