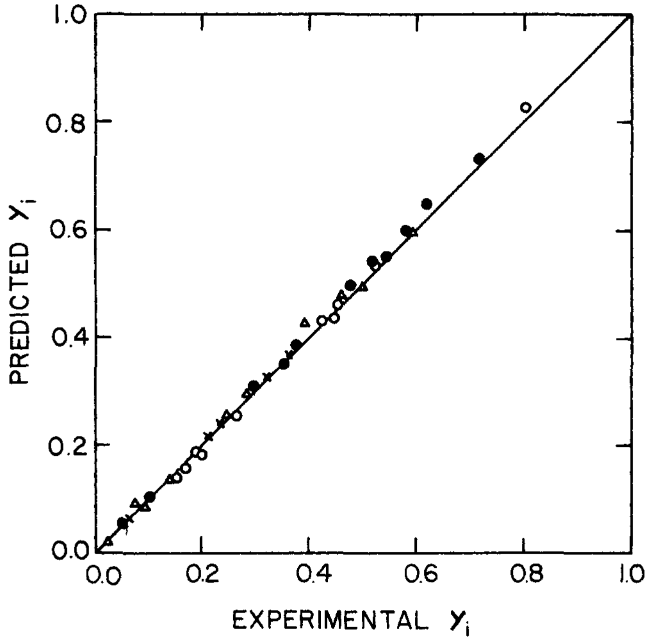

Figure 2. Comparison of calculated and experimental vapor phase compositions for the quaternary system methyl acetate (○)—chloroform (△)—methanol (●)—benzene (×) at 101.325 kN/m². Experimental data were reported by Hudson and Van Winkle (1969).

The parameter values reported in Table 1 were used to generate VLE values for one quinary, three quaternary, 54 ternary and 207 binary systems (including the binaries used for establishing the parameters) for a total of 677 isothermal/isobaric sets of data in the temperature range of 298.15 to 454.15°K. For simplicity, the vapor phase was assumed to be ideal in all the calculations. The calculated values are in reasonably good agreement with the experimental values reported in the literature with an average absolute deviation of 0.013 mol fraction in the vapor phase concentration, indicating that the proposed equation for representing the temperature dependence of these parameters is acceptable. To illustrate the agreement, the calculated vapor phase compositions for the quaternary system methyl acetate-chloroform-methanol-benzene at 101.325 kN/m² are compared with the experimental values reported by Hudson and Van Winkle (1969) in Figure 2. In addition, the calculated γ values for the xylene-di-isobutyl ketone system at 423.15°K are very close to unity, providing another evidence which supports the validity of the proposed equation.

ACKNOWLEDGMENT

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NOTATION

a_{kl} = temperature-dependent group interaction parameter, Eq. 4
b_{kl} = temperature-independent group interaction parameter, Eq. 7
m_{kl} = temperature-independent group interaction parameter, Eq. 6
n_{kl} = temperature-independent group interaction parameter, Eq. 6
N = number of components
s = number of data points
x = liquid phase mole fraction
y = vapor phase mole fraction

Greek Letters

γ_i = activity coefficient of component i
Γ_k = activity coefficient of group k
ν_i = number of non-hydrogen atoms in molecule i
ν_k = number of non-hydrogen atoms in group k
ν_{ki} = total number of non-hydrogen atoms in all groups of kind k in a molecule of component i
χ = liquid phase group fraction

Subscripts

i, j = component i and j
k, l, m = group k, l, and m
ki = group k in molecule i

Superscripts

G = contribution due to the interaction of the functional groups
(i) = standard state (pure component i)
s = size contribution

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Catalyst Decay by a Leaching Mechanism

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A number of heterogeneous catalysts decay through the loss of a particular specie that is leached or vaporized from the catalyst. Kavasmaneck and Sherman (1980) reported on the advantage of using a recycle reactor to accelerate the decay of catalyst activity for hydration of olefins. Millidge (1969) had previously shown that the activity of a supported phosphoric acid catalyst is dependent on the retention of acid on the support. A theoretical frame work for correlating the catalyst

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decay with loss of an active specie for tubular reactors and recycle reactors is presented.

Consider the reaction

$$B \rightarrow D \quad r_B = k_o\, \alpha^a C_B^n \tag{1}$$

that is catalyzed by a catalyst which decays due to leaching or vaporization of a catalytic specie. Designate this catalyst specie as component A. Furthermore assume that the rate of leaching or vaporization of this specie can be represented by

$$r_A = k_A(C_{Ae} - C_A) \tag{2}$$

where

C_A = concentration of A in the fluid phase that is leaching from the catalyst

C_{Ae} = equilibrium concentration of A in the fluid phase with the solid A impregnated on the catalyst surface, i.e., $C_{Ae} = HC_{AS}$. Where H = constant.

k_A = a rate constant that is a function of the velocity of the fluid flowing through the catalyst. If the loss is due to vaporization into a gas stream k_A is related to k_{GA}, a mass transfer coefficient (Holland and Anthony, 1979).

r_A = moles of A lost from the catalyst surface per unit time per unit volume of catalyst

The material balance on A in the fluid phase for a plug flow reactor at steady state yields

$$\frac{d\, n_A}{S\, d\, Z} = k_{AP}(C_{Ae} - C_A) \tag{3}$$

where

$$n_A = \frac{\text{moles of A flowing in the fluid phase}}{\text{unit time}}$$

k_{AP}= decay constant for plug flow reactor.

