Reaction Kinetic Studies: Catalytic Dehydrogenation of Sec-butyl Alcohol to Methyl Ethyl Ketone

JOSEPH J. PERONA and GEORGE THODOS

Northwestern Technological Institute, Evanston, Illinois

Reaction kinetics for the catalytic dehydrogenation of sec-butyl alcohol to methyl ethyl ketone has been investigated at atmospheric pressure and temperatures ranging from 650° to 750°F. in the presence of solid brass spheres, 1/8 in. in diameter. The nature of this catalyst permitted a direct evaluation of the surface involved in this reaction and allowed the definition of a surface-feed ratio to be expressed as S/F in place of the conventional weight-feed ratio W/F commonly used in catalytic studies. Feed compositions ranged from sec-butyl alcohol to mixtures containing high percentages of methyl ethyl ketone and hydrogen.

In these studies mass transfer effects were found to be significant and, for a proper representation of conditions at the catalyst surface, must be taken into account. The effect of feed compositions on the initial rates of reaction showed that the rate-controlling step was the desorption of hydrogen involving a single-site mechanism.

In addition, the results of these studies have been used to produce values of height of reactor unit HRU which have been found to correlate with mass velocity and temperature. The HRU provides a simple means of calculating the depth of catalyst necessary to effect a designated conversion.

The design of catalytic reactors according to fundamental principles requires an exacting background knowledge of the reaction mechanism taking place on the surface of the catalyst. Although empirical approaches have proved expedient for the design of commercial units, a more fundamental approach to the solution of such problems becomes increasingly significant. As a result of the developments of the reaction-rate mechanisms proposed by Hougen and Watson (*2*) and involving the participation of active centers on the catalytic surfaces, it is now possible to associate the rate of reaction with the behavior of the reactants and products on these active centers. Several possible mechanisms have been produced, and to date these constitute the fundamental background for comprehension of the various steps taking place in the course of a reaction. The possible rate mechanisms are numerous, and the development of the corresponding rate equations is presented elsewhere (*2*).

The preponderance of catalytic reactions has been carried out in the presence of porous catalysts which provide an extensive network through which the reactants and products must diffuse in order for the reaction to proceed. The variables influencing the diffusional phenomena occurring within the catalyst pores have been considered theoretically by Thiele (*12*). These diffusional effects have been shown to decrease with the size of the catalytic particles and to become insignificant for fluidized beds. For larger particles in fixed beds, diffusion to or from the interior of the catalyst may be significant and presents an additional variable in the fundamental study of reaction mechanisms. The use of solid brass as catalyst for the dehydrogenation of sec-butyl alcohol, besides eliminating this possible variable, also permits the direct calculation of the surface taking part in the reaction. Since it is possible to account for the surface participating in the reaction, the relationship of space velocity and conversion dx_A taking place in an elementary section of reactor volume whose surface is dS may be expressed as

$$F\,dx_A = r_A\,dS \tag{1}$$

From Equation (1) the surface-feed ratio S/F, which is directly related to space velocity, now can be defined in terms of conversion and reaction rate as follows:

$$\frac{S}{F} = \int_0^{x_A} \frac{dx_A}{r_A} \tag{2}$$

The surface-feed ratio S/F is a more direct relationship and is used in these studies rather than the conventional weight-feed ratio W/F. For porous catalysts the use of the weight-feed ratio W/F proves more expedient and is found to be specific to the type of catalyst, method of preparation, and size. On the other hand, the ratio S/F is more fundamental in this application since it deals only with the specific nature of the reaction and not the method of preparation and size of the catalyst. Therefore, whenever the surface of the catalyst can be conveniently obtained, the surface-feed ratio S/F may be applied.

EXPERIMENTAL EQUIPMENT

The experimental unit used in these studies, which is presented diagrammatically in Figure 1, consisted of a small continuous pilot plant having a stainless steel tubular reaction heated by an electric furnace. Liquid mixtures of sec-butyl alcohol and methyl ethyl ketone were pumped into the reactor from a calibrated feed tank. The introduction of hydrogen, nitrogen, and air to the system was regulated by means of a needle valve, and the flow rates were measured with a rotameter. The reactor effluent was passed through a water-cooled condenser to a phase separator, from which noncondensable gases could be collected over salt water in the gas-sampling bottle or passed through the wet-test meter to measure the rate of production.

Reactor

Figure 2 shows the details of the reactor, which was fabricated from 1½-in., type-304 stainless steel pipe and was 40 in. long. Two stainless steel sleeves, 1 and ½ in. I.D., provided a variation of cross-sectional area of the catalyst bed. In this manner greater ranges of mass velocity through the catalyst were conveniently obtained with the equipment available. Thermowells provided on the top flange and bottom plug permitted the establishment of temperature profiles over the full length of the reactor. The entire volume of the reactor, with the exception of the catalyst zone, was filled with 3- to 5-mm. glass shot. The glass shot above the catalyst bed provided adequate heat transfer surface and insured a uniform fluid flow pattern; whereas this packing below the catalyst bed acted as a support and also decreased the void volume of the reactor, causing the rapid removal of the effluents.

