$\vec{V}_o'$ = mean superficial velocity

V, V_r, V_z = dimensionless superficial velocity, its components

y_A', y_A = mass fraction of A, mass fraction of A normalized with feed concentration

z', z = dimensional, dimensionless axial coordinate

Greek Letters

ϵ = void fraction

μ = dynamic viscosity

ψ = dimensionless stream function

ξ = ratio of viscous and turbulent resistance parameters

ρ', ρ = dimensional, dimensionless density

ρ_A' = mass concentration of A

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Manuscript received April 22, 1976; revision received July 20, and accepted July 21, 1976.

Part II. Experimental Studies

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The modeling equations formulated for a catalytic packed-bed reactor with distributed resistance to flow have been applied to the alumina catalyzed isomerization of 1-butene to cis- and trans-2-butene. Flow maldistribution was deliberately created in a 5.25 cm I.D. reactor by packing different radial sections with alumina particles of different size. Effluent gas composition, monitored by gas chromatography, was found to vary with radial position in a manner consistent with the modeling equations and with the reaction rate constant previously established in a microreactor.

SCOPE

Problems associated with maldistributed flow through a catalytic packed-bed reactor are of major importance in determining the efficiency and life of the catalytic reactor. Modeling equations describing point conversion as a function of position in a reactor having distributed resistance to flow were developed in Part I. The present paper is an experimental study to verify the extent of validity of these equations in model systems. The double-bond isomerization of 1-butene over alumina was chosen as the model reaction for study. The reaction has the advantages of following first-order kinetics, being essentially thermoneutral, and showing stable activity at 200°C over an extended period of time. The rate constant for the reaction with the particular alumina studied (a Davison product) was first established independently in a flow microreactor system. The fractional conversion of 1-butene, as a function of radial position in the effluent stream, was then followed in a 5.25 cm I.D. reactor for four packing configurations: uniformly sized large particles throughout, uniformly sized small particles throughout, small particles in the central core and large particles in the outer annulus, and large particles in the central core and small particles in the outer annulus. Temperatures in the catalyst bed were monitored by thermocouples at various axial stations, both at the center of the bed and at the wall. Composition of the gas leaving the bed, as a function of radial position, was monitored with a small, movable probe which led directly to a gas chromatograph. Good resolution of all the butene isomers was obtained.

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CONCLUSIONS AND SIGNIFICANCE

The experimental results on the isomerization of 1-butene over alumina confirm the results predicted by the isothermal theory developed in Part I. The rate constant determined independently in microreactor experiments permits computation of the conversions obtained in a macroreactor uniformly packed with either large or small catalyst particles. Reasonable agreement is also obtained for the radial dependence of conversion with reactors packed to give either a high flow resistance core or a high flow resistance outer annulus. This confirmation of the isothermal theory now encourages one to solve the describing equations for reactor configurations which may be more complex than those already treated and to extend the theory to nonisothermal reactors.

In Part I of this work, modeling equations were formulated for a packed-bed reactor having a distributed resistance to flow. In the present paper, experimental results are reported for a model reaction, the double-bond isomerization of 1-butene catalyzed by alumina. After preliminary studies were made in a flow microreactor to establish operating conditions and the isothermal rate constant, the reaction was conducted in a macroreactor in which flow maldistribution was deliberately created by packing different radial sections of the reactor with particles of different size. Effluent gas composition as a function of radial position was monitored by gas chromatography. The isomerization of 1-butene over alumina is an attractive reaction for such a study: the reaction is almost thermoneutral, the kinetics are first order, and catalyst activity is stable.

Numerous studies have been made of the kinetics of the alumina catalyzed isomerization of the several *n*-butenes (1-butene, cis- and trans-2-butenes). Particularly useful for the present work was the determination of all the individual (relative) rate constants by Haag and Pines (1960) and Hightower et al. (1967). The paper of Hightower et al. established that all reaction paths exist in this three-isomer system and that catalyst activity for the isomerization of 1-butene can be conveniently followed by using the simplified reaction scheme

$$\text{1-butene} \rightleftarrows \text{2-butene (cis + trans)} \qquad (1)$$

At 200°C, the temperature used for the present study, the equilibrium constant for this simplified scheme is about 8 (Kilpatrick et al., 1946). An apparent first-order rate constant was computed on the basis that the isomerization of 1-butene can be treated as an irreversible, first-order reaction. Since fractional conversion of 1-butene was below 0.5 in all the experiments, the error introduced by the use of an irreversible reaction rate expression was negligible. The first-order behavior of butene isomerization over alumina has been reported by several investigators, for example, Hightower et al. (1967). We did not test our system for first-order kinetics but rather used an apparent first-order rate constant as a convenient method of expressing conversion.

