$S^2(\log \hat{N}_{Sh})$ = estimate of variance of log $\hat{N}_{Sh}$
t = time of contact, sec.
t_c = time of contact during free fall
t_o = time of fall for the shortest distance (from detachment at the nozzle to arrival at the coalesced layer), sec.
t_f = time of fall for any other fall distance, sec.
T = temperature, °C.
U = gross terminal velocity of droplet, cm./sec.
V = volume of droplet, cc.
X_d = weight percentage of continuous phase in dispersed phase
X_c = weight percentage of dispersed phase in continuous phase
λ_n = eigenvalues
μ_c, μ_d = viscosity of continuous and dispersed phase, respectively, poise
ρ_c, ρ_d = density of continuous and dispersed phase, g./cc.
σ = interfacial tension, dynes/cm.

LITERATURE CITED

1. Calderbank, P. H., and I. J. O. Korchinski, *Chem. Eng. Sci.*, **6**, 65 (1956).
2. Colburn, A. P., and D. B. Welsh, *Trans. Am. Inst. Chem. Engrs.*, **38**, 179 (1942).
3. Coulson. J. M., and S. J. Skinner, *Chem. Eng. Sci.*, **1**, 197 (1952).
4. Davies, J. T., *Trans. Inst. Chem. Engrs.*, **38**, 289 (1960).
5. Elzinga, E. R., and J. T. Banchero, *Chem. Eng. Progr. Symposium Ser. No. 29*, **55**, 149 (1959).
6. Garner, F. H., A. Foord, and M. Tayeban, *J. Appl. Chem.*, **9**, 315 (1959).
7. Garner, F. H., and P. J. Haycock, *Proc. Royal Soc.*, **A252**, 457 (1959).
8. ———, and M. Tayeban, *Anales de la Real Sociedad Espanola, de Fisica y Quimica*, Serie B-Quimica, Tomo LVI (B), 479 (1960).
9. ———, and A. H. P. Skelland, *Ind. Eng. Chem.*, **46**, 1255 (1954).
10. —————, *Chem. Eng. Sci.*, **4**, 149 (1955).
11. —————, *Trans. Inst. Chem. Engrs.*, (*London*), **29**, 315 (1951).
12. —————, *Ind. Eng. Chem.*, **48**, 51 (1956).
13. Griffith, R. M., *Chem. Eng. Sci.*, **12**, 198 (1960).
14. Hadamard, J., *Compt. Rend.*, **152**, 1735 (1911).
15. Hamielec, A. E., and A. I. Johnson, *Can. J. Chem. Eng.*, **4**, 41 (1962).
16. Handlos, A. E., and Thomas Baron, *A.I.Ch.E. Journal*, **3**, 127 (1957).
17. Heertjes, P. M., W. A. Holve, and H. Talsma, *Chem. Eng. Sci.*, **3**, 122 (1954).
18. Hu, Shengen, and R. C. Kintner, *A.I.Ch.E. Journal*, **1**, 42, (1955).
19. Johnson, A. I., and A. E. Hamielec, *ibid.*, **6**, 145 (1960).
20. —————, D. Wood, and A. Golding, *Can. J. Chem. Eng.*, 221 (1958).
21. Kronig, R., and J. C. Brink, *Appl. Sci. Res.*, **A-2**, 142 (1950).
22. Leeson, D., IBM-1620 Program Library, No. 6.0. 002, available prior to July (1962).
23. Licht, William, and J. B. Conway, *Ind. Eng. Chem.*, **42**, 1151 (1950).
24. ———, and W. F. Pansing, *ibid.*, **45**, 1855 (1953).
25. Linton, M., and K. L. Sutherland, *Chem. Eng. Sci.*, **12**, 214 (1960).
26. Newman, A. B., *Trans. Am. Inst. Chem. Engrs.*, **27**, 203 (1931).
27. Olander, D. R., *A.I.Ch.E. Journal*, **7**, 175 (1961).
28. Sherwood, T. K., J. E. Evans, and J. V. A. Longcor, *Ind. Eng. Chem.*, **31**, 1144 (1939).
29. Thorsen, G., and S. G. Terjesen, *Chem. Eng. Sci.*, **17**, 137 (1962).
30. Wilke, C. R., and Pen Chang, *A.I.Ch.E. Journal*, **1**, 264 (1955).

Manuscript received February 11, 1963; revision received November 18, 1963; paper accepted November 19, 1963. Paper presented at A.I.Ch.E. New Orleans meeting.

