Hydration of Isobutene in a Trickle-bed Reactor: Wetting Efficiency and Mass Transfer

Reaction rates for the hydration of isobutene were measured at 323 K and atmospheric pressure in a trickle-bed reactor over a sixfold range of liquid rates. Three widely different feed conditions were used to vary the effect of mass transfer and wetting efficiency. The effect of wetting efficiency on the rate was analyzed using the additive procedure of Tan and Smith. The results showed that mass transfer from liquid to particle, wetting efficiency, and intraparticle kinetics all influenced the total rate, but that the gas-to-liquid mass transfer resistance was unimportant. Most of the resultant values of wetting efficiency and liquid-to-mass transfer coefficients were a little lower than literature values. This may be due to the high surface tension of our aqueous system. The derived total rate equations agreed well with the experimental rates, suggesting that the additive procedure is a satisfactory method of accounting for wetting efficiency.

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Introduction

In trickle-bed reactors gas and liquid flow concurrently downward through a fixed bed of catalyst particles. Such reactors are widely used, particularly when one reactant is very volatile and another is normally a liquid, as in processes involving hydrogen (hydrogenation and desulfurization of oils) or oxygen (oxidation of liquid-phase reactants). Interphase mass transfer and wetting efficiency, as well as intraparticle diffusion and intrinsic kinetics, can affect the performance of such systems (Satterfield, 1975; Herskowitz and Smith, 1983).

Wetting efficiency refers to the extent of liquid-solid contacting and is important at low liquid flow rates. Under these conditions part of the outer surface of the catalyst particles is covered by only a thin film of liquid through which there is little mass transfer resistance. The actual flow pattern of liquid and gas is complicated, involving nearly stagnant filaments of liquid, liquid rivulets, and thin films. Wetting efficiency, f, is used to account for mass transfer to the particle in this complex system. It has been defined in different ways (Colombo et al., 1976; Ramachandran et al., 1986; Satterfield, 1975). The definition we used is based upon dividing the outer particle surface into two parts, a fraction f covered by flowing liquid rivulets, and a fraction $1-f$ covered with only a thin film of liquid (the so-called gas-covered part). The internal volume of the particles has been shown to be completely filled with liquid (Colombo et al., 1976; Schwartz et al., 1976). Because of the low mass-transfer resistance on the gas-covered surface, and because this surface increases as the liquid rate decreases, the global reaction rate does not necessarily increase with liquid rate. When the rate depends upon the concentration of a gaseous reactant for an active catalyst, the curve of reaction rate vs. liquid flow rate exhibits a minimum. This has been observed experimentally by Mata and Smith (1981) and Herskowitz and Smith (1978) for the oxidation of sulfur dioxide in water with activated carbon catalyst and for the hydrogenation of α-methyl styrene with a palladium catalyst.

Two methods have been prominent among those used to evaluate the wetting efficiency. In the dynamic method an adsorbing or nonadsorbing tracer is introduced into the liquid feed under nonreacting conditions. Then the response curve in the effluent is measured to determine f (Ramachandran et al., 1986; Schwartz et al., 1976). Alternatively, the reaction rate is measured vs. liquid flow rate at steady state. From this information,

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and with intrinsic kinetics and intraparticle diffusivity known, f is evaluated (Herskowitz et al., 1979).

The key problem is determining wetting efficiency from experimental reaction rates is that the usual effectiveness factor concepts are not applicable when f is not equal to zero or unity. This is because the concentration of reactant on the gas-covered outer surface is not the same as the concentration of the liquid-covered part. Herskowitz et al. (1979) solved this problem for discrete values of f by assuming a cube-shaped particle with one or more faces gas-covered. Tan and Smith (1980) generalized this approach for any f by assuming that the total rate of reaction was equal to that if all the surface was covered by liquid, multiplied by f, plus the rate if all the surface was covered by gas, multiplied by $(1 - f)$. Comparison with the experimental data of Herskowitz et al. (1979) showed that this additive procedure gave excellent agreement for $f = 1/6, 2/6, 3/6$, etc.

Herskowitz et al. could quantitatively analyze data only for liquid and gas feed streams in equilibrium with respect to the reactant, hydrogen in their case. However, nonequilibrium feed streams with reactant primarily in the liquid or the gas provide a more accurate measurement of both interphase mass transfer and wetting efficiency. As an illustration, if the limiting reactant is only in the gas entering the catalyst bed, there must be mass transfer from gas to liquid or from gas to particle if reaction is to occur. If $f = 1$, the extent of reaction is expected to be much less than if $f < 1$, where reaction can occur with less mass transfer resistance by direct transfer of reactant from gas to particle surface. Our objectives were to measure f and interphase mass transfer rates by the reaction method for widely different feed stream compositions: absorption runs where the reactant was primarily in the gas entering the bed, desorption runs for which reactant was primarily in the liquid, and equilibrium runs in which the reactant concentration in gas and liquid were in equilibrium. The additive assumption was used to obtain the wetting efficiency.

The reaction system chosen was the hydration of isobutene to tertiary butyl alcohol using ion-exchange resin Amberlyst-15 as a catalyst. This reaction is first order in isobutene, zero order in water, and irreversible at 323 K and atmospheric pressure, the conditions of the experiments. The first-order rate constant and intraparticle diffusivity is known for the same catalyst (Leung et al. 1986). Also, the alcohol product is not very volatile, so the reaction rate can be determined from the tertiary butyl alcohol content in the effluent liquid. Side reactions do not occur. A batch recycle reactor for the liquid was employed. This permitted accurate concentration measurements, yet the conversion per pass was low, so the rate could be obtained from the simple differential reactor equation.

Using the additive procedure for treating the wetting efficiency, expressions for the total reaction rate were derived for the three feed conditions. These equations and the rate data were sufficient to establish f and the mass transfer coefficients $k_{Ls}a_s$ from liquid to particle, and $k_{gL}a_L$ from gas to liquid. In the analysis the mass transfer between gas and liquid in the regions above and below the catalyst bed had to be accounted for. These mass transfer corrections were evaluated from separate experimental data obtained by removing the catalyst bed.

The reaction results showed that f and $k_{Ls}a_s$ were sensitive to the rate data and could be accurately determined. The wetting efficiencies were a little lower than those of Herskowitz et al. (1979), Morita and Smith (1978), and Satterfield (1975). The higher surface tension for the aqueous system may explain the lower values. The liquid-to-particle mass transfer coefficients agreed with those of Morita and Smith but were lower than those of Dharwadkar and Sylvester (1977) and Goto and Smith (1975). The rate data were not sensitive to $k_{gL}a_L$. Hence gas-to-liquid mass transfer did not significantly influence the rate data, and accurate values of $k_{gL}a_L$ could not be determined. The derived rate equations predicted the observed rates, lending confidence to the additive procedure for treating the wetting efficiency.

Experimental Procedure

Water containing different amounts of isobutene flowed downward through the catalyst bed and was returned to a reservoir where the isobutene content was readjusted to the desired feed condition. From the reservoir the aqueous solution was recycled back to the reactor. The gas feed, containing different amounts of isobutene, flowed on a once-through basis downward concurrently with the liquid. The reactor consisted of a 1.5×10^{-2} m ID glass reactor equipped with a liquid distributor containing twelve 10^{-3} m ID capillary tubes. The reactor, reservoir, and auxiliary apparatus are shown in Figure 1. Reaction runs were made with and without a small bed of glass beads as prepacking. Operating conditions and dimensions are listed in Table 1. A complete description of the apparatus and operating procedure is available (Leung, 1986).

The catalyst particles, Amberlyst-15, are spherical beads that consist of agglomerates of gel-type microparticles of sulfonated copolymers of styrene, crosslinked with 20% divinyl benzene. Catalyst properties are given by Leung, et al. (1986). A small amount, 0.788×10^{-3} kg, of catalyst was used in order to achieve differential reactor operation. Conversions of isobutene were less than 15% per pass. For a first-order reaction Massaldi and Maymo (1969) have shown that negligible error is introduced in assuming a constant rate of reaction when the conversion does not exceed 15%. With proper pretreatment, as described by Leung et al., the catalyst activity does not decay over a period of several months.

