Performance of Slurry and Trickle-Bed Reactors: Application to Sulfur Dioxide Removal

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Methods are developed for predicting the performance of different types of three-phase reactors for removal of a gaseous reactant by catalytic reaction. The removal is assumed to occur by mass transport of reactant from *gas-to-liquid and liquid-to-catalyst particle and then by intraparticle diffusion* and reaction in the liquid filled pores. The method is applied to the oxidation of sulfur dioxide at 25°C and 1 atm using activated carbon, in the presence of water, as a catalyst. Slurry, trickle-bed, and counterflow packed-bed reactors are compared in terms of the key variables affecting the fraction of sulfur dioxide reacted.

SCOPE

Three-phase reactors are necessary for systems involving a solid catalyst and gaseous and liquid reactants (for example, desulfurization of petroleum fractions). Such reactors are also used when the gaseous reactant must be dissolved in a liquid phase, as in polymerization of ethylene or hydrogenation of oils. Another application is for removal of a pollutant from a gas stream. All such three-phase processes involve steps of gas-liquid, liquid-catalyst, *and intraparticle mass transfer and chemical reaction.* The relative importance of these individual steps depends upon the type of contacting of the three phases. Hence, the choice of reactor is important for optimum performance.

In this paper, methods and equations are presented for predicting the fraction x_B of gaseous pollutant reacted for slurry, trickle, and counterflow packed-bed reactors. Analytical solutions for x_B are given for first-order intrinsic kinetics. The air oxidation of sulfur dioxide fits this situation, since the intrinsic rate in water filled pores of activated carbon particles has been found to be first order in oxygen and zero order in sulfur dioxide (for gas concentrations of 0.3 to 9.0% sulfur dioxide). Both kinetic and mass transfer coefficients are available from the experiments of Komiyama and Smith (1975*a*, *b*) in a slurry reactor. The same intrinsic kinetics and the mass transfer results of Goto and Smith (1975) in a trickle bed may be used to predict the behavior of packed-bed reactors. Hence, sufficient information is available for *comparing the performance of various reactor types* for this reaction system.

There are several earlier studies involving sulfur dioxide and activated carbon in three-phase reactors. One is the review of Hartman et al. (1971). Also, Seaburn and Engel (1973) used a slurry reactor to evaluate the adsorption capacities of various kinds of carbon. Hartman and Coughlin (1972) studied the oxidation reaction in a countercurrent, packed-bed arrangement. These authors suggested that the outer surface of the catalyst particles might not be completely covered with liquid and obtained a value of about 90% coverage from their data.

CONCLUSIONS AND SIGNIFICANCE

For first-order intrinsic kinetics, the mass conservation equations for three-phase reactors can be solved analytically. This has been done for slurry, trickle-bed, and counterflow packed-bed reactors. The resultant equations give the fraction of gas-phase reactant removed in terms of dimensionless groups of mass transfer coefficients, equilibrium parameters, kinetic rate constant, and liquid and gas flow rates. Derivations are given for two flow models for slurry reactors: plug flow of gas bubbles and a residence time distribution of gas bubbles corresponding to complete mixing. The liquid phase is supposed to be well mixed. For the packed-bed reactors, plug flow of both gas and liquid is assumed.

The equations are applied by using experimental kinetics for the oxidation of sulfur dioxide with an activated carbon catalyst. Since the data were obtained in a slurry reactor, the theoretical prediction for this

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reactor type could be tested. The experiments were carried out with no flow of liquid so that the equations had to be adapted to a batch type of reactor. When this was done, predicted and experimental results were in good agreement.

The comparison of predicted results for different reactors showed that for all types the fraction of sulfur dioxide removed from the gas flow increased as catalyst particle size decreased, as liquid flow rate increased, and as sulfur dioxide concentration in the feed gas decreased. However, the effect of these variables varied from reactor to reactor. For the same reactor volume and flow rates, the countercurrent packed bed gave the highest sulfur dioxide removal and the trickle bed the lowest x_B. In contrast, for the same mass of catalyst the slurry reactor gives the highest sulfur dioxide removal. For this reaction system, gas-to-liquid and liquid-to-particle mass transfer, intraparticle diffusion, and the intrinsic reaction rate all influenced the results. However, the most rate limiting step was gas-to-liquid mass transfer for the packed-bed reactors and intraparticle diffusion combined with intrinsic rate for the slurry reactor.

The coupling of transport and kinetic rates and great range of the latter values, along with the practical necessity of employing different catalyst loadings and particle sizes in the various reactors, prevent general statements about the optimum reactor type. However, if kinetics data are available, the methods given here may be useful for determining the preferred reactor. While explicit solutions are limited to first-order reactions, numerical solution of the same type of equation would provide results for any type of intrinsic kinetics. The evaluation methods are based solely upon extent of reaction and do not take into account such practically important factors as pressure drop and means of retaining small particles in the slurry type of reactor.

The catalytic oxidation of sulfur dioxide on activated carbon in the presence of liquid water is a useful reaction for studying the performance of three-phase reactors. Komiyama and Smith (1975*a,b*) studied the intrinsic kinetics of the reaction

$$2SO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$$

at 25°C and 1 atm pressure and also measured intraparticle diffusivities for the activated carbon catalyst. For sulfur dioxide concentrations of as low as 0.3% in air, the rate was zero order in sulfur dioxide and first order in oxygen. The data were obtained in a slurry reactor operated so that the catalyst pores were filled with liquid. Then, the above reaction and an expression for the intrinsic rate (per unit volume of reactor) may be written

$$A(l) + qB(l) \rightarrow \text{product} \tag{1}$$

$$R_{A,\text{int}} = kC_{l,A}(1 - \epsilon) \tag{2}$$

For comparing different types of three-phase reactors, equations for predicting extent of reaction will be derived for first-order kinetics for a gaseous reactant. Then the results will be applied to sulfur dioxide oxidation by using the quantitative kinetics determined by Komiyama. Isothermal, steady state behavior, with constant physical properties and mass transfer coefficients, will be assumed.