Selectivity in Hydrocarbon Oxidation

MAURICE SPIELMAN
Esso Research and Engineering Company, Madison, New Jersey

In many chemical reactions of commercial interest the desired product is an intermediate in a sequence of reactions. For example in liquid phase hydrocarbon oxidations it is often found that overoxidation results in a host of useless and undesirable tars and condensation products. These degrade feedstock to waste value and often cause fouling and plugging in process vessels. On the other hand low conversion, underoxidation, reduces the amount of undesirable materials made but increases the complexity and cost of operation by requiring large equipment to handle high recycle rates.

Operating conditions selected are often those near the highest conversion possible without getting into process difficulties. In many cases optimization with respect to balancing the cost of recycle against the value of high selectivity to product is not adequately explored. By means of kinetic studies optimum conversion levels can be shown to be well below those usually considered normal.

This article presents an analytical study of two reaction sequences postulated for liquid phase hydrocarbon oxidation. Major differences between reactor types are found. The relationship between conversion of feed and selectivity to intermediate product is strongly influenced by the type of reactor used. At any conversion level selectivity and yield of intermediate are higher in a batch or plug flow reactor than in a continuous flow stirred reactor. The undesirable result of conversion beyond the point of maximum yield is also shown. Choice of an optimum conversion level is thus simplified.

Application of the calculated results to experimental data on ordinary and boric acid modified air oxidation of cyclohexane are given.

The results of this study are not limited to oxidation. They can provide a helpful tool for planning and interpreting experimental studies, for visualizing fundamental process limitations at an early stage of development, and for making maximum use of existing data.

KINETIC MODELS

The two reaction schemes studied are shown in Figure 1. In each sequence feedstock is oxidized to desired intermediate products which are then further oxidized to degradation products.

Case 1 represents a three-component consecutive reaction sequence in which a is the feedstock, b is the desired intermediate, and c is the overoxidized final product. This relatively simple sequence is no newcomer to the literature and will not be discussed at length. However it is unexpectedly powerful when applied to actual data on oxidation. It also leads directly into the next case.

Case 2 illustrates a five-component sequence of simultaneous and consecutive reactions. Starting with feedstock x desired intermediates y and z are formed and from them final products u and w. Note that there are two possible routes to intermediate z.

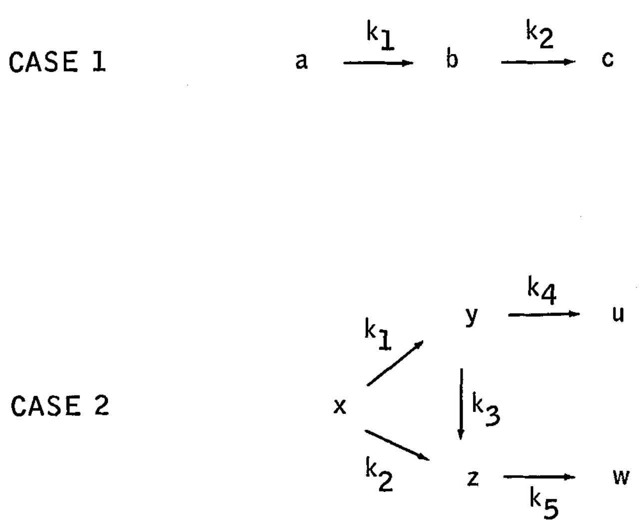

Fig. 1. Reaction schemes.

The material balance and kinetic equations describing each system of reactions are shown in Tables 1 to 4 for a continuous flow stirred reactor and for a batch reactor, mathematically equivalent to an ideal plug flow reactor. The tables also present analytical solutions for pure feedstock. They contain expressions for the concentration of each component for any degree of reaction and expressions for conversion of feed and selectivity to desired products at any point in the reaction.*

Two different expressions for selectivity are shown for the five-component cases. The first is for selectivity to intermediates y and z only. The second includes one final product, in agreement with a practical scheme for cyclohexane oxidation which will be discussed.

Assumptions, Mathematical Limitations

The basic assumptions required in setting up the material balances, solving the equations, and applying the results to isothermal liquid phase oxidation reactions are as follows:

1. The reaction system is irreversible. This should be valid for oxidations wherein highly reacted materials would not be expected to return to a state of lower oxidation.

2. The reactions are first order with respect to hydrocarbon. This appears justified by available data in the literature on various oxidations (5).

3. The number of moles of oxidate made is equal to the number of moles of feed reacted. Thus the reactor contains a fixed number of moles at all times, regardless of the degree of conversion. This implies either that no cleavage or condensation of oxidized material takes place, or else that the number of moles appearing owing to cleavage is equal to the number of moles disappearing owing to condensation. In this way the formation of water and carbon dioxide may be neglected.

4. For a liquid filled reactor to contain the same number of moles of hydrocarbon at all times in a fixed volume, regardless of product distribution, it is required that the ratio of density to molecular weight be the same for feed and products (same volume per mole). This is a minor assumption here.

