Pulsation in a Fixed-Bed Reactor

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Rates of reaction were measured for the liquid phase hydrogenation of α-methyl styrene in a pulsed, fixed bed reactor. Data at 80 psia and 55°C., using 0.5 wt. % palladium on ⅛" Al_2O_3 spheres as a catalyst, indicated that the mass transfer of dissolved hydrogen to the catalyst surface controlled the rate of conversion of styrene to cumene. Hence the data were employed to calculate mass transfer coefficients as a function of pulse frequency and amplitude.

Comparison with non-pulse data at the same Reynolds number showed that pulsation increased the mass transfer rate as much as 80%.

The effect of flow pulsation on the performance of liquid-liquid extraction and heat transfer apparatus has been extensively investigated (*2, 8, 10, 11*). In general these studies indicate that the transfer rates increased as a result of pulsations, and the improvement is most pronounced at low average flow rates. If it is assumed that the improvement is due to a decrease in resistance near the fluid-surface boundaries, pulsation should increase reaction rates in fluid-solid catalytic reactions. The effect, although not measured heretofore, is expected to be significant if resistance to mass transfer plays an important role in determining the reaction rate. This situation is likely to occur in liquid-solid catalyst systems, but may occur also for gas-solid catalyst reactions.

To evaluate this phenomenon quantitatively, the rates of hydrogenation of α-methylstyrene have been studied under both pulsed and nonpulsed conditions. A liquid phase of hydrogen dissolved in the styrene flowed through a fixed-bed reactor containing ⅛ in. spherical pellets of alumina coated with 0.5 wt. % palladium as the catalyst. This system possessed the advantages of a specific reaction with well-studied kinetics (*3, 8*) and relatively large external diffusion resistance. Side reactions are negligible; palladium is known to catalyze only the hydrogenation of the isopropyl group in the methylstyrene. To eliminate the possibility of a gas phase, the hydrogen concentration was limited by its solubility in the liquid styrene. This maximum value is so low, about 0.4 mole % at 60°C. and 150 lb./sq. in. abs. (*9*), that a single-pass, differential reactor cannot provide concentration changes large enough for accurate rate measurements. Hence, a recycle differential reactor, such as described by Butt, Bliss and Walker (*6*), was used to build up the product (cumene) concentration.

EXPERIMENTAL

To obtain a reproducible liquid phase of reactants, the styrene was saturated with hydrogen at a known pressure and temperature upstream from the reactor. To maintain the advantage of a constant composition feed, a positive displacement pump was used to achieve pulsed flow. Even then complete solution of hydrogen was possible only when a temperature higher than that in the absorber was maintained until the stream emerged from the reactor. Since the solubility increases with temperature for the hydrogen-α-methylstyrene system, this procedure gave satisfactory results.

The six chief components of the reactor loop shown in Figure 1 operated as follows:

1. In the absorber the styrene is saturated with hydrogen at a measured temperature (T) and pressure.
2. The liquid is heated to T + 15°C. between the absorber and pump.
3. The positive displacement pump acts as a pump, pulse generator, and positive displacement meter.
4. After it has passed through another heater, the liquid enters the reactor in a pulsed manner, and a fraction of the hydrogen and α-methylstyrene is converted to cumene at about T + 10°C.
5. The effluent stream is cooled to absorber temperature T before it enters the top of the absorber.
6. The liquid stream is resaturated with hydrogen at T as it flows countercurrent to hydrogen gas in the absorber.

The preparation of the reactant and the hydrogen exhaust system are also shown in Figure 1. In general, the apparatus consisted of stainless steel or Teflon, and the loop system was made of ¼ or ⅜ in. tubing to reduce pressure drop. Because palladium is susceptible to poisoning, only stainless steel, silver solder, Teflon, and Sauereisen were allowed to be in contact with the reaction fluid.

The reactor, 1-in. I.D., was packed with ⅛-in. alumina spheres on both sides of the catalyst pellets. Bare thermocouple junctions were installed at different radial positions within the catalyst bed and in the inert packing before and after the bed to check radial and axial temperature gradients. The location of the 30-gauge copper-constantan couples and other details of the reactor are given in Figure 2. The thermocouples were calibrated at the freezing and boiling points of water.

In the absorber the hydrogen entered the vertical 2-in. pipe through a porous sparger, bubbled through a few inches of styrene, and then flowed countercurrent to the liquid through a 16-in. section packed with glass helices.

The pump was equipped with a variable speed drive which provided 10 to 87 strokes/min. and 0.5 in. to 4.0 in. plunger amplitude.