SLURRY REACTOR THEORY

In treating slurry systems, it will be assumed that the liquid phase is well mixed. This will not introduce significant errors except in special situations, for example, where the liquid has a high viscosity and the reactor contains considerable internal equipment (cooling or heating coils, etc.). The situation with respect to the gas phase is less certain. With very strong agitation, the gas bubbles may coalesce and redisperse (Hanhart et al., 1963) and also have a residence time approaching that of a completely mixed fluid. That is, the concentration of soluble reactant would be the same in all the bubbles in the reactor. With less agitation, the bubbles will approach plug flow as they rise through the liquid. Fortunately, it is only for cases of intermediate solubility of the gaseous reactant in the liquid that the residence time of the bubbles is important. Niiyama and Smith (1976) have shown that for either very soluble or slightly soluble gases, the residence time of the gas bubbles in the liquid has no effect on reactor performance. While the limiting reactant in our application is oxygen, which is but slightly soluble in water, equations are presented for both plug flow (model I) and for the complete mixing condition (model II).

Plug Flow of Gas Bubbles

Mass balance equations for reactants A and B and for steady state flow of both gas and liquid phases are

$$\frac{Q_g}{S_t}\frac{dC_{gA}}{dz} + N_{lA} = 0 \tag{3}$$

$$\frac{Q_g}{S_t}\frac{dC_{gB}}{dz} + N_{lB} = 0 \tag{4}$$

$$Q_l(C_{lA,f} - C_{lA}) + (\overline{N}_{lA} - N_{sA})V = 0 \tag{5}$$

$$Q_l(C_{lB,f} - C_{lB}) + (\overline{N}_{lB} - N_{sB})V = 0 \tag{6}$$

where N_{lA}, N_{lB}, N_{sA}, and N_{sB} are the interphase mass transfer rates per unit volume of reactor. The boundary conditions are

$$\begin{aligned} C_{gA} &= C_{gA,f} \quad \text{at} \quad z = 0 \\ C_{gB} &= C_{gB,f} \quad \text{at} \quad z = 0 \end{aligned} \tag{7}$$

Mass transport rates between gas and liquid can be expressed in terms of gas interface and interface-liquid coefficients; that is

$$N_{lA} = (ka)_{gA}(C_{gA} - C_{i,gA}) = (ka)_{lA}(C_{i,lA} - C_{lA}) \tag{8}$$

If we assume that Henry's law holds at the interface

$$C_{i,gA} = H_A{}^{*}C_{i,lA} \tag{9}$$

Equation (8) may be written

$$N_{lA} = (ka)lA\eta_{bA}(C_{gA}/H_A{}^{*} - C_{lA}) \tag{10}$$

Here η_{bA}, the gas-liquid effectiveness factor, is given by

$$\eta_{bA} = \left[1 + \frac{(ka)_{lA}}{(ka)_{gA} H_A^*} \right]^{-1} \tag{11}$$

The average mass transport rate of A from gas to liquid, as the bubble rises through the slurry, may be expressed as

$$\overline{N}_{lA} = \frac{1}{z_t} \int_0^{z_t} N_{lA} dz = (ka)_{lA} \eta_{bA} \left(\frac{\overline{C}_{gA}}{H_A^*} - C_{lA} \right) \tag{12}$$

where

$$\overline{C}_{gA} = \frac{1}{z_t} \int_0^{z_t} C_{gA} dz \tag{13}$$

Analogous equations for $\overline{N}_{lB}$, η_{bB}, and $\overline{C}_{gB}$ are obtained by replacing subscript A with B in Equations (10) to (13).

Mass transport rates between liquid and catalyst particle may be expressed in terms of mass transfer coefficients:

$$N_{sA} = (ka)_{sA} (C_{lA} - C_{sA}) \tag{14}$$

$$N_{sB} = (ka)_{sB} (C_{lB} - C_{sB}) \tag{15}$$

Furthermore, the global reaction rate R_A can be written, using Equation (2), as

$$R_A = \eta k C_{s,A} (1 - \epsilon) \tag{16}$$

For a first-order, irreversible reaction, the effectiveness factor for a spherical catalyst particle is given by

$$\eta = \frac{1}{\phi} \left(\frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right) \tag{17}$$

$$\phi = \frac{V_p}{S_p} \sqrt{\frac{k}{D_{e,A}}} \tag{18}$$

Combining Equations (14) and (16) to eliminate C_{sA} and noting that $N_{sA} = N_{sB}/q = R_a$, we obtain

$$N_{sA} = \frac{N_{sB}}{q} = k \eta \eta_l C_{lA} (1 - \epsilon) \tag{19}$$

where the liquid-particle effectiveness factor is defined as

$$\eta_l = [1 + k\eta(1 - \epsilon)/(ka)_{sA}]^{-1} \tag{20}$$

The transverse rate of accumulation of A in the liquid phase can be written, using Equation (12), as

$$(\overline{N}_{lA} - N_{sA}) = (ka)_{lA} \eta_{bA} \left(\frac{\overline{C}_{gA}}{H_A^*} - \frac{C_{lA}}{\eta_{oA}} \right) \tag{21}$$

Here η_{oA} is an overall effectiveness factor, defined as

$$\eta_{oA} = \left[1 + k \eta \eta_l \frac{(1 - \epsilon)}{(ka)_{lA} \eta_{bA}} \right]^{-1} \tag{22}$$

Equations (3) to (6) can now be expressed in terms of the pertinent parameters and the unknown concentrations C_{lA}, C_{gA}, C_{lB}, and C_{gB}. This is done by substituting Equations (10), (19), and (21) into Equations (3) to (6). Expressing the results in dimensionless variables (defined in nomenclature), we get

$$\frac{dy_{gA}}{d\zeta} + Da_{gA} (y_{gA} - y_{lA}) = 0 \tag{23}$$

$$\frac{dy_{gB}}{d\zeta} + Da_{gB} (y_{gB} - y_{lB}) = 0 \tag{24}$$

$$y_{lA,f} - y_{lA} + Da_{lA} (\overline{y}_{gA} - y_{lA}/\eta_{oA}) = 0 \tag{25}$$

$$y_{lB,f} - y_{lB} + Da_{lB} (\overline{y}_{gB} - y_{lB}) - \beta_l Da_{lB} y_{lA} = 0 \tag{26}$$