Analytical methods

Reaction rates were obtained by periodically sampling the liquid leaving the reactor (location 3 in Figure 1) and analyzing for tertiary butyl alcohol. The analysis was carried out in a gas chromatograph with flame ionization detector and a column of 15% Carbowax 20M on 80/100 mesh Chromosorb W, operated at 358 K. Nitrogen was used as carrier gas, and isopropyl alcohol was employed as an internal standard to improve accuracy.

In order to evaluate isobutene concentrations in the liquid entering the distributor and leaving the reactor, 2×10^{-9} m^3 samples were taken using a gas-tight syringe, and were immediately injected into the gas chromatograph. The necessary calibration curve was obtained by injecting samples of known isobutene concentration. The isobutene analyses were carried out with the same chromatograph column operated at 358 K.

Feed conditions

For the equilibrium feed condition, pure isobutene gas (Phillips Chemical Co., 99% purity) and distilled water saturated with isobutene were fed to the reactor. Since the streams were in equilibrium, there was no mass transfer in the regions above the

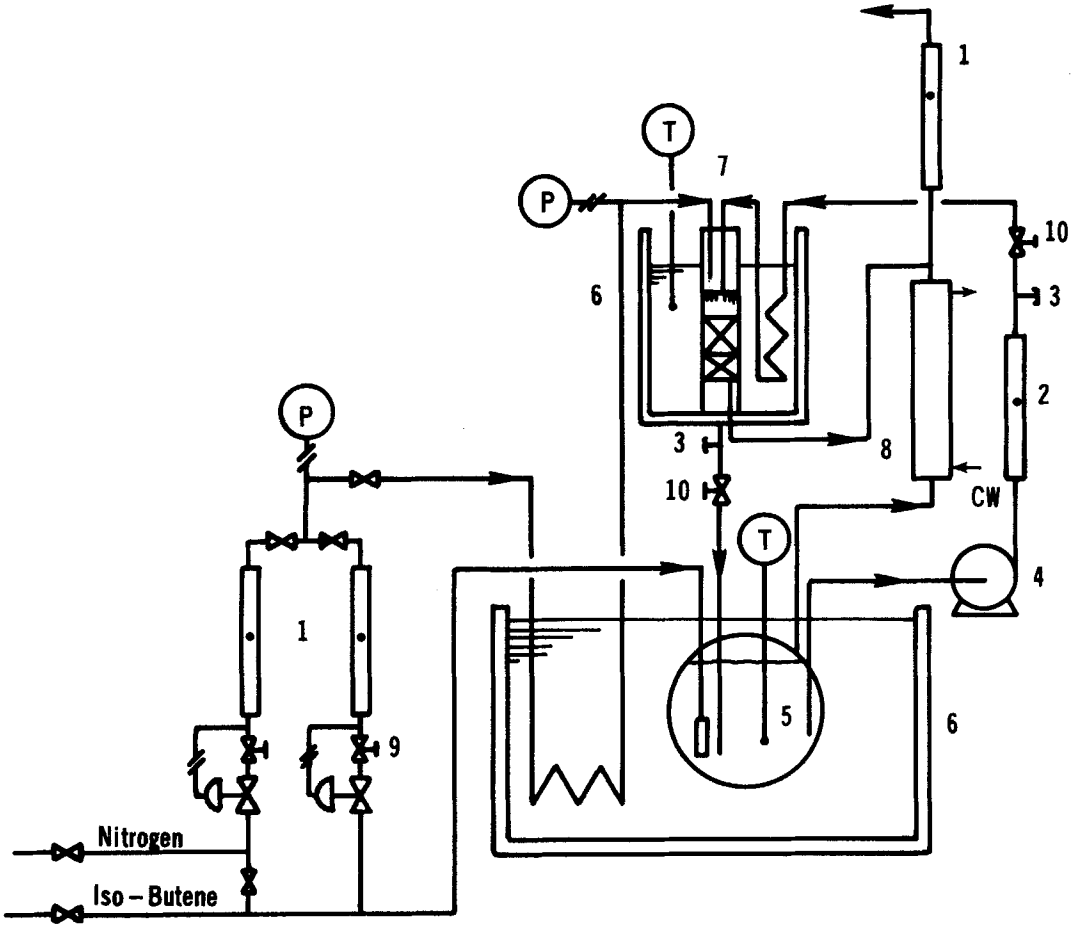

Figure 1. Apparatus.

1. Gas rotameters
2. Liquid rotameter
3. Sampling septa
4. Recycle pump
5. Reservoir with isobutene sparger
6. Constant-temperature bath
7. Trickle-bed reactor
8. Reflux condenser
9. Flow controllers
10. Needle valves

Table 1. Operating Conditions

Reactor ID	1.5×10^{-2} m
Catalyst	Amberlyst-15D
Catalyst* and prepacking particle size, d_p	0.45×10^{-3} m
Mass of catalyst, m	0.788×10^{-3} kg
Glass bead prepacking height, z_p	13×10^{-3} m
Height of empty column above prepacking, z_1	5×10^{-3} m
Height of empty column below prepacking, z_2	50×10^{-3} m
Catalyst bed height, z_c	10×10^{-3} m
Liquid flow rate, Q_L	0.55 to 3.42×10^{-6} m^3/s
Gas flow rate** to reactor, Q_g	1.7 and 5.5×10^{-6} m^3/s
Gas flow rate** to reservoir	4.2×10^{-6} m^3/s
Reactor temp.	323 K
Reactor press.	1×10^5 Pa
Liquid volume in reservoir and lines, V_T	10^{-3} m^3

*Effective wet size, after conditioning dry-sieved fractions of catalyst particles (35–50 mesh)

**At room temperature and atmospheric pressure

catalyst bed. Isobutene was continuously bubbled through the water in the reservoir. Analysis of the data showed that mass transfer resistance from gas to liquid in the catalyst bed was much less than the resistance of the other rate steps. Therefore, the gas and liquid streams were in near equilibrium with respect to isobutene throughout the catalyst bed.

For the absorption runs, pure isobutene gas and water partially stripped of isobutene (in the reservoir) were fed to the reactor. Nitrogen was continuously bubbled through the water returned to the reservoir to remove isobutene. Stripping was not complete and also there was some transfer of isobutene to the liquid in the regions above the catalyst bed. The concentration of isobutene entering the catalyst bed was calculated from independent mass transfer data as described later.

For desorption runs, pure nitrogen and water partially saturated with isobutene were fed to the reactor. Isobutene was continuously bubbled through the water in the reservoir during a run. However, there was considerable transfer from the liquid to the nitrogen gas in the region above the catalyst bed. Hence, the water entering the catalyst bed was not saturated. Again separate mass transfer data were used in order to evaluate the isobutene concentration entering the catalyst bed.

Calculation of Reaction Rates

Figure 2 shows alcohol concentration vs. time for a typical equilibrium run. The linear relationship verifies that the rate is constant during a run. The line does not pass through the origin because pure water was not used at the beginning of each run. Earlier data in a liquid-full reactor (Leung et al., 1986) indicated that alocohol concentrations as high as 3×10^{-3} kmol/m^3 did not affect the solubility of isobutene or influence the reaction rate.

Because of the slight volatility of the alcohol, a small amount was stripped from the liquid in the reservoir and the reactor. The method of accounting for this loss is described by Leung, et al. The result is the inclusion of a correction factor β in the following batch-recycle reactor expression for the rate:

$$r = (1 + \beta)\left(\frac{V_T}{m}\right)\frac{dC_{TBA}}{dt} \qquad (1)$$

The value of β, the ratio of the evaporation rate to the accumulation rate of alcohol, is 0.087 at the operating conditions of 323 K and atmospheric pressure. Equation 1 and the alcohol concentration vs. time measurements were used to calculate reaction rates.