EXPERIMENTAL

Materials

All gases were obtained from the Linde Corporation and used without further purification. The 1-butene used as reactant was of minimum 99.0% purity, as were the cis-2-butene and trans-2-butene used for calibration purposes. Nitrogen of minimum 99.99% purity (moisture $\leqq 3$ p.p.m.) was used as diluent, and the helium was used as carrier gas in the chromatograph.

Two samples of extruded alumina were furnished by the Davison Chemical Division, W. R. Grace and Company; these were identified as SMR7-5001 Item 1 and Item 2. The physical properties of these samples, provided by Davidson, are listed below:

	Item 1	Item 2
Diameter	1/16 in.	1/8 in.
Surface area (BET)	205 m^2/g	205 m^2/g
Pore volume (BET)	0.77 cm^3/g	0.68 cm^3/g*
Pore volume (water)	0.80 cm^3/g	0.80 cm^3/g
Average pore diam. (calc.)	150Å	132Å
Loss on ignition, 955°C	2.3%	1.6%

Before it was used, the catalyst was heated in air for 3 hr. at 550°C. Fresh catalyst was used for each experiment.

Flow Rates

Flow rates were monitored by rotameters. The rotameter used for 1-butene in the microreactor experiments (see below) was calibrated with a soap bubble burette. The rotameters used for nitrogen and for 1-butene in the macroreactor experiments were calibrated with a wet test meter.

Analysis

Butene isomer analysis was conducted with a Perkin-Elmer Vapor Fractometer Model 154C, having a thermal conductivity detector. Excellent resolution of 1-butene, cis-2-butene, and trans-2-butene was obtained with a 4m column, 0.63 cm in diameter packed with 20% BMEA (bis-2-methoxy ethyl adipate) on 60-80 mesh Chromosorb P. The column was operated at 40°C. Calibration curves, obtained with gas sample loops of three sizes (¼, ½, and 1 cm^3), were straight lines passing through the origin. The calibration factors for the three isomers were essentially indistinguishable. This is consistent with the report of Gerberich and Hall (1966) that the relative sensitivities of 1-butene, trans-2-butene, and cis-2-butene were in the ratio 1.00:1.00:1.07. Observed retention times on the BMEA column at 40°C were 1-butene, 4.0 min; trans-2-butene, 4.6 min; and cis-2-butene, 5.2 min.

Microreactor Experiments

The microreactor consisted of a length of ¼ in. (0.635 cm O.D., 0.457 cm I.D.) stainless steel tubing surrounded by an electric furnace. The lower section of the tube, which served as preheater, was filled with 0.30 cm diameter glass beads to a height of 11.5 cm; the beads were supported on glass wool and were separated from the catalyst by glass wool. One gram of predried catalyst, normally 28 to 35 mesh (0.059 to 0.042 cm), was then introduced above the glass beads. The furnace temperature was controlled by a Honeywell controller. Catalyst bed temperature was monitored by an iron constantan couple which touched the reactor wall in the catalyst section.

Exit gas composition was measured as described above. The flow rate of pure 1-butene into the reactor was held constant at 28 cm^3/min, measured at 21°C and 1 atm by a calibrated rotameter; this is equivalent to 45 cm^3/min at 200°C.

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* There appears to be some inconsistency in the supplier's data for BET pore volume and the calculated average pore diameter for Item 2. However, since in this work only the water pore volume is used, this matter was not investigated.

