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*Manuscript received July 8, 1964; revision received October 15, 1964; paper accepted Octobed 23, 1964.*

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# Effect of Packing on the Catalytic Isomerization of Cyclopropane in Fixed and Fluidized Beds

**TADAO ISHII and G. L. OSBERG**

**National Research Council of Canada, Ottawa, Canada**

**An experimental study with fixed and fluidized beds in the isomerization of cyclopropane on a silica alumina catalyst is reported for a temperature range of 150° to 250°C. and of 5 to 150 *W/F* (g-catalyst, hr./g.-mole). The effects of various cylindrical screen packing, 0.2-, 0.4-, and 1.0-in. diameter, and 1.0-in. diameter pall ring, on final conversion were determined. Reactor scale effects were also considered with reactors of 0.9-, 1.8-, and 6.0-in. diameter and bed heights 1.8 to 11.0 in.**

**Overall conversions were higher in a fluidized bed with packing than in a normal fluidized bed but were less than in a fixed bed, though approaching it in some cases. Rate data from the fixed bed closely followed first-order kinetics. When the same catalyst was tested in a normal fluidized bed, the rate was dependent on linear gas velocity and catalyst bed height. With packing present in the fluidized bed, this dependency was much less, but packing size and shape had some effect.**

**Several previously proposed reactor models were considered for correlating the data.**

The fluidization technique has become a widely used method of solid-gas contact over the last twenty years because of a large amount of research and development effort in both industry and universities. The quantitative design of fluidized bed reactors is, however, complicated by the bypassing of the gas via bubbles and channels, with the result that in many reactions lower conversions are obtained in a fluidized bed than in a fixed bed at the same space velocity.

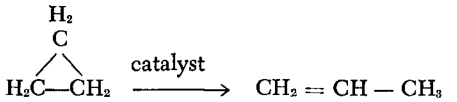
Consequently, many modified reactors have been proposed to control the nature of the gas and the solid flow in the fluidized bed. For example baffles, various packings, or stirring devices have been suggested to break a deep bed into a series of shallow beds or to obtain a uniform dispersion of small gas bubbles (*1, 2, 3, 4*). Overcashier et al. (*5*), Lewis et al. (*6*), and Massimilla et al. (*7*) have found that horizontal baffles improve the homogeneity of fluidized solid-gas systems, and this effect was most pronounced at high gas flow rates. Volk et al. (*8*) have used vertical surfaces such as tubes or half-rounds successfully and report that the conversion rates were the same in a 6.5-ft. diameter modified reactor as were obtained in 6-in. diameter reactor. Very little quantitative information regarding the effect of fixed packing on conversions in a fluidized bed reactor has been published. Sutherland et al. (*9*) as a result of a study of the effect of packing on fluidized bed properties such as minimum fluidization velocity, pressure drop, and heat transfer suggested that cylindrical screen packing should have useful applications in fluidized beds of free flowing materials. Gabor and Mecham (*10*) have reported data on radial gas mixing in fluidized beds containing spheres and solid cylindrical packing as part of a study on the reprocessing of spent nuclear fuels.

The work described in this paper is an investigation of the effect of perforated wall packing on a first-order catalytic reaction. Kinetic data between the fixed bed (with and without packing) and the fluidized bed (with and without packing) were obtained so that direct comparisons could be made.

## EXPERIMENTAL PROCEDURE

### Reaction Used

The reaction chosen for this study was the catalytic isomerization of cyclopropane to propylene,



The rate of isomerization was measured in the temperature range from 150° to 250°C. Inlet stream composition to the catalyst beds averaged about 2% cyclopropane and 98% air.

Roberts (*11*) studied the isomerization of cyclopropane using acidic solid catalysts. On silica-zirconia-alumina the apparent activation energy of isomerization was 19.0 Kcal. in the temperature range of 100° to 135°C. The most important side reaction was the dimerization of propylene. The material retained by the catalysts was probably largely propylene and polymers of propylene. Kinetics of the reaction were investigated with gas chromatographic methods by Bassett and Habgood (*12*). The reaction was first order at 370°C. on Na-Zeolite. The overall activation energy was 19.0 Kcal. in the temperature range 263° to 378.5°C. No hydrocarbons other than propylene were observed in the reaction products. This investigation also suggested that the presence of water or available protons is essential to the formation of a reaction intermediate in the isomerization of cyclopropane. Studies by Davis and Scott (*13*) have indicated that this isomerization behaves as an ideal homogeneous first-order reaction in contact with borosilicate glass equipment at constant pressure and at temperatures up to 620°C.

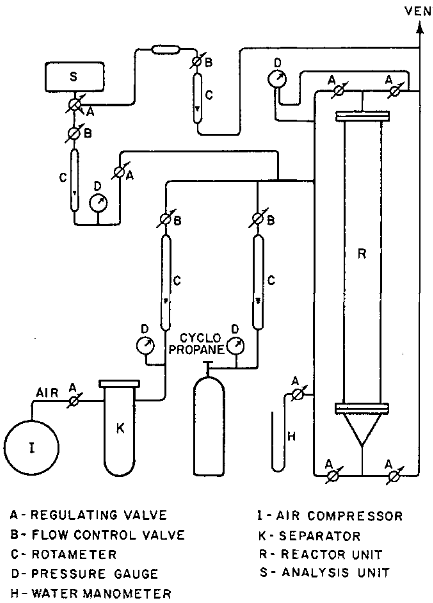


Fig. 1. Arrangement of experimental equipment.

### Catalyst

The catalyst used in the studies was the 150 to 200 Tyler mesh fraction of an equilibrated silica-alumina cracking catalyst. The bulk density of catalyst containing 2.2% water was 0.87 g./cc. A particle density of catalyst dried at 105° and 200°C. was 2.13 and 2.25 g./cc., respectively. The catalyst particles were generally round but not truly spherical. The catalyst contained 2.2% water when charged to the reactor.

### Apparatus

A flow diagram of the experimental system is shown in Figure 1. Cyclopropane of 99.5% purity was employed without further purification. Compressed air from a compressor was employed without drying or purification so that air contained some water vapor. Individual gases were metered by flow meter and mixed to about 2% cyclopropane. The combined feed stream was preheated before entering the catalyst bed. The experiments for both fixed bed and fixed bed with packing were carried out with downward flow of the gas. For the fluidized bed runs upward flow was used. The kinetic data were obtained with three reactors, *A*, *B*, and *C*. Details of the reactors are shown in Figure 2.