For the runs at steady flow rates it was easiest to depulse the system used for pulsed runs. This was accomplished by operating the pump at a high frequency (65 strokes/min.), using two surge tanks, partially filled with hydrogen, installed in series, and in capacitance positions at the pump outlet, and using flexible hose couplings on the inlet and outlet of the pump. A rotameter measured the flow rate in the nonpulsed runs.

The conversion in the reactor was obtained by measuring the refraction index of samples of reaction mixture. With a dipping refractometer and constant temperature bath, the cumene content of the styrene-cumene samples was determind to 0.05 mole %.

Details of the equipment and its operation are given by Biskis (*4*).

Chemicals

The technical grade of α-methylstyrene used was 98.5 wt. % pure and contained 1.0 wt. % β-methylstyrene. Complete analysis and physical properties are available (*1*). The polymer content was negligible.

Microscopic examination of the catalyst indicated that the palladium coating did not extend a significant distance within the pellets. The inert packing consisted of alumina spheres. Measurements of the diameter of the catalyst and the alumina indicated an average value of 0.123 in. with a standard deviation of about 0.007 in. Preliminary tests with the alumina showed no catalytic activity.

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For calibration of the refractometer reagent grade cumene was used.

RANGE OF MEASUREMENTS

Since the purpose of this investigation was to study the effect of pulsation, most of the data were obtained at 80 lb./sq.in.abs. and 55°C; conditions where mass transfer controlled the rate of reaction. At these conditions the flow parameters were varied over the following ranges:

Modified Reynolds number = 47-484
Pulse amplitude number = S = 21-55.9
(catalyst pellet diameter)
Pulse frequency = ω = 10.3-52 min.$^{-1}$
α-methylstyrene mole fraction = 0.7-1.0.

Twelve additional pulsation runs were made at pressures from 64 to 117 lb./sq.in.abs. and at amplitudes and frequencies within the given ranges.

RESULTS

The reaction involves the conversion of 1 mole of styrene to cumene:

$$H_2 + C_6H_5C(CH_3) = CH_2 \rightarrow C_6H_5\,CH(CH_3)_2$$

Since the hydrogen mole fraction is maintained constant by the absorber at about 0.4 mole % and the conversion per pass in the reactor is small, the total moles Q in the closed loop system is essentially constant. Hence the cumene formed from time 0 to t is $Q(x - x_o)$. This quantity can also be expressed in terms of the rate of reaction per unit mass of catalyst, r, and the time:

$$Q(x - x_o) = W \int_o^t r\,dt \qquad (1)$$

If the diffusion resistance between the bulk fluid and the catalyst controls the overall rate of reaction, r will be a constant, and Equation (1) becomes

$$x - x_o = \frac{rW}{Q} t \qquad (2)$$

This is based upon the fact that the hydrogen concentration in the feed is constant at the saturation value throughout the run. The experimental data agree with this linear relationship between r and t; data for typical runs are shown in Figure 3 where the styrene mole fraction varies from 1.0 to 0.72. Equation (2) would also be applicable if the rate of reaction on the surface of the catalyst controlled the process and if the rate was independent of α-methylstyrene concentration. However, earlier kinetic studies (3, 9) have shown that the surface rate is di-