5. In considering reactor volume the space occupied by any inert diluent or solid is excluded, as is the volume occupied by the oxidizing gas.

6. A further mathematical limitation applies to the batch reactor solutions. No rate constants which allow a denominator to be zero in the expressions for concentration of intermediate or final products are permitted. However physically feasible solutions may be derived from most of the resulting indeterminate forms by means of L'Hôpital's rule. No such restrictions apply to the continuous flow stirred reactor solutions.

7. Concentration of dissolved oxygen influences each of the reactions equally and is uniform throughout the reactor. It may thus be combined with true reaction rate constants yielding effective rate constants. Such constants may then be strictly valid for only one value of dissolved oxygen concentration. However if oxidation is carried out with a constant oxygen concentration in the off-gas (tail gas), as is usual for continuous operation, the dissolved oxygen concentration should also be constant.

Handling the oxygen concentration this way avoids making any assumption as to reaction order with respect to oxygen. Runs with different oxygen content in the tail gas might not be comparable. But in commercial operations safety considerations dictate a low oxygen concentration in the tail gas. Major variations are not permitted.

Influence of Reactor Type

Several important differences between batch and continuous stirred reactor systems are apparent from the

TABLE 1. BATCH (OR PLUG FLOW) REACTOR,
THREE-COMPONENT SYSTEM
Consecutive Reactions
First-Order, Irreversible

Material balances
$a + b + c = 1$
$da/dt = -k_1a$
$db/dt = k_1a - k_2b$
$dc/dt = k_2b$

Solution with $a_o = 1$; $b_o, c_o = 0$
$a = e^{-k_1t}$
$b = (a - a^{p+1})/p$
where $p = (k_2 - k_1)/k_1, p \neq 0$
$c = 1 + (a)^{p+1}/p - a(p + 1)/p$

Conversion $= 1 - a$

Selectivity $= b/(b + c) = (a)(1 - a^p)/(1 - a)(p)$

Note:
When $p = 0$, the following are valid:
$b = -a \ln a$
$c = 1 + a \ln a - a$

Selectivity $= b/(b + c) = [a \ln (1/a)]/(1 - a)$

---

* For the three-component system conversion is defined as 1-a. Selectivity to intermediate is defined as the fraction of desired product in the feed-free oxidate ($= b/(b + c)$), and yield as b.

TABLE 2. CONTINUOUS STIRRED REACTOR,
THREE-COMPONENT SYSTEM
Consecutive Reactions
First-Order, Irreversible

Material balances
$a + b + c = 1$
At steady state
$da/dt = 0 = Ia_o - k_1a - Ia$
$db/dt = 0 = Ib_o + k_1a - k_2b - Ib$
$dc/dt = 0 = Ic_o + k_2b - Ic$

Solution with $a_o = 1$; $b_o, c_o = 0$; $I \neq 0$
$a = I/(k_1 + I) = 1/(1 + \theta k_1)$
$b = k_1I/(k_1 + I)(k_2 + I)$
$\qquad = a(1 - a)/[a + (1 - a)(p + 1)]$
$c = k_1k_2/(k_1 + I)(k_2 + I)$
$\qquad = (1 - a)^2(p + 1)/[a + (1 - a)(p + 1)]$
$I = k_1a/(1 - a)$

Conversion $= 1 - a$

Selectivity $= b/(b + c) = 1 - (p + 1)(b/a)$
$\qquad = a/(1 + p - ap) = k_1a/(1 - a)(k_2 + I) = I/(k_2 + I)$

TABLE 3. BATCH REACTOR, FIVE-COMPONENT SYSTEM
Simultaneous and Consecutive Reactions
First-Order, Irreversible

Material balances
$x + y + z + u + w = 1$
$dx/dt = -(k_1 + k_2)x$
$dy/dt = k_1x - (k_3 + k_4)y$
$dz/dt = k_2x + k_3y - k_5z$
$du/dt = k_4y$
$dw/dt = k_5z$
Solution with $x_o = 1$; $y_o, z_o, u_o, w_o = 0$

$$x = e^{-\beta t}$$

$$y = \frac{k_1}{(\beta - \alpha)}[x^{\alpha/\beta} - x]$$

$$z = \left[\frac{\gamma + k_2(\alpha - k_5)}{(\beta - k_5)(\alpha - k_5)}\right]x^{k_5/\beta} + \left[\frac{\gamma - k_2(\beta - \alpha)}{(\beta - \alpha)(\beta - k_5)}\right]x - \left[\frac{\gamma}{(\beta - \alpha)(\alpha - k_5)}\right]x^{\alpha/\beta}$$