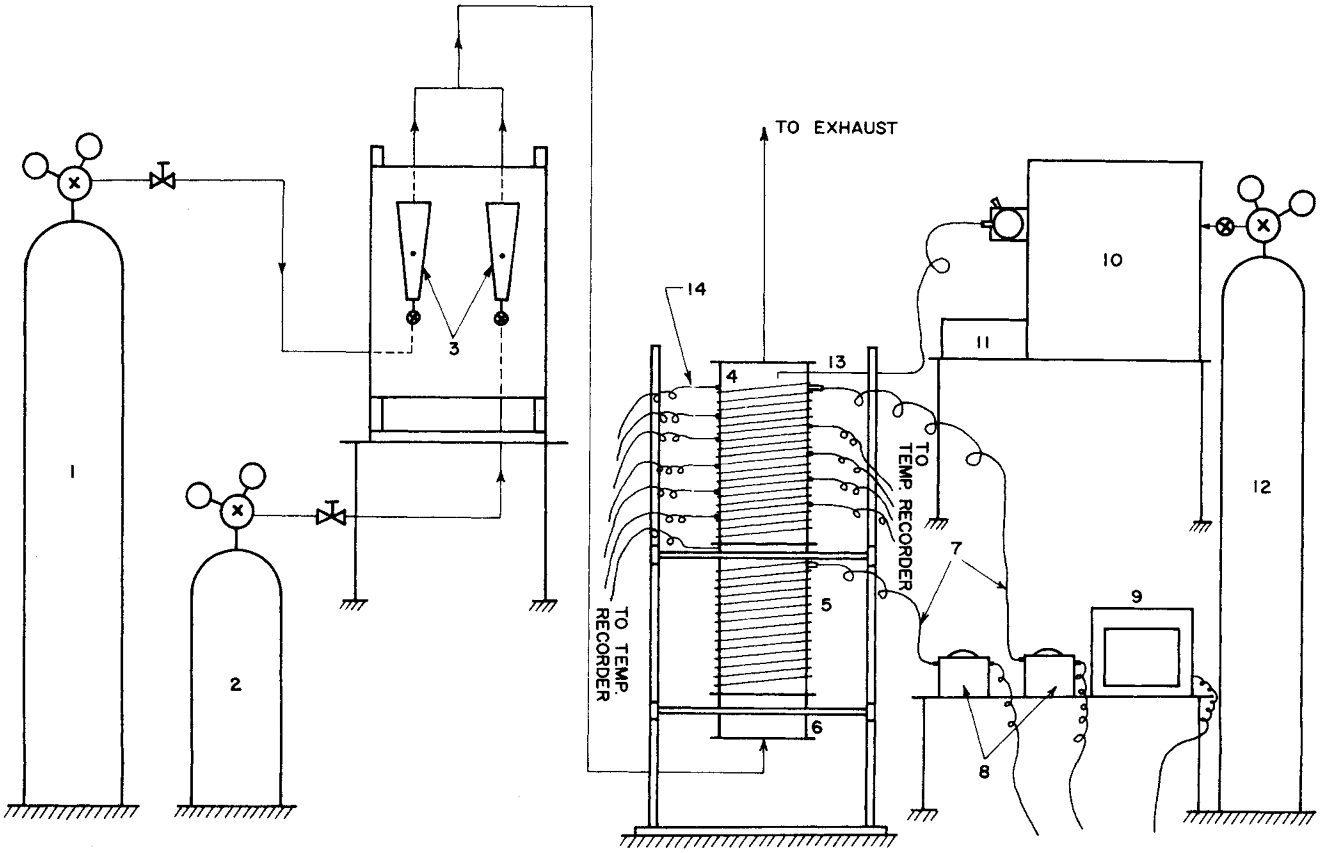

Fig. 1. Schematic of the setup for the macroreactor experiment.

1. Nitrogen cylinder
2. Butene-1 cylinder
3. Rotameters
4. Reactor
5. Preheater
6. Flow straightener
7. Connections for the heating tapes
8. Power stats
9. Temperature recorder
10. Chromatograph
11. Recorder for the chromatograph
12. Helium (carrier gas) cylinder
13. Sample probe
14. Thermocouples

Macroreactor Experiments

A schematic of the equipment is shown in Figure 1. Individual elements are described below:

1. Two rotameters (3) were used to measure the flow rates of 1-butene and nitrogen.

2. The reactor assembly (4, 5, 6). This consisted of three sections: a flow straightener, 6.35 cm long and packed with 0.3 cm diameter glass beads supported on a stainless steel screen; the preheater, 15.25 cm long, also packed with 0.3 cm diameter glass beads supported on a screen; and the reactor, of total length 20.3 cm. The reactor was packed with catalyst to a height of 15.25 cm. All of the assembly components were made of Type S304 stainless steel of I.D. 5.25 cm, O.D. 6.03 cm. The sections were connected by mild steel flanges equipped with Type S321 stainless steel O rings (O.D. 7.30 cm) to prevent gas leakage. Twelve chromel-alumel thermocouples were used for temperature measurement. One was inserted at the top of the preheater to determine the temperature of the gas leaving the preheater; the other eleven were located in the reactor section as shown in Figure 2 to measure catalyst temperature at the wall and at the center for a number of axial positions. Temperatures were continuously recorded by a multipoint L and N Speedomax recorder.