The boundary conditions, Equation (7), become

$$y_{gA} = y_{gB} = 1 \quad \text{at} \quad \zeta = 0 \tag{27}$$

Equations (23) to (26) are applicable to any reaction of the form of Equation (1) for which the kinetics are first order in A and zero order in B. For sulfur dioxide oxidation with an activated carbon catalyst in an aqueous slurry (Komiyama, 1975*a*), the reaction was zero order because C_{l,SO_2} was in excess. In this case, $y_{sB} > 0$. Then, from Equations (19) and (21), the following restriction is obtained:

$$y_{sB} = y_{lB} - \beta_s y_{lA} > 0 \tag{28}$$

Equations (23) to (27) can be solved analytically. With the restriction of Equation (28), the solution for the concentrations leaving the reactor may be written:

$$y_{lA,e} = \frac{Da_{lA}[1 - \exp(-Da_{gA})] + y_{lA,f} Da_{gA}}{Da_{gA}(1 - Da_{lA} + Da_{lA}/\eta_{oA}) + Da_{lA}[1 - \exp(-Da_{gA})]} \tag{29}$$

$$y_{gA,e} = y_{lA,e} + (1 - y_{lA,e}) \exp(-Da_{gA}) \tag{30}$$

$$y_{lB,e} = \frac{Da_{lB}[1 - \exp(-Da_{gB})] - \beta_l Da_{gB}(Da_{lB}) y_{lA,e} + y_{lB,f} Da_{gB}}{Da_{lB}[1 - \exp(-Da_{gB})] + Da_{gB}} \tag{31}$$

$$y_{gB,e} = y_{lB,e} + (1 - y_{lB,e}) \exp(-Da_{gB}) \tag{32}$$

For gas purification, the important quantity is the fraction x_B of pollutant that is removed in the reactor. This is simply related to $y_{gB,e}$:

$$x_B = 1 - y_{gB,e} \tag{33}$$

Well-mixed Gas Bubbles

For well-mixed behavior of the gas phase, Equations (25) and (26) still apply, but differential Equations (23) and (24) are replaced by the algebraic expressions for well-mixed bubbles:

$$1 - y_{gA} - D_{gA} (y_{gA} - y_{lA}) = 0 \tag{34}$$

$$1 - y_{gB} - Da_{gB} (y_{gB} - y_{lB}) = 0 \tag{35}$$

The solution of Equations (25), (26), (34), and (35) is

$$y_{lA,e} = \frac{\eta_{oA}(Da_{lA} + y_{lA,f} + y_{lA,f} Da_{gA})}{(1 + Da_{gA})(\eta_{oA} + Da_{lA}) - Da_{gA} Da_{lA} \eta_{oA}} \tag{36}$$

$$y_{gA,e} = \frac{Da_{lA} + \eta_{oA} + y_{lA,f} Da_{gA} \eta_{oA}}{(1 + Da_{gA})(\eta_{oA} + Da_{lA}) - Da_{gA} Da_{lA} \eta_{oA}} \tag{37}$$

$$y_{gB,e} = \frac{Da_{lB} + 1 - \beta_l Da_{gB} Da_{lB} y_{lA,e} + y_{lB,f} Da_{gB}}{Da_{gB} + Da_{lB+1}} \tag{38}$$

$$y_{lB,e} = \left(1 + \frac{1}{Da_{gB}} \right) y_{gB,e} - \frac{1}{Da_{gB}} \tag{39}$$

Equations (32) and (38) are employed later to evaluate the performance of slurry reactors for gas purification.

PACKED-BED REACTOR THEORY

Axial dispersion in the gas phase of trickle-bed and counterflow packed-bed reactors is probably negligible. Axial dispersion in the liquid may be significant at high conversions in some instances, for example, in laboratory reactors (that is, short beds) with low flow rates. A summary of the correlations of the several experimental studies of liquid axial dispersion coefficients is given in the review of Goto et al. (1977). Since in most instances axial dispersion is unimportant in the liquid, it will be neglected here.

Dimensionless mass balance equations for plug flow through a fixed bed of catalyst particles, in which reaction (1) occurs, are as follows:

$$\frac{dy_{gA}}{d\zeta} \pm Da_{gA}(y_{gA} - y_{lA}) = 0 \tag{40}$$

$$\frac{dy_{gB}}{d\zeta} \pm Da_{gB}(y_{gB} - y_{lB}) = 0 \tag{41}$$

$$\frac{dy_{lA}}{d\zeta} - Da_{lA}(y_{gA} - y_{lA}/\eta_{oA}) = 0 \tag{42}$$

$$\frac{dy_{lB}}{d\zeta} - Da_{lB}(y_{gB} - y_{lB}) + \beta_l Da_{lB} y_{lA} = 0 \tag{43}$$

In Equations (40) and (41), the plus sign indicates concurrent gas and liquid flow (trickle bed), and the minus sign designates countercurrent flow. Boundary conditions for concurrent flow are

$$y_{gA} = y_{gB} = 1; \quad y_{lA} = y_{lA,f}; \quad y_{lB} = y_{lB,f}; \quad \text{at} \quad \zeta = 0 \tag{44}$$

and for countercurrent flow

$$y_{lA} = y_{lA,f}; \quad y_{lB} = y_{lB,f}; \quad \text{at} \quad \zeta = 0 \tag{45}$$

$$y_{gA} = y_{gB} = 1 \quad \text{at} \quad \zeta = 1 \tag{46}$$

An analytical solution of Equations (40) to (43) can also be obtained. For concurrent flow, the solution is

$$y_{gA,e} = \alpha_1 \exp(\lambda_1) + \alpha_2 \exp(\lambda_2) \tag{47}$$

$$y_{lA,e} = \alpha_3 \exp(\lambda_1) + \alpha_4 \exp(\lambda_2) \tag{48}$$

$$\begin{aligned} y_{gB,e} = {} & \alpha_5 \exp(\lambda_3) + \alpha_6 \\ & - \beta_l Da_{gB} Da_{lB} \left[\frac{\alpha_3 \exp(\lambda_1)}{\lambda_1(\lambda_1 - \lambda_3)} + \frac{\alpha_4 \exp(\lambda_2)}{\lambda_2(\lambda_2 - \lambda_3)} \right] \end{aligned} \tag{49}$$