$$u = -\left[\frac{k_1k_4}{\alpha(\beta - \alpha)}\right]x^{\alpha/\beta} + \left[\frac{k_1k_4}{\beta(\beta - \alpha)}\right]x + \frac{k_1k_4}{\alpha\beta}$$

$$w = -\left[\frac{\gamma + k_2(\alpha - k_5)}{(\beta - k_5)(\alpha - k_5)}\right]x^{k_5/\beta} - \frac{k_5}{\beta}\left[\frac{\gamma - k_2(\beta - \alpha)}{(\beta - \alpha)(\beta - k_5)}\right]x + \frac{k_5}{\alpha}\left[\frac{\gamma}{(\beta - \alpha)(\alpha - k_5)}\right]x^{\alpha/\beta} + \frac{k_2}{\beta} + \frac{\gamma}{\alpha\beta}$$

The solution is not valid where division by zero is indicated. Thus none of the following conditions are admissible:*

$\alpha = \beta \qquad \alpha = k_5 \qquad \alpha = 0 \qquad \beta = k_5 \qquad \beta = 0$

Conversion $= 1 - x$

Selectivity to intermediates $= (y + z)/(y + z + u + w)$
$\qquad = (y + z)/(1 - x)$

$$= \frac{1}{(1 - x)}\left[\left[\frac{k_1(k_4 - k_5)}{(\beta - \alpha)(\alpha - k_5)}\right]x^{\alpha/\beta} - \left[\frac{\beta(\beta - \alpha) + k_1(k_4 - k_5)}{(\beta - \alpha)(\beta - k_5)}\right]x + \left[\frac{\gamma + k_2(\alpha - k_5)}{(\beta - k_5)(\alpha - k_5)}\right]x^{k_5/\beta}\right]$$

Selectivity† $= (y + z + u)/(y + z + u + w)$
$\qquad = 1 - (w)/(1 - x)$

$$= 1 - \frac{1}{(1 - x)}\left[\left[\frac{k_2\alpha + \gamma}{\alpha\beta}\right] + \frac{k_5}{\alpha}\left[\frac{\gamma}{(\beta - \alpha)(\alpha - k_5)}\right]x^{\alpha/\beta} - \frac{k_5}{\beta}\left[\frac{\gamma - k_2(\beta - \alpha)}{(\beta - \alpha)(\beta - k_5)}\right]x - \left[\frac{\gamma + k_2(\alpha - k_5)}{(\beta - k_5)(\alpha - k_5)}\right]x^{k_5/\beta}\right]$$

* Solutions valid for the first four of these conditions can be determined by L'Hôpital's rule. The condition $\beta = 0$ is the only truly degenerate case.

† This definition of selectivity includes one final product u in agreement with the product scheme for cyclohexane discussed in the text.

tables, the most significant being the presence of the flow rate term I in the equations for the continuous stirred reactor. This term corresponds to a molal space velocity. In effect it acts as an additional rate constant. It characterizes the appearance and disappearance of all components and may be considered as an external rate constant due to flow. If it is greater than all of the (internal) chemical rate constants, then it is clearly the dominant process. Similarly if it is smaller than the chemical rate constants, the effect of flow rate can only be minor.

The effect of change in the flow rate will be most pronounced when the flow rate is of the same order of magnitude as the rate constants.

Another difference between batch and continuous stirred reactors is seen in the expressions for the concentrations of desired and undesired products. These yield different distributions of the reactor products for any degree of feed conversion and hence different values of selectivity. In turn this leads to the result that for the reaction schemes shown selectivity to intermediate is higher in a batch reactor or plug flow reactor (PFR) than in a continuous stirred reactor (CSR) at any conversion level.*

Expressions for the final products approach limiting, positive values at high conversion, while those for the intermediates approach zero. Thus only final products will be present when the feedstock is entirely consumed (at infinite time).

One more important difference follows from the fact that the ideal CSR is completely backmixed, while the PFR has no backmixing. Thus the two solutions serve to give upper and lower limits as to the effect of backmixing on selectivity. Various definitions of degree of backmixing exist which enable interpolation between these two solutions (*9*, *10*).

The effects of staging CSR are also shown, since a PFR may be considered to be the equivalent of an infinite series of CSR. The two solutions thus serve to give upper and lower limits to the effect on selectivity of staging a series of continuous stirred reactors. References 8 and 9 show how interpolation may be made. These effects as well as the rate of feedstock conversion are discussed in detail in (*11*).

The main result here is that insofar as chemical rate limitations apply, no degree of agitation will give results poorer than the CSR or better than the PFR. This does not take into account any mass transfer limitations. However a uniform concentration of dissolved oxygen has already been postulated.

Modifications for a Cyclohexane System

The oxidation of cyclohexane to cyclohexanone and cyclohexanol was the process of immediate interest in this

---

* Selectivities are obviously equal at zero and at 100% conversion.

study. Some practical aspects of this process have influenced the final form in which the Case 2 results were applied to experimental data.