Isobutene Concentration Entering Catalyst Bed

Figure 3 displays the three arrangements used to evaluate the mass transfer between gas and liquid in the regions above the catalyst bed and then the isobutene concentration in the liquid entering the catalyst bed. When data were taken with prepacking there were two such regions, labeled *top* and *pp* in Figure

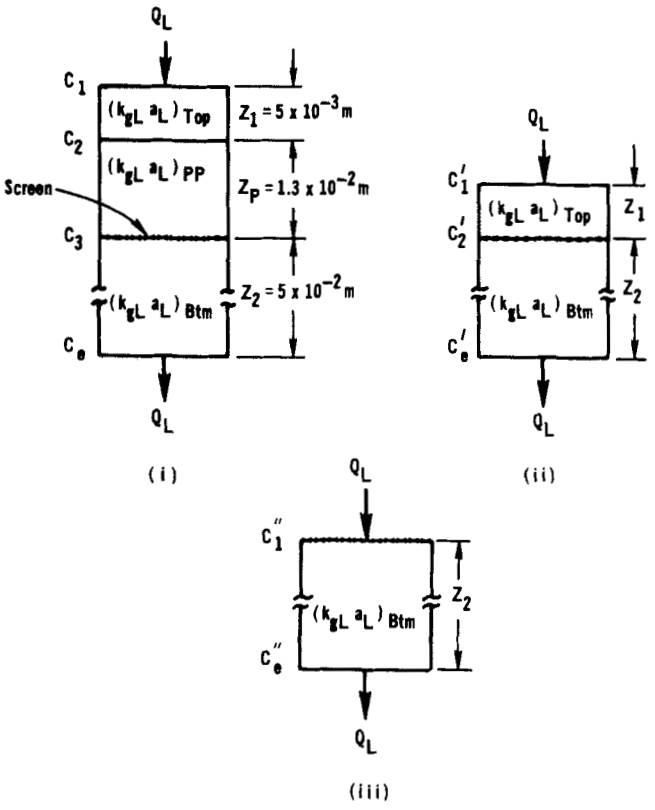

Figure 3. Apparatus arrangements for mass transfer study.

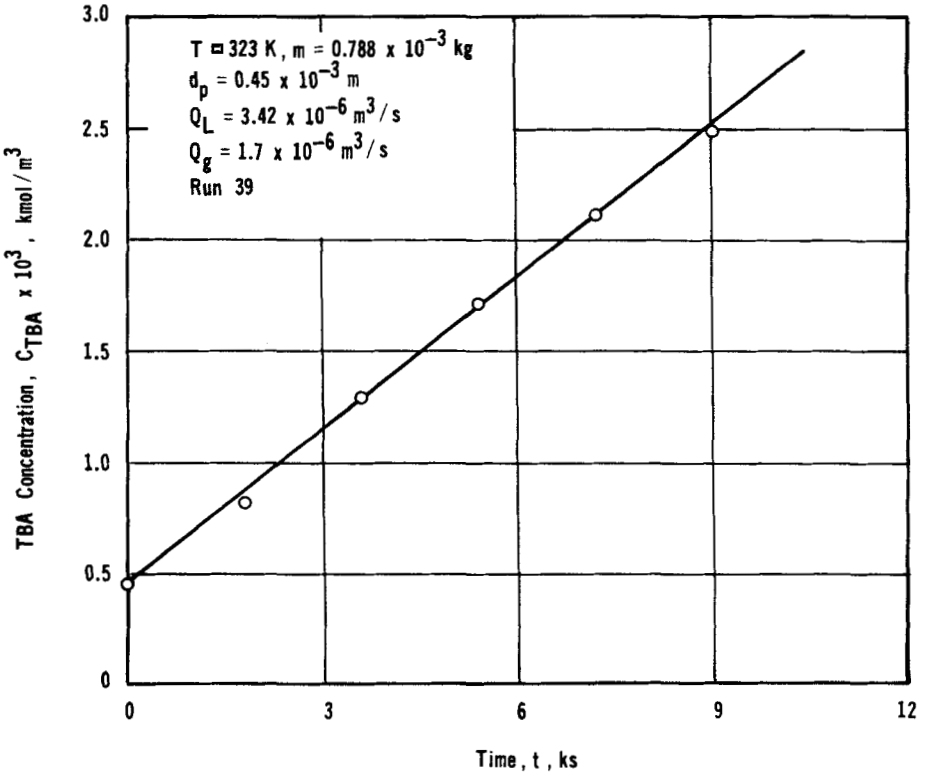

Figure 2. Accumulation of TBA vs. time in trickle-bed recycle reactor.
A-15D catalyst, equilibrium run

3(i). The top region refers to the empty tube space (5×10^{-3} m in length) between the outlet of the distributor and the top of the prepacking, Figure 3(i), or the screen, Figure 3(ii). In all cases the catalyst bed was removed, leaving only the screen that held the catalyst bed. The mass transfer rates of isobutene from gas to liquid were measured at 323 K and atmospheric pressure. The dimensions of the top, prepacking, and bottom (between screen and liquid exit) were the same as for the reaction runs, Table 1.

The method of analyzing the data was to write mass balances for each of the three arrangements. These equations were then solved for the rate coefficients $(k_{gL}a_L)z$ for each region, z_1, z_p, and z_2. Figure 4 shows the results for combinations of the three coefficients as a function of flow rate. The two curves that include the prepacking show a maximum at an intermediate flow rate. This may be due to a change in flow regime in the prepacking region. The flow regime map of Tosun (1984) indicates that at a liquid rate in our reactor of about 2.5×10^{-6} m^3/s, transition from trickling to pulsing flow occurs.

The values of $(k_{gL}a_L)z$ for the top and prepacking sections were then used with the measured liquid feed concentrations C_f to calculate the concentrations $C_{cat,a}$ and $C_{cat,d}$ of isobutene in the liquid entering the catalyst bed. Figures 5 and 6 show these results, as well as the feed concentrations, for absorption and desorption conditions, with and without prepacking. For the absorption runs with prepacking the concentrations entering the catalyst bed were as high as 42% of saturation, while for desorption the concentrations were as low as 60% of saturation. Without prepacking these values were no more than 20% for absorption and more than 80% for the desorption condition. Details of the method of calculation are given in the Supplementary Material.

The absorption and desorption concentrations were sufficiently different to provide independent equations relating f, $k_{gL}a_L$, and $k_{Ls}\,a_s$ in the catalyst bed. The C_{cat} values shown in Figures 5 and 6 were used along with the measured reaction rates to analyze the reaction data.

Experimental Rates and Derived Rate Equations

Equilibrium feed condition

Reaction rates calculated from the experimental data are shown in Figure 7 (with prepacking) and Figure 8 (without prepacking) for the three feed arrangements. The maxima and minima in the curves at a liquid flow rate of about 2.5×10^{-6} m^3/s are likely due to a change in flow regime. This phenomenon was also noted in the mass transfer experiments involving a packed section, Figure 4. In Figure 7 the experimental point for a threefold change in gas flow rate (equilibrium runs) indicates a negligible effect of gas rate.

According to the additive procedure of Tan and Smith (1980), the total rate of reaction for a first-order reaction is given by

$$r_{eq} = f k\eta C_{iB,s} + (1 - f) k\eta C^*_{iB,L} \qquad (2)$$

The concentration $C_{iB,s}$ is that on the liquid-covered outer surface, and the whole term represents the contribution to the reaction rate from this part of the surface. The second term represents the contribution from the gas-covered surface. Since the mass transfer resistance through the thin film of liquid on the gas-covered surface is very low, the concentration is assumed to