3. The preheater and reactor sections were heated with electric heating tapes (7), controlled by variable transformers (8), and insulated with ceramic wool.

4. The sample probe (13) consisted of a 0.08 cm I.D. (0.16 cm O.D.) pitot tube, inserted through a silicone septum 2.5 cm above the top of the catalyst bed. The tube was bent downwards at a right angle so that its tip was about 0.32 cm above the catalyst bed. The end of the pitot tube, outside the reactor, was inserted in a 0.317 cm copper tube bearing reference marks. By matching these marks with a reference mark on the support plate, the radial position of the probe inside the reactor could be established and varied in a known way during the course of a run.

Two particle sizes of alumina were used: 0.317 cm diameter extruded and particles crushed and sieved to be 10 to 18 mesh (0.168 to 0.100 cm, avg. = 0.134 cm). The temperature was kept at 200°C in the macroreactor experiments, and the gas flow rates were held at 1.30 l/min of 1-butene plus 3.02 l/min of nitrogen, measured at 21°C and 1 atm. Exit gas samples were withdrawn from relative radial positions (r/R) of 0, 0.25, 0.50, 0.75, and 1.00.

Two types of experiment were performed. In one, the catalyst bed was packed with uniformly sized particles, either large or small. In the other mode, the bed was packed nonuniformly. These configurations were sketched in Figure 1 of Part I. The nonuniform packing was done in two configurations. In one, the central core (of diameter equal to the radius of the reactor) was packed with small particles (0.134 cm avg.) and the outer annulus packed with large particles (0.317 cm). In the other the central core was packed with the large particles and the outer annulus with the small particles. These nonuniform packings were achieved by first inserting a thin Plexiglas tube (I.D. 2.54 cm, thickness 0.08 cm) coaxially in the reactor, filling the central core and the annulus with particles of the desired size, and slowly withdrawing the Plexiglass tube.

The preheater and reactor were initially heated to about 200°C with no flow of gas. Flow of the desired butene-nitrogen mixture was then begun, while temperature was regulated by the variable transformers. Since the catalyst bed temperature was kept close to that of the incoming gas, and since the isomerization is almost thermoneutral, the small power supply to the reactor was largely used to compensate for heat losses to the surroundings.

After a relatively uniform temperature profile had been obtained in the reactor, gas samples at various radial positions were taken for gas chromatographic calculation of fractional conversion. Two or three samples were taken at each probe

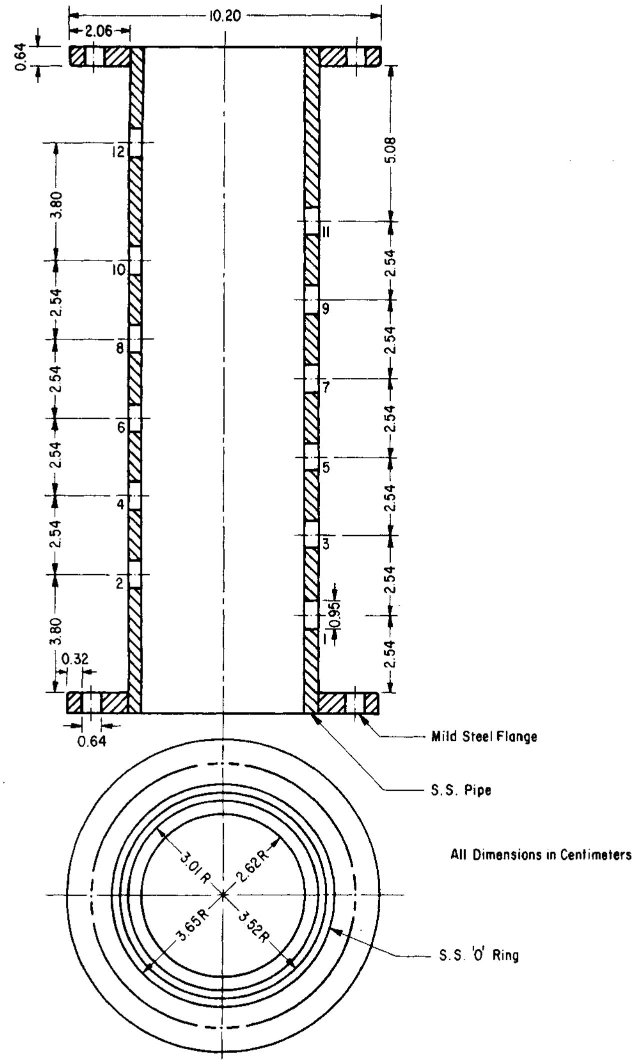

Fig. 2. Details of the reactor. Holes 1-11 are for thermocouples; hole 12 is for sample probe. Thermocouples 1, 4, 5, 8, and 9 located at wall; thermocouples 2, 3, 6, 7, 10, and 11 located at center.