1. Two different expressions for selectivity are given in Tables 3 and 4. The first defines selectivity as $(y + z)/(y + z + u + w)$, a rigorous definition for selectivity to intermediate. The second defines selectivity as $(y + z + u)/(y + z + u + w)$. Here the desired oxidate product is $(y + z + u)$, a mixture of two intermediates and one final product. This definition was used in the subsequent correlation of experimental data, since it conforms to a possible product sequence in cyclohexane oxidation.* In this sequence (Figure 1) x = cyclohexane, y = cyclohexanol, z = cyclohexanone, u = cyclohexyl esters, w = organic acids.

The end product u is not an unwanted degradation product since it is practical to recover cyclohexanol from cyclohexyl esters present in the oxidate by subsequent hydrolysis and saponification of the reactor effluent.

2. When boric acid is used as a reaction modifier in the oxidation, borate esters are formed:

$$y + H_3BO_3 \rightarrow u$$

Thus, when solid boric acid is present in the reactor, the expressions for du in Tables 3 and 4 are valid for the borate esters.

In the absence of boric acid, and to some extent even in the presence of boric acid, esters are produced by reaction of alcohol with organic acid as

$$y + w \rightarrow u$$

or, for a diacid, diesters result:

$$2y + w \rightarrow u$$

In this case the material balance expressions for du and du/dt in Tables 3 and 4 are oversimplified. This point will be left open in the interest of reaching a solution. It is usually ignored.

TABLE 4. CONTINUOUS STIRRED REACTOR,
FIVE-COMPONENT SYSTEM
Simultaneous and Consecutive Reactions
First-Order, Irreversible

Material balances

$x + y + z + u + w = 1$

At steady state

$dx/dt = 0 = Ix_o - (k_1 + k_2)x - Ix$

$dy/dt = 0 = Iy_o + k_1x - (k_3 + k_4)y - Iy$

$dz/dt = 0 = Iz_o + k_2x + k_3y - k_5z - Iz$

$du/dt = 0 = Iu_o + k_4y - Iu$

$dw/dt = 0 = Iw_o + k_5z - Iw$

Solution with $x_o = 1$; $y_o, z_o, u_o, w_o = 0$; $I \neq 0$

$$x = \frac{I}{\beta + I}$$

$$y = \frac{k_1 I}{(\alpha + I)(\beta + I)} = \frac{k_1}{(\alpha + I)} x$$

$$z = \frac{I[(\alpha + I)k_2 + \gamma]}{(\alpha + I)(\beta + I)(I + k_5)} = \left[\frac{(\alpha + I)k_2 + \gamma}{(\alpha + I)(I + k_5)}\right] x$$

$$u = \frac{\delta}{(\alpha + I)(\beta + I)} = \frac{\delta}{I(\alpha + I)} x = \frac{k_4}{I} y$$

$$w = \frac{k_5[(\alpha + I)k_2 + \gamma]}{(\alpha + I)(\beta + I)(I + k_5)}$$

$$= \frac{k_5}{I}\left[\frac{(\alpha + I)k_2 + \gamma}{(\alpha + I)(I + k_5)}\right] x = \frac{k_5}{I} z$$

$I = \beta x/(1 - x)$

Conversion $= 1 - x$

Selectivity to intermediates $= (y + z)/(y + z + u + w)$

$$= (y + z)/(1 - x)$$

$$= \frac{I}{I + k_5}\left[1 - \frac{k_1(k_4 - k_5)}{\beta(\alpha + I)}\right]$$

Selectivity* $= (y + z + u)/(y + z + u + w)$

$$= 1 - (w)/(1 - x) = 1 - (k_5 z/\beta x)$$

$$= 1 - \frac{k_5}{\beta}\left[\frac{(\alpha + I)k_2 + \gamma}{(\alpha + I)(I + k_5)}\right]$$

* This definition of selectivity includes one final product u in agreement with the product scheme for cyclohexane discussed in the text.

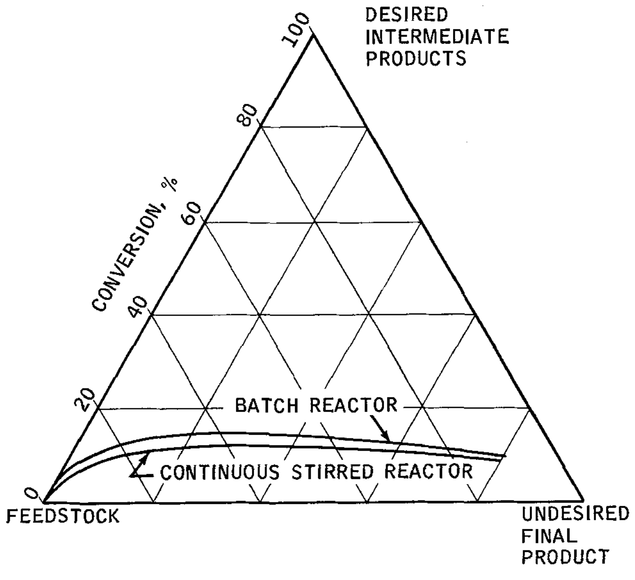

Fig. 2. Reaction path for cyclohexane oxidation.