Equation 3 is readily integrated to yield

$$C_A = C_{Ae}\left[1 - \exp\left(- \frac{k_{AP}\theta}{L} Z\right)\right] \tag{4}$$

where

$C_A = 0$ at $Z = 0$

L = length of the reactor

$n_A = C_A v_T$

v_T = volumetric flow rate of the fluid, $\frac{\text{vol}}{\text{time}}$

$\theta = \frac{V}{v_T}$ the residence time

For the concentration of A on the catalyst at a particular point Z in the reactor a material balance on A yields,

$$-\frac{dC_{AS}}{dt} = k_{AP}(C_{Ae} - C_A) \tag{5}$$

By substituting for C_A from Eq. 4 and integrating for a particular Z,

$$\alpha_p = 1 - \frac{k_{AP}C_{Ae}}{C_{AS}^{\circ}}\left[\exp\left(- \frac{k_{AP}\theta}{L} Z\right)\right]t \tag{6}$$

where

C_{AS}° = concentration of A on the catalyst at $t = 0$

α_p = C_{AS}/C_{AS}° for the plug flow reactor

The average acid concentration or activity of the catalyst as a function of time on stream is obtained as follows.

$$\bar{\alpha}_p = \frac{1}{L}\int_0^L \alpha_p\, dZ \tag{7}$$

By eliminating α_p from Eq. 7 by use of Eq. 6 and integrating, the average activity is given by the following equations

$$\bar{\alpha}_p = 1 - \frac{C_{Ae}}{C_{AS}^{\circ}\theta}[1 - \exp(-k_{AP}\theta)]t \tag{8}$$

$$\bar{\alpha}_p = 1 - \frac{(C_A)_{\text{exit}}}{C_{AS}^{\circ}\theta}\, t \tag{9}$$

In order to determine the effect of leaching on the conversion of B as given by Eq. 1, α_p from Eq. 6 is utilized. For the case of a first order reaction and for first order deactivation, one obtains

$$-\frac{d\, C_B}{S\, d\, Z} = k_o\, \alpha_p\, C_B$$

then

$$-\int_{C_B^{\circ}}^{C_B} \frac{dC_B}{C_B} = S\int_0^L k_o\left[1 - \frac{k_{AP}C_{Ae}}{C_{AS}^{\circ}}\left(\exp\left(- \frac{k_{AP}\theta}{L} Z\right)\right)t\right]dZ \tag{10}$$

By assuming that the reactor is being operated isothermally, Eq. 10 is integrated and rearranged to yield

$$X_p = 1 - \exp(k_o\bar{\alpha}_p\theta) \tag{11}$$

where $\bar{\alpha}_p$ is given by Eq. 8.

X_p = conversion from the plug flow reactor, $X_p = 1 - C_B/C_B^{\circ}$.

The equations for the recycle reactor are presented as follows. At steady state (Holland and Anthony 1979)

$$C_A = \frac{k_{AR}C_{Ae}}{1 + k_{AR}\theta} \tag{12}$$

where

k_{AR} = rate constant for loss of catalyst specie A from catalyst surface for a recycle reactor

As indicated by Kavasmaneck and Sherman (1980) the velocity through the catalyst for the recycle reactor is independent of the volumetric flow rate, v_T, entering and leaving the reactor, whereas for the plug flow reactor the velocity through the catalyst is fixed for a given holding time. Thus the rate of decay for the recycle reactor is independent of the holding time. However, for the assumption of a perfectly mixed reactor the recycle ratio must be greater than 20/1 and preferably greater than 30/1 (Holland and Anthony, 1979).

The concentration of A on the catalyst is given by

$$-\frac{dC_{AS}}{dt} = k_{AR}(C_{Ae} - C_A) \tag{13}$$

Elimination of C_A from Eq. 13 by use of Eq. 12, and integrating from $C_{AS} = C_{AS}^{\circ}$, $t = 0$ to $C_{AS} = C_{AS}$ and $t = t$ yields

$$\alpha_R = 1 - \frac{k_{AR}C_{Ae}}{C_{AS}^{\circ}}\left(\frac{1}{1 + k_{AR}\theta}\right)t \tag{14}$$

To calculate the conversion for B the following equation results for the first order reaction (Holland and Anthony, 1979).

$$\frac{C_B}{C_B^{\circ}} = \frac{1}{1 + k_o\alpha_R\theta} \tag{15}$$

and

$$X = 1 - C_B/C_B^{\circ}$$

where α_R is given by Eq. 14 for a specified time on stream.

