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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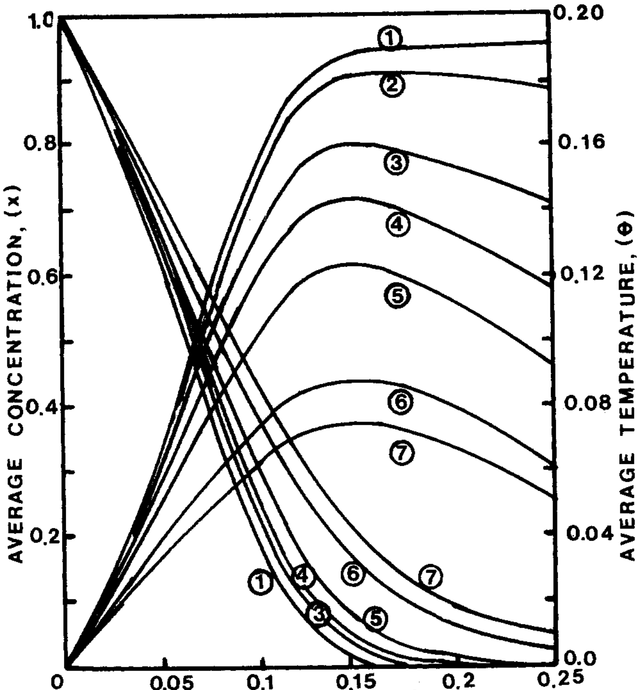

Figure 1. The effect of wall heat transfer on overall conversions and temperature rises—laminar flow reactor. (1) Adiabatic reaction conditions; (2)$G_5 = 0.1$; (3)$G_5 = 0.5$; (4)$G_5 = 1.0$; (5)$G_5 = 2.0$; (6)$G_5 = 10.0$; (7) CWTR. $G_2 = 17.92$; $G_3 = 1.709 \times 10^8$; $G_4 = 0.1902$.

ever, in practice it can be considered that a tubular reactor does not operate at either of these limiting conditions but is subject to wall heat transfer corresponding to the following boundary condition;

$$-k_e \frac{\partial \theta}{\partial a} = hR_i\theta_w \quad \text{at} \quad a = 1.0 \qquad (1)$$

The present study was undertaken to determine the effect of wall heat transfer in a chemically reacting system. A first order reaction was assumed together with the following flow models: (i) plug flow, (ii) laminar or annular flow, and (iii) laminar flow accompanied by radial diffusion.

THEORETICAL DEVELOPMENT AND NUMERICAL SOLUTION

The basic differential equations and the appropriate numerical approximations were developed previously by Golding and Dussault for constant physical properties and fully developed velocity profiles. It was assumed that under non-isothermal conditions the effect of change in physical properties on concentration and temperature profiles was small when compared to the effect of the heat of reaction. In addition, the variation of the rate constant with temperature was assumed to follow the Arrhenius relationship. Dimensionless continuity and energy equations were developed and at the wall the energy equations were as follows: for plug flow;

$$\frac{\partial \theta}{\partial w} = 2\left(\frac{\partial \theta}{\partial a} + \frac{\partial^2 \theta}{\partial a2}\right) + 2xG_3G_4e^{-G_2}/(\theta_w + 1) \quad a = 1.0 \qquad (2)$$

and for laminar flow;

$$\frac{\partial \theta}{\partial a} + \frac{\partial^2 \theta}{\partial a^2} + G_3G_4e^{-G_2}/(\theta_w + 1) = 0 \quad a = 1.0 \qquad (3)$$

In the case of wall heat transfer the dimensionless boundary condition equation required to complete the sets of equations was;