$$\begin{aligned} y_{lB,e} = {} & \alpha_5 \left(1 + \frac{\lambda_3}{Da_{gB}}\right) \exp(\lambda_3) + \alpha_6 \\ & - \beta_l Da_{gB} Da_{lB} \left[\left(\frac{1}{\lambda_1} + \frac{1}{Da_{gB}}\right) \frac{\alpha_3(\exp \lambda_1)}{\lambda_1 - \lambda_3} \right] \\ & + \left(\frac{1}{\lambda_2} + \frac{1}{Da_{gB}}\right) \frac{\alpha_4 \exp(\lambda_2)}{\lambda_2 - \lambda_1} \end{aligned} \tag{50}$$

where

$$\begin{aligned} \lambda_1 = \frac{1}{2} \Bigg\{ & -\frac{Da_{lA}}{\eta_{oA}} - Da_{gA} + \Bigg[\left(\frac{Da_{lA}}{\eta_{oA}} - Da_{gA} \right)^2 \\ & + 4(Da_{gA}) Da_{lA} \Bigg]^{1/2} \Bigg\} \end{aligned} \tag{51}$$

$$\begin{aligned} \lambda_2 = \frac{1}{2} \Bigg\{ & -\frac{Da_{lA}}{\eta_{oA}} - Da_{gA} - \Bigg[\left(\frac{Da_{lA}}{\eta_{oA}} - Da_{gA} \right)^2 \\ & + 4(Da_{gA}) Da_{lA} \Bigg]^{1/2} \Bigg\} \end{aligned} \tag{52}$$

$$\lambda_3 = -(Da_{gB} + Da_{lB}) \tag{53}$$

$$\alpha_1 = (\mu_A - \lambda_2)/(\lambda_1 - \lambda_2) \tag{54}$$

$$\alpha_2 = (\mu_A - \lambda_1)/(\lambda_2 - \lambda_1) \tag{55}$$

$$\alpha_3 = (1 + \lambda_1/Da_{gA})\alpha_1 \tag{56}$$

$$\alpha_4 = (1 + \lambda_2/Da_{gA})\alpha_2 \tag{57}$$

$$\alpha_5 = \frac{\mu_B}{\lambda_3} + \frac{\beta_l(Da_{gB})Da_{lB}}{\lambda_3} \left(\frac{\alpha_3}{\lambda_1 - \lambda_3} + \frac{\alpha_4}{\lambda_2 - \lambda_3} \right) \tag{58}$$

$$\alpha_6 = 1 - \frac{\mu_B}{\lambda_3} - \beta_l(Da_{gB})Da_{lB} \left(\frac{\alpha_3}{\lambda_1 \lambda_3} + \frac{\alpha_4}{\lambda_2 \lambda_3} \right) \tag{59}$$

and

$$\mu_A = Da_{gA}(y_{lA,f} - 1) \tag{60}$$

$$\mu_B = Da_{gB}(y_{lB,f} - 1) \tag{61}$$

For countercurrent flow, the solution of Equations (40) to (43) and (45) and (46) is a set of equations similar to Equations (47) to (50). These results are available (Goto and Smith, 1977).

For those cases where axial dispersion is important, Equations (40) to (43) and the boundary conditions must be modified. A formal analytical solution is possible, but the evaluation involves numerical determination of roots of fourth- or higher-order algebraic equations. A solution method has been reported (Goto and Smith, 1978).

RESULTS

Slurry Reactors: No Liquid Flow

The experimental data of Komiyama and Smith (1975*b*) for oxidation of sulfur dioxide in a slurry reactor provide a means for testing some of the results of the preceding section. These authors measured rates of reaction R_A as a function of catalyst loading M_s and particle diameter for semibatch operation, that is, continuous gas flow but no flow of liquid. Operating conditions were such that intraparticle diffusion, gas-liquid and liquid-particle mass transfer, and intrinsic kinetics affected the rate of consumption of oxygen. From such rate data, the fraction x_B of sulfur dioxide removed from the gas can be calculated from the expression

$$x_B = \frac{R_B V}{Q_g C_{gB,f}} \tag{62}$$

Actually, Komiyama and Smith reported in Table 2 the rate constant k'_{rm} rather than R_A. However, the k'_{rm} values can be converted to experimental rates by using Equation (4) of their paper. Thus

$$R_B = qR_A = qk'_{rm} \frac{C_{gA,f}}{H_A^*} \left(\frac{M_s}{\rho_p V} \right) \tag{63}$$

and from Equation (62)

$$x_B = qk'_{rm} \frac{(C_{gA,f}/C_{gB,f})M_s}{Q_g H_A^* \rho_p} \tag{64}$$

TABLE 1. OPERATING CONDITIONS AND RATE PARAMETERS FOR OXIDATION OF SULFUR DIOXIDE IN SLURRY REACTOR (KOMIYAMA AND SMITH, 1975 *a,b*)

a. Pressure and temperature
   $P = 1$ atm
   $T = 273 + 25 = 298°K$
b. Particle density of Pittsburgh Activated Carbon, type BPL
   $\rho_p = 0.80$ g/cm³
c. Total volume of reactor
   $V = 963$ cm³ (volume of water = 900 cm³)
d. Gas flow rate
   $Q_g = 33.3$ cm³/s
e. Concentrations in the feed gas
   $C_{gA,f} = 8.59 \times 10^{-6}$ mole/cm³; 21% in air
   $C_{gB,f} = 0.49 \times 10^{-6}$ mole/cm³; 1.2%
f. Henry's Law constant for O_2
   $H_A{}^* = C_{gA}/C_{lA} = 35.4$
g. Intrinsic reaction rate constant
   $k = 6.6\ s^{-1}$
h. Effective diffusivity of O_2
   $D_{eA} = 5.35 \times 10^{-6}$ cm²/s
i. Mass transfer coefficient from bubble to liquid
   $k_L a_b = 1.54\ s^{-1}$
j. Negligible resistance of mass transfer from gas to interface of gas liquid
   $(ka)_{gA} = (ka)_{gB} \to \infty, \eta_{bA} = \eta_{bB} = 1.0$

The stoichiometric coefficient q is 2 for sulfur dioxide oxidation, and all other quantities in Equation (63) are given in the Komiyama paper.