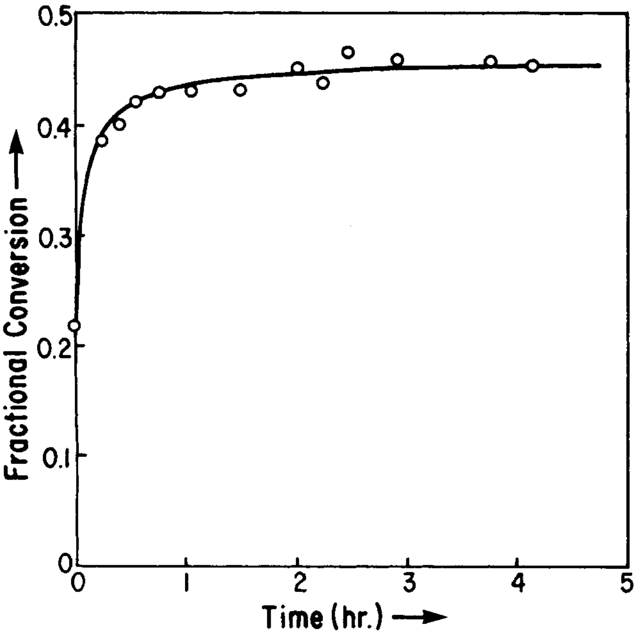

Fig. 3. Catalyst activity (microreactor) vs. time, 200°C.

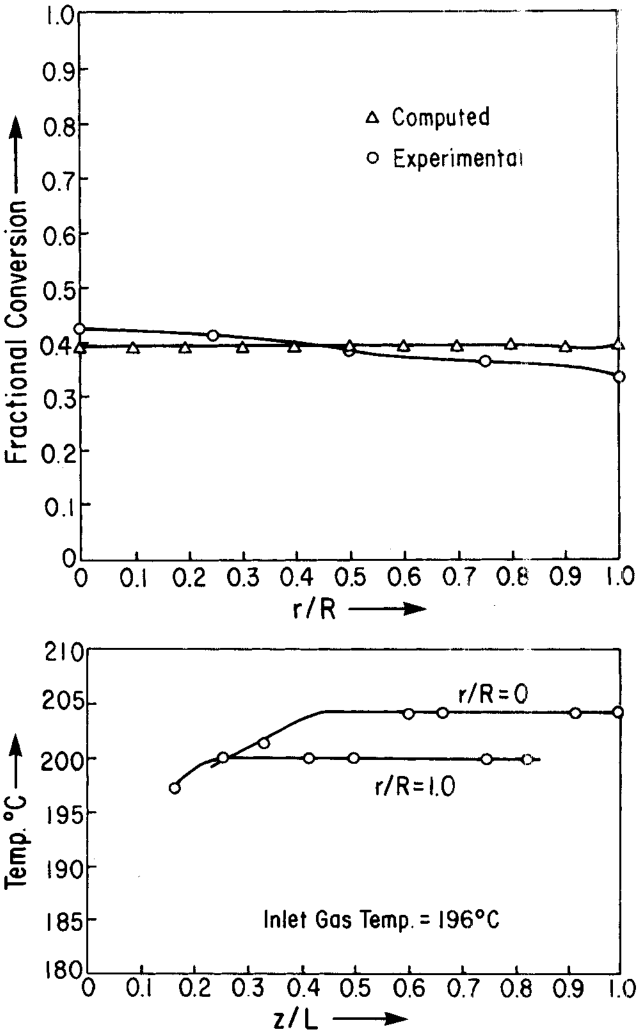

Fig. 4. Computed and experimental results for bed uniformly packed with large particles. *a*. Fractional conversion in effluent vs. radial position. *b*. Axial temperature profiles in the center and at the wall.

position in order to ensure reproducibility. Samples were also taken at one of the radial positions at the conclusion of each run to check on possible deactivation; no deactivation was observed.