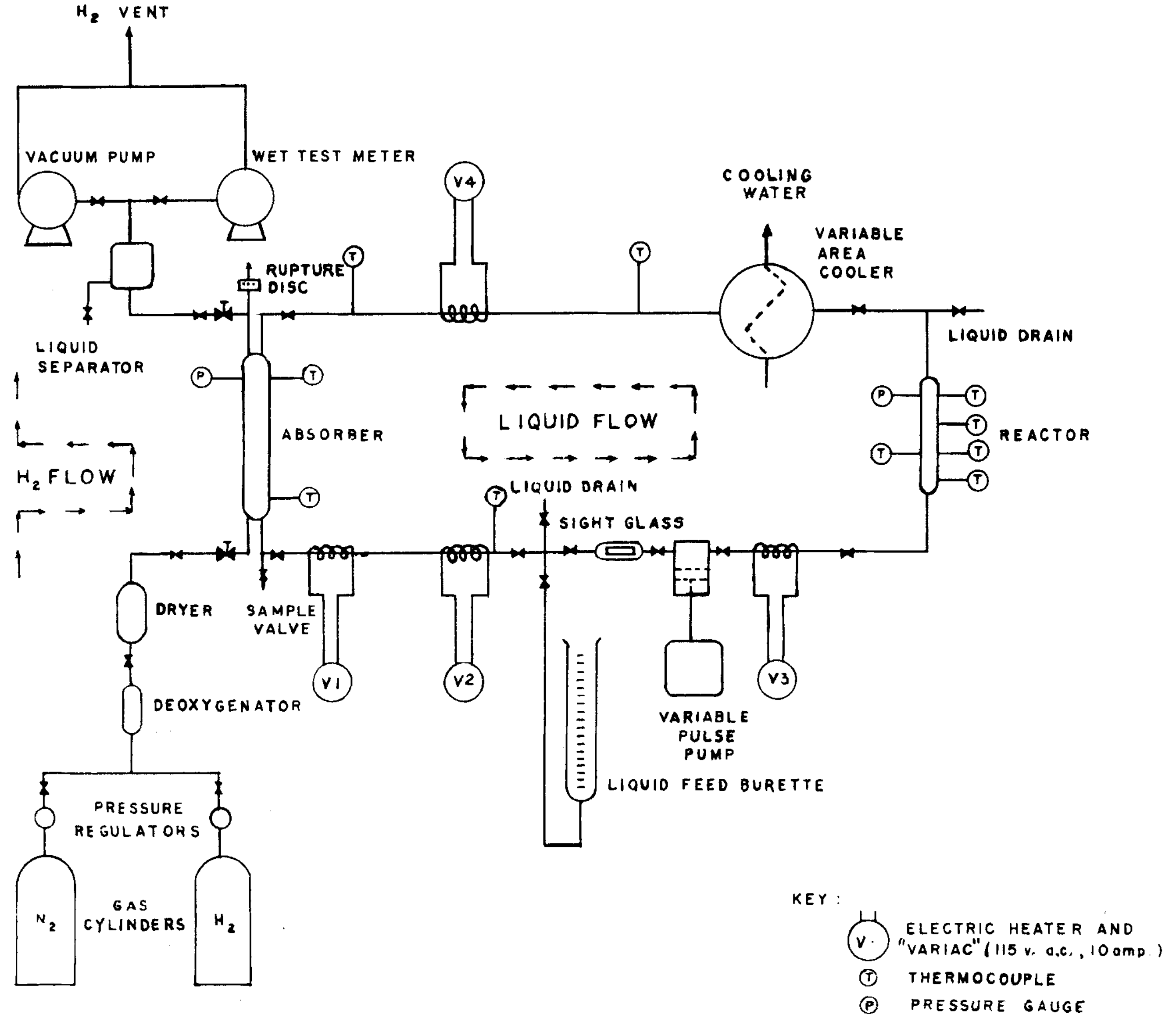

Fig. 1. Process flow diagram

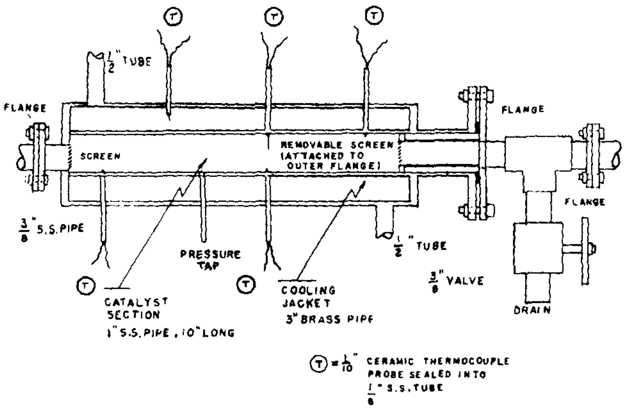

Fig. 2. Reactor.

rectly proportional to styrene mole fraction. Hence, the data indicate that at 55°C. external diffusion controls the process. Substantiating evidence was available from the temperature effect observed in the present data. For example, it was difficult to maintain constant temperature in the catalyst bed over total run times of as much as 21 hr. In run C4 shown in Figure 3, for example, the temperature varied from 53.4 to 59°C. but the rate remained constant. Babcock's investigation (3) of the surface rate indicated an increase of about 4%/1°C. By contrast, a change in flow rate always resulted in a rate change.

In view of these arguments, Equation (2) was used to calculate the rate for both pulse and nonpulse runs. Results at 80 lb./sq. in. abs. are shown in Figure 4 for pulsed conditions at two amplitude numbers and for nonpulse operation. Since pulse frequency and flow rate were not independent in these measurements, Equation (4), each Reynolds number corresponds to a specific frequency. Hence, each point on a curve for a given amplitude number S in Figure 4 is associated with a different frequency.