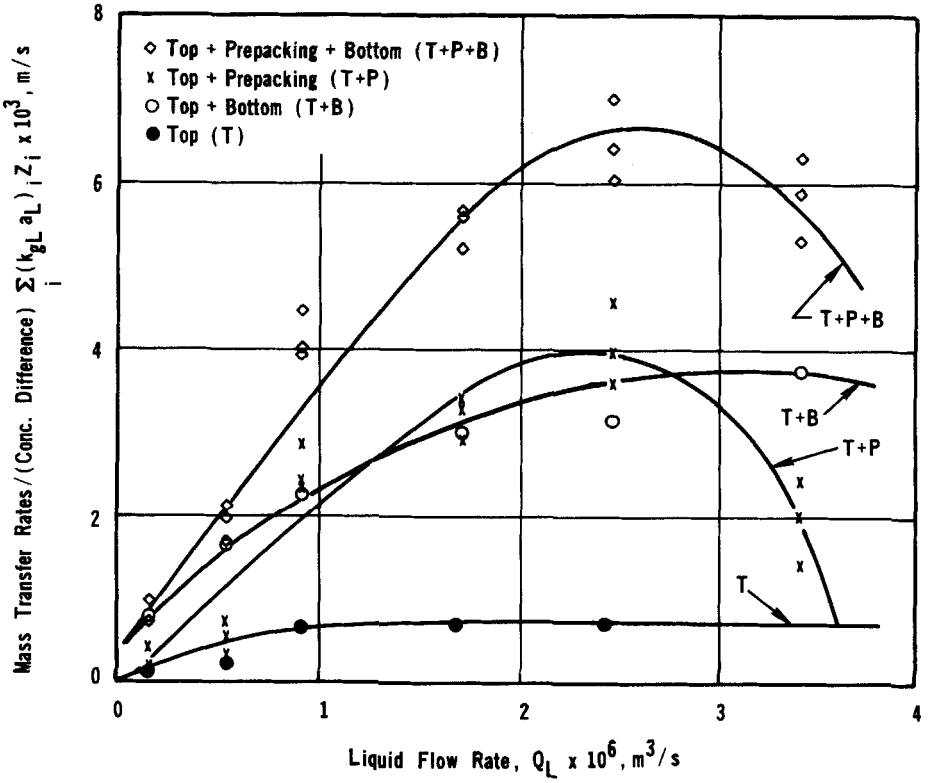

Figure 4. Effect of liquid rate on gas-to-liquid mass transfer in the three regions.

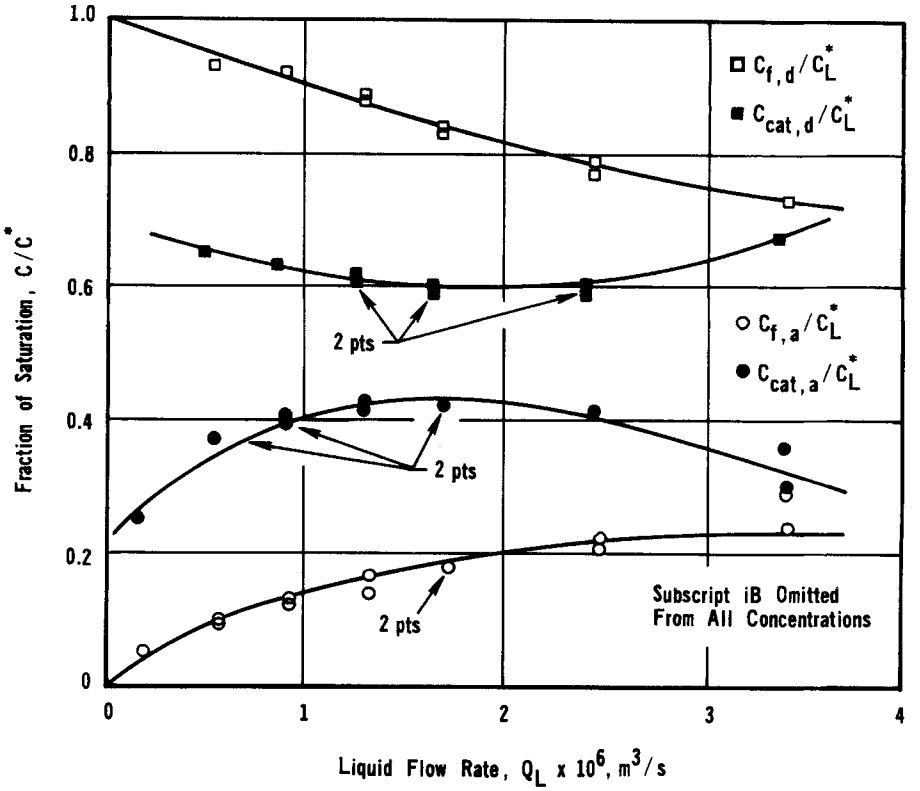

Figure 5. Concentration of isobutene in liquid feed and at top of catalyst bed.
Absorption and desorption runs with prepacking

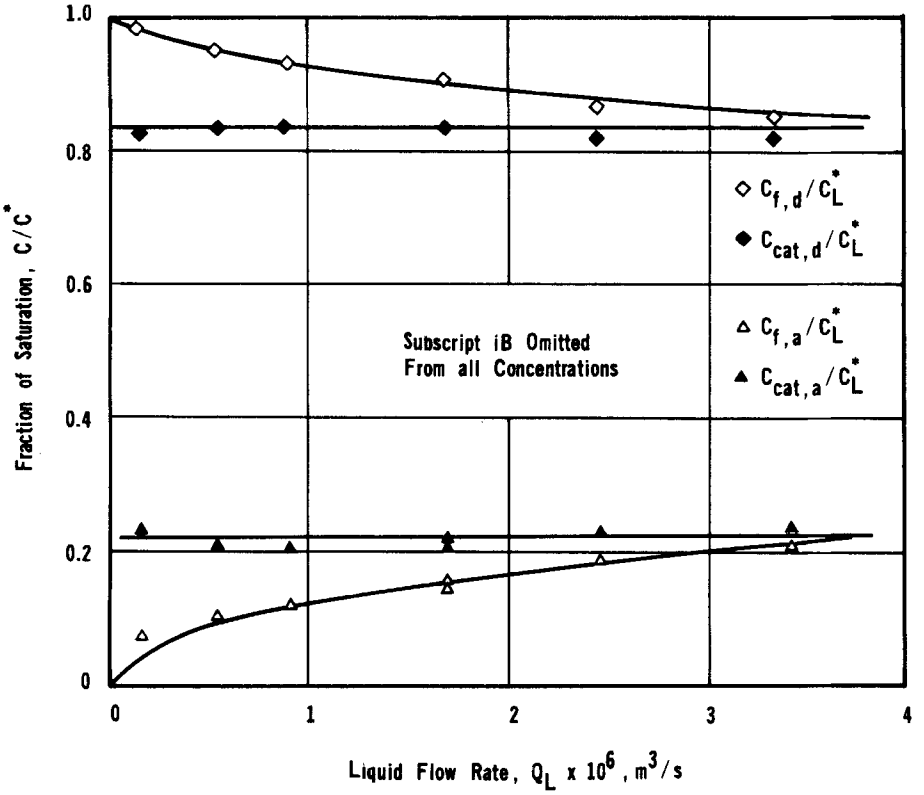

Figure 6. Concentration of isobutene in liquid feed and at top of catalyst bed.
Absorption and desorption runs without prepacking

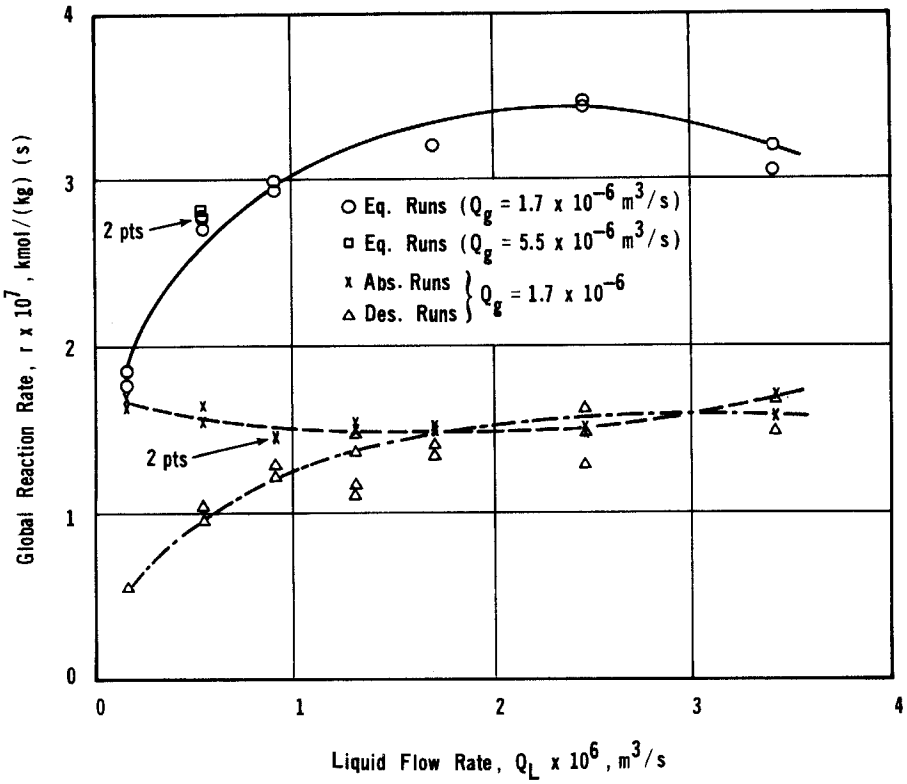

Figure 7. Trickle-bed reaction rates with prepacking.