### Reactors

Reactor *A* consisted of a 16 in. length of 0.9-in. I.D. Pyrex tubing surrounded by a heated oil jacket to maintain the desired reaction temperature. The oil in the jacket was heated electrically, and its temperature was controlled automatically to about 1° to 2°C. A glass porous plate in the bottom of the tube supported the catalyst bed and distributed the gas uniformly. Temperature measurements of the catalyst bed were made with chromel-alumel thermocouple inserted in a small centrally located thermowell. A small glass cyclone separator was connected to the outlet of the reactor.

Reactor *B* consisted of a 30 in. length of 1.81-in. I.D. stainless steel tube surrounded by a sand bath fluidized by air. The reactor temperature was controlled by heating the sand bath with externally mounted electrical resistance heaters. Temperature measurements of the bed were made with a chromel-alumel thermocouple inserted in a small centrally located stainless steel tube of 0.12-in. O.D. A stainless steel porous plate was welded into the lower part of reactor to support the catalyst bed and to distribute the up-flow gas uniformly. Elutriated catalyst particles were collected by a small cyclone connected to the outlet of the fluidized reactor. The catalyst carry-over was generally negligible under the experimental conditions employed.

Reactor *C* consisted of a 48 in. length of 6.0-in. I.D. stainless steel tube. The lower flange held a stainless steel porous plate and was connected to a conical preheating section. The reactor temperature was automatically controlled by external heaters. The column was wound with four separate sections of heating wires and was insulated with asbestos insulation. The temperatures within the bed were measured by chromel-alumel thermocouples in stainless steel wells located on the axis and at the inside reactor wall. The temperature distribution of the bed was occasionally checked by moving the thermocouples in the wells. The upper flange supported a porous stainless steel filter which removed suspended catalyst from the upward flowing gas stream. In down-flow experiments, the upper part of reactor was used as a preheater.

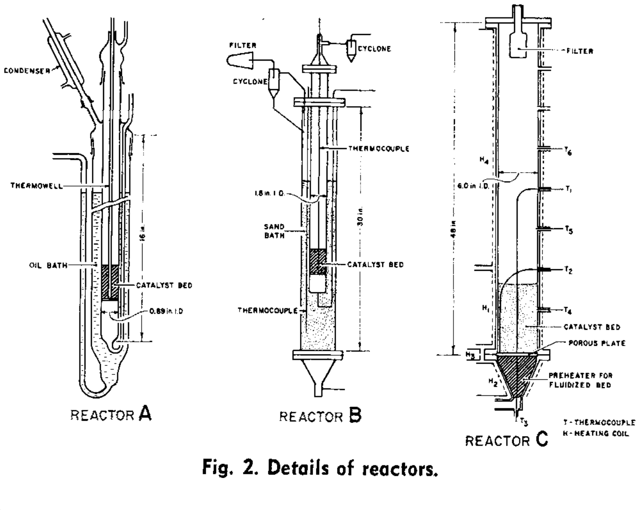


Fig. 2. Details of reactors.

### Packings

The packings used in the fixed and fluidized bed runs consisted of open-ended 14-mesh/in. stainless steel screen cylinders (wire 0.024 in. in diameter) of two sizes (0.2 × 0.2 in. and 0.4 × 0.4 in.). In addition, a 1.0 × 1.0 in. open-ended 14-mesh/in. mild steel screen cylinder and commercially available pall ring (1.0 × 1.0 in., mild steel) were used in fluidized bed runs as more probable sizes for possible industrial applications. In a typical run, the packing was poured into the reactor to a height greater than that of the catalyst bed. A known weight of bed was then added. In general, the ratio of the height of packing to the catalyst bed was maintained at 2.0 to 3.0, to make ample allowance for bed expansion in the fluidized bed runs. The catalytic activity of packing in the isomerization reaction was tested. All the packings used in the bed were inactive at temperatures less than 250°C., but some catalytic activity appeared above this temperature.

### Gas Analysis

Samples of inlet and outlet gas were analyzed for cyclopropane and propylene by gas chromatography with a chromatograph equipped with a hydrogen flame detector. Separations were made by a 10-ft column of propylene carbonate on fire brick with helium as the carrier gas. The temperature of the column was 40°C. and the pressure within the column 30 lb./sq. in. gauge. The sample volume was approximately 1.5 ml.

### Preliminary Experiments

Prior to establishing a standard testing procedure, preliminary experiments on catalyst stability were carried out in a 0.9-in. I.D. × 25-in. glass tube fitted with a porous plate and heated by an electrical resistance wire. Bed temperature was regulated with a temperature controller.

In a typical test, the catalyst activity decreased gradually during the first 70 hr. then became steady for the period 70 to 400 hr. for the temperature range 200° to 250°C. This reactor also served to evaluate the effects of inlet cyclopropane concentration, the effect of air as compared with nitrogen as the diluent and the catalyst. At the low cyclopropane concentration (about 1 to 2%) used in these experiments, no significant effects on conversion were observed for concentration fluctuations within ± 0.2%. With 1% cyclopropane concentration used the conversions were the same in air as in nitrogen, and so the oxygen in the air had no noticeable effect on the isomerization reaction. The selectivity of the reaction to propylene formation was studied at temperatures from 300° to 450°C. At 300°C. the selectivity was 92% and it decreased to 18.7% at 450°C. Although propylene was relatively stable over the whole temperature range investigated, a small portion of propylene was consumed at temperatures above 250°C.

From these preliminary experiments, the test reaction conditions were chosen to be in the temperature range from 150° to 250°C. with an inlet gas mixture of 2 ± 0.2% cyclopropane in air.

### Procedure

Prior to a set of runs, the required amount of catalyst was charged into the reactor and the various heater settings adjusted to give the desired line-out temperature. Before each run, the catalyst bed was dried for about 15 hr. in air at 200°C. Following this pretreatment, the reaction mixture was fed at the prescribed rate. For fixed bed operation, the gas flowed down through the bed but up through the bed for fluidized bed runs. The catalyst was allowed to reach a steady activity which took from 50 to 70 hr. before a run was begun at the test conditions. In order to compare the conversions at the same experimental conditions between the fixed and fluidized beds, the up-flow gas stream was switched to down flow for the fixed bed operation at the end of the sampling for the fluidized bed runs.