Predicted values of x_B can be obtained from Equations (29) and (33) or (36) to (39). For no liquid flow, Da_{lA} and Da_{lB} are infinite, and the equations reduce to the following form:

Plug flow of gas (model I):

$$x_B = q\left(\frac{C_{gA,f}}{C_{gB,f}}\right)\left[\frac{1}{1 - \exp(1 - Da_{gA})} + \frac{\eta_{oA}}{(1 - \eta_{oA})Da_{gA}}\right]^{-1} \quad (65)$$

Well-mixed gas bubbles (model II):

$$x_B = q\left(\frac{C_{gA,f}}{C_{gB,f}}\right)\left[1 + \frac{1}{(1 - \eta_{oA})Da_{gA}}\right]^{-1} \quad (66)$$

The operating conditions and parameters necessary for the calculations are given in Table 1. The calculations are made for a gas flow rate of 33.3 cm³/s to a reactor of total (water plus catalyst particles) volume of 963 cm³. The intrinsic rate constant, effective diffusivity, and bubble-to-liquid mass transfer coefficient $k_L a_b$ are those determined by Komiyama and Smith (1975*b*) by analysis of a large amount of experimental data taken at various operating conditions. For oxygen and sulfur dioxide, which are of limited solubility in water, it is assumed that the bubble-to-liquid transport resistance is predominantly in the liquid film. Then, $(ka)_{gA} = (ka)_{gB} \to \infty$ and $\eta_{bA} = \eta_{bB} = 1.0$. The values used for the liquid-to-particle mass transfer coefficient k_s are those reported in Table 2 of the Komiyama paper. The adaptation of these rate parameters to the form needed for use

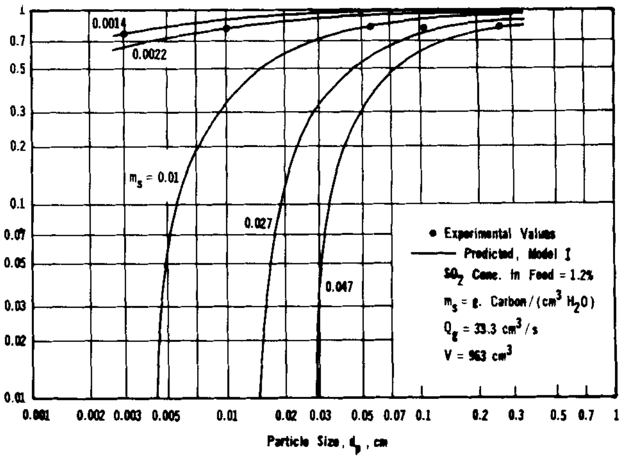

Fig. 1. Effect of catalyst particle size and loading on SO_2 removal in a slurry reactor ($Q_l = 0$).

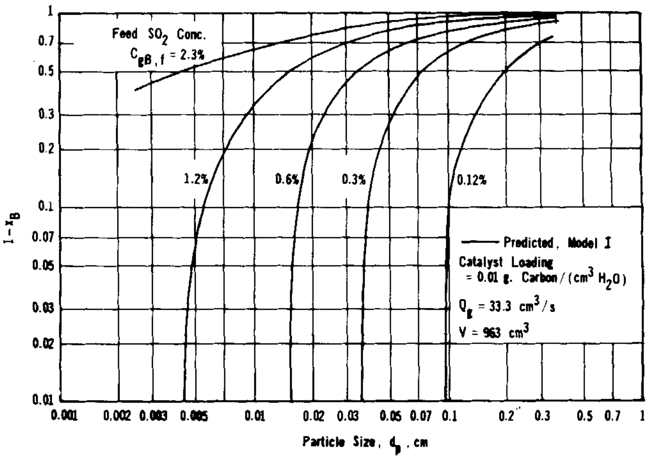

Fig. 2. Effect of feed concentration on removal of SO_2 in a slurry reactor ($Q_1 = 0$).

TABLE 2. PREDICTED AND EXPERIMENTAL RESULTS OF SULFUR DIOXIDE IN A SLURRY REACTOR WITH NO LIQUID FLOW

								Predicted		
d_p, cm	M_s, g	$(ka)_{lA}$[a], s^{-1}	$(ka)_{sA}$[b], s^{-1}	η[c]	$k\eta(1-\epsilon)$[d], s^{-1}	η_l[e]	η_{oA}[f]	x_B model I	x_B model II	Exp, x_B
0.0030	1.25	0.101	0.190	0.853	0.00914	0.954	0.921	0.229	0.228	0.241
0.0099	2.0	0.101	0.0548	0.446	0.00765	0.877	0.938	0.180	0.179	0.182
0.0541	9.0	0.101	0.0330	0.0964	0.00743	0.816	0.943	0.163	0.163	0.166
0.105	24.6	0.101	0.0443	0.0506	0.0107	0.806	0.922	0.226	0.225	0.198
0.259	42.4	0.101	0.0309	0.0207	0.00753	0.804	0.943	0.163	0.162	0.176

[a] $(ka)_{lA} = k_L a_b V_b/V = 1.54\ (63/963) = 0.101\ s^{-1}$.
[b] $(ka)_{sA} = k_s a_s\ (M_s/\rho_p)/V = k_s\ (6/d_p)\ (M_s/0.08)/963 = 0.00779\ k_s M_s/d_p$. Values of k_s from Table 2 of Komiyama and Smith (1975*b*).
[c] $\phi = (d_p/6)\sqrt{k/D_{e,A}} = (d_p/6)\sqrt{6.6/5.35 \times 10^{-6}} = 185.1\ d_p$. This ϕ was used to estimate η from Equation (17).
[d] $k\eta(1 - \epsilon) = k\eta(M_s/\rho_p)/V = 6.6\eta\ (M_s/0.8)/963 = 0.00857\ \eta M_s$.
[e] From Equation (20).
[f] From Equation (22).