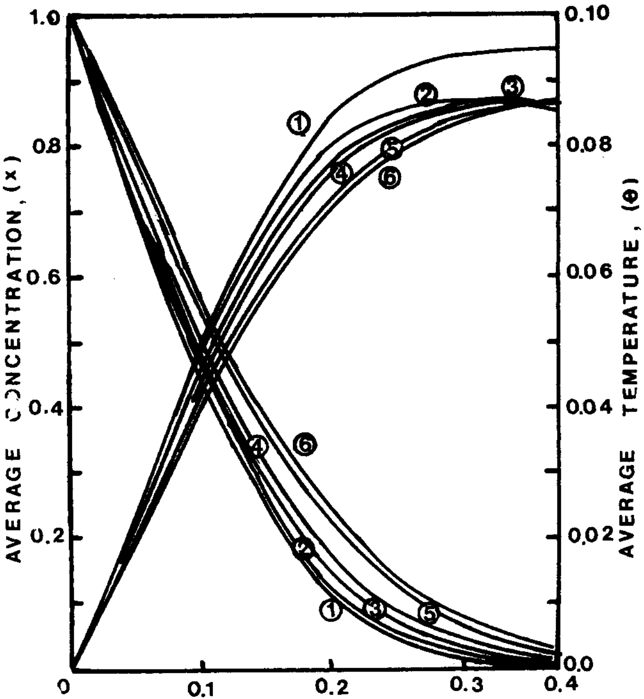

Figure 2. The effect of flow model on conversions and temperature rises in a tubular reactor with natural convection heat transfer at wall. Adiabatic reaction conditions: 1) Plug flow reactor—$G_5 = 0.0$. Natural convection wall heat transfer: 2) Plug flow reactor; 3) Laminar flow reactor with radial diffusion—$G_1 = 1.0$; 4) Laminar flow reactor with radial diffusion—$G_1 = 0.5$; 5) Laminar flow reactor with radial diffusion—$G_1 = 0.05$; 6) Laminar flow. $G_2 = 17.92$; $G_3 = 1.28 \times 10^8$; $G_4 = 0.0951$; $G_5 = 0.1626\,\theta_w^{0.25}$.

$$\frac{\partial \theta}{\partial a} = \frac{-hRi}{k_e}\theta_w = -G_5\theta_w \qquad (4)$$

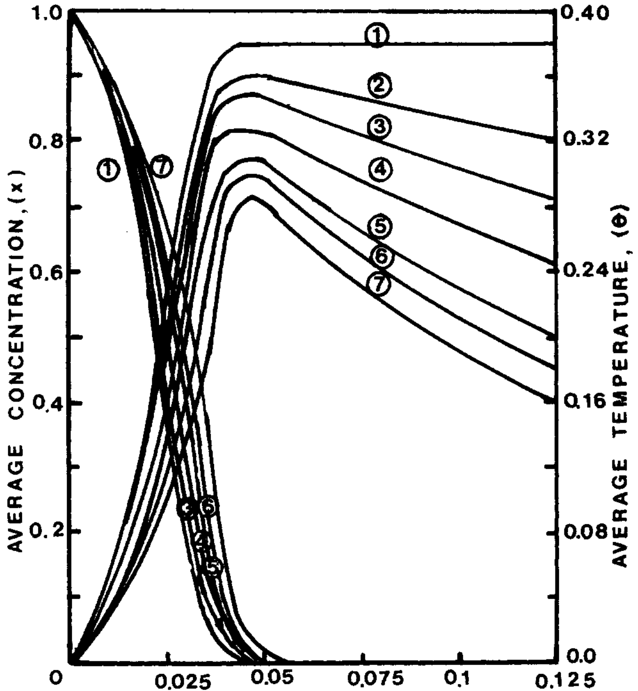

Figure 3. Effect of wall heat transfer on conversion and temperature rises at high heat of reaction—laminar flow reactor. (1) Adiabatic reaction conditions; (2)$G_5 = 0.5$; (3)$G_5 = 1.0$; (4)$G_5 = 2.0$; (5)$G_5 = 5.0$; (6)$G_5 = 10.0$; (7) CWTR. $G_2 = 17.92$; $G_3 = 2.51 \times 10^{-8}$; $G_4 = 0.3802$.

It should be noted that the heat of convection group, G_5, is equal to one half the wall Nusselt number defined by Rothenberg and Smith as $Nu_w = hd/k_c$. Equations 2, 3 and 4 were then approximated numerically to obtain the algebraic equations required and solved using an IBM 360/65. The numerical solutions were first checked for numerical consistency with previously computed results by comparing computations at large and small values of G_5 corresponding to CWTR and adiabatic reaction conditions respectively. In the case of the annular velocity profile no computational problems arose and the mesh size was chosen using the procedures suggested by Santarelli and Foraboschi. However, for the plug flow model computational instability was observed at the reactor wall. This was overcome by using a lower order explicit numerical approximation as given in Lapidus and selecting values of the radial and axial increment such that the solution would always converge.