Precision of Results

A key assumption in the analysis of the data was that the hydrogen concentration corresponded to the saturation value at the absorber conditions. To evaluate this assumption, rate measurements were made at constant conditions, but the hydrogen flow rate to the absorber was varied. No observable effect on rate was found when the hydrogen rate was varied from 0.83 to 4.23 cu. ft./hr. (standard conditions).

The chief error in the data was probably due to difficulties in measuring the flow rate of an almost saturated liquid under pulsing conditions. Reproducibility tests were therefore made at different amplitude factors with the following results:

S	No. of runs	Deviation in rate, % Average	Maximum
55.9	8	5.4	11.6
35.0	11	4.3	11.0
21.0	8	5.3	13.1

The moles of reaction liquid in the system diminished during a run due to withdrawal of samples for analysis. However, the total amount withdrawn was small, less than 5%, and known so that a corrected value of Q could be employed.

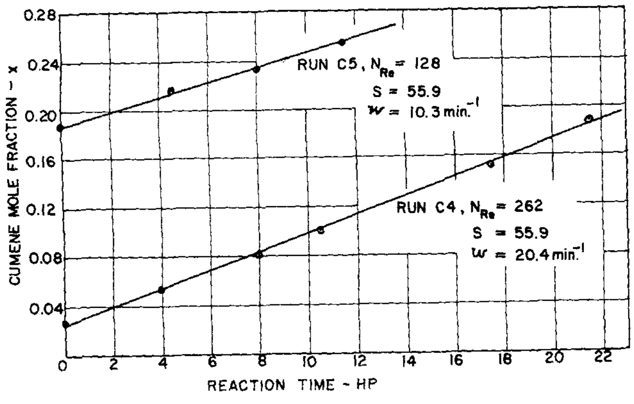

Fig. 3. Cumene concentration vs. time for typical runs at 55°C. and 80 lb./sq.in.abs.

ANALYSIS OF RESULTS

Calculation of Mass Transfer Coefficients

Mass transfer coefficients were determined from the expression

$$r = kA(C_B - C_s) \tag{3}$$

where A is the surface area for mass transfer per unit mass of catalyst. This was arbitrarily chosen as the external surface of the spherical pellets, 11.1 sq. cm./g. The bulk concentration C_B and the rate were measured. For a diffusion-controlled process C_s is zero, and k values were determined on this basis. As an approximate check, the kinetic expression proposed by Babcock and co-workers (3) for the surface rate was used to estimate C_s. These investigators used the same type of catalyst, carrier, and pellet size but a different batch and, most probably, a different activity. In the calculations, values of C_s were determined for the conditions of each nonpulse run of the present study with the experimental rate measurement. The results gave values of C_s which were a few percent of C_B; the maximum ratio was 0.06.

Figure 5 gives the mass transfer results obtained for the pulse and nonpulse rate data in Figure 4. The curve for nonpulse conditions may be compared with mass transfer coefficients determined from diffusion measurements in nonreactive systems. The k_{NP} values given in the literature vary considerably. Typical results, such as those of Hougen and Wilke (7), are higher than those given in Figure 5 by 50 to 100%. Differences in bed conditions (thickness, etc.) and effective areas for transfer may be responsible for the difference in results. Since variations of this magnitude occur between various investigations in nonreactive systems, it was believed most reliable to use the nonpulse data of the present study to evaluate the pulsation effect. This is done in the next section.

Effect of Pulsation

Since it was necessary to use the pulse generator as a pump, the time-average flow rate, pulse frequency, and pulse amplitude were not independent variables. Thus the

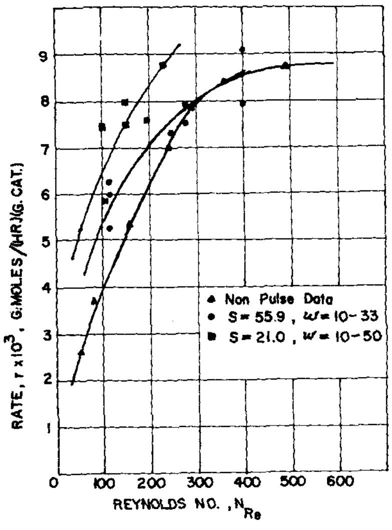

Fig. 4. Effect of pulsation on rate.