RESULTS AND DISCUSSION

Microreactor Experiments

Figure 3 shows the fractional conversion of 1-butene to the other isomers as a function of time on stream, at 200°C. It is seen that there is an increase in conversion during the first half hour, after which the conversion remains essentially constant for a 4 to 5 hr period.

At 200°C the steady activity level occurs at a conversion of 45% of the 1-butene to 2-butenes. If we assume first-order, irreversible reaction and ideal plug flow behavior in the reactor, the rate constant k may be calculated from the following expression:

$$k = \frac{q\rho_s}{w} \ln\left[\frac{1}{1-x}\right] \tag{2}$$

The particle density ρ_s was taken from the manufacturer's data as 0.90 g/cm^3, although values of 1.00 to 1.10 have been reported in the literature for other aluminas. The weight of catalyst w was always 1 g, and the volumetric flow rate q was always 45.0 cm^3/min (at 200°C). From the observed value of $x = 0.45$ at 200°C, k is then calculated from Equation (2) to be 24.2 min^{-1} at 200°C.

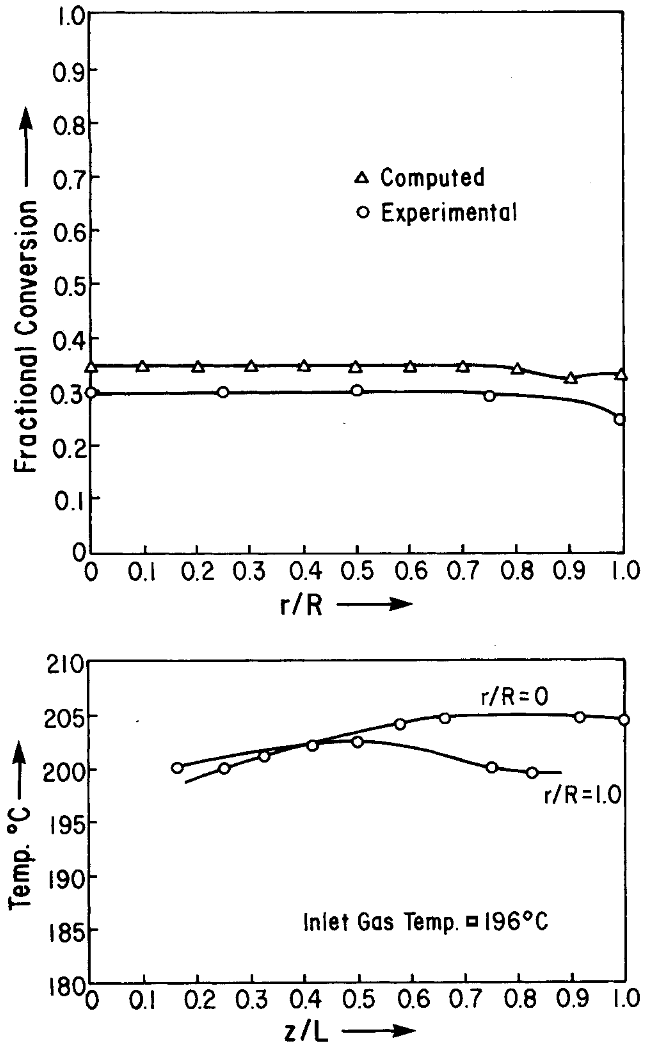

Fig. 5. Computed and experimental results for bed uniformly packed with small particles. *a*. Fractional conversion in effluent vs. radial position. *b*. Axial temperature profiles in the center and at the wall.

This rate constant was used in the calculation of the Damköhler number for the macroreactor experiments.

Macroreactor Experiments

The modified Damköhler number Da appearing in Equation (21) of Part I of this work can be written as

$$Da = Rr_{Af}/G_o \qquad (3)$$

The mole fraction of 1-butene in the feed was 0.30. Direct measurement of the gas pressure in the gas straightener section showed it to be 1.004 atm. With the assumption of ideal gas behavior, the calculated values are

C_f $= 7.73 \times 10^{-6}$ g moles 1-butene/cm^3 in feed
r_{Af} $= 1.04 \times 10^{-2}$ g 1-butene converted (cm^3 cat.)$^{-1}$ (min)$^{-1}$
G_o $= 0.322$ g cm^{-2} min^{-1}
Da $= 0.082$

The viscosity of the gas mixture was needed for the Reynolds number Re. The viscosity was calculated from the viscosities of the pure components (Perry and Chilton, 1973) with the use of Wilke's semiempirical formula as reported by Bird et al. (1960). The calculated viscosity was 191 × 10^{-6} poise. From this and the above value of G_o, the following values of Re were obtained:

$Re = 3.8$ for small particles

$Re = 9.0$ for large particles

With these parameters, it is now possible to compute, by numerical solution of the modeling equations, the fractional conversion in the effluent gas as a function of radial position.