PRELIMINARY INVESTIGATIONS

The catalytic dehydrogenation of secondary alcohols to ketones was first reported by Ipatieff (*4*) with metals such as iron, zinc, brass, manganese, and nickel. No significant dehydrogenation was noted with aluminum, lead, tin, bismuth, antimony, or magnesium. Balandin and Liberman (*1*) and Neish (*9*) showed that copper has initial dehydrogenating properties which gradually diminish owing to irreversible poisoning effects. Ivannikov, Tatarskaya, and Gavrilova (*5*) showed that uranium acts as a promoter to copper, which did not

---

Joseph J. Perona is at present with the Oak Ridge National Laboratory, Oak Ridge, Tennessee.

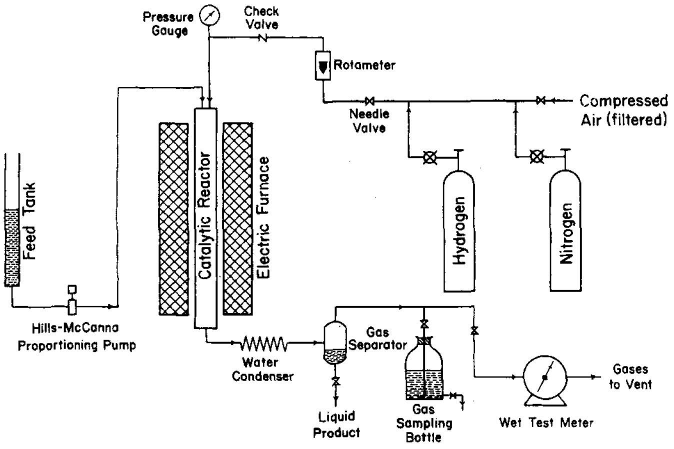

Fig. 1. Flow diagram of experimental equipment.

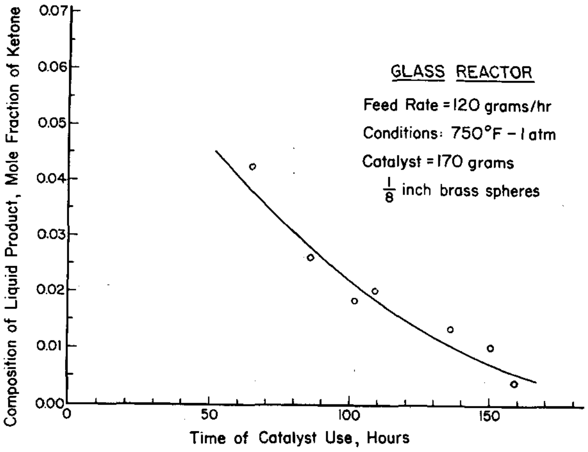

Fig. 3. Activity of catalyst in glass reactor vs. time.

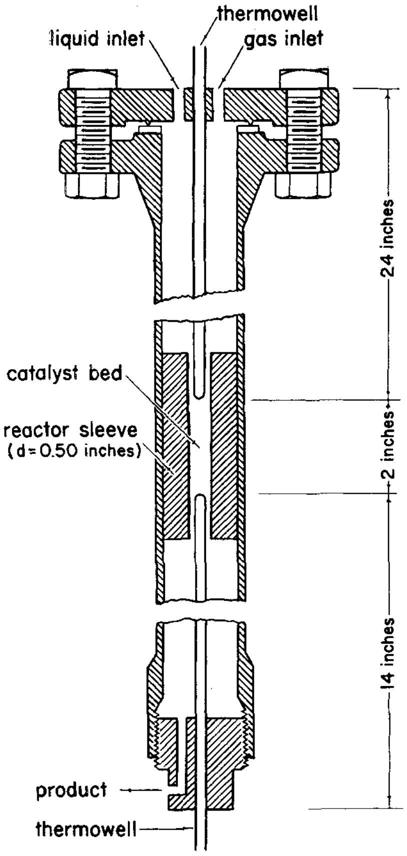

Fig. 2. Experimental reactor.

show poisoning effects after 60 hr. of use. Several dehydrogenating catalysts of the zinc oxide type are reported in the literature (*7*, *8*, *10*). Iron, manganese, and nickel, although capable of dehydrogenating secondary alcohols to ketones, have the added catalytic ability to decompose the ketones produced into olefins and oxides of carbon (*4*). In addition, Ipatieff (*4*) noted that zinc tended to oxidize in the course of the reaction involving the dehydrogenation of alcohols.

Considerable importance has been attached to the use of brass for the commercial production of methyl ethyl ketone. The technical information in the literature involving the use of brass for the production of ketones is essentially nonexistent despite the current commercial interest and activity on this subject. Therefore, it was found necessary to conduct a series of exploratory investigations in order to study the behavior of this catalyst under varying conditions of operation.

Brass ball bearings $\frac{1}{8}$-in. in diameter having a tolerance of ±0.001 in. and composed of 65% copper and 35% zinc were used throughout this study.