Temperature distribution within the bed was occasionally checked by moving the thermocouple in the wells. Experimental results were obtained at a constant bed temperature (generally 150° to 250°C. ± 1.0°C.) to eliminate the need for temperature corrections. The pressure drop across the catalyst bed compared with the operating pressure, which was atmospheric, was assumed negligible. At the maximum flow rates the outlet reactor pressure was 70 in. of water, but the greater part of the experimental data were obtained with the reactor pressure less than 20 in. of water. No corrections for pressure drop across the bed or for total reactor pressure were made to the reaction rate calculations. The weights of catalyst collected in the cyclone separator were negligible compared with the bed weights. The catalyst bed height $L$ was calculated by dividing the catalyst bed weight by the cross-sectional area of the reactor and by an average settled catalyst density of 0.87 g./cc. Thus $L$ as used in correlations in this report does not take into account bed expansion which occurred during fluidization. With packing present, $L$ was estimated from the total volume of the bed which was the sum of the packing volume and the settled bed volume. Separate reproducibility studies demonstrated that no noticeable change in catalyst activity took place during the runs. The activity was checked during each run by returning to the reference conditions of 200°C. and $W/F$ ratios within the range 28.6 to 57.6. The activity was found to be reproducible to within ± 0.5 to ± 2.0%.

### Velocity at Minimum Fluidization

The minimum fluidization velocity was taken as the point at which the pressure drop across the reactor (not the catalyst bed) vs. air flow curve showed a discontinuity. In cases where this sharp discontinuity did not occur, the intersection of the two parts of the curve was selected as the point defining $u_f$. No large effects of reactor size, bed height, packing size except for pall ring, or temperature on $u_f$ were observed. The average value of $u_f$ over the experimental range used was 0.0108 ± 0.0007 ft./sec.

## RESULTS

### Determination of Reaction Order and Rate Constants

The conversion of cyclopropane, that is the fraction of cyclopropane consumed as a function of $W/F$, and temperature for fixed beds with packing are shown in Figure 3. The conversions at high $W/F$ and high temperature approached 100%, and for this reason it may be concluded that the reaction is irreversible. The pressure drop across the catalyst bed was negligible, because a relatively small bed height and a low flow velocity were used for these fixed bed runs. All the data except a few points fall on single isothermal curves. The data represent three different diameters of reactor, three different $L/D$ ratios, various flow velocities, and five reaction temperatures. Although the data on the isothermal curves were a little scattered, no scale effects were observed in these fixed bed runs.

In order to compare the effect of packing on conversion in a fixed bed, a series of runs without packing present were performed. The experimental conditions were the same as for the fixed bed with packing. No large effects

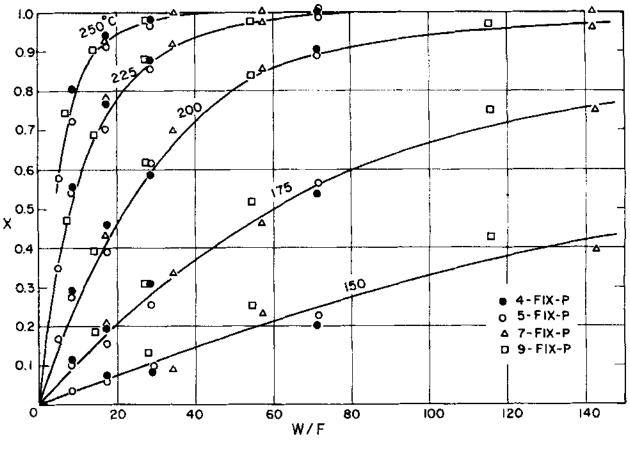


Fig. 3. Conversion as a function of $W/F$ for a fixed bed with packing.

TABLE 1. THE OVERALL FIRST-ORDER RATE CONSTANTS FOR A FIXED BED AND A FIXED BED WITH PACKING

| Temp, °C. | Rate constants<br>No packing<br>$k_o \times 10^2$ | <br>With packing<br>$k_p \times 10^2$ | Mean rate constants<br>$k_m \times 10^2$ | $\frac{k_p}{k_o}$ |
|---|---|---|---|---|
| 150 | 0.36 | 0.41 | 0.39 | 1.14 |
| 175 | 1.05 | 1.12 | 1.09 | 1.07 |
| 200 | 2.88 | 3.17 | 3.03 | 1.10 |
| 225 | 6.65 | 7.10 | 6.88 | 1.07 |
| 250 | 13.30 | 14.30 | 13.80 | 1.08 |

due to packing were found, although the data for the fixed bed with packing were slightly higher than for the runs without packing. In both series nearly isothermal conditions (± 1.0°C.) were obtained within the beds.

The rate equation for a catalytic reaction in a flow system may be written as

$$-r_A = yF\frac{dx}{dW} = y\frac{dx}{d(W/F)} \tag{1}$$

Thus, the rate of conversion corresponding to any given value of $W/F$ in Figure 3 will be given by the slope of the tangent to the curve at that point. A linear relationship between the conversion rate and the fractional conversion was found for both series. On the assumption that the total moles of gas undergoes no change during the reaction, the reaction follows approximately a first-order process, for which the equation is

$$r_A = -k\,y\,(1-x) \tag{2}$$

The values of first-order overall rate constant as defined by Equation (2) are given in Table 1. The rate constant $k_p$ for fixed bed with packing runs is slightly larger than the rate constant $k_o$ for runs without packing. The mean value of $k_p/k_o$ ratio within the temperature range 150° to 250°C. is 1.09. It is not clear why this ratio is larger. The mean value $k_m$ between $k_o$ and $k_p$ was, however, used in this paper as a measure of the activity of the catalyst bed.

Temperature dependency of rate constants was evaluated from an Arrhenius' plot over the temperature range from 150° to 250°C. An overall activation energy of 15.7 Kcal. was calculated from the slope of the curve log $k_m$ vs. $1/T$.

**Fluidized Bed Runs**

Fluidized bed runs without packing were made in the 0.9-, 1.8-, and 6.0-in. reactors at temperatures ranging from 150° to 250°C. and with various gas velocities and ratios of $L/D$. The fractional conversions as a function of $W/F$ are given in Table 2.* A typical run is shown in Figure 4. The conversions from the fluidized bed runs were usually less than those from the fixed bed runs. The data indicate that the $L/D$ ratio, gas velocity, and reactor diameter influence the final conversion. Furthermore these effects on conversion were much more evident at the higher temperatures.

The effect of packing on total conversion was also studied with various packings in a fluidized bed. These data listing conversions as a function of $W/F$ for the same temperature range and reactors are given in Table 3.* A typical run is shown in Figure 4. When these curves are compared with the fixed bed curves for the same bed temperatures, the conversions approach the fixed bed values but are lower especially at the higher temperatures. Thus, the first-order relationship which applied to the fixed bed data is not strictly applicable to the fluidized bed data. An apparent rate constant may be calculated on the assumption of the first-order rate form, however, and used for considering the effects of parameters such as $L/D$ ratio, gas velocity, reactor diameter, and bed temperature on conversion.