Table 3. Operating Conditions and Rate Parameters for Oxidation of Sulfur Dioxide in Packed-Bed Reactors

a. Reactor dimensions
$V = 963$ cm^3
$d_t = 8.0$ cm and $S_t = 50.3$ cm^2
$z_t = 19.2$ cm

b. Void fraction in bed; mass of catalyst
$\epsilon = 0.45$ and $M_s = (1 - \epsilon)\ \rho_p V = 0.55\ (0.8)\ (963) = 423$g

c. Gas flow rate
$Q_g = 33.3$ cm^3/s

d. Mass transfer coefficient from gas to liquid (Goto and Smith, 1975)
For $d_p = 0.0541$ cm, $(ka)_{lA} = 5.14 \times 10^{-3}\ Q_l^{0.39}$, s^{-1}
For $d_p = 0.291$ cm, $(ka)_{lA} = 4.01 \times 10^{-3}\ Q_l^{0.41}$, s^{-1}
$(ka)_{lB}/(ka)_{lA} = (D_{l,B}/D_{l,A})^{1/2} = 1.7 \times 10^{-5}/2.6 \times 10^{-5})^{1/2} = 0.809$

e. Mass transfer coefficient from liquid to solid (Goto and Smith, 1975)
For $d_p = 0.0541$ cm, $(ka)_{sA} = 4.76 \times 10^{-2}\ Q_l^{0.67}$
For $d_p = 0.291$ cm, $(ka)_{sA} = 1.28 \times 10^{-2}\ Q_l^{0.56}$
$(ka)_{sB}/(ka)_{sA} = (D_{lB}/D_{lA})^{2/3} = 0.753$

f. Apparent reaction rate constant
For $d_p = 0.0541$ cm, $k\eta(1 - \epsilon) = 6.6(0.0964)\ (0.55) = 0.350$ s^{-1}
For $d_p = 0.291$ cm, $(k\eta(1 - \epsilon) = 6.6(0.0185)\ (0.55) = 0.0672$ s^{-1}

g. Temperature = 25°C
Pressure = 1 atm

in Equations (65) and (66) are given in the footnotes to Table 2.

The last three columns of Table 2 show predicted and experimental values for the fraction of sulfur dioxide removed from the gas. The near coincidence of the results for models I and II verifies the previous conclusion that the residence-time distribution of the gas bubbles has no effect for slightly soluble gases (oxygen in this case). The agreement between predicted and experimental x_B lends confidence to the theory proposed in the previous section.

The individual effects of catalyst loading and particle size are not evident from Table 2, since both variables were changed from run to run. Figure 1 shows the separate influence of these variables as calculated from Equation (65). Note that for small particles and a large catalyst loading, for example, $d_p = 0.004$ cm and $M_s =$

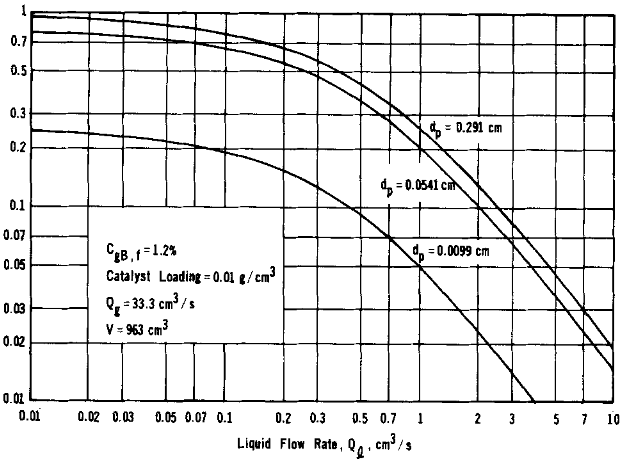

Fig. 4. Effect of liquid flow rate on SO$_2$ removal in packed-bed reactors for $C_{gB,f} = 1.2\%$ ($Q_g = 33.3$ cm^3/s, $V = 963$ cm^3).

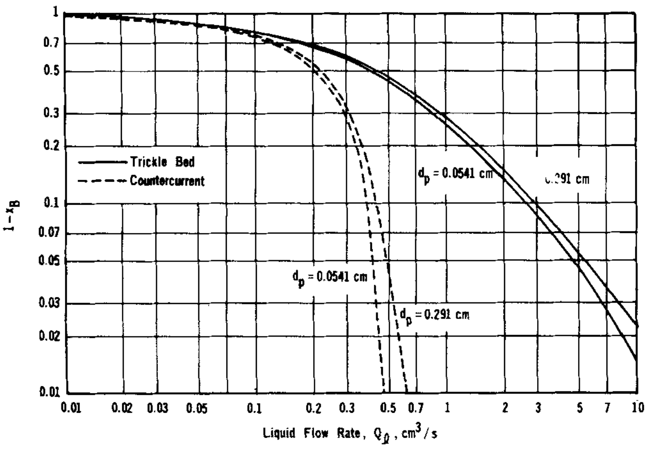

Fig. 3. Effect of liquid flow rate on SO$_2$ removal in a continuous-flow slurry reactor.

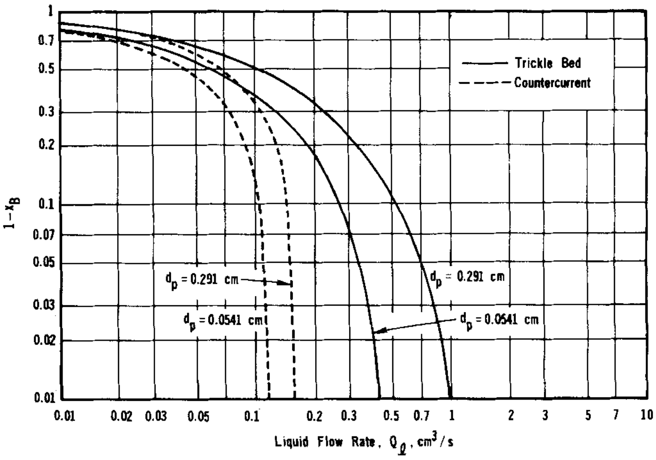

Fig. 5. Effect of liquid flow rate on SO$_2$ removal in packed-bed reactors for $C_{gB,f} = 0.12\%$ ($Q_g = 33.3$ cm^3/s, V = 963 cm^3).

