Correlating Kinetic Data in Reactors

Application to Tertiary Butanol Dehydration

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The reactor-unit concept proposed by Hurt is extended in this paper to include fractional-order reactions and to show the effect of volume change on the system. Equations defining the reactor unit for homogeneous and heterogeneous reactions are derived.

The catalytic dehydration of tertiary butanol was chosen as a means of studying the validity of the extended reactor-unit concept. The experimental investigation was conducted over a wide range of flow rates, catalyst bed heights, and temperatures. The result of the application of this modified reactor-unit expression to the correlation of the data was excellent.

A need exists for a simple, straightforward method of correlating performance and design of industrial reactors. Hurt's reactor-unit concept (*1* and *2*) is a significant stride toward the answer to this need but has a rather limited range of applicability.

The present work extends the reactor-unit concept to reactions of apparent fractional order and shows a method of accounting for the effect of volume change during the reaction. The classical concepts of homogeneous and heterogeneous reactions formulated by Benton (*3* and *4*) have been utilized in the reactor-unit concept to give a mathematical expression which predicts the relationship among bed height, flow rate, and conversion.

PREVIOUS WORK

Reactions may be characterized in general as either homogeneous or heterogeneous. In the case of homogeneous reactions occurring isometrically, the reaction is described by Hurt as zero, first, or second order by the following equations:

zero order

$$ {}_0N_R = f = kt \qquad (1a)$$

first order

$$ {}_1N_R = \ln \frac{1}{1-f} = kt \qquad (1b)$$

second order

$$ {}_2N_R = \frac{f}{1-f} = kt \qquad (1c)$$

where it is assumed that the rate of reaction is determined primarily by the presence of a single component or limiting reactant. Other forms of Equation (1*c*) may also occur (*2*) but bimolecular reactions will not be discussed.

In the heterogeneous case for first-order isometric reactions the height of a reactor unit is defined by Hurt to be

$$ HRU = \frac{Z}{\displaystyle\int \frac{dy}{y-y^*}} = \frac{Z}{{}_1N_R} \qquad (2)$$

Hay, Coull, and Emmett (*5*) have shown mathematically that this equation is valid regardless of the number of series resistances: rates of surface reaction, absorption, desorption, and diffusion, provided that each of these resistances is a first-order process; e.g., the concentration gradient from one step to the next appears to the first power.

Simply speaking, the height of a reactor unit, as used here, is a comparative measure of the resistance of a given system to chemical conversion, and the number of reactor units is a measure of the amount of conversion. The product of these two terms is the catalyst-bed height.

Frequently the impression is given in the kinetics literature that the order of a reaction is numerically equal to the molecularity of the system; such an erroneous conclusion will lead to general confusion on the subject. Nor is selecting as the order of the reaction the integer which most nearly describes the data good practice, because a significant error may be introduced when one is extrapolating to higher conversion rates if the reaction happens to be of fractional order. Chemical reactions of noninteger orders are known to exist and are frequently encountered.

GENERAL REACTOR-UNIT EXPRESSION

The usual form of the kinetic rate equation for isothermal homogeneous reactions, in which a limiting component controls the rate, is

$$ -\frac{dN}{dt} = kNC^{n-1} \qquad (3a)$$

where

$$ C = \frac{N}{V} $$

Equation (3*a*) reduces to the more familiar form shown below for reactions conducted at constant volume.

$$ -\frac{dC}{dt} = kC^n \qquad (3b)$$

A general solution for isometric homogeneous reactions may be found by substituting $N = N_0(1-f)$, $dN = -N_0\,df$, and $N = VC$ into Equation (3*a*) and integrating. The result is

$$ {}_nN_R = C_0^{1-n}\left[\frac{(1-f)^{1-n}-1}{n-1}\right] = kt \qquad (4)$$

This equation is a general definition for the number of reactor units because each of the expressions shown in Equations (1*a*), (1*b*), and (1*c*) may be obtained from Equation (4) by the selection of appropriate values of n; in addition, this general definition also includes reactions of noninteger order. Substitution of $n = 1$ into Equation (4) results in an indeterminant form, but application of L'Hôpital's rule gives Equation (1*b*).