Brass spheres in a glass reactor packed with glass shot showed a continued decrease in activity with time as indicated in Figure 3. Inspection showed a black carbonaceous deposit on both the brass catalyst and the glass spheres which was completely removed by the passage of air at approximately 800°F. The appearance of the oxidized catalyst is essentially black and is compared with a new catalyst in Figure 4.

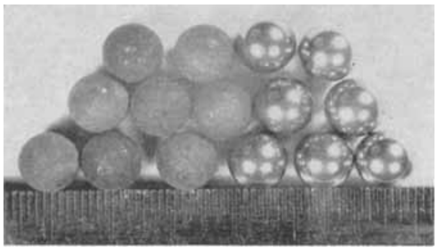

Fig. 4. Appearance of new and used brass ball bearings as catalyst.

Several blank runs were made with the glass reactor without a catalyst. With a temperature of 750°F. in the zone ordinarily occupied by the catalyst, an effluent gas rate of approximately 300 cc./hr. was observed for sec-butyl alcohol feed rates of 200 to 600 g./hr. A typical analysis of the effluent gases was found by mass spectrometer measurements to have the following composition:

	Mole fraction
Hydrogen	0.959
Methane	0.033
Ethane	0.001
Ethylene	0.007
	1.000

This indicates that the reaction in the absence of catalyst is basically of a cracking nature with a preponderance of hydrogen resulting in the effluent gases while no ketone was noted in the effluent liquid. In all cases the alcohol involved in this decomposition reaction consumed less than 1% of the alcohol introduced into the reactor.

Experimentation with the stainless steel reactor revealed that blank runs following a regeneration period with air produced relatively high rates of cracked gases which decreased rapidly with time. Average rates of gas production in the course of a run were measured and are expressed as the zigzag lines presented in Figure 5. Instantaneous rates of gas production can be established from the straight-line relationship drawn through these average rates and presented in Figure 5. These observations strongly suggest that the cracking reactions might have been catalyzed to some extent by the metallic oxides produced during the regeneration period and that the decrease in gas rate was due to the reduction of the metallic oxides by the product hydrogen. In order to test this theory, a regeneration period with air was followed by a nitrogen purge and then hydrogen was passed through the reactor at 800°F. for 10 hr. before the start of a run with sec-butyl alcohol and without a catalyst. The rate of cracked gases produced under these conditions was found to be only about 25 cc./hr. in comparison with a rate of about 400

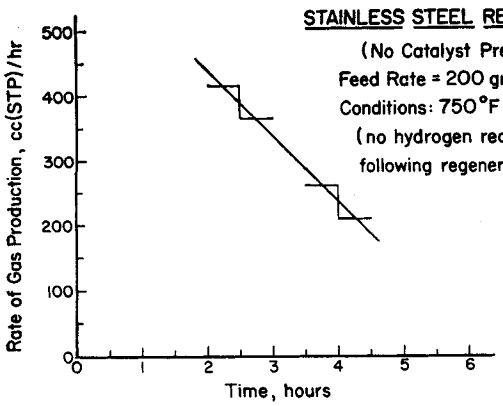

Fig. 5. Cracking activity of blank reactor after regeneration (no hydrogen reduction).

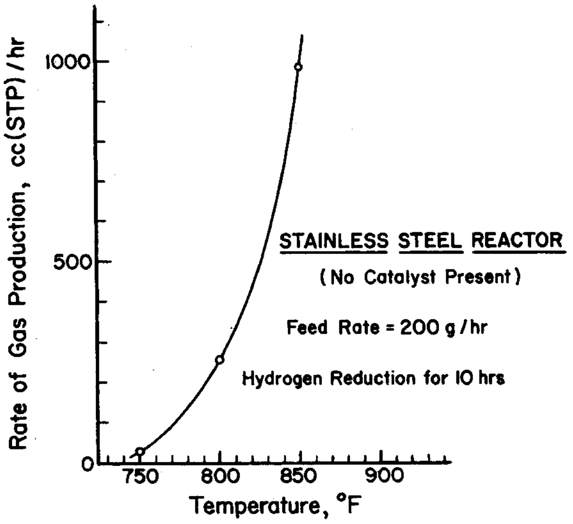

Fig. 6. Cracking activity of blank reactor vs. temperature after regeneration followed by hydrogen reduction.

cc./hr. found initially with the stainless steel reactor and no hydrogen reduction following regeneration.

The rate of the cracking reaction was found to increase sharply with temperature, as shown by Figure 6. Therefore, in order to keep the rate of cracking as low as possible and at the same time to obtain a reasonable conversion, a temperature of 750°F. was selected as the maximum to be investigated.

A 24-hr. cycle of 5 hr. of reaction time, 5 hr. of regeneration with air at 800°F., and 14 hr. of reduction with hydrogen at 800°F. was found to yield consistent and reproducible data. The first 2 hr. of feed introduction was used to bring the reactor up to reaction temperature and to allow the reactants to attain chemical equilibrium with the catalyst. Hourly liquid samples were collected, and product gas rates were observed during the last 3 hr. of the reaction time. The decrease in conversion over the 3-hr. period, due to loss in catalyst activity, was of the same order as conversion changes due to slight temperature variations (±5°F.). Values of conversion and temperature over the 3-hr. period were averaged for each run.