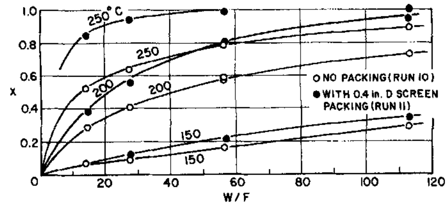


Fig. 4. Conversion as a function of $W/F$ and temperature for a fluidized bed with and without packing.

**Apparent Rate Constants for a Fluidized Bed**

When Equation (2) is substituted into Equation (1) and integrated for an idealized piston-flow reactor, the rate constant is given by

$$k = \frac{F}{W}\ln\left(\frac{1}{1-x}\right) \tag{3}$$

For an idealized piston-flow reactor, $k$ calculated from Equation (3) is numerically equal to the catalytic activity and is independent of the conversion, the flow rate, and the amount of catalyst. An apparent rate constant $k'$ may be estimated from Equation (3) for other types of reactors such as fluidized beds, but it is a function of the catalyst activity, the gas-solid contact, and the temperature. When the catalyst activity and the temperature are held constant, $k'$ becomes a measure of the effectiveness of the gas-solid contact and will generally be smaller than $k$ for a piston-flow reactor, because a fluidized bed reactor, for example, will usually not make so efficient use of the catalyst. Apparent rate constants as a function of the $L/D$ ratio, gas velocity, and temperature for the fluidized bed alone in the 1.8- and 6.0-in. reactor are plotted in Figure 5. When the temperature and the reactor diameter are held constant, $k'$ is a measure of the effects of the catalyst bed height and the gas velocity on gas-solid contact in a fluidized reactor. The fixed bed value is also shown in this figure for comparison. At the bed temperature of 250°C., $k'$ appears to decrease rapidly with increasing

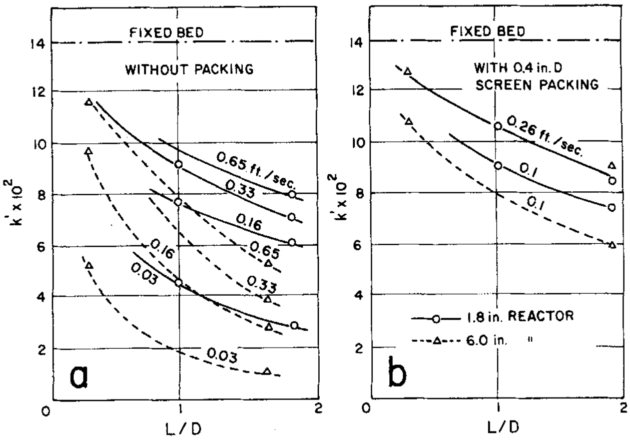


Fig. 5. Apparent rate constant as a function of $L/D$ ratio and gas velocity for a fluidized bed (*a*) without and (*b*) with 0.4-in. screen packing in the 1.8- and 6.0-in. diameter reactor. T-250°C.

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* Tabular material has been deposited as document 8257 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$1.25 for photoprints or \$1.25 for 35-mm. microfilm.

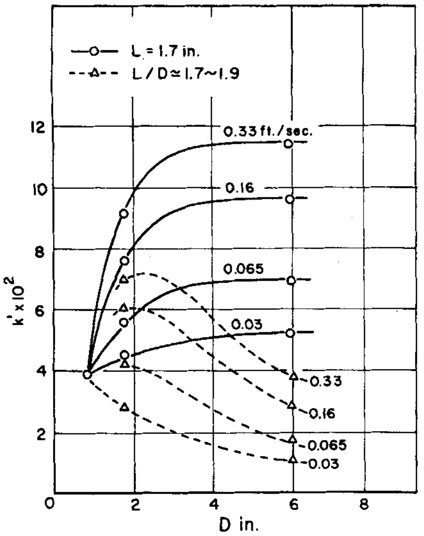

**Fig. 6. Apparent rate constant as a function of reactor diameter and gas velocity at constant bed height and at $L/D \simeq 1.7$ to 1.9 for a fluidized bed without packing.**

bed height and decreasing gas velocity. At lower temperatures the effects of these parameters on $k'$ were not as large.

Figure 6 shows the effects of the reactor diameter on $k'$ as a function of the gas velocity and the bed temperature at a constant settled bed height ($L = 1.75$ in.) for the fluidized bed. At small reactor diameters, the value of $k'$ increased, rapidly at first, then more slowly with increasing reactor diameter. These results suggest that at constant bed temperature and gas velocity the effectiveness of a gas-solid contact in a fluidized bed should depend only on the catalyst bed height for reactor diameters approaching 6-in. diameter. It is also interesting to note in Figure 6 that $k'$ for the 0.9-in. reactor is independent of the gas velocity, whereas for the 1.8- and 6.0-in. reactor the effect of the gas velocity on $k'$ is large. The effect of reactor diameter on $k'$ as a function of the gas velocity at an $L/D$ ratio in the range 1.7 to 1.9, that is geometrical similarity, is also illustrated in Figure 6. This plot shows that at small reactor diameters $k'$ increases initially with increasing reactor diameter because of the dominating effect of diameter, but as the reactor diameter is increased $k'$ finally decreases because of the diminishing effect of the reactor diameter and the increasing effect of the bed height.

The effect of the $L/D$ ratio on $k'$ as a function of the gas velocity was also determined for the fluidized bed with packing. The data for the fluidized bed with 0.4-in. screen packing in a 1.8-in. reactor and in a 6.0-in. reactor are shown in Figure 5*b*. The relationship between $k'$ and $L/D$ is similar in shape to that shown for the fluidized bed alone, but the values of $k'$ are appreciably higher, and the effect of reactor diameter is less.

The effect of packing size on $k'$ as a function of the ratio of the reactor diameter $D$ to the packing diameter $d$ was also considered. The data from the 6-in. reactor at $L/D = 1.7$ are shown in Figure 7. In this figure, $k'$ from the fluidized bed alone are plotted at $D/d = 1$. It is clear that the apparent rate constants for the fluidized bed with packing increased approximately inversely with $d$, when the bed diameter, the bed height, the gas velocity, and the bed temperature were held constant. It may also be expected that at larger values of $D/d$ the value of $k'$ for a fluidized bed with packing would be close to the fixed bed value, especially at a high gas velocity.