Due to the differences in the mixing patterns in the two reactors, a catalyst with greater activity is required for the recycle reactor to obtain the same conversion at the same holding time and feed concentrations as the plug flow reactor.

Kavasmaneck and Sherman (1980) suggest that the rate of loss of specie A is a function of the mass velocity through the

TABLE 1. ACTIVITIES AND CONVERSIONS AT VARIOUS RATE CONSTANTS, TIME ON STREAM = 100 HOURS

$k_o(10^3)s^{-1}$	G_R/G_P	$k_{AR}(10^4)s^{-1}$	α_R	$\bar{\alpha}_P$	$X_R\%$	$X_P\%$
2	20	11.71	0.97	0.99	11.0	11.8
2	50	20.11	0.94	0.99	10.7	11.8
10	20	11.71	0.97	0.99	38.1	46.7
10	50	20.11	0.94	0.99	37.4	46.7
50	20	11.71	0.97	0.99	75.5	95.7
50	50	20.11	0.94	0.99	74.9	95.7

TABLE 2. ACTIVITIES AND CONVERSIONS AT VARIOUS RATE CONSTANTS. TIME ON STREAM = 1,000 HOURS

$k_o(10^3)s^{-1}$	G_R/G_P	$k_{AR}(10^4)s^{-1}$	α_R	$\bar{\alpha}_P$	$X_R\%$	$X_P\%$
50	20	11.7	0.65	0.94	67.4	94.6
50	50	20.1	0.44	0.94	58.3	94.6
50	100	30.3	0.19	0.94	37.6	94.6

catalyst. Mass transfer coefficients have been measured by evaporating a liquid from the catalyst (Satterfield, 1970). The coefficients are proportional to mass velocity to the 0.59 power. By assuming that k_A is proportional to mass velocity to the n^{th} power, k_{AR} and k_{AP} are related as follows

$$k_{AR} = k_{AP}(G_R/G_P)^n \tag{16}$$

Equation 16 is used in the following example with $n = 0.59$ to illustrate the relative deactivation of a catalyst. For $\theta = 63.5$ s, $C_{Ae}/C^{\circ}_{AS} = 8.8 \times 10^{-5}$ and $k_{AP} = 2 \times 10^{-4}$ s^{-1}, the following results are obtained (Table 1).

These results show that the differences in conversion are due to the reactor type and not catalyst activity. For a time on stream of 1000 hours the following results are obtained (Table 2).

These results illustrate the increase in decay that can be achieved in the recycle reactor as compared to the plug flow reactor.

NOTATION

a = reaction order for the decay, Eq. 1
A = catalyst specie
B = reactant gas
C_A = concentration of A in the bulk stream, mol/m^3
C_{Ae} = equilibrium concentration of A in the bulk stream, mol/m^3
C_{AS} = concentration of A on the catalyst, mol/m^3
C°_{AS} = initial concentration of A on the catalyst mol/m^3
C_B = concentration of B, mol/m^3
C°_B = initial concentration of B, mol/m^3
D = product gas
G = mass velocity, kg/m$^2 \cdot$ s
H = Henry's constant
k_A = rate constant of the mass transfer of A from catalyst to bulk stream k_A is a function of the bulk stream flow rate
k_o = chemical reaction rate constant
L = length of the tubular reactor
n = reaction order, Eq. 1
n_A = molar flow rate of A, mol/s
r_A = moles of A lost from the catalyst surface per unit time per unit volume of reactor
r_B = moles of B reacted per unit time per unit volume of reactor
S = cross sectional area of the tabular reactor, m^2
t = time, s
V = volume of the recycle reactor
v_T = volumetric flow rate of the fluid, m^3/s
X = conversion of B
Z = length from the entrance of the tubular reactor

Greek Letters

α = C_{AS}/C°_{AS}, a reference of catalyst activity
θ = residence time, (volume of reactor)/volumetric flow rate
$\bar{\alpha}$ = average α

Subscripts

P = plug flow tubular reactor
R = recycle reactor

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Conversions and Temperature Rises in a Tubular Reactor with Heat Transfer at the Wall-Exothermic Reaction

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CANADA

In studies predicting the performance of non-isothermal tubular reactors such as those of Anderson and Coull, Christiansen and Shinohara, Golding and Dussault, Santarelli and Foraboschi or Rothenberg and Smith, the reaction has been considered to be taking place either in a constant wall temperature reactor (CWTR) or under adiabatic reaction conditions. These corresponded to the following boundary conditions; for adiabatic reaction conditions $\partial\theta/\partial a = 0.0$ at $a = 1.0$, while for the CWTR: $\theta = 0.0$ at $a = 1.0$, where θ, was the dimensionless temperature and, a, the dimensionless radial distance. How-

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