EXPERIMENTAL RESULTS AND INTERPRETATION OF DATA

Rate data were taken at 650° and 700°F. for four different feed compositions and at 750°F. for five different feed compositions. All runs were made at atmospheric pressure. The extent of conversion was calculated from the composition of the liquid samples, which were analyzed in a Baird infrared spectrophotometer, and from the effluent gases, which were considered to be hydrogen. The material balances resulting from the liquid composition and gases produced were always in good agreement. The experimental data obtained from these studies are presented in Table 1.*

TABLE 2. CALCULATED INITIAL RATES OF REACTION

Temperature, °F.	Feed composition, mole fraction: Alcohol	Ketone	Hydrogen	Average pressure	Partial pressures of feed components, atm.: Alcohol	Ketone	Hydrogen	r_0, Initial rate of reaction, lb.-moles alcohol converted/(hr.)(sq. ft.)
650	1.000			0.988 atm	0.988			0.00620
650	0.594	0.406		0.978	0.581	0.397		0.00415
650	0.196	0.804		0.979	0.192	0.787		0.00178
650	0.550		0.450	0.990	0.545		0.445	0.00640
700	1.000			0.978	0.978			0.0255
700	0.594	0.406		0.962	0.571	0.391		0.0150
700	0.196	0.804		0.979	0.192	0.787		0.0061
700	0.529		0.471	0.986	0.521		0.465	0.0254
750	1.000			0.984	0.984			0.0425
750	0.594	0.406		0.985	0.585	0.400		0.0233
750	0.394	0.606		0.965	0.380	0.585		0.0174
750	0.196	0.804		0.978	0.192	0.786		0.0100
750	0.607		0.393	0.987	0.600		0.388	0.0425

Plots of conversion x_A vs. the surface-feed ratio S/F were produced for all feed compositions at 650°, 700°, and 750°F. and graphically differentiated to obtain the initial rate of reaction corresponding to conversion, $x_A = 0$, and surface-feed ratio, $S/F = 0$. A plot of x_A vs. S/F at 700°F. is presented in Figure 7 for the following four different feed compositions.

Feed Compositions for 700°F., Mole Fraction

	1	2	3	4
Alcohol	1.000	0.594	0.196	0.529
Ketone		0.406	0.804	
Hydrogen				0.471
	1.000	1.000	1.000	1.000

The initial rate obtained through these means is directly related to the composition of the feed; at the value $S/F = 0$ any mass transfer contributions are eliminated, thus permitting a direct association of the initial rate only with the composition of the incoming feed. A summary of initial reaction rates is presented in Table 2 for the different compositions at 650°, 700°, and 750°F.

Establishment of Surface Mechanism

The data presented in Table 2 were subjected to a rigorous analysis along the lines proposed by Hougen and Watson (*2*) in order to establish the reaction mechanism at the catalyst surface controlling this dehydrogenation step. Equilibrium constants K used in this investigation were calculated from the relationship

$$\log K = -\frac{2{,}790}{T} + 1.510 \cdot \log T + 1.865 \quad (3)$$

where T is expressed in degrees Kelvin. This equation was developed by Kolb

---

*Tabular material has been deposited as document 5219 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

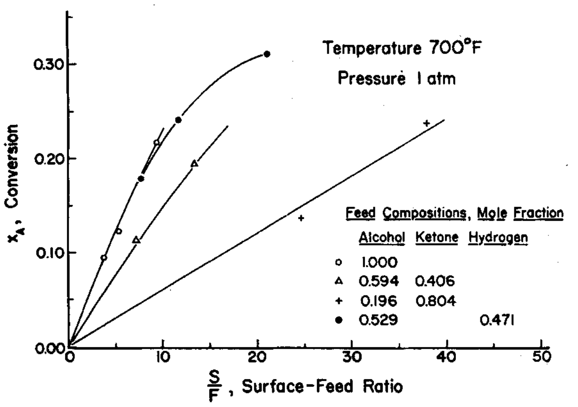

Fig. 7. Experimental results of conversion vs. surface-feed ratio at 700°F. and atmospheric pressure.