APPLICATION TO DESIGN

Previous sections have indicated the effects of reactor type, backmixing, staging, and feed stream purity on the conversion selectivity relationship. Some other factors important in design may now be briefly mentioned. These are covered in detail by Levenspiel (*11*).

High or Low Conversion?

The conversion selectivity relationships are directly translatable to a form which shows the reaction path and the actual yield of products. For example the results given in Figure 2 are based on the same calculations as the five-component system shown in Figure 4.*

The triangular plot shows that the actual yield of desired products quickly reaches a plateau. For the example given maximum yield in a CSR is 11%, reached at 48% conversion. Yet the yield is 9% at 19% conversion. Relative to low conversion operation, high conversion only results in the degradation of feed and intermediate to undesired final product.

---

* A cyclohexyl hydroperoxide intermediate might also be postulated here (*1, 7*). However for reasons of safety the experimental oxidations studied were catalyzed by cobalt or manganese salts, thus maintaining hydroperoxide concentration at negligibly low levels. Presence of this intermediate could be significant in noncatalyzed oxidations, and it is known that different product distributions can result.

* References *2* and *13* illustrate the extreme usefulness of triangular coordinates and discuss various other reaction paths.

Thus from the standpoint of feedstock cost and product value low conversion operation, while yield is still rising, is desirable, regardless of reactor type.

Maximum Yield

Analytical expressions for maximum yield in the five-component systems are cumbersome and are not particularly useful for a flat yield curve of the type shown in Figure 2.

Expressions for the maximum yield of intermediate and the corresponding effluent feedstock concentration in the three-component system are given in Table 5 for both CSR and PFR. These will be most useful when yield has a well-defined maximum. It has already been shown that much lower conversions are practical when the yield curve is flat, such as would correspond to large k_2/k_1. For the latter case limiting the conversion level to that corresponding to 75% of maximum yield is offered as an empirical rule-of-thumb.

What Residence Time?

For first-order disappearance of feedstock conversion depends on residence time as follows:

$$1 - x = 1 - e^{-K\theta} \qquad \text{(PFR)}$$

$$1 - x = K\theta/(1 + K\theta) \qquad \text{(CSR)}$$

The dimensionless product $K\theta$ may be considered to be a reduced time. It is directly proportional to residence or batch time and hence proportional to reactor volume for a given throughput. For any given residence time or reactor volume PFR conversion is higher than CSR for this first-order case.

TABLE 5. THREE-COMPONENT SYSTEM
Maximum yield

Batch reactor
a for maximum $b = [1/(p + 1)]^{1/p}$
where $p \neq 0, p = (k_2 - k_1)/k_1$
$= 1/e$
where $p = 0$
b max $= a/(p + 1)$

Continuous stirred reactor
a for maximum $b = [(p + 1) - \sqrt{(p + 1)}]/p$
where $a \neq (p + 1)/p$ and $p \neq 0$
$= 1/2$ where $p = 0$
b max $= a(1 - a)/[a + (1 - a)(p + 1)]$

Still another basis for comparison is the yield of desired product per unit time or volume. For the three- and five-component cyclohexane oxidation cases to be described the PFR shows a 10% advantage over the CSR.

For the reaction schemes considered all of these comparisons show that from the standpoint of minimum required reactor size the use of a plug flow reactor to prepare a degradable intermediate product is preferable to the use of a continuous stirred reactor.

What Temperature?

Denbigh (*6*) shows how knowledge of the differences in temperature dependence of the rate constants may be used to select a temperature or temperature sequence which can increase yield over isothermal operation. When the temperature effect is not known, or if the actual reaction sequence is uncertain, he recommends hit or miss experimentation on the effect of temperature.

Effect of Catalysts

Carberry (*3*) analyzes catalyst performance in heterogeneous catalysis for the isothermal Case 1. He is not interested in reactor type but rather considers interparticle and intraparticle transport phenomena. His expressions for yield of intermediate reduce to the expressions for b in Table 1 when all diffusional effects are assumed absent. This corresponds to maximum yield. The author states that for favorable ratios of k_1/k_2 ($>> 1$) bulk transport control of consecutive (surface) reactions inevitably leads to severe yield losses.