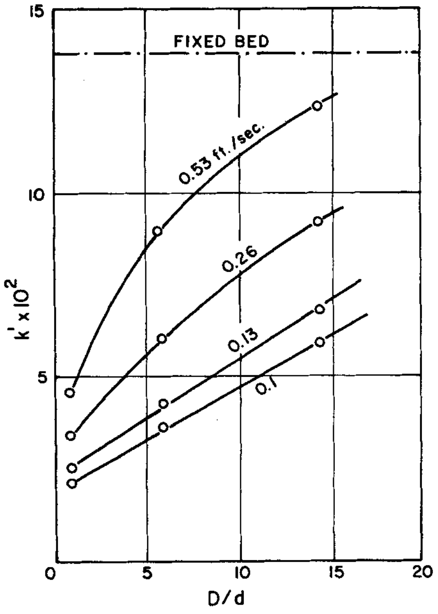

**Fig. 7. The effect of packing size on $k'$ as a function of $D/d$ ratio and gas velocity at $L/D = 1.7$ for a fluidized bed with packing in 6-in. reactor. T-250°C.**

## DISCUSSION OF RESULTS

### Fluidized Bed Without Packing

The conversion data for the fluidized bed alone are plotted as a function of dimensionless group $kW/F$, gas velocity, and settled bed height in Figure 8. The dashed line represents the conversion curve if the reaction took place in a completely mixed bed without bypassing. Except for the results at $L/D = 0.3$ in 6.0-in. reactor, Figure 8*b*, which lie above the dashed curve, all the data

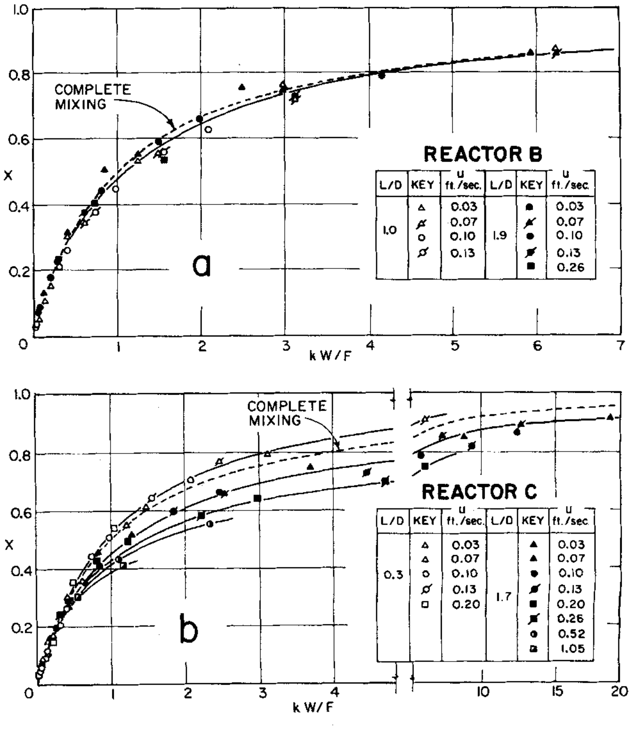

**Fig. 8. Conversion as a function of $k$ $W/F$ at various superficial gas flow rates for a fluidized bed without packing. *(a)* 1.8-in. diameter reactor, *(b)* 6-in. diameter reactor.**

fall below or on the completely mixed curve. Data obtained from the 0.9-in. reactor all fall below the line for complete mixing and were a function of gas velocity. The data in Figure 8*a* represent the conversions for five gas velocities and two $L/D$ ratios in the 1.8-in. reactor. All the data appear to be independent of the gas velocity and the bed height and fall on a single curve which approaches closely to the completely mixed system. Actually, $k'$ does depend upon gas velocity and bed height as shown in Figure 6, but the insensitiveness of the curves in Figure 8 to velocity and bed height is surprising but has been noted previously by Orcutt et al. (*14*). The data in Figure 8*b* represent the conversions for five gas velocities at $L/D = 0.3$ and for eight gas velocities at $L/D = 1.7$. All the data obtained at $L/D = 0.3$, which was the same bed height as shown in Figure 8*a*, fall on a single curve which is slightly higher than the line calculated for the completely mixed system. When such a shallow bed, that is $L = 1.75$ in., is used, the effects of the reactor diameter on conversions would be expected to be small and gas-catalyst contact would be expected to follow approximately the completely mixed system. When a bed of 10.2 in. height was used, the conversions as a function of $kW/F$ were clearly dependent upon the gas velocity. The data for the velocity range 0.03 to 1.0 ft./sec. at $L/D = 1.7$ show that the higher the gas velocity the lower the conversion.

### Fluidized Bed With Packing

All the data as a function of dimensionless group, $kW/F$, gas velocity, and settled bed height for fluidized bed with three different size screen packing, 0.2, 0.4, and 1.0 in., and with 1.0-in. pall ring in the two different reactors, 1.8- and 6.0-in. diameter, are given in Figure 9. The two dashed lines were calculated with the assumption of piston flow or of a completely mixed system. All the data in those figures lie between the piston flow and the completely mixed lines, whereas almost all the data for fluidized beds alone were lower than the completely mixed line. This illustrates a major effect of the presence of packing on the fluidized bed conversions.

In Figure 9*a* the results at 1.9 in. settled bed height for a fluidized bed with 0.2-in. screen packing in the 1.8-in. reactor are shown. The data represent five temperatures (150° to 200°C.) and five gas velocities (0.03 to 0.16 ft./sec.). All the data fall on the single curve which is close to the piston flow line. Thus it may be concluded that reaction temperature and gas velocity contribute no secondary effects. In Figure 9*b* the results for the fluidized bed with 0.4-in. screen packing in 1.8-in. reactor are shown. The data represent two bed heights (1.8 and 3.6 in.), five gas velocities (0.03 to 0.16 ft./sec. and 0.03 to 0.26 ft./sec., respectively), and five temperatures (150° to 250°C.). These data also fall on a single curve which lies between the piston flow and the completely mixed system within a deviation of about ± 2.0%. The curve through the data is lower than that for the 0.2-in. screen packing used in Figure 9*a*, and the effects of packing size are clearly indicated. However, again no significant difference due to the reaction temperature, the gas velocity, and the bed height were observed. In Figure 9*c* the results obtained with 0.4-in. screen packing in 6.0-in. reactor are given. The data represent two bed heights (1.8 and 11.0 in.), five gas velocities (0.03 to 0.20 ft./sec. and 0.10 to 0.53 ft./sec., respectively), and five temperatures (150° to 250°C.). Most of the data fall on a single curve within a deviation of about ± 2.0%. Although the same 0.4-in. screen packing as in Figure 9*b* was used in this case, the curve is very similar to the curve shown in Figure 9*a* for which a 0.2-in. packing was used. In Figure 9*d* the results for a 1.0-in. packing in 6.0-in. reactor are shown. The data represent two different packings (1.0-in. screen packing and 1.0-in. pall ring), five gas velocities (0.1 to 0.52 ft./sec.), and five temperatures. All the data fall on a single curve for each packing with a deviation of about ± 2.0%. The curve for a 1.0-in. pall ring is higher than