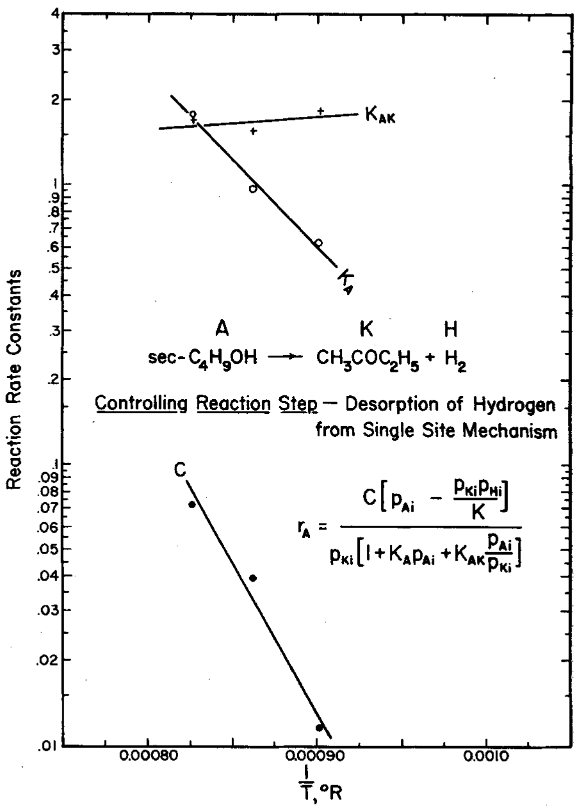

Fig. 8. Relationships of rate constants and temperature.

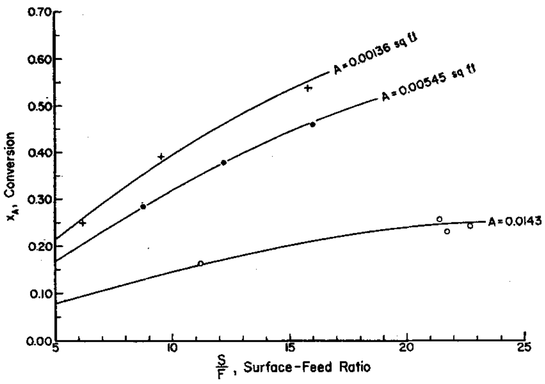

Fig. 9. Effects of mass transfer associated in the catalytic dehydrogenation of sec-butyl alcohol in the presence of brass at 750°F. and 1 atm.

and Burwell (*6*), who approached equilibrium for this reaction from both directions. Altogether, ten possible reaction model mechanisms were assumed to apply, and the corresponding rate equations were derived for them. The resulting equations are presented in Table 3*, along with the corresponding calculated constants. The solution of simultaneous equations involving the feed compositions and initial rates of reaction produced the rate constants summarized in Table 3. A review of these constants shows that the desorption of hydrogen from a single site is the only mechanism for which the constants were all positive at 650°, 700°, and 750°F. Therefore, the rate of reaction for the dehydrogenation of sec-butyl alcohol to methyl ethyl ketone in the presence of brass becomes

$$r_A = \frac{C\left[p_{Ai} - \frac{p_{Ki}p_{Hi}}{K}\right]}{p_{Ki}\left[1 + K_A p_{Ai} + K_{AK}\frac{p_{Ai}}{p_{Ki}}\right]} \qquad (4)$$

For the derivation of this equation the reaction was assumed to take place in three steps: (1) the adsorption of the alcohol onto an active site, (2) decomposition of the alcohol–active site complex to form methyl ethyl ketone in the vapor phase and adsorbed molecular hydrogen, (3) desorption of the hydrogen in the vapor phase. The first two steps were assumed to be at equilibrium, with the third step controlling the rate of the reaction. In Equation (4) K_A is the adsorption equilibrium constant for step 1, and K_{AK} is the product of K_A and the equilibrium constant for step 2.

The constants C, K_A, and K_{AK} are summarized in Table 3 and are correlated

TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL REACTION RATES AT 700°F.

Run	$(x_A)_{avg}$ Conversion	S/F at $(x_A)_{avg}$	Average partial pressures In main gas stream, atm. Alcohol	Ketone	Hydrogen	At interface, atm. Alcohol	Ketone	Hydrogen	Average reaction rate, lb.-moles/(hr.)(sq. ft.) Calculated	Experimental
M-1	0.0476	1.9	0.879	0.042	0.042	0.859	0.056	0.056	0.0236	0.0246
M-4	0.097	6.4	0.490	0.419	0.049	0.472	0.426	0.052	0.0137	0.0150
M-8	0.089	3.7	0.453	0.042	0.489	0.445	0.052	0.491	0.0230	0.0233
M-13	0.068	11.3	0.177	0.791	0.013	0.172	0.792	0.014	0.0057	0.0061

TABLE 6. PERTINENT DATA FOR THE CALCULATION OF REACTION RATES OF ILLUSTRATIVE EXAMPLE

Conversion	Partial pressure of components in main gas stream, atm.			Mass transfer coefficients, lb.-moles/(hr.)(sq. ft.)(atm.)			Partial pressures of components at catalyst surface, atm.			Reaction rate, lb.-moles/(hr.)(sq. ft.)
x_A	p_A	p_K	p_H	k_{gA}	k_{gK}	k_{gH}	p_{Ai}	p_{Ki}	p_{Hi}	r_A
0.00	1.000	0.000	0.000							0.000
0.0471	0.910	0.045	0.045	0.720	1.015	3.72	0.859	0.081	0.055	0.0371
0.1285	0.772	0.114	0.114	0.788	1.167	4.07	0.727	0.144	0.123	0.0352
0.229	0.626	0.187	0.187	0.892	1.420	4.63	0.593	0.208	0.193	0.0297
0.310	0.526	0.237	0.237	0.970	1.640	5.05	0.498	0.253	0.242	0.0270
0.600	0.251	0.375	0.375	1.275	2.86	6.70	0.236	0.381	0.378	0.0181
0.800	0.113	0.444	0.444	1.490	4.47	7.83	0.105	0.446	0.445	0.0106
0.900	0.052	0.474	0.474	1.600	6.05	8.46	0.048	0.475	0.475	0.00578