Table 4. Comparison of Slurry and Packed-Bed Catalytic Reactors for Sulfur Dioxide Removal by Oxidation with Air (25°C, 1 atm)

$V = 963$ cm^3 $\quad C_{gA,f} = 21\%$ $\quad C_{gB,f} = 1.2\%$
$Q_g = 33.3$ cm^3/s $\quad Q_l = 1.0$ cm^3/s

Reactor type	d_p, cm	M_s, g	$(ka)_{lA}$, s^{-1}	$(ka)_{sA}$, s^{-1}	$k\eta(1 - \epsilon)$s^{-1}	η_l	η_{oA}	Fraction removed x_B	
Slurry	0.0541	9.0	0.101	0.0330	0.00743	0.816	0.943	0.791*	
	0.291	9.0	0.101	0.00583	0.00142	0.804	0.989	0.739*	
Packed bed	0.0541	423	0.00514	0.0476	0.350	0.120	0.109	0.737†	~1.0**
	0.291	423	0.00401	0.0128	0.0672	0.160	0.272	0.720†	~1.0**

* Model I.
† Concurrent flow.
** Countercurrent flow.

9g carbon [or 9/900 = 0.01g/(cm^3 of water)], sulfur dioxide removal is 100%.

The influence of the concentration of sulfur dioxide in the feed is shown in Figure 2 for a catalyst loading of 0.01 g carbon/(cm^3 of water). Lower feed concentrations give higher fractional removals of sulfur dioxide because the intrinsic rate was found to be zero order in sulfur dioxide. This was based upon data for 0.3% $< C_{gB,f} <$ 9.0% (Komiyama and Smith, 1975a). Hence, the curve for 0.12% sulfur dioxide involves the assumption that zero-order kinetics extends to this low feed concentration. The curves in Figure 2 suggest that catalytic oxidation in water is particularly effective for dilute sulfur dioxide gas streams.

These results for no liquid flow are based upon a steady-state period of operation. Komiyama and Smith (1975a) found such a period to last for several hours. Ultimately, the sulfuric acid concentration in the water would become large and reduce the reaction rate. This limitation does not apply when there is a continuous flow of liquid.

Continuous Flow Slurry Reactors

For comparing slurry and packed-bed reactors, the liquid feed is considered to be saturated with oxygen and to contain no sulfur dioxide. Hence, $y_{lA,f} = 1$ and $y_{lB,f} = 0$. Then, the fraction of sulfur dioxide removed from the gas can be calculated from Equations (29) to (33) for model I. For these calculations, values of $(ka)_{lB}$, $(ka)_{sB}$, and $H_B{}^*$ are necessary. The two mass transfer coefficients were evaluated from the correlations of Satterfield (1970). The solubility of sulfur dioxide in water at 25°C was found by Komiyama and Smith (1975a) to follow a Freundlich type of equation $C_{lB} = 2.24\, C_{gB}{}^{0.768}$. Then

$$H_B{}^* = (C_{gB}/C_{lB})_{\text{equil}} = (C_{gB,f}{}^{0.232}/2.24)\, y_{gB}{}^{0.232} \tag{67}$$

Since $H_B{}^*$ is a function of y_{gB}, a trial and error method is required to determine Da_{gB}, β_l, and β_s corresponding to the concentration of B(sulfur dioxide) leaving the reactor.

Figure 3 shows values of x_B calculated from Equations (29) to (33). The results are plotted as a function of liquid flow rate and catalyst particle size for a specific loading [(0.01 g carbon)/(cm^3 of water)], feed concentration ($C_{gB,f}$ = 1.2% and $C_{gA,f}$ = 21%), gas flow rate (Q_g = 33.3 cm^3/s), and reactor volume (963 cm^3). Liquid flow rates per unit volume of reactor (Q_l/V) greater than (0.1/900) 3 600 = 0.4 (hr)$^{-1}$ are needed, at this gase rate, before large fractions of the sulfur dioxide can be removed. Primarily because of intraparticle diffusion resistance, the fractional removal increases with a decrease in particle size.

Packed-Bed Reactors

For comparison, the performance of trickle-bed and counterflow packed-bed reactors will be evaluated for the same gas composition and flow rate, and reactor volume, as employed in obtaining the slurry reactor results. Other operating conditions and the rate parameters used in the calculations are given in Table 3. Results were determined for two catalyst particle sizes, and the required values of $(ka)_l$ and $(ka)_s$ were obtained for these particle sizes from the correlations of Goto and Smith (1975). While these correlations are based upon measurements for trickle-bed operation, the same values are assumed to be valid for countercurrent flow. Since gas flow rate does not have a significant effect on these mass transfer coefficients in trickle beds (Goto and Smith, 1975), this assumption may not be serious. The intrinsic rate constant k (Table 3) is the same as employed for the slurry reactor calculations.

The fraction of sulfur dioxide removed was predicted from model Equations (47) to (50) and (33) for the trickle-bed condition and from the analogous equations (Goto and Smith, 1977b) for counterflow of gas and liquid. Figure 4 shows the results for a sulfur dioxide content of 1.2% in the feed gas. The advantage of counterflow is significant at higher liquid rates. Also, the benefit gained by using small particles, owing to decreased intraparticle diffusion resistance, is greater in counterflow. Figure 5 displays similar results for a lower feed concentration (0.12%) of sulfur dioxide. Here again, the zero-order rate with respect to sulfur dioxide is responsible for the much larger x_B values shown in Figure 5.

COMPARISON OF SLURRY AND PACKED-BED REACTORS

The equations developed in the theory section provide a basis for comparing three-phase reactors for a reaction that is first-order with respect to a reactant in the gas phase. It has been assumed that the outer surface of the catalyst particles are completely covered with liquid and that the interior pores are filled with liquid. Hence, no provision for direct reaction between gas and catalyst is allowed.

The equations have been applied to the air oxidation of sulfur dioxide, and Figures 3 to 5 illustrate the effect of key variables on the fraction of sulfur dioxide removed from the gas phase. From these figures, the effectiveness of the reactors at different operating conditions can be compared. Such a comparison is given in Table 4 for the specific case of gas and liquid (water) flow rates of 33.3 and 1.0 cm^3/s, for a reactor volume of 963 cm^3, and for two catalyst particle sizes. The sulfur dioxide content of the gas feed is 1.2%.