From Equation (2) the differential equation for a heterogeneous reaction is

$$ \frac{dy}{dt} = k(y-y^*)^n \qquad (5)$$

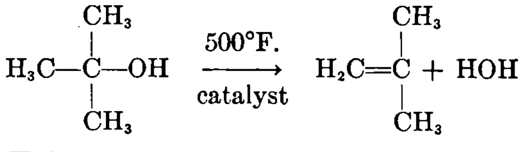
or in the integrated form

$$ \frac{(y_0-y^*)^{1-n}-(y-y^*)^{1-n}}{1-n} = kt \qquad (6)$$

THE DEHYDRATION OF TERTIARY BUTANOL

General Considerations

Tertiary butanol may be dehydrated at 500°F. over an alumina catalyst, the equilibrium conversion being essentially 100%. A literature survey on this reaction indicated that side reactions were unlikely. With primary alcohols there is some evidence that the dehydration proceeds through an intermediate ether formation (*6*), but tertiary alcohols are thought to have a much higher dehydration rate than ether-formation rate (*7*). Of course there is complete equivalence as to the position of the double bond in the isobutylene formed during reaction.



$$ H_3C{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH \xrightarrow[\text{catalyst}]{500°\text{F.}} H_2C{=}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} + HOH $$

Reactor-unit Expression

The dehydration of tertiary butanol was selected as a suitable test reaction for studying the reactor-unit equation for two principal reasons: the reaction (1) involves a volume change and (2) is probably of fractional order. Substituting

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f, the ratio of moles converted to the moles converted at equilibrium, for partial pressure in Equation (6) yields

$$\frac{1}{1-n}\left[y_0^{1-n} - \left\{\frac{y_0(1-f)}{(y_0 f + 1)}\right\}^{1-n}\right] \cdot \left[1 + \frac{y_0 f}{2}\right] = k\,\frac{V_R}{V_0} = {}_nN_R \quad (7)$$

where reciprocal space velocity V_R/V_0 is employed rather than residence time. If the feed to the reactor is 100% limiting reactant ($y_0 = 1.00$) the previous result reduces to

$$\frac{1}{1-n}\left[1 - \left\{\frac{1-f}{1+f}\right\}^{1-n}\right] \cdot \left[1 + \frac{f}{2}\right] = k\,\frac{V_R}{V_0} = {}_nN_R \quad (8)$$

Equipment and Procedure

The investigation was conducted in a fixed-bed, isothermal catalytic reactor donated by Gulf Research and Development Company. The 3-ft. reactor consisted of a ¾-in. stainless steel tube concentric with a 3-in. steel jacket which contained Dowtherm heating medium.

The research-grade tertiary butanol was pumped from a reservoir through a preheating coil where the alcohol was vaporized and carried to the top of the reactor. The vapors flowed downward through the catalyst bed, and the effluent stream was totally condensed at constant (atmospheric) pressure.

The condensed product was analyzed by fractionally distilling the isobutylene from the water-alcohol mixture. This mixture was further analyzed for water content, and thus an accurate material balance was provided.

The reactor was operated at temperatures ranging from 480° to 580°F. over a mass velocity range of from 20 to 250 lb./(hr.)(sq.ft.) at bed heights of 1 to 4 in. and with both pure and diluted feed.

Catalyst

Alcoa F-10 alumina of particle size passing 8 and stopping on 9 U.S. standard mesh sizes was used as the dehydrating catalyst throughout this study. The activity of the catalyst diminished with use, presumably owing to the coking of active centers. In order to correlate data taken with a catalyst of varying activity, it was necessary to make a standard conversion run at the beginning and end of each day.

Results

The correlation of the data* by the reactor-unit method is presented in Figure 1. Most of the data were taken at a reaction temperature of 530°F. Equation (8) was successfully employed in correlating all the data taken with a feed containing pure tertiary butyl alcohol. The value of n was found to be 0.615. When this same value of n was used in Equation (7), the correlation of the runs employing a diluent was equally satisfactory. Water was used as the diluent in one case and normal heptane in another. As water is many times more strongly adsorbed on alumina than is heptane, it was considered possible that the water in the reaction may reversibly poison the catalyst, but this situation was not observed, as the data from both types of diluents fitted nicely in the correlation.