---

*See footnote on page 232.

with reciprocal temperature to produce the linear relationships presented in Figure 8. The positive temperature coefficient exhibited with K_A, the adsorption equilibrium constant of the alcohol, may appear inconsistent with present concepts which point out that this variation should be negative. The majority of catalytic reactions found in the literature show these constants to have a negative temperature coefficient; however, a few exceptions have been reported. In the hydrogenation studies of Sussman and Potter (*11*) over a copper-magnesia catalyst a positive temperature coefficient for the adsorption equilibrium constant of propylene is similarly reported. These constants can be expressed in equation form with temperature as follows:

$$\log C = -\frac{10{,}735}{T} + 7.776 \qquad (5)$$

$$\log K_A = -\frac{6165}{T} + 5.327 \qquad (6)$$

$$\log K_{AK} = \frac{486}{T} - 0.1968 \qquad (7)$$

Mass Transfer Effects

The establishment of the rate-controlling step on the surface of the catalyst involved initial rates at $S/F = 0$ corresponding to infinite feed flow rates. At these conditions mass transfer contributions are eliminated, and the partial pressures of the components in the main gas stream become identical to those existing at the solid-gas interface. Therefore, the reaction rate taking place at the surface of the catalyst and expressed by Equation (4) becomes applicable only when the partial pressures of the components are known at the interface.

The effects of mass transfer on this reaction were studied by varying the cross-sectional area of the reactor and observing the influence of the surface-feed ratio S/F on the conversion x_A. These investigations were conducted at 750°F. with a feed consisting only of sec-butyl alcohol. The results of these observations, presented in Figure 9, indicate that mass transfer contributions at this temperature are significant and must be accounted for in the proper design of a reactor. The details involving mass transfer calculations to permit evaluation of the partial pressures of the components at the interface are presented by Hougen and Watson (*2*) and utilize mass transfer coefficients for these components that were produced from the mass transfer factor:

$$j_d = \frac{k_g M_m p_f}{G}\left[\frac{\mu}{\rho D_m}\right]_f^{2/3} \qquad (8)$$

where $\mu/\rho D_m$ = Schmidt group, dimensionless. Through these means it becomes possible to evaluate the partial pressure difference of a component across the gas film, thus permitting the use of the rate equation, which becomes applicable to conditions existing at the surface of the catalyst. Partial pressures at the interface were calculated for four runs at 700°F. and covered a wide range of compositions of alcohol, ketone, and hydrogen. The reaction rates calculated from these interfacial partial pressures are presented in Table 4 and compared with the average experimental rates obtained from the x_A vs. (S/F) curves at conditions of average conversion. The approach involving mass transfer calculations, illustrated in a later section, is found to be, although rigorous, somewhat unwieldy for expediency.

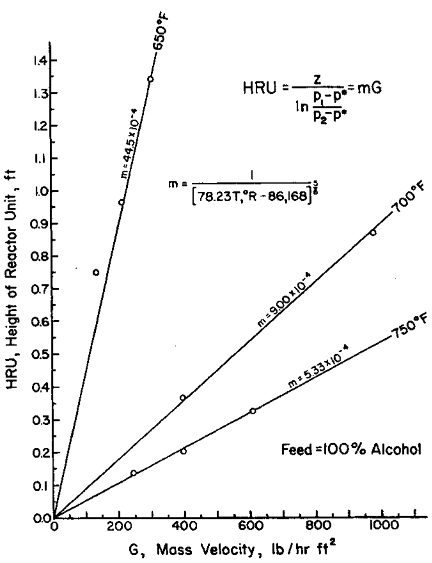

Fig. 10. Relationships of height of reactor unit and mass velocity for the dehydrogenation of sec-butyl alcohol at 650°, 700°, and 750°F. (catalyst: brass spheres 1/8 in. in diameter).

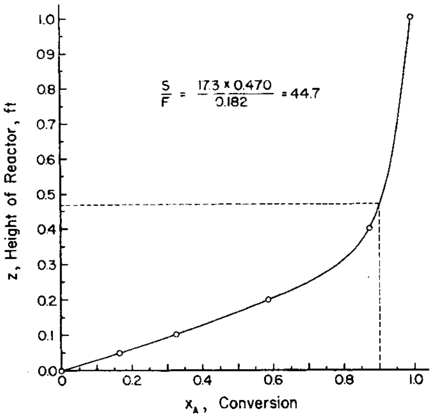

Fig. 11. Reactor height vs. conversion relationship for illustrative example (HRU approach).