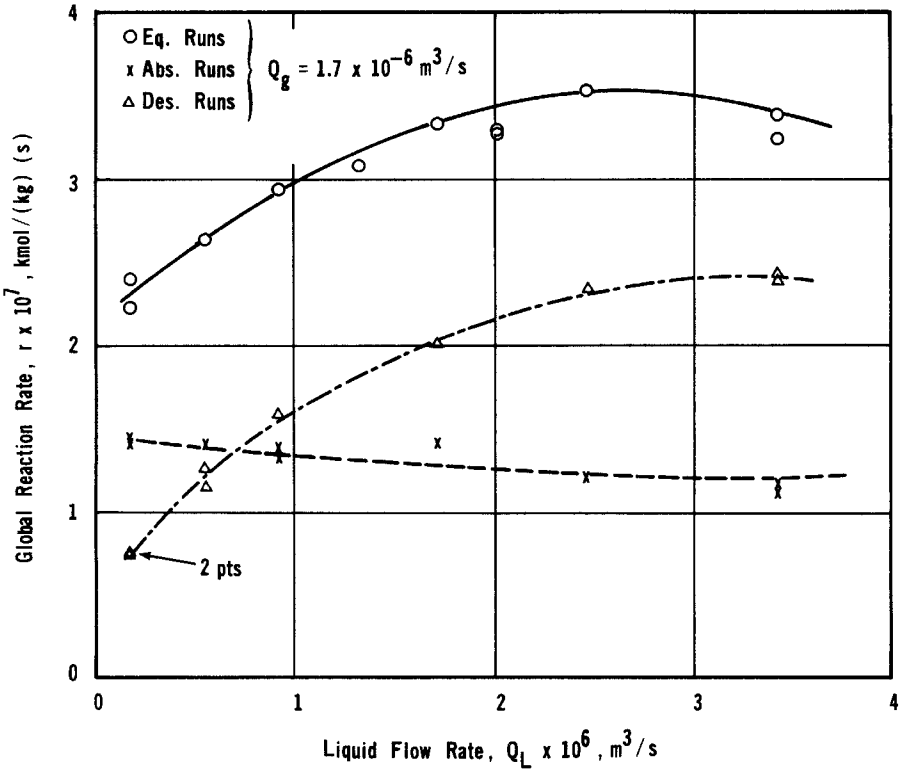

Figure 8. Trickle-bed reaction rates without prepacking.

be that in equilibrium with the concentration in the gas, that is $C^*_{iB,L}$.

To apply Eq. 2, $C_{iB,s}$ needs to be expressed in terms of known concentrations and the rate parameters. This is done by first writing the following mass balance of isobutene in the liquid phase around the differential reactor:

$$Q_L(C^*_{iB,L} - C_{iB,e}) = f(k_{Ls}a_s)(C_{iB,L} - C_{iB,s})_{ave}Sz_c - f(k_{gL}a_L)(C^*_{iB,L} - C_{iB,L})_{ave}Sz_c \quad (3)$$

where $C_{iB,e}$ is the concentration in the effluent liquid. The mass transfer term from gas to liquid in Eq. 3 includes the factor f. This assumes that the gas-liquid area is proportional to the fraction of the particle surface area covered by liquid. Whether or not f is included in this term has little effect on the final equation for the rate (Eq. 8).

The mass transfer rate to the liquid-covered surface is equal to the contribution to the reaction rate from this surface. Again using the Tan and Smith (1980) concept, this contribution is given by

$$f(k_{Ls}a_s)(C_{iB,L} - C_{iB,s})_{ave} = f k\eta C_{iB,s}\,(m/Sz_c) \quad (4)$$

The average concentration differences are nearly equal to the arithmetic averages for the differential reactor. Thus,

$$(C_{iB,L} - C_{iB,s})_{ave} = \tfrac{1}{2}[(C^*_{iB,L} - C_{iB,s}) + (C_{iB,e} - C_{iB,s})] = \tfrac{1}{2}(C^*_{iB,L} + C_{iB,e}) - C_{iB,s} \quad (5)$$

and

$$(C^*_{iB,L} - C_{iB,L})_{ave} = \tfrac{1}{2}[(C^*_{iB,L} - C^*_{iB,L}) + (C^*_{iB,L} - C_{iB,e})] = \tfrac{1}{2}(C^*_{iB,L} - C_{iB,e}) \quad (6)$$

Using Eqs. 5 and 6 for the average concentration differences, and Eqs. 4 and 5 to eliminate $C_{iB,e}$, Eq. 3 can be solved for $C_{iB,s}$:

$$C_{iB,s} = \frac{C^*_{iB,L}}{1 + k\eta\left(\frac{m}{Sz_c}\right)\left(\frac{1}{k_{Ls}a_s} + \frac{1}{\frac{2Q_L}{fSz_c} + k_{gL}a_L}\right)} \quad (7)$$

Substitution of this expression for $C_{iB,s}$ in Eq. 2 gives a predictive equation for the rate for the equilibrium feed condition:

$$r_{eq} = \frac{fC^*_{iB,L}}{\frac{1}{k\eta} + \frac{m}{Sz_c}\left(\frac{1}{k_{Ls}a_s} + \frac{1}{\frac{2Q_L}{fSz_c} + k_{gL}a_L}\right)} + (1-f)k\eta C^*_{iB,L} \quad (8)$$

In Eq. 8, η is the conventional first-order effectiveness factor corresponding to a uniform concentration on the outer surface of the particle. For the same catalyst, temperature, and particle size, Leung et al. (1986) determined, from liquid-full experiments, $k\eta$ to be 1.66×10^{-4} m^3/kg cat · s. If the mass transfer surface from gas to liquid in Eq. 3 does not include the factor f, then f also appears in the $k_{gL}a_L$ term in Eq. 8.

Since $2Q_L/fSz_c \gg k_{gL}a_L$, the inclusion of f has a negligible effect on the rate.

Equation 8 is in terms of three rate parameters f, $k_{Ls}a_s$, and $k_{gL}a_L$.

Absorption feed condition

For this condition of a relatively high concentration of isobutene in the gas feed and a low concentration in the liquid feed, Figures 7 and 8 show that the rate increases slightly at low liquid flow rates. Since the mass transfer rate from liquid to particle should decrease as Q_L decreases, the rate is expected to decrease. The opposite result is because f is less than unity at low liquid rates. Hence, an increasing amount of reaction occurs on the gas-covered surface for which the mass transfer rate is high. The desorption results in Figures 7 and 8 provide further evidence for this interpretation, as discussed later.

The same analysis employed for the equilibrium runs can be used to obtain a predictive equation for the rate r_a. The mass balance of isobutene in the liquid phase for the absorption condition is

$$Q_L(C_{iB,cat} - C_{iB,e}) = f(k_{Ls}a_s)(C_{iB,L} - C_{iB,s})_{ave}Sz_c - f(k_{gL}a_L)(C^*_{iB,L} - C_{iB,L})_{ave}Sz_c = 0 \quad (9)$$

where $C_{iB,cat}$ is the concentration in the liquid entering the catalyst bed, as obtained from Figures 5 and 6. Equations similar to Eqs. 5 and 6 may be written for the average concentration differences. Equation 4 also is applicable. The resulting expression for $C_{iB,s}$ is

$$C_{iB,s} = \frac{\left(\frac{2Q_L}{fSz_c}\right)C_{iB,cat} + (k_{gL}a_L)C^*_{iB,L}}{k\eta\frac{m}{Sz_c}\left[\left(\frac{2Q_L}{fSz_c} + k_{gL}a_L\right)\left(\frac{Sz_c}{k\eta m} + \frac{1}{k_{Ls}a_s}\right) + 1\right]} \quad (10)$$

Substituting Eq. 10 in Eq. 2 gives the following expression for the rate for the absorption feed condition:

$$r_a = \frac{\left(\frac{2Q_L}{Sz_c}\right)C_{iB,cat} + f(k_{gL}a_L)C^*_{iB,L}}{\frac{m}{Sz_c}\left[\left(\frac{2Q_L}{fSz_c} + k_{gL}a_L\right)\left(\frac{Sz_c}{k\eta m} + \frac{1}{k_{Ls}a_s}\right) + 1\right]} + (1-f)k\eta C^*_{iB,L} \quad (11)$$

Since $k\eta$ is known, Eq. 11 is also an expression for the reaction rate in terms of the three parameters f, $k_{Ls}a_s$, and $k_{gL}a_L$.