Figure 4*a* shows a comparison of the calculated and experimental conversions, as a function of dimensionless radial position, for the case of the macroreactor uniformly packed with the large particles ($d_p/R = 0.12$). Figure 4*b* shows the measured axial temperature profiles in these experiments at the center line and at the wall. The agreement between calculated and experimental conversion is quite good except near the wall, where, with large particles, the wall effect cannot be adequately taken into account in the machine computation. It should be recalled that the calculated results for the macroreactor make use of the rate constant determined from the microreactor experiments.

Results for uniform packing with small particles ($d_p/R = 0.051$) are shown in Figures 5*a* and 5*b*. Conversions were slightly lower than in the previous case because in these experiments the smaller particles packed less densely than did the larger ones. Here again there is

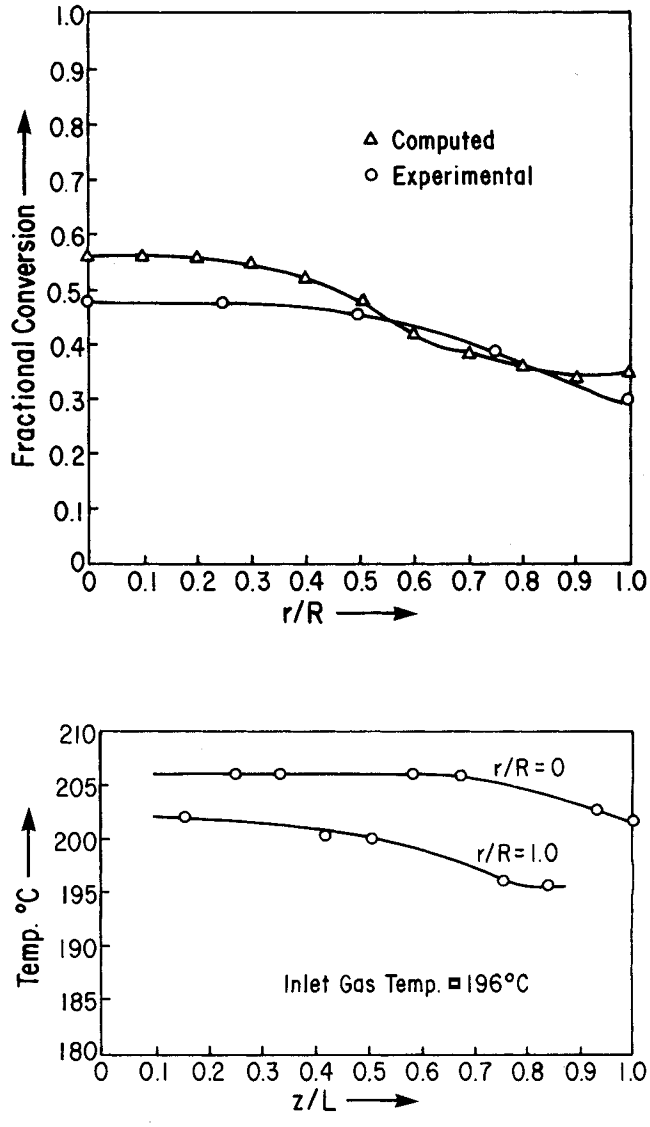

Fig. 6. Computed and experimental results for nonuniform packing (high resistance core). *a*. Fractional conversion in effluent vs. radial position. *b*. Axial temperature profiles in the center and at the wall.