APPLICATION TO EXPERIMENTAL DATA

Cyclohexane Oxidation, Three-Component Case

Batch laboratory and continuous stirred reactor pilot unit data for the boric acid modified air oxidation of cyclohexane are shown in Figure 3.

Here selectivity is defined as the mole fraction of cyclohexanol plus cyclohexanone in the oxidate, and conversion is defined as the mole fraction of oxidate in caustic-washed reactor effluent. (Saponification regenerates cyclohexanol from the cyclohexyl esters formed.) In this process both cyclohexanol and cyclohexanone are desired intermediate products. The practical simplification of lumping them together enables the three-component system to be used.

The open circle at the top of the figure represents the best of the batch data, namely 85% selectivity at 15% conversion. The full circles represent pilot unit data with a single continuous stirred reactor.

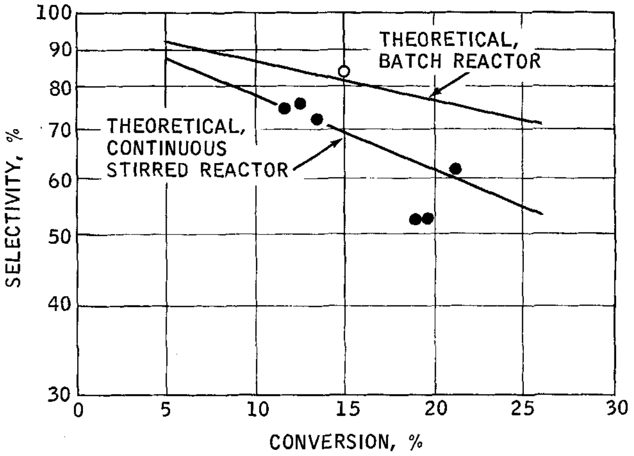

Fig. 3. Boric acid modified oxidation of cyclohexane. ○ batch lab data, ● CSR pilot unit data. Theoretical curves are based on a three-component system with $k_2/k_1 = 2.5$.

The two lines in the figure show the selectivity conversion relationships predicted for a three-component system with $p = 1.5$.* Agreement with the data is satisfactory over the range studied. Thus if one accepts the three-component mechanism, it follows that the difference between batch and pilot unit results is mainly due to differences in reactor type.

Cyclohexane Oxidation, Five-Component Case

Both batch and continuous stirred reactor data were available for comparison in the three-component case described above. Batch data for the unmodified air oxidation of cyclohexane were not available, but three independent sets of CSR data were. These have been compared, with each considered as a five-component system. Two sets of data were taken from the literature (*4*, *12*), and a third set was obtained by the Humble Oil and Refining Company. All were taken under approximately similar conditions of operation.

---

* This value was selected as follows. Several values of $p[=(k_2/k_1) - 1]$ were assumed, and the theoretical selectivity conversion relationships calculated and plotted for both batch and CSR operation. The experimental data best fit the calculated curves when $p = 1.5$.

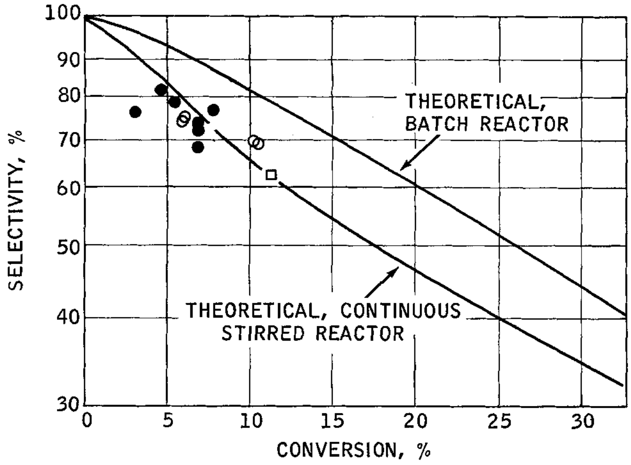

Fig. 4. Cyclohexane oxidation. ● CSR pilot unit data, ○ reference *12*, run series *V*, □ reference *4*. Theoretical curves are based on the five-component system discussed in the text.

The five constants needed for calculation were estimated from the detailed product analysis of reference 4.* The constants were then used to predict conversion selectivity relationships for batch and CSR operation. These are shown as the upper and lower curves, respectively, in Figure 4.

The three sets of data are also shown in the figure. It can be seen that the points scatter about the predicted CSR curve and that only a rather narrow range of conversion is covered. However the agreement is satisfactory when one considers that the data came from three different sources and that differences undoubtedly exist in such variables as reactor geometry, feedstock purity, and mixing energy input.