Desorption feed condition

The rate data shown in Figures 7 and 8, for a feed condition of zero isobutene in the gas (pure N_2 feed) and much isobutene in the liquid, show a continuous increase with liquid flow rate. The rate is very low at the lowest liquid rate, where $f < 1$, because there is little contribution from the gas-covered surface. The increase in rate with Q_L is explainable by the increased contribution from the liquid-covered surface due to increasing turbulence, i.e., an increase in $K_{Ls}a_s$.

Since the gas feed is pure nitrogen, the concentration of isobutene in the gas entering the catalyst bed is very low. Mass bal-

ances of isobutene in the gas and liquid phases in the region above and in the catalyst bed show that the average liquid concentrations, in equilibrium with the gas entering and leaving the catalyst bed, are of the order of 1.6×10^{-5} kmol/m^3. This is only about 1% of concentration in the bulk liquid. Neglecting this liquid concentration ($C^*_{iB,L} \sim 0$), the mass balance of isobutene in the liquid, analogous to Eqs. 3 and 9, is

$$Q_L(C_{iB,cat} - C_{iB,e}) = f(k_{Ls}a_s)(C_{iB,L} - C_{iB,s})_{ave}Sz_c - f(k_{gL}a_L)(0 - C_{iB,L})_{ave}Sz_c \quad (12)$$

Again Eq. 4 is applicable, and appropriate expressions, similar to Eqs. 5 and 6, may be written for the average concentration differences. Then Eq. 2 becomes

$$r_d = f k\eta C_{iB,s} \quad (13)$$

Proceeding as before, the expressions for $C_{iB,s}$ and r_d are

$$C_{iB,s} = \frac{\left(\frac{2Q_L}{fSz_c}\right)C_{iB,cat}}{k\eta\frac{m}{Sz_c}\left[\left(\frac{2Q_L}{fSz_c} + k_{gL}a_L\right)\left(\frac{Sz_c}{k\eta m} + \frac{1}{k_{Ls}a_s}\right) + 1\right]} \quad (14)$$

$$r_d = \frac{\left(\frac{2Q_L}{Sz_c}\right)C_{iB,cat}}{\frac{m}{Sz_c}\left[\left(\frac{2Q_L}{fSz_c} + k_{gL}a_L\right)\left(\frac{Sz_c}{k\eta m} + \frac{1}{k_{Ls}a_s}\right) + 1\right]} \quad (15)$$

Equation 15 provides a third expression for the rate in terms of f, $k_{Ls}a_s$, and $k_{gL}a_L$.

Evaluation of Rate Parameters

Only two of Eqs. 8, 11, and 15 are independent. The three rates are related by the equation

$$\frac{r_{eq} - r_a}{r_d} = \frac{C^*_{iB,L} - (C_{iB,cat})_a}{(C_{iB,cat})_d} \quad (16)$$

where $(C_{iB,cat})_a$ and $(C_{iB,cat})_d$ are the concentrations in the liquid entering the catalyst bed for the absorption and desorption feed conditions, respectively. Therefore only two of the rate parameters can be evaluated from the three sets of rate data in Figures 7 and 8. The sensitivity of the rate to each parameter was evaluated using available correlations for $k_{Ls}a_s$ and $k_{gL}a_L$ from Dharwadkar and Sylvester (1977), Goto and Smith (1975), and Fukushima and Kusaka (1977). All the results are shown in Figure 9. Three of the curves are for $f = 1$, 0.9, and 0.8 with $k_{Ls}a_s$ and $k_{gL}a_L$ evaluated from the correlation of Goto and Smith. The relatively large deviation between the curves indicates that the equations are sensitive to the wetting efficiency. The effect of $k_{Ls}a_s$ on the rate is shown by the two curves, both for $f = 1$ and $k_{gL}a_L$ from Goto and Smith, but $k_{Ls}a_s$ evaluated in one case from Goto and Smith and in the other Dharwadkar and Sylvester. The two correlations for $k_{Ls}a_s$ differ significantly, but still the two curves show a strong dependency on $k_{Ls}a_s$. Finally, two curves are shown, both for $f = 1$ and $k_{Ls}a_s$ from Goto and Smith, but $k_{gL}a_s$ from Fukushima and Kusaka for one curve and from

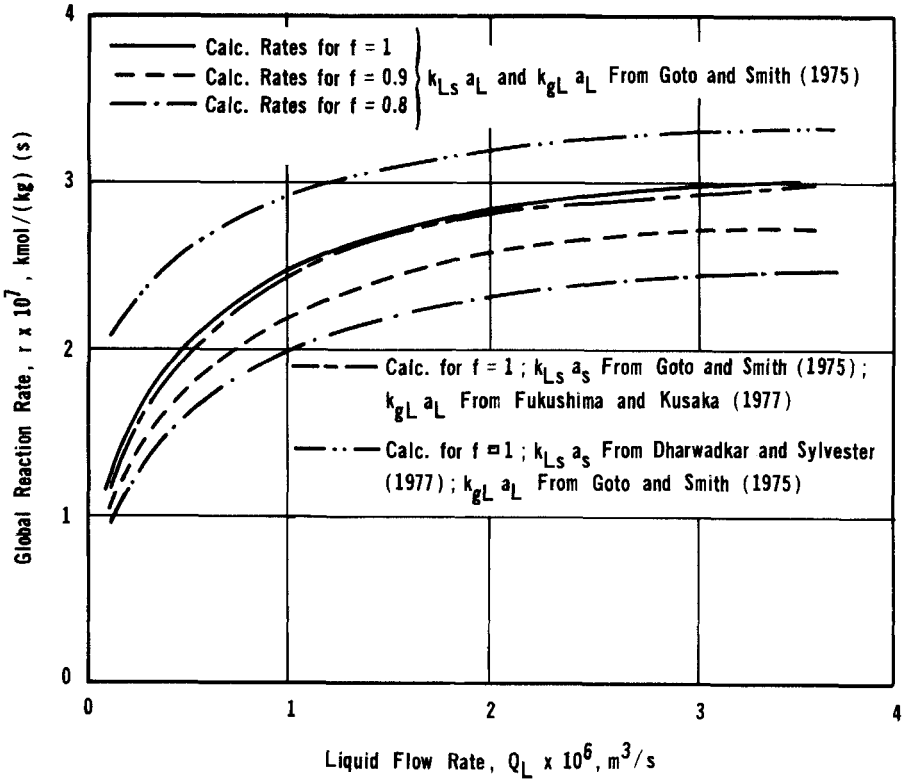

Figure 9. Sensitivity of reaction rates to f, $k_{Ls}a_s$, and $k_{gL}a_L$.
Desorption runs without prepacking

Table 2. Results of Two-Parameter Optimization*

$Q_L \times 10^6$ m³/s	With Prepacking f	With Prepacking $k_{Ls}a_s$ s⁻¹	Without Prepacking f	Without Prepacking $k_{Ls}a_s$ s⁻¹
3.42	0.83	0.187	0.89	0.259
2.46	0.89	0.230	0.85	0.281
1.70	0.88	0.187	0.79	0.205
1.31	0.86	0.158	—	—
0.92	0.85	0.141	0.78	0.129
0.55	0.77	9.64×10^{-2}	0.75	8.29×10^{-2}
0.16	0.71	2.71×10^{-2}	0.72	4.85×10^{-2}

*Using Subroutine ZXMWD with $k_{gL}a_L$ from Goto and Smith (1975)

Goto and Smith for the second curve. Even though the two correlations gave $k_{gL}a_L$ values that differ by two- to threefold, the two curves nearly coincide. It is concluded, for the reaction and conditions of this study, that gas-to-liquid mass transfer had little effect on the reaction rate. Hence, the rate can be analyzed to provide accurate results for $k_{Ls}a_s$ and f, but the data are not sensitive to $k_{gL}a_L$.