The results in Table 4 indicate that the largest fractional removal (1.0) of sulfur dioxide is for a counterflow packed-bed arrangement, and the least removal (0.72 to 0.737) for a trickle bed with values of 0.739 to 0.791 for a slurry reactor. The values of $(ka)_{lA}$, $(ka)_{sA}$, and $k\eta(1-\epsilon)$ show that the rate limiting step for the slurry reactor is the particle rate $[k\eta(1-\epsilon)]$ and the mass transfer from gas to liquid $(ka)_{lA}$ for the packed-bed arrangements. The low value of $k\eta(1-\epsilon)$ for the slurry is due to the small amount of catalyst in the reactor [that is, small $(1-\epsilon)$ value]. Performance based upon sulfur dioxide removal per unit mass of catalyst would show the slurry arrangement to be superior to the other forms because of the larger mass transfer rates (ka) from gas bubble to liquid. Hence, for very active, expensive catalysts, this factor, combined with the higher effectiveness factors associated with the possibility of using smaller particle sizes favors slurry reactors.

An advantage of trickle-bed reactors, with respect to the counterflow arrangement, is that the liquid rate is not limited by flooding. Hence, a comparison at constant liquid rates, as in Table 4, may not always be appropriate.

The results of this study show that in addition to the design parameters of feed rates and compositions, catalyst particle size, catalyst loading, and intrinsic rate can have a pronounced effect on reactor performance. Hence, the preferred three-phase reactor for one reaction will not necessarily be the optimum for a different reaction. However, the theory presented here should be useful in illustrating how performance can be evaluated for different types of reactors. While numerical solution of the mass balance equations would be required for nonlinear kinetics, the same form of equations would be applicable for any kinetics. In any practical comparison, other considerations than extent of reaction would be important. Such considerations would include energy costs and means of retaining the small catalyst particles in a continuous-flow, slurry reactor. For example, Lemay, et al. (1975) compared trickle-bed and slurry reactors on the basis of power consumption. The reaction rate was controlled by external mass transfer. For a finely divided catalyst and for pulsing flow in the trickle bed, the slurry reactor was preferable.

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NOTATION

a_b = surface area of bubbles per unit volume of bubbles, cm^{-1}
a_s = outer surface area of particles per unit volume of particles, cm^{-1}
C = concentration ($\overline{C}$ designates average value), mole/cm^3 (or %)
Da_{gA} = $(ka)_{lA}\eta_{bA}V/Q_gH_A^*$
Da_{gB} = $(ka)_{lB}\eta_{bB}V/Q_gH_B^*$
Da_{lA} = $(ka)_{lA}\eta_{bA}V/Q_l$
Da_{lB} = $(ka)_{lB}\eta_{bB}V/Q_l$
$D_{e,A}$ = effective intraparticle diffusivity of A, cm^2/s
D_l = molecular diffusivity in liquid, cm^2/s
d_p = particle diameter, cm
d_t = reactor diameter, cm
H^* = Henry's Law constant, C_g/C_l
k = intrinsic first-order reaction rate constant, s^{-1}
k'_{rm} = measured reaction rate constant defined by Equation (63), s^{-1}
k_L = mass transfer coefficient from gas bubbles to liquid, cm/s
k_s = mass transfer coefficient from liquid to particle, cm/s
$(ka)_g$ = volumetric, gas-phase mass transfer coefficient (in gas-to-liquid transport), s^{-1}
$(ka)_l$ = volumetric, liquid-phase mass transfer coefficient (in gas-liquid transport), s^{-1}
$(ka)_s$ = volumetric, liquid-phase mass transfer coefficient (in liquid-to-solid transport), s^{-1}
N_l = rate of mass transport from gas to liquid, ($\overline{N_l}$ designates average value), mole/(s) (cm^3 of bed)
N_s = rate of mass transport from liquid to solid, mole/(s) (cm^3 of bed)
M_s = total mass of catalyst particles in reactor, g
m_s = mass of catalyst per unit volume of liquid, g/cm^3
q = stoichiometric coefficient (2 for sulfur dioxide oxidation)
R_{int} = intrinsic reaction rate based on volume of reactor, mole/(s) (cm^3 of reactor)
R = global reaction rate based on volume of reactor mole/(s) (cm^3 of reactor)
S_p = external surface area of particles, cm^2
S_t = cross-sectional area of bed, cm^2
T = temperature, °K
V = volume of reactor, cm^3
V_b = total volume of bubbles in reactor, cm^3
V_p = volume of catalyst particles, cm^3
Q_g = volumetric flow rate of gas (25°C, 1 atm), cm^3/s
Q_l = volumetric flow rate of liquid, cm^3/s
x_B = fraction of reactant B removed from gas phase
y_{gA} = $C_{gA}/C_{gA,f}$
y_{gB} = $C_{gB}/C_{gB,f}$
y_{lA} = $C_{lA}H_A^*/C_{gA,f}$
y_{lB} = $C_{lB}H_B^*/C_{gB,f}$
y_{sA} = $C_{sA}H_A^*/C_{gA,f}$
y_{sB} = $C_{sB}H_B^*/C_{gB,f}$
z = axial coordinate in bed, cm
z_t = total length of packed bed, cm

Greek Letters

α_1,α_2 = parameters defined by Equations (54) to (59)
β_l = $q(C_{gA,f}/C_{gB,f})(H_B^*/H_A^*)k\eta\eta_l(1-\epsilon)/(ka)_{lB}\eta_{bB}$
β_s = $q(C_{gA,f}/C_{gB,f})(H_B^*/H_A^*)k\eta\eta_l(1-\epsilon)/(ka)_{sB}$
$1-\epsilon$ = catalyst volume fraction in reactor
ζ = z/z_t
$\lambda_1, \lambda_2, \lambda_3$ = parameters defined by Equations (51) to (53)
η = catalytic effectiveness factor, Equation (17)
μ_A, μ_B = parameters defined by Equations (60) and (61)
η_b = gas-liquid effectiveness of reactant, Equation (11)
η_l = liquid-particle effectiveness, Equation (20)
η_{oA} = overall effectiveness of reactant A, Equation (22)
ρ_l = density of liquid, g/cm^3
ρ_p = density of particle, g/cm^3
ϕ = Thiele modulus, Equation (18)

Subscripts

A = reactant A (O_2)
B = reactant B (SO_2)
e = exit
f = feed
g = gas phase
i = interface
l = liquid phase
s = outer surface of catalyst particle

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