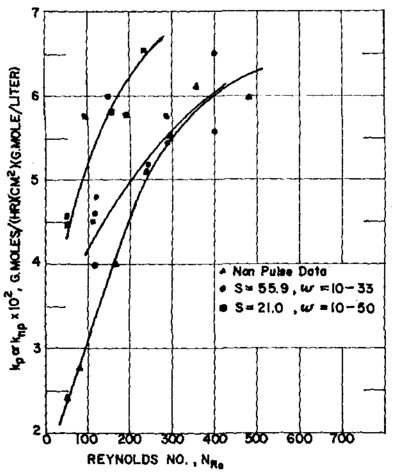

Fig. 5. Effect of pulsation on mass transfer coefficient.

average flow rate expressed in terms of the Reynolds number is

$$N_{Re} = a\omega S \qquad (4)$$

This situation made it difficult to express the effect of frequency and amplitude on the mass transfer coefficients. However, the combined effect of these two variables can be observed directly by a comparison of k_p with k_{NP} at the same time-average Reynolds number. Figure 6 shows the fractional improvement in mass transfer plotted as $(k_p - k_{NP})/k_{NP}$. The solid curves were obtained from data such as that illustrated in Figure 5 by comparing pulse and nonpulse results at the same Reynolds number. These results, which are for 80 lb./sq. in. abs., indicate increases in mass transfer rates as high as 80% at low frequencies and amplitudes; that is, at low Reynolds numbers, according to Equation (4). It cannot be concluded from Figure 6 that the effect of pulsation increases as the amplitude decreases because the Reynolds number is less at the lower values of S and comparison of ordinates at the same frequency does not give the effect of amplitude alone. The improvement in k approaches zero as the frequency approaches infinity since the flow approaches steady state at these conditions.

The only other mass transfer results of a similar nature are those of Bradford (5). He reported coefficients for the solution of β-naphthol spheres in water in a packed column. The frequency range was somewhat higher (w = 24 and 170 min.$^{-1}$) and the amplitude numbers much lower (S = 1.5 and 3.0) than those studied in the present work. Bradford's results showed smaller effects of pulsation on k. This is believed to be due to the smaller amplitude numbers employed. The two sets of data predict a decreasing effect as the frequency and the steady flow rate (Reynolds number) increase.

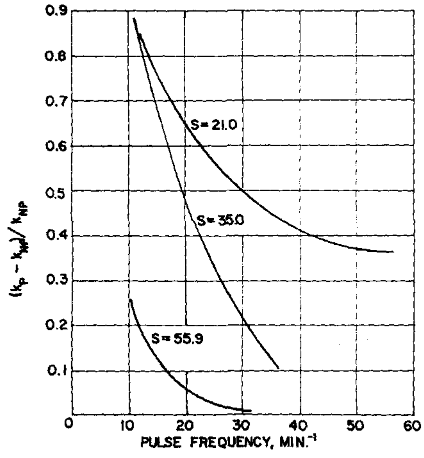

Fig. 6. Increase in mass transfer coefficient due to pulsation

CONCLUSION

This study shows that a pulsating flow can significantly increase the rate of reaction in a fixed-bed reactor operating at conditions where external diffusion resistance is important. The improvement in rate due to pulsation decreases as the steady flow rate increases.

ACKNOWLEDGMENT

The Union Carbide Corporation, through a Fellowship Grant, provided financial assistance for this project.

NOTATION

A = external area of catalyst pellets, sq. cm./g.
a = constant in Equation (4)
C = hydrogen concentration, g. mole/liter
C_B = concentration in bulk fluid
C_s = concentration at catalyst surface
d_p = catalyst pellet diameter, ft.
k = mass transfer coefficient for hydrogen, g. mole/(hr.) (sq. cm.) (g. mole/liter); k_{NP} and k_p = nonpulse and pulse conditions, respectively
N_{Re} = modified Reynolds number, $d_p v_s \rho/\mu$
Q = total liquid charge in closed system, g. moles
r = rate of reaction, g. moles of cumene formed per hour per g. of catalyst
S = amplitude number, amplitude in empty reactor, due to one stroke of pump, (pellet diameter)
T = temperature, °K.
t = reaction time, hr.
v_s = time-average superficial velocity in reactor, ft./sec.
W = catalyst charge, g.
x = cumene mole fraction at time t; x_o refers to $t = 0$

Greek Letters

μ = viscosity of liquid reaction mixture at reactor conditions, lb./(ft.) (sec.)
ω = pulse frequency, min.$^{-1}$
ρ = density of liquid reaction mixture, lb./cu. ft.
$\phi(S)$, $\theta(S)$ = functions of S used in Equation (5)
π = total pressure, lb./sq. in. abs.

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Manuscript received January 3, 1963; revision received March 21, 1963; paper accepted March 22, 1963. Paper to be presented at A.I.Ch.E. San Juan meeting.