Optimal values of f and $k_{Ls}a_s$ were determined by minimizing the sum of the squares of the deviations between the predicted rates from Eq. 8, 11, and 15 and the experimental rates shown in Figures 7 and 8. The Goto and Smith correlation was used for $k_{gL}a_L$. Separate results were obtained for the runs with and without the prepacking section above the catalyst bed. The calculations were carried out utilizing an IMSL (1984) *Library User Manual* subroutine called ZXMWD (1984). This subroutine employed a quasi-Newton method for the optimization process.

The results for f and $k_{Ls}a_s$ are listed in Table 2. As expected,

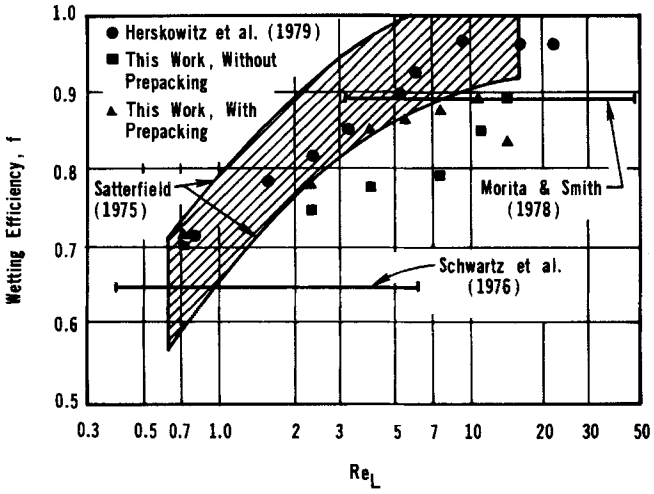

Figure 10. Comparison of wetting efficiencies.

both wetting efficiency and $k_{Ls}a_s$ decreased with decreasing liquid flow rate. The f values with prepacking are a little higher than f without prepacking at all the intermediate liquid rates. This may indicate that an improved liquid distribution increased the wetting efficiency. However, the ratio of reactor diameter to particle size, about 33, along with the liquid distributor met the criteria for uniform liquid distribution (Herskowitz and Smith, 1978). A more plausible explanation is that the difference in f values with and without prepacking is a measure of the accuracy of the data.

Figures 10 and 11 compare f and $k_{Ls}a_s$ with data from the literature. Most of the f values in Figure 10 are somwhat lower

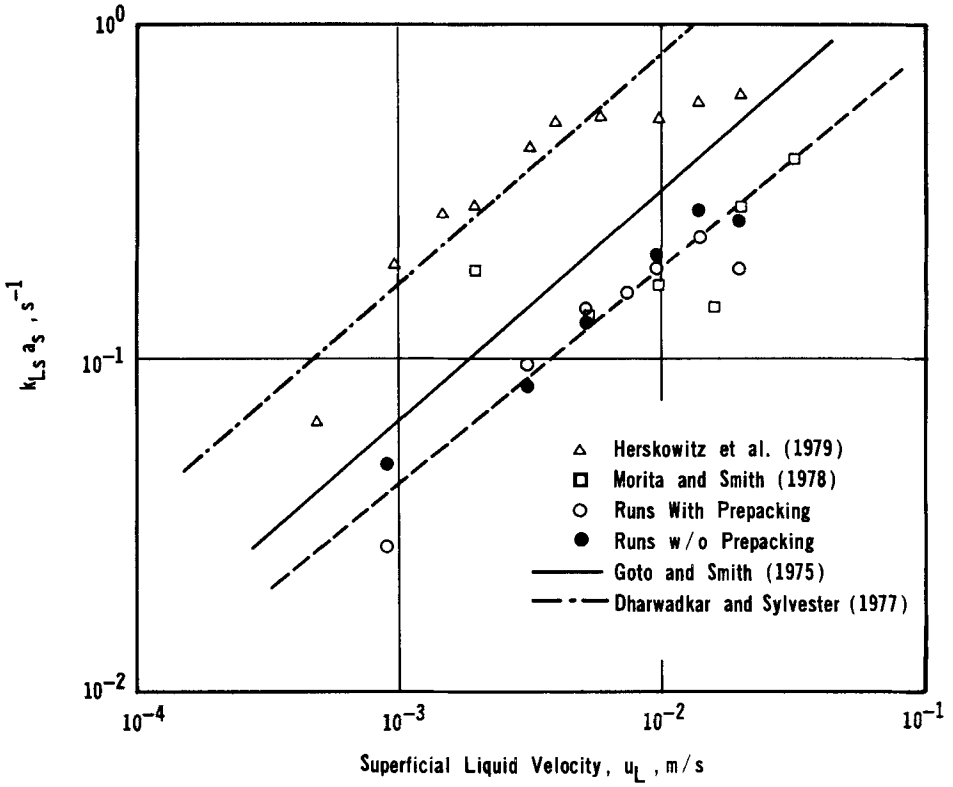

Figure 11. Comparison of liquid-to-particle mass transfer coefficients.

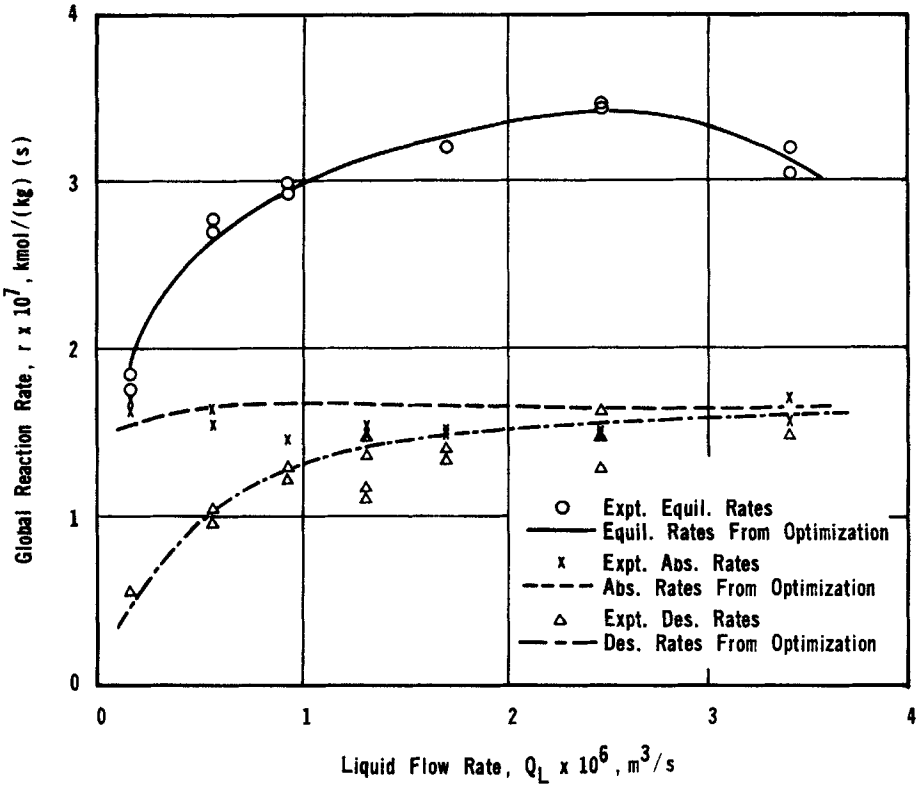

Figure 12. Predicted and experimental rates for runs with prepacking.