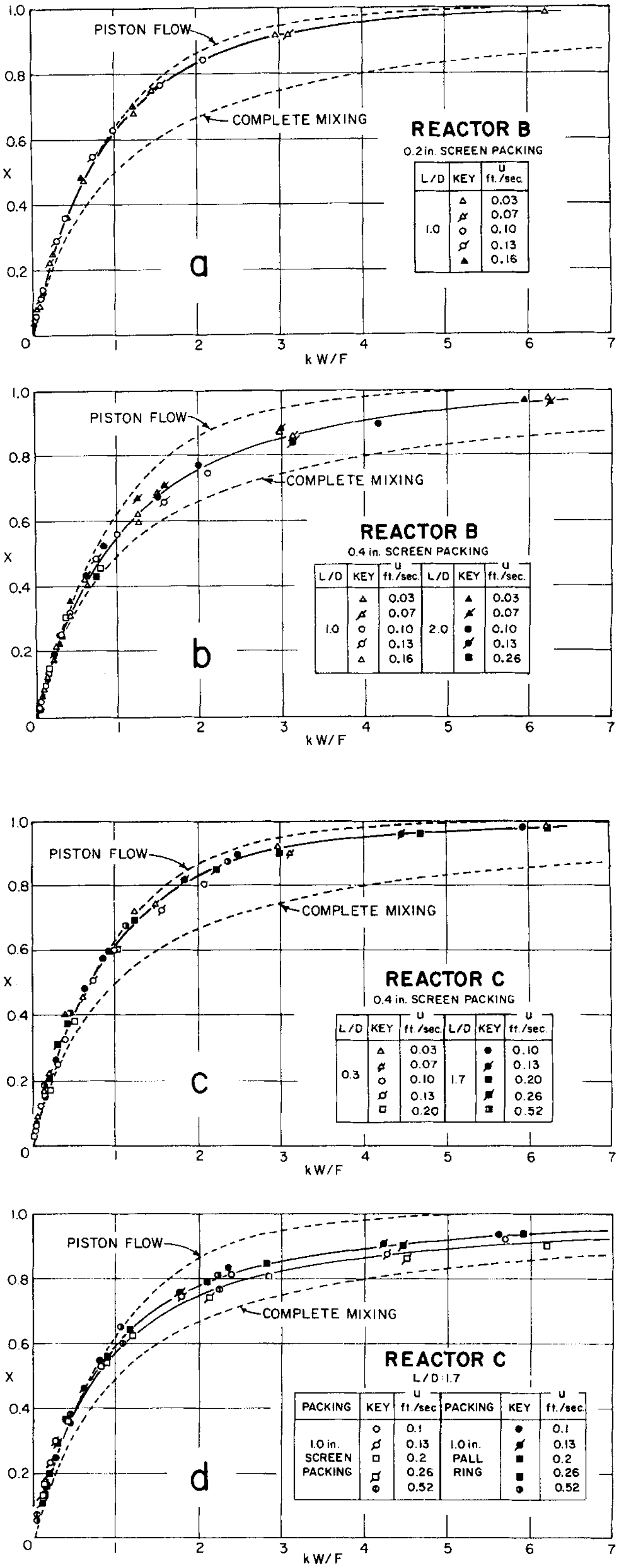

**Fig. 9. Conversion as a function of $k\ W/F$ at various superficial gas flow rates for a fluidized bed with packing. *(a)* 0.2-in. screen packing in 1.8-in. diameter reactor, *(b)* 0.4-in. screen packing in 1.8-in. diameter reactor, *(c)* 0.4-in. screen packing in 6.0-in. reactor, *(d)* 1-in. screen and pall rings in 6-in. diameter reactor.**

for a 1.0-in. screen packing, and so it should be noted that packing characteristics other than size should be taken into account.

In general, for fluidized beds with packing the most important factors affecting the conversion as a function of $kW/F$ seems to be the $D/d$ ratio and packing characteristics such as size, geometric form, etc., rather than the effects of bed height, reactor diameter, linear velocity, etc.

### Application of Various Reactor Models

Since the piston flow and the completely mixed models do not correlate well with fluidized bed data, various other models which have been proposed (*13*) to account for the deviations from these idealized models were examined. Three have been selected for trial in correlating the data in this study.

*Dispersion model.* The dispersion model assumes that the flow of gas through a bed involves some longitudinal mixing which is characterized by an effective diffusion or dispersion coefficient. The steady state differential equation in dimensionless form is

$$\frac{1}{N_{Pe}}\frac{d^2f(z)}{dz^2}-\frac{df(z)}{dz}-Rf(z)=0 \tag{4}$$

where the dimensionless Peclet group contains the dispersion coefficient. Assuming that there is no volume change during the reaction, Equation (4) has been solved analytically by Wehner and Wilhelm (*16*) for a first-order reaction. Their solution modified in this paper by a different ratio of the characteristic length $z = w/W$ reduces to Equation (5) for a closed vessel:

$$1-x_A = \frac{4a\exp\left(\frac{1}{2}\frac{FW}{D_{e'}}\right)}{(1+a)^2\exp\left(\frac{a}{2}\frac{FW}{D_{e'}}\right)-(1-a)^2\exp\left(-\frac{a}{2}\frac{FW}{D_{e'}}\right)} \tag{5}$$

where

$$a=\sqrt{1+4K\frac{W}{F}\left(\frac{D_{e'}}{FW}\right)}$$

$D_{e'}$ is a modified axial dispersion coefficient, [g. g.-mole/hr.]. It is assumed in this solution that no stagnant gas pockets or gross bypassing occurs. This model usually represents quite satisfactorily flow which deviates only moderately from piston flow. In the limit of an infinitely large diffusivity the solution is identical with that of the completely mixed model. With zero diffusivity the solution approaches that for a piston flow.

Since the conversion data reported in this study for nonpacked fluidized beds are generally below the conversion line based on a completely mixed model (see Figure 8), it is concluded that the dispersion model can not be applied to this case. However, when packing is used, the final conversions obtained fall in the region between the piston flow and the completely mixed models, and so a dispersion model may be applicable. In Figure 10 the dispersion model has been used to correlate the data obtained from the 6-in. reactor. The data represent two different settled bed heights (1.8 and 10.0 to 11.0 in.), the gas velocity ranges (0.03 to 0.2 and 0.1 to 0.52-ft./sec.), and two packing sizes (0.4 and 1.0 in.). The two solid lines were calculated from Equation (5) with assumed values for the dimensionless group $FW/D_{e'}$. The calculated curve is lower at small $kW/F$ and higher at large $kW/F$, but the deviations were within ± 2% over the range of $kW/F$ from 1.0 to 7.0. In this case, that is for a fluidized bed containing 0.4-in. packing, the curve represents a reasonably good fit.