Height of Reactor Unit

The combined contributions of mass transfer effects and the reaction at the surface are conveniently represented by the height of reactor unit, HRU. For a reaction which is unimolecular in both directions and for which the partial-pressure changes of the components across the film are equal and the adsorption terms in the denominator of the rate equation are negligible, Hurt (*3*) defines the height of a catalytic reactor through the expression

$$z = (HCU + HTU)N_R = (HRU)N_R \qquad (9)$$

where *HCU* represents the height of catalytic unit resulting from the surface reaction; *HTU*, the height of transfer unit due to mass transfer effects; and *HRU*, the height of reactor unit, which represents the contribution of both mass transfer and surface-reaction effects.

Although Hurt in the development of these concepts has postulated a unimolecular reaction, these units have been assumed to apply in the dehydrogenation of sec-butyl alcohol, where

$$N_R = \ln\frac{p_1 - p^*}{p_2 - p^*} \qquad (10)$$

From the data of Table 1, *HRU* values have been calculated for a feed consisting of sec-butyl alcohol at 650°, 700°, and 750°F. The resulting *HRU* values and data from which they were derived appear in Table 5† and are plotted in Figure 10 as straight lines against mass velocity which pass through the origin. Consequently this relationship of *HRU* becomes

$$HRU = mG \qquad (11)$$

where G represents the mass velocity, pounds per hour per square feet, and m is a constant which may be expressed in terms of temperature through the relationship

$$m = \frac{1}{(78.23T - 86{,}168)^{5/6}} \qquad (12)$$

in which T is the reaction temperature in degrees Rankine. Although the theoretical background involving the definition of *HRU* for this reaction is not rigorous, the relationships resulting from the application of Equation (11) to produce the straight lines of Figure 10 affords an expedient means for the design of reactors which incorporate the simultaneous contribution of both mass transfer and the reaction taking place on the surface of the catalyst. This approach eliminates the unavoidable and laborious trial-and-error procedure resulting from the application of the multiconstant rate equation and necessary mass transfer calculations for the establishment of the proper rate of reaction.

Illustrative Example

The catalytic dehydrogenation of secondary butyl alcohol to methyl ethyl ketone is to be carried out at 750°F. and atmospheric pressure in a cylindrical reactor 3 in. in diameter and packed with ⅛-in. brass spheres. A feed stream of 2 gal./hr. of

---

†See footnote on page 232.

secondary butyl alcohol is introduced to the reactor.

Calculate the reactor height required to effect a 90% conversion using the following:

a. the height-of-reactor-unit (HRU) approach
b. the reaction-rate equation with associated mass transfer calculations

Solution

Feed rate = 2 × 6.7 = 13.4 lb./hr. = 0.182 lb.-moles/hr.

Cross-sectional area of reactor = $\pi/4[3/12]^2 = 0.0490$ sq. ft.

Mass velocity = 13.4/0.0490 = 275 lb./(hr.)(sq. ft.)

Catalyst surface: For a void volume fraction, $\epsilon = 0.40$, the catalyst surface becomes 17.3 sq. ft./ft. of reactor height

PART A. From Figure 10, *HRU* = 0.147 ft. at *G* = 275 lb./(hr.)(sq. ft.) and 750°F. The equilibrium constant at this temperature $K_p = 95.94$ was used to calculate the equilibrium composition, which is

	Mole fraction
Alcohol	0.0026
Ketone	0.4987
Hydrogen	0.4987
	1.0000

The height of the reactor required when sec-butyl alcohol is charged to the reactor becomes

$$z = (HRU)N_R = (HRU)\ \ln \frac{p_{A_1} - p_A{}^*}{p_{A_2} - p_A{}^*}$$

$$= 0.147\ \ln \frac{1.000 - 0.0026}{p_{A_2} - 0.0026}$$

Assumed values of z produced the following partial pressures of alcohol leaving the reactor p_{A_2}, corresponding to conversions x_A.

z, ft.	p_{A_2}, atm.	x_A
0.00	1.000	0.000
0.05	0.713	0.168
0.10	0.508	0.326
0.20	0.259	0.588
0.40	0.0682	0.872
1.00	0.0037	0.993

The relationship of reactor height z vs. conversion x_A is presented in Figure 11. From this figure a reactor height of $z = 0.47$ ft. is required to effect a 90% conversion.

PART B. A rigorous solution to this problem involving the use of the reaction-rate equation and mass transfer contributions necessitates a trial-and-error procedure, in which the composition of alcohol, ketone, and hydrogen must be established at the catalyst surface in order to produce the proper rate. For a designated conversion x_A a preliminary rate of reaction was calculated by using the component compositions of the main gas stream. Mass transfer calculations involving the use of j_d factors for granular packings (*2*) permitted the evaluation of mass transfer coefficients k_g for alcohol, ketone, and hydrogen from which the partial-pressure differences of these components across the gas film were calculated. With the composition of these components defined at the interface, a new reaction rate was calculated and the mass transfer calculations repeated until the reaction rate no longer changed. The final rates taking place at the catalyst surface are presented in Table 6 along with their corresponding conversions x_A and other pertinent data.