RESULTS AND CONCLUSIONS

Calculations were carried out to determine the influence of wall heat transfer on conversions and temperature rises in a flow reactor. A first order reaction was studied as exemplified by the hydration of acetic anhydride and the effect of the variation of the wall heat transfer group, G_5 is shown in Figure 1. The computed results fall between the two limiting cases, i.e., approaching the results obtained for adiabatic reaction conditions at low G_5 values and tending towards the results obtained for a CWTR at high G_5 values. It should be noted for this reaction even low rates of wall heat transfer noticeably reduced temperature rises, curves (2) and (3). The G_5 values of 0.1 and 0.5 corresponding to heat transfer coefficient values of around 6.0 and 31.0 W $m^{-2}K^{-1}$ respectively (0.935 cm inside diameter reactor). This is also shown in Figure 2 when the effect of heat loss due to free convection at the wall was estimated for a slower reaction and lower value of the heat of reaction group, G_4. The wall heat transfer coefficient for free convection was approximated using the equation given in Kern for long vertical tubes;

$$h = 1.05(\Delta T/d_o)^{0.25} \tag{5}$$

Also shown in Figure 2 is the effect of flow model and indicates that for a fixed laminar velocity profile radial transport will significantly increase conversions.

In the case of other reaction systems the effect of wall heat transfer will depend on the reaction rate and the heat of reaction. This is illustrated in Figure 3 for larger values of G_3 and G_4 and indicates that heat transfer coefficients must be in the forced convection range before conversions will be reduced when compared to adiabatic reaction conditions. Conversely it is also indicative of the magnitude of wall heat transfer required if temperature rises are to be minimized. Wall temperatures were also computed and the results were consistent with the results reported by Sparrow et al., for varying wall heat flux in a parallel plate channel.

Radial concentration and temperature profiles were computed and showed the same trends as were observed for overall conversions and temperature rises. It was found however that when wall heat transfer was present depending on distance along the reactor wall temperature profiles would be considerably flatter than those predicted for either an adiabatic reactor or a CWTR. Further work is being carried out to check these profiles in comparison to experimental data.

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NOTATION

a = dimensionless radial distance defined as r/R_i
A = frequency factor for a first order reaction, s^{-1}
C_p = specific heat, J kg^{-1} K^{-1}
d = reactor inside diameter, m
d_o = reactor outside diameter, m
D_{AM} = effective diffusivity of component A in reaction mixture, m^2 s^{-1}
E = activation energy J kg mol^{-1}
G_1 = Lewis number defined as $\rho C_p D_{AM}/kc$
G_2 = activation energy group defined as E/RT_o
G_3 = frequency factor group defined as $R_i^2 \rho C_p A/k_c$
G_4 = heat of reaction group defined as $-\Delta H \rho_{Ao}/\rho C_p T_o$
G_5 = wall heat transfer group defined as hR_i/kc
h = wall heat transfer coefficient, W m^{-2} K^{-1}
ΔH = heat of reaction, J kg mol^{-1}
k_c = thermal conductivity, W m^{-1} K^{-1}
Nu_w = wall Nusselt number defined as hd/k_c
R = gas constant, J kg mol^{-1} K^{-1}
R_i = inside tube radius, m
T = temperature, °K
T_o = inlet temperature or ambient temperature, °K
T_w = wall temperature, °K
ΔT = temperature difference at wall, °K
$\langle u \rangle$ = average velocity, m s^{-1}
x = dimensionless concentration defined as ρ_A/ρ_{Ao}
x_o = inlet mole fraction of component A
w = dimensionless axial distance defined as, $k_c z/2 R_i^2 < u > C_p \rho$
z = reactor length, m

Greek Letters

ρ = density, kg m^{-3}
ρ_A = concentration, kg mol m^{-3}
ρ_{Ao} = inlet concentration, kg mol m^{-3}
θ = dimensionless temperature defined as $(T - T_o)/T_o$
θ_w = dimensionless wall temperature
μ = viscosity, kg m^{-1} s^{-1}

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