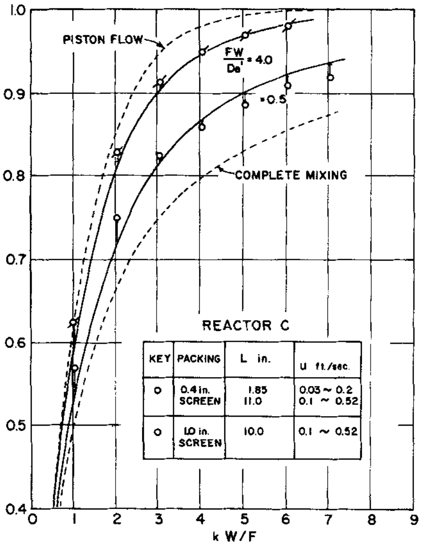

**Fig. 10. A test of the data from a fluidized bed with packing in a 6-in. diameter reactor with the dispersion model.**

*Tanks-in-series model.* For this model it is assumed that the reactor can be represented by a series of equally sized fully mixed compartments as proposed by McMullin and Weber (*17*). This model has been applied to fluidized beds fitted with horizontal baffles to form compartments and to fluidized beds in series. Overcashier et al. (*5*) reported that the spread in residence times may be effectively narrowed by the use of baffles, although not to the extent corresponding to an equivalent number of completely mixed stages.

Although gas-solid contacting behavior between the fluidized beds with packing and beds divided by horizontal baffles may be essentially different, a comparison between the results on a fluidized bed with packing and with the tanks-in-series model was made. It was found that the data for the 6.0-in. reactor could be fitted to the tanks-in-series model, but the data for the 1.8-in. reactor were slightly higher than the calculated line. These results suggested that the fluidized reactor efficiency may be increased by the use of packing to or above the extent corresponding to an equivalent number of completely mixed unit stages.

*Two-phase model.* Various two-phase models which have been proposed to fit the conditions prevailing in a fluidized bed are based on the observation that in a fluidized bed bubbles form at the bottom and grow or coalesce as they rise through the bed. The dynamics and size of these bubbles have a large effect on conversion in a fluidized bed. Studies on bubble flow (*14, 18, 19, 20*) have resulted in useful models. Orcutt et al. (*14*) developed a bubble-flow model which assumes that all but the gas required for minimum fluidization passes through the bubble phase. For the completely mixed case, it is also assumed that within the dense phase there is complete mixing and a first-order reaction, that within each rising bubble there is complete mixing and no reaction, and that there is an exchange of gas between the two phases. The fraction of the reactant which is unconverted as a function of $kW/F$ is given by

$$\Phi(k)=1-x=\beta e^{-n_K}+\frac{1-\beta e^{-n_K}}{\frac{K}{1-\beta e^{-n_K}}+1} \tag{6}$$

where

$$\beta = 1 - (u_f/u)$$

$$n_K = qh/u_b V$$

$$K = kW/F$$

For the piston-flow case, it is assumed that there is complete mixing within each rising bubble but piston flow in the dense phase. The expression giving the fraction of unconverted reactant is

$$\Phi(K) = 1 - x = \frac{1}{m_2 - m_1} m_2 e^{-m_1}\left(1 - \frac{m_1 u_f}{n_K u}\right) - m_1 e^{-m_2}\left(1 - \frac{m^2 u_f}{n_K u}\right) \qquad (7)$$

where $m_1$ and $m_2$ are the roots of

$$m^2 - m(n_K + K)/(1-\beta) + K n_K/(1-\beta) = 0$$

The limiting cases of Equations (6) and (7) are

$$(a)\ \lim_{K=0} \Phi(K) = 1$$

$$(b)\ \lim_{K=\infty} \Phi(K) = \beta e^{-n_K} = f_b$$

$$(c)\ \lim \frac{d}{dK} \Phi(K) = -1$$

As $n_K$ approaches infinity, the system tends to complete mixing with no bypassing for the complete mixing case and to piston flow with no bypassing for the piston flow case, respectively.

In Figure 11 correlations for all the data from the fluidized bed with packing runs and part of the data for fluidized bed without packing based on the bubble-flow model by Orcutt et al. are given. As shown previously, all of the data with packing are in a region between the idealized piston-flow line and the complete mixing line, and nearly all of the data without packing fall on the complete mixing line or below the line. The solid lines through the data for the packing runs were calculated from Equation (7) (piston-flow case), whereas Equation (6) (complete mixing case) was used for the nonpacked fluidized bed runs. These solid lines are calculated at $u_f/u$ equal to 0.1 for various assumed values of $f_b$. Satisfactory agreement between the experimental data and the calculated lines was obtained. For the fluidized beds with packing, the experimental data are more dependent on the packing than on reactor diameter, bed height, and gas velocity, but for the fluidized bed alone the data are very sensitive to these latter parameters. Thus, the gas velocity range was limited to the lower values from 0.1- to 0.13-ft./sec. for the fluidized bed alone. In general, for fluidized beds alone, the fractional degree of bypassing seems to depend on reactor size, bed height, and flow conditions. Bubbles appear not to be uniformly distributed over the height of the bed. A good correlation over a wide experimental range is therefore unlikely. When packing is used in the fluidized bed, such scale effects as reactor size, bed height, etc., are much smaller or perhaps negligible. Consequently, the comparatively simple models described earlier should be useful in designing fluidized beds containing packing.

On the assumption that bubbles in the bed are uniformly distributed over the height of the bed, the number of mass transfer units $n_K$ as a function of the equivalent bubble diameter $d_b$ was estimated at various fluidized bed heights at minimum fluidization $h_f$ with the method proposed by Davidson (21). The molecular diffusion coefficient of propylene, 1.04 sq. ft./hr., instead of cyclopropane through the air was used and was calculated by the method of Fair and Lerner (22). Then, $n_K$ as a function of the fraction gas bypassing the bed $f_b$ at $\beta = 0.9$ was calculated from the following equation:

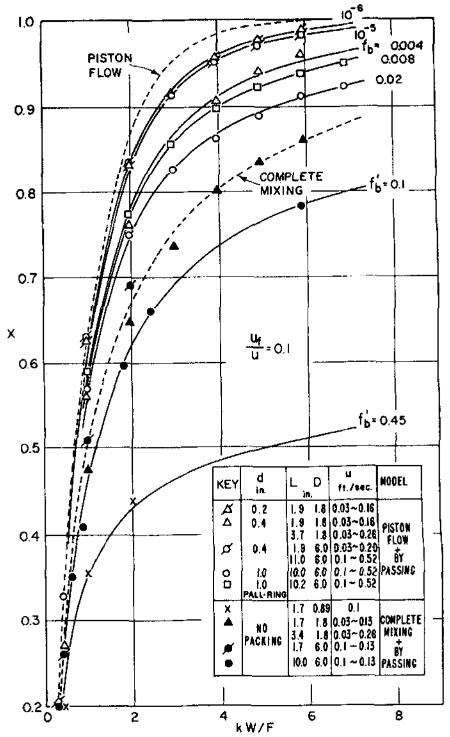

**Fig. 11. A test of the data from a fluidized bed with and without packing with the model by Orcutt-Davidson-Pigford (14) used.**

$$f_b = \beta e^{-n_K} = \left(1 - \frac{u_f}{u}\right) e^{-n_K} \qquad (8)$$

When one combines these two relationships, $d_b$ as a function of $f_b$ at a constant value of $u_f/u$ may be estimated.

The estimated values of the equivalent bubble diameter $\overline{d}_b$ as a function of the catalyst bed height at a linear velocity of 0.1 ft./sec. for both the fluidized bed, with and without packing, in the 1.8- and 6.0-in. reactor are shown in Figure 12*a*. The curve for the fluidized bed increases with increasing catalyst bed and shows that the bubble sizes are increasing as they rise through the bed. Since the curve with packing is flat, it is concluded that the bubbles are approximately similar in size and are uniformly distributed over the height of the bed owing to the packing which impedes the growth of large bubbles.

$\overline{d}_b$ as a function of the linear velocity at a bed height of 9.9 to 11.0 in. in 6.0-in. reactor is also shown in Figure 12*b*. $\overline{d}_b$ for the fluidized bed increased with increasing linear velocity, whereas with the packing present the effect of the linear velocity on $\overline{d}_b$ is small enough to ignore. $\overline{d}_b$ as a function of the packing size at $L/D = 1.0$ to 2.0 and $u = 0.1$ ft./sec. for a fluidized bed with packing in 1.8- and 6.0-in. reactor are shown in Figure 12*c*. This curve shows that $\overline{d}_b$ increases with the packing diameter and thus emphasizes the importance of the packing diameter *d*.

## CONCLUSIONS

A comparison of the kinetic data obtained from the same catalyst in flow reactors operated as a fixed bed, a

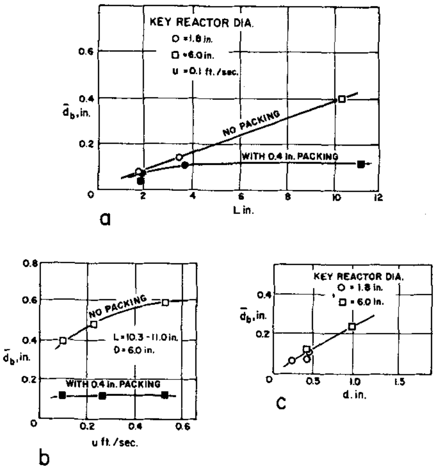

**Fig. 12. The calculated equivalent bubble diameter as a function of *(a)* bed height, *(b)* superficial gas velocity, *(c)* packing diameter for a fluidized bed with and without packing.**

fluidized bed, and a fluidized bed containing packing showed that the highest conversions for a particular set of flow and temperature conditions were obtained in the fixed bed, the lowest in the fluidized bed, and with conversions falling in between these limits for the fluidized bed with packing. Thus packing improved gas-catalyst contact efficiency in the modified fluidized bed. The magnitude of the improvement depended on catalyst activity, bed variables such as bed diameter and height, and on packing variables such as shape and size. With a well-designed packing in a fluidized bed conversion levels approaching fixed bed values should be obtained.

Data obtained from fluidized beds alone could not be correlated over the whole range of operating conditions employed with simplified reactor models used because of the complex effect of gas velocity and bed height on conversions.

Kinetic data obtained from fluidized beds containing packing were much less dependent on gas velocity and bed height and could be fairly well correlated by the dispersion, the tanks-in-series, or the two-phase model of Orcutt-Davidson-Pigford by a suitable choice of appropriate empirical factors. These models do not take into account packing variables such as shape and size which are new factors introduced by the presence of packing.

The improvement in gas-solid contact obtained in packed-fluidized bed is believed to be due to reduced backmixing of the gases to a smaller average bubble size and a more uniform distribution of bubbles throughout the modified fluidized bed.

## NOTATION

$c_A$ = concentration of cyclopropane, mole/cu. ft.
$c_B$ = concentration of reaction intermediate, mole/cu. ft.
$D$ = diameter of reactor, in.
$D_{e'}$ = modified axial dispersion coefficient, g. g.-mole/hr.
$d$ = diameter of packing, in.
$\bar{d}_b$ = mean equivalent bubble diameter, in.
$F$ = feed rate, mole/hr.
$f$ = fraction of reactant remaining
$f_b$ = fraction gas bypassing the fluidized bed with packing
$f_{b'}$ = fraction gas bypassing the fluidized bed without packing
$h$ = fluidized bed height, in.
$k$ = first-order rate constant, g.-mole/g.-hr.
$k'$ = apparent rate constant for fluidized bed, g.-mole/g.-hr.
$k_m$ = mean value between $k_o$ and $k_p$, g.-mole/g.-hr.
$k_o$ = first-order rate constant for no packing present, g.-mole/g.-hr.
$k_p$ = first-order rate constant for with packing present, g.-mole/g.-hr.
$L$ = catalyst bed height under settled conditions, in.
$n_K$ = number of mass transfer units
$N_{Pe}$ = Peclet group, $Lu/D_e$
$q$ = volumetric flow through a bubble, cu.ft./sec.
$R$ = dimensionless rate group, $kL/u$
$r$ = reaction rate, that is cyclopropane consumed, g.-mole/g.-hr.
$T$ = reaction temperature, °C. or °K.
$t$ = time
$u$ = superficial linear velocity, ft./sec.
$u_b$ = bubble rising velocity, ft./sec.
$u_f$ = minimum fluidization velocity, ft./sec.
$V$ = bubble volume, cu. ft.
$W$ = weight of catalyst bed, g.
$x$ = fraction of cyclopropane reacted
$y$ = mole fraction of cyclopropane in the feed
$z$ = dimensionless distance in the axial direction $w/W$
$\beta$ = $1 - (u_f/u)$
$\Phi$ = fraction of reactant unconverted

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*Manuscript received May 8, 1964; revision received November 30, 1964; paper accepted December 2, 1964. Paper presented at A.I.Ch.E. Houston meeting.*