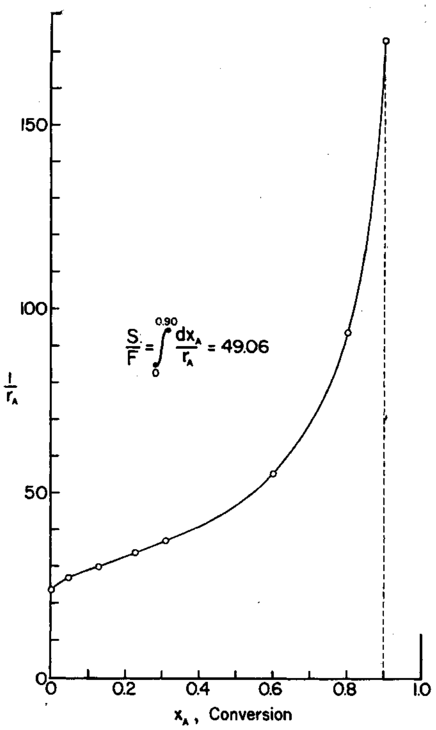

Fig. 12. Reciprocal rate-conversion relationship for illustrative example (rigorous approach involving reaction rate and mass transfer effects).

A plot of reciprocal rates and conversions is presented in Figure 12, which upon integration between the limits of conversion, $x_A = 0$ to $x_A = 0.90$, yields a value of

$$\frac{S}{F} = \int_0^{0.90} \frac{dx_A}{r_A} = 49.06$$

The height of the reactor required to effect a 90% conversion therefore becomes

$$\frac{S}{F} = \frac{(17.3)(h)}{0.182} = 49.06$$

$$h = 0.51 \text{ ft.}$$

The results produced by both methods are in fair agreement. The method involving the use of the rate equation and mass transfer contribution is rigorous and accurate but is quite demanding from a calculation point of view. On the other hand, the approach involving the use of the height of reactor unit proves somewhat less exact, but far less time consuming for a reasonable conclusion. This inexactness is inherently associated in the proper number of reactor units N_R as reflected in the differences involved in the logarithmic expression at high conversions.

NOTATION

C = constant in rate equation
D_m = diffusivity of transferable component, sq. ft./hr.
F = feed rate, lb.-moles of alcohol/hr.
G = mass velocity of gas stream, lb./(hr.)(sq. ft.)
HCU = height of catalytic unit, ft.
HRU = height of reactor unit, ft.
HTU = height of transfer unit, ft.
j_d = mass transfer factor
k_g = mass transfer coefficient, lb.-moles/(hr.)(sq. ft.)(atm.)
K = chemical equilibrium constant
K_A = adsorption equilibrium constant for sec-butyl alcohol
K_{AK} = constant in rate equation
m = slope of HRU vs. G
M_m = mean molecular weight of gas stream
N_R = number of reactor units
p^* = partial pressure of alcohol at thermodynamic equilibrium, atm.
p_1 = partial pressure of alcohol entering reactor, atm.
p_2 = partial pressure of alcohol leaving reactor, atm.
p_f = partial pressure of non-transferable component, atm.
p_{Ai} = partial pressure of alcohol at interface, atm.
p_{Ki} = partial pressure of ketone at interface, atm.
p_{Hi} = partial pressure of hydrogen at interface, atm.
r_A = reaction rate, lb.-moles of alcohol converted/(hr.)(sq. ft.)
S = surface area of catalyst, sq. ft.
T = absolute temperature, °K. or °R.
W = weight of catalyst, lb.
x_A = conversion, lb.-moles of alcohol converted/lb.-mole of alcohol in feed
z = height of catalyst bed, ft.
μ = viscosity of gas, lb./(hr.)(ft.)
ρ = density of gas, lb./cu. ft.

LITERATURE CITED

1. Balandin, A. A., and A. L. Liberman, *Compt. rend. acad. sci.* (*U.S.S.R.*), **28**, 794 (1940).
2. Hougen, O. A., and K. M. Watson, *"Chemical Process Principles,"* pp. 902–926 and 982–990, John Wiley and Sons, New York (1947).
3. Hurt, D. M., *Ind. Eng. Chem.*, **35**, 522 (1943).
4. Ipatieff, V. N., "Catalytic Reactions at High Pressures and Temperatures," pp. 16–18, The Macmillan Company, New York (1936).
5. Ivannikov, P. Y., M. G. Tatarskaya, and E. Y. Gavrilova, *Sintet. Kauchuk*, **9**, 16 (1936).
6. Kolb, H. J., and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **67**, 1084 (1945).
7. Mottern, H. O., U. S. Pat. 2,586,694 (February 19, 1952).
8. McNeil, Donald, and F. R. Charlton, British Pat. 636,743 (May 3, 1950).
9. Neish, A. C., *Can. J. Research*, **23B**, 49 (1945).
10. Padovani, Carlo, and Giuseppe Salvi, *Riv. combustibili*, **5**, 81 (1951).
11. Sussman, M. V., and Charles Potter, *Ind. Eng. Chem.*, **46**, 457 (1954).
12. Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916 (1939).

Presented at A.I.Ch.E. Seattle meeting