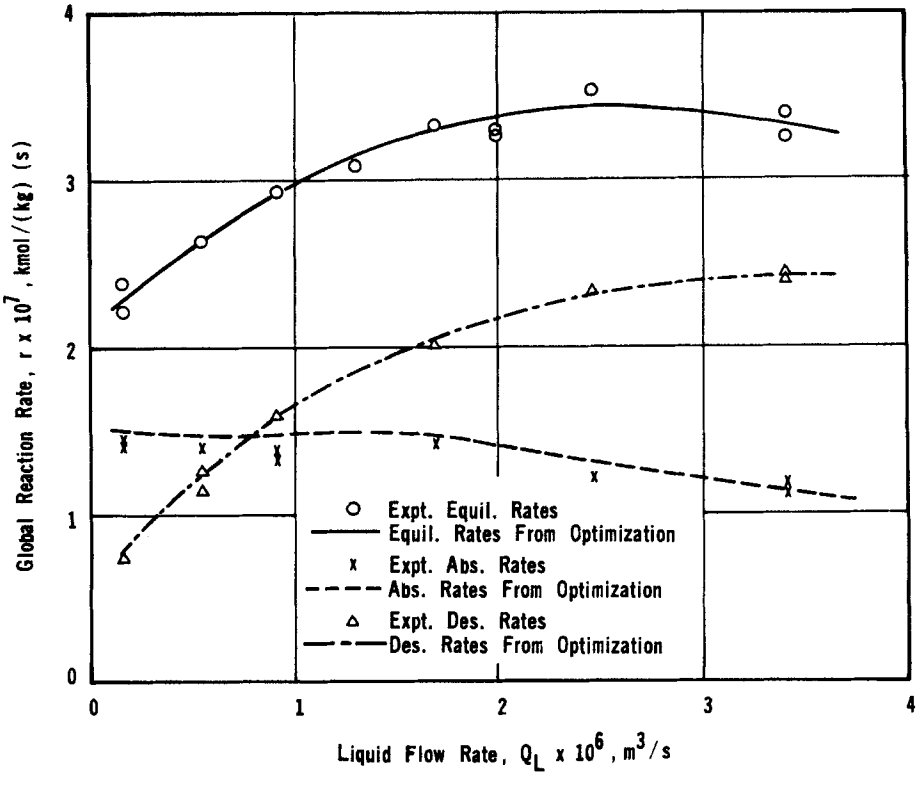

Figure 13. Predicted and experimental rates for runs without prepacking.

than the band proposed by Satterfield (1975) and most of the specific literature results. It may be that the high surface tension of water (73×10^{-3} N/m at 293 K; Weast [1982]) in our system explains why f is lower than the values found by Herskowitz et al. (1979) and Morita and Smith (1978), who used α-methyl styrene (surface tension = 32×10^{-3} N/m at 292K; Weast [1982]). The comparison shown in Figure 11 indicates lower values of $k_{Ls}a_s$ than the results from the literature. Again the reason may be due to differences in surface tension that could affect the effective mass-transfer area. The dependency of $k_{Ls}a_s$ on liquid velocity from our data agrees with that of the earlier studies.

Figures 12 and 13 compare the experimental rates with those predicted using the optimal values of f and $k_{Ls}a_s$. Good agreement is obtained with and without the prepacking section. The predicted rates exhibit the slight increase with decreasing liquid rate for the absorption feed condition and the strong decrease in rate with decreasing liquid rate observed for the desorption feed condition. These trends are required of a predictive method that satisfactorily explains the effect of a wetting efficiency less than unity at low liquid rates.

Thus the results of this study support the additive method, Eq. 2, of accounting for wetting efficiency.

Acknowledgement

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Notation

a_L = effective gas-liquid mass transfer area, m^2/m^3
a_s = effective liquid-solid mass transfer area, m^2/m^3
C = concentration, $kmol/m^3$
d_p = particle diameter, m
f = wetting efficiency
k = intrinsic rate constant, $m^3/kg\ cat \cdot s$
k_{Ls} = liquid-solid mass transfer coefficient, m/s
k_{gL} = gas-liquid mass transfer coefficient, m/s
m = mass of catalyst bed, kg
Q = flow rate, m^3/s
r = total reaction rate, $kmol/kg\ cat \cdot s$
Re_L = liquid Reynolds number, $d_p u_L \rho_L / \mu_L$
S = cross-sectional area of reactor, m^2
u_L = superficial liquid velocity, m/s
V_T = total liquid volume, m^3
z = reactor length, m
z_1 = height of empty column above bed, 5×10^{-3} m
z_2 = height of empty column below bed, 5×10^{-2} m
z_c = height of catalyst bed = 1.0×10^{-2} m
z_p = height of prepacking = 1.3×10^{-2} m

Greek letters

β = ratio of evaporation rate to accumulation rate of TBA
ρ_L = liquid density, kg/m^3
η = effectiveness factor
μ_L = liquid viscosity, $N \cdot s/m^2$

Subscripts

a = absorption feed condition
ave = average
btm = bottom section below catalyst bed
cat = catalyst bed
d = desorption feed condition
e = exit
eq = equilibrium feed condition
f = feed
g = gas
gL = gas-liquid
iB = isobutene
L = liquid
Ls = liquid-solid
pp = prepacking section above catalyst bed
$r \times n$ = reaction
s = outer surface of particle
T = total
TBA = tertiary butyl alcohol
top = top section above catalyst bed or prepacking section

Superscript

* = equilibrium or saturated value

Literature Cited

Colombo, A. J., G. Baldi, and S. Sicardi, "Solid-Liquid Contacting Effectiveness in Trickle-Bed Reactors," *Chem. Eng. Sci.*, **31**, 1101 (1976).

Dharwadkar, A., and N. D. Sylvester, "Liquid-Solid Mass Transfer in Trickle Beds," *AIChE J.*, **23**, 376 (1977).

Fukushima, S., and K. Kusaka, "Interfacial Area and Boundary of Hydrodynamic Flow Regime in Packed Column with Cocurrent Downward Flow," *J. Chem. Eng. Japan*, **10**, 461 (1977).

Goto, S., and J. M. Smith, "Trickle-Bed Reactor Performance," *AIChE J.*, **21**, 707 (1975).

Herskowitz, M., R. G. Carbonell, and J. M. Smith, "Effectiveness Factors and Mass Transfer in Trickle-Bed Reactors," *AIChE J.*, **25**, 272 (1979).

Herskowitz, M., and J. M. Smith, "Liquid Distribution in Trickle-Bed Reactors. I: Flow Distribution," *AIChE J.*, **24**, 439 (1978).

———, "Trickle-Bed Reactors: A Review," *AIChE J.*, **29**, 1 (1983).

Leung, P. C., "Hydration of Isobutene in Trickle-Bed Reactors," Ph.D. Thesis, Univ. California, Davis (1986).

Leung, P. C., C. Zorrilla, F. Recasens, and J. M. Smith, "Hydration of Isobutene in Liquid-Full and Trickle-Bed Reactors," *AIChE J.*, **32**, 1839 (1986).

Massaldi, H. A., and J. A. Maymó, "Error in Handling Finite Conversion Reactor Data by the Differential Method," *J. Catal.*, **14**, 61 (1969).

Mata, A. R., and J. M. Smith, "Oxidation of Sulfur Dioxide in a Trickle-Bed Reactor," *Chem. Eng. J.*, **22**, 229 (1981).

Morita, S., and J. M. Smith, "Mass Transfer and Contacting Efficiency in a Trickle-Bed Reactor," *Ind. Eng. Chem. Fundam.*, **17**, 113 (1978).

Ramachandran, P. A., M. P. Dudukovic, and P. L. Mills, "A New Model for Assessment of External Liquid-Solid Contacting in Trickle-Bed Reactors from Tracer Response Measurements," ISCRE 9, Philadelphia (May, 1986).

Satterfield, C. N., "Trickle-Bed Reactors," *AIChE J.*, **21**, 209 (1975).

Schwartz, J. G., E. Wegér, and M. P. Dudukovic, "A New Tracer Method for Determination of Liquid-Solid Contacting Efficiency in Trickle-Bed Reactors," *AIChE J.*, **22**, 894 (1976).

Tan, C. S., and J. M. Smith, "Catalyst Particle Effectiveness with Unsymmetrical Boundary Conditions," *Chem. Eng. Sci.*, **35**, 1601 (1980).

Tosun, G., "A Study of Cocurrent Downflow of Nonfoaming Gas-Liquid Systems in a Packed Bed. 1: Flow Regimes: Search for a Generalized Flow Map," *Ind. Eng. Chem. Process Des. Dev.*, **23**, 29 (1984).

Weast, R. C., ed., *Handbook of Chemistry and Physics*, 62nd ed., CRC Press, Boca Raton, FL (1982).

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