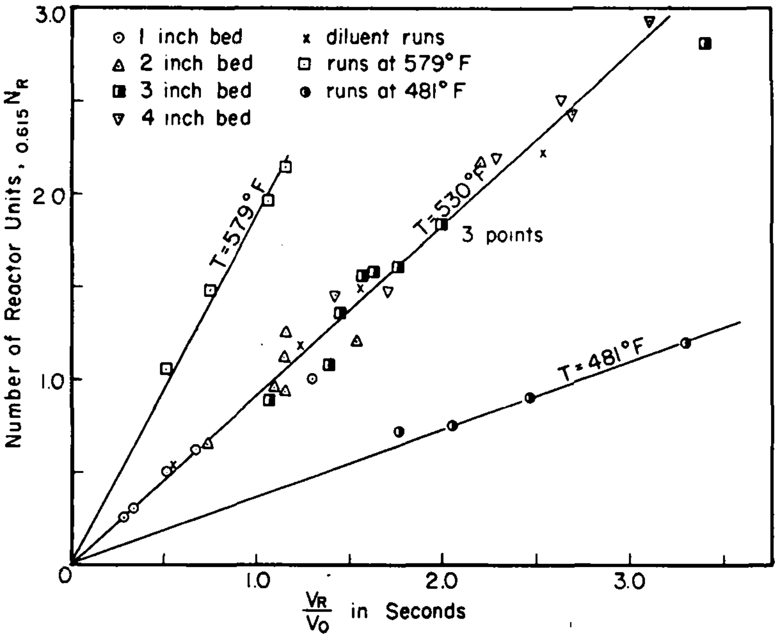

Fig. 1. Plot of reactor units vs. $\frac{V_R}{V_0}$.

The dehydration observed at other temperatures similarly followed the same equation and at the same value of n (0.615). The slopes of the isotherms on Figure 1 were used in preparing the pseudo Arrhenius plot in Figure 2. Although the absolute specific reaction-rate constants were not used, the slope of the isotherm in an N_R vs. V_R/V_0 plot should be proportional to the absolute reaction rate. The linearity of this plot indicated that the chemical reaction rate rather than diffusion or adsorption rates was the controlling step in the dehydration.

SUMMARY

This study shows that for this system the simple reactor-unit expressions presented here correlate data from a heterogeneous reaction of over-all fractional order over substantially the entire range of conversion, over a fourfold change in bed height, over a tenfold change in flow rate, over a 100° temperature range, and for both pure and dilute feed.

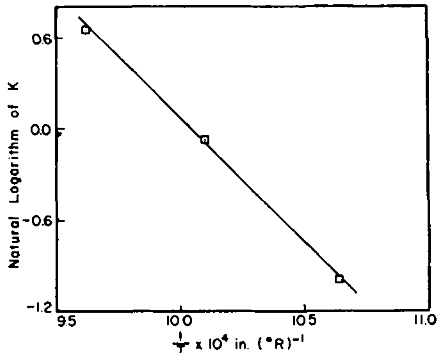

Fig. 2. Arrhenius plot for the dehydration of tertiary butanol.

It may be concluded that the reactor-unit concept has been extended to cover fractional-order reactions occurring nonisometrically. It is possible to use this simple method to correlate the performance of various existing reactors and to design new reactors more accurately from limited pilot plant data.

NOTATION

f = fraction of equilibrium conversion
HRU = height of reactor unit
k = reaction rate constant
n = order of reaction
N = number of molecules
N_R = number of reactor units
t = residence time
y = mole fraction of the reactant in gas
y_0 = initial mole fraction of the reactant in gas
y^* = mole fraction at equilibrium
V = volume or, in flow systems, volumetric rate
V_0 = initial volume, or in flow systems, initial volumetric rate
V_R = volume of catalyst
Z = catalyst-bed depth

LITERATURE CITED

1. Hurt, D. M., *Ind. Eng. Chem.*, **35**, 522 (1943).
2. Caddell, J. R., and D. M. Hurt, *Chem. Eng. Progr.*, **47**, 333 (1951).
3. Benton, A. F., *Ind. Eng. Chem.*, **19**, 494 (1927).
4. ——, *J. Am. Chem. Soc.*, **53**, 2984 (1931).
5. Hay, R. G., James Coull, and P. H. Emmett, *Ind. Eng. Chem.*, **41**, 2809 (1949).
6. Dohse, H., and W. Kalberger., *Z. Physik. Chem., Abt.*, **B5**, 131 (1929).
7. Conant, J. B., and A. H. Blatt, "The Chemistry of Organic Compounds," The Macmillan Company, New York (1947).

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*Complete data may be obtained as document 4962 from the American Documentation Institute Photoduplication Service, Library of Congress, Washington 25, D. C., for $1.25 for photoprints or 35-mm. microfilm.