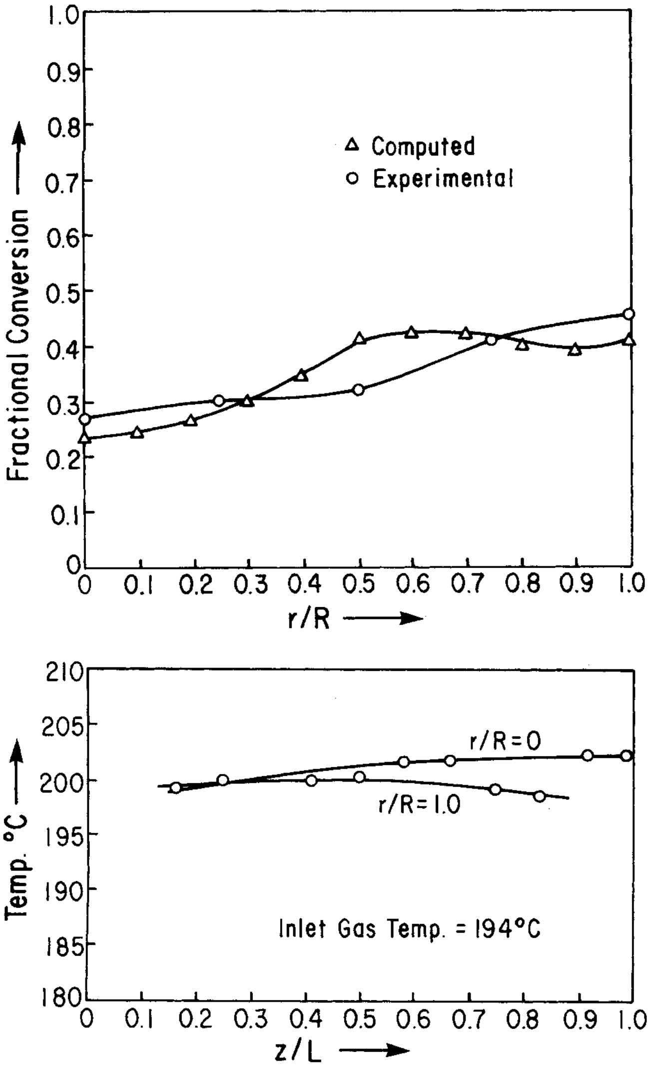

Fig. 7. Computed and experimental results for nonuniform packing (high resistance annulus). *a*. Fractional conversion in effluent vs. radial position. *b*. Axial temperature profiles in the center and at the wall.

reasonable agreement between the measured and the predicted conversion profiles.

The case of nonuniform packing with a high resistance (small particle size) core is shown in Figures 6*a* and 6*b*. Worthy of note is the fact that the computed results predict a considerably steeper change in conversion across the interface than was actually measured. The discrepancy is actually greater than is evident from Figure 6*a* because the temperature difference between center and wall in this run (Figure 6*b*) should have resulted in even lower experimental conversions near the wall. The discrepancy is attributed to the interpenetration of small and large particles at the interface, an effect which is not considered in the modeling. Aside from this, the major result is the expected one: conversions are highest in the central core, where resistance to flow and residence time of the reacting gas are higher than in the annulus.

Finally, Figures 7*a* and 7*b* show the results for the opposite case of nonuniform packing with high resistance in the annulus. Maximum discrepancy between the computed and experimental conversions again occurs in the interfacial region between the small and the large particles; elsewhere, the agreement is relatively good. As expected, the conversions are substantially higher in the high resistance annulus, where greater residence time for reaction is afforded.

In broad terms, the experimental results on the isomerization of 1-butene confirm the results predicted on the basis of the theory developed in Part I. The apparent first-order rate constant deduced from microreactor experiments at 200°C permitted computation of the conversions observed with a (nominally isothermal) macroreactor uniformly packed with either large or small catalyst particles, with acceptable accuracy. Reasonable agreement was also obtained for conversion as a function of radial position for a macroreactor deliberately packed to give nonuniform flow distribution for the alternate cases of a high flow resistance core or a high flow resistance outer annulus.

It is concluded, therefore, that the coupling of the vectorial form of the Ergun equation with appropriate kinetic expressions provides a reasonable means for modeling conversion in isothermal packed-bed reactors where flow maldistribution occurs. The extension of this approach to nonisothermal systems would seem to be the logical approach for the modeling of hot spot formation in packed-bed reactors.

NOTATION

C_f = concentration of 1-butene in the feed
d_p = particle diameter
Da = Rr_{Af}/G_o = Modified Damköhler number
G_o = average mass velocity/cross sectional area of the reactor
k = reaction rate constant
L = length of the macroreactor
q = volumetric flow rate of gas in the microreactor
r = radial position in the macroreactor
r_{Af} = rate of reaction at feed conditions
R = radius of the macroreactor
Re = Reynolds number
w = weight of catalyst sample in the macroreactor
x = fractional conversion of butene-1 to 2-butenes in the microreactor
z = axial position in the macroreactor
ρ_s = particle density of catalyst

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Manuscript received April 22, 1976; revision received July 20 and accepted July 21, 1976.