CONCLUSIONS

Several conclusions relevant to planning and correlating a pilot program or selecting a set of design conditions have become clear in this study. The frame of reference is that of hydrocarbon oxidation, but the conclusions appear to be of more general validity. It has been seen that even an approximate knowledge of reaction mechanism or of reaction order permits useful generalizations to be made and provides a rational basis for extrapolation of data. Thus the results have practical usefulness even when they are not unqualifiedly rigorous.

If the desired products are degradable intermediates in a sequence of first-order irreversible reactions, it was seen that:

1. Selectivity in batch or plug flow reactor is higher than in a continuous stirred reactor for any conversion level.
2. High conversion operation may be useless. An optimum practical yield of intermediate is obtained at relatively low conversion.
3. The upper and lower limits of the relationships between conversion, selectivity, and yield for any reactor type may be quantitatively established from a small number of laboratory runs to define the reaction rate constants. In this way excessively optimistic or pessimistic extrapolations can be avoided.

If the desired products are terminal ones in a sequence of irreversible reactions rather than intermediates, the first two of these conclusions are reversed. This shows how important it is to have an idea of reaction mechanism.

Whenever possible the early phases of a laboratory or pilot plant study should include data taken over a wide range of operating conditions, even those far removed from what might be considered reasonable. This could involve operating a continuous unit at unrealistically low and high conversions or carrying a batch reaction on much longer than the normal reaction time.

Such data should permit definition of the reaction mechanism, of the optimum reactor type, and of the best conversion level. The mechanism derived from such a wide range of data will be more reliable and useful than one derived from a narrow cluster of data. It is believed that this approach can reduce the total amount of experimental effort expended on a study and still permit meaningful data to be taken at commercially practical operating conditions.

NOTATION

a = mole fraction of feedstock, Case 1
b = mole fraction of intermediate, Case 1
c = mole fraction of final product, Case 1
e = base of natural logarithms
I = flow rate, moles/hr./mole of reactor contents, $\text{hr.}^{-1} = 1/\theta$
K = reaction rate constant describing disappearance of feed, hr.^{-1}
k = reaction rate constant, hr.^{-1}
$K\theta$ = reduced time factor
p = $(k_2 - k_1)/k_1$
t = time, hr.
u = mole fraction of final product, Case 2
w = mole fraction of final product, Case 2
x = mole fraction of feedstock, Case 2
y = mole fraction of intermediate, Case 2
z = mole fraction of intermediate, Case 2

Greek Letters

α = $(k_3 + k_4)$, hr.^{-1}
β = $(k_1 + k_2)$, hr.^{-1}
γ = (k_1k_3), hr.^{-2}
δ = (k_1k_4), hr.^{-2}
θ = batch reaction time or residence time, hr.

Subscripts

o = value at zero time
1,2,3,4,5 = various reaction paths

LITERATURE CITED

1. Berezin, I. V., N. F. Kazanskaya, and V. F. Privalov, *Proc. Acad. Sci. USSR*, Phys. Chem. Sect., Engl. Transl., **126**, 809 (1959).
2. Bilous, Olegh, and E. L. Piret, *A.I.Ch.E. Journal*, **1**, 480 (1955).
3. Carberry, J. J., *Chem. Eng. Sci.*, **17**, 675 (1962).
4. Ciborowski, S., *Przemysl Chemiczny*, **40**, 32 (1961).
5. De Maria, F., J. E. Longfield, and G. Butler, *Ind. Eng. Chem.*, **53**, 259 (1961).
6. Denbigh, K. G., *Chem. Eng. Sci.*, **8**, 125 (1958).
7. Denisov, E. T., and N. M. Emanuel, *Russ. Chem. Reviews*, **29**, 645 (1960).
8. Eldridge, J. W., and E. L. Piret, *Chem. Eng. Progr.*, **46**, 290 (1950).
9. Lessels, G. A., *Chem. Eng.*, **64**, No. 8, 251 (1957).
10. Levenspiel, O., and K. B. Bischoff, *Ind. Eng. Chem.*, **51**, 1431 (1959).
11. Levenspiel, O., "Chemical Reaction Engineering," Wiley, New York (1962).
12. Steerman, J. W. M., S. Kaarsemaker, and P. J. Hoftyzer, *Chem. Eng. Sci.*, **14**, 139 (1961).
13. Trambouze, P. J., and E. L. Piret, *A.I.Ch.E. Journal*, **5**, 384 (1959).

Manuscript received December 14, 1962; revision received January 7, 1964; paper accepted January 8, 1964.

---

* Here too the values were derived on a best fit basis. The constants are $k_1 = 0.150$, $k_2 = 0.038$, $k_3 = 2.88$, $k_4 = 0.375$, $k_5 = 1.71$.