steady state flow rate
R = the inside radius of a tube at any given point
R_u = the unstressed radius of a tube
r = spatial coordinate in the radial direction
T = the duration of a pulse
t = the variable time
Δt = $t_n - t_{n-1}$
u = component of fluid velocity parallel to the axis of the tube
$\overline{u}$ = axial velocity of the fluid averaged over a cross sectional area of the tube
$\Delta\overline{u}$ = $\overline{u}_n - \overline{u}_{n-1}$
v = radial component of velocity
z = spatial coordinate in the axial direction of the tube
Δz = $z_n - z_{n-1}$

Greek Letters

δ = thickness of the tubing wall
μ = absolute viscosity
ν = kinematic viscosity
ρ = density of flowing fluid
ψ = an undefined functional relationship

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Effect of Imperfect Mixing on Autorefrigerated Reactor Stability

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This paper discusses the effects of imperfect mixing on the stability of autorefrigerated chemical reactors. Mixing is shown to strongly influence stability in these evaporatively-cooled systems. A modified van Heerden steady state stability analysis is presented. Computer simulation of a typical system illustrates the occurrence of runaways and local hot spots. Both continuous stirred tank reactors and batch reactors are considered.

Stability of perfectly mixed continuous autorefrigerated chemical reactors was discussed in a previous paper (*1*). The effects of removing the heat of reaction by evaporative cooling, instead of by conventional cooling jackets or coils, was studied by various stability analysis techniques. The decrease in latent heat of vaporization near the critical temperature was shown to be a source of positive feedback.

The purpose of this paper is to consider the case where mixing is not complete so that spacial concentration and temperature gradients can develop. This effect, resulting in local hot spots, would be expected to occur in industrial scale reactors, particularly in highly viscous or slurry systems.

Mixing is shown to significantly influence the stability of these evaporatively cooled reactors. A modified van Heerden steady state stability analysis and a computer simulation of a typical system are presented. Both continuous stirred tank reactors and batch reactors are discussed.

SYSTEM

A binary mixture of reactant A and product B is considered. Product B is the higher boiler, being of higher molecular weight and stoichiometrically requiring R_m moles of reactant A:

$$R_m A \xrightarrow{k} B \tag{1}$$

Reaction rate is assumed to be first-order in A. Vapor pressures for less volatile B and more volatile A are given by

$$\begin{aligned} \ln P_A &= C_1\left(\frac{1}{T}\right) + C_2 \\ \ln P_B &= C_3\left(\frac{1}{T}\right) + C_4 \end{aligned} \tag{2}$$

Raoult's law is used to calculate liquid and vapor compositions.

The process equipment studied is the typical reactor-condenser system shown in Figure 1. The exothermic heat

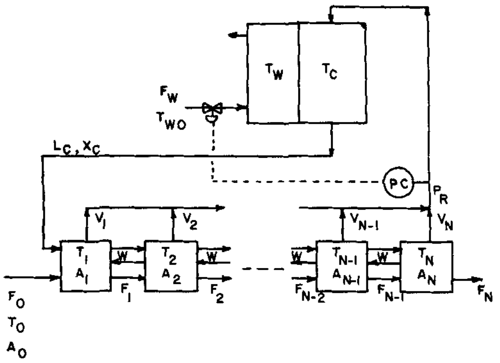

Fig. 1. Imperfectly mixed autorefrigerated reactor.

of reaction vaporizes reactor liquid. Vapor passes to the condenser where its heat of condensation is removed. Liquid returns to one end of the reactor by gravity flow or by pump. In the continuous case, a feed stream is added and product withdrawn. In the batch case no material is removed or added.

To model imperfect mixing the reactor is assumed to consist of N perfectly mixed stages. Interstage mixing transports material and sensible heat between stages. The parameter, W, is defined as the interstage mixing rate. It is an effective dispersion coefficient or degree of mixing, and would be related to the system geometry and properties and the agitator speed through the Reynolds and Froude Numbers. Holdup in each stage is assumed constant.

The condenser is assumed to consist of perfectly mixed stages on both the process and coolant sides. Holdups of vapor and liquid on the process side of the condenser are assumed negligible.

Other assumptions are constant physical properties, phase equilibrium in both condenser and reactor, constant and equal heats of vaporization of A and B.

TEMPERATURE DEPENDENCE OF REACTION RATES

A preliminary discussion of reaction rates in autorefrigerated systems is presented to introduce the steady state stability analysis.

In the staged reactor system defined, liquid vaporizes in each stage of the reactor due to the reaction. Since reactant A is more volatile it is the main component vaporized. But for component A to be transported down the reactor to subsequent stages by bulk flow and interstage mixing, concentration differences must exist along the reactor. Of course the higher the degree of mixing, the larger W, the smaller the concentration gradients will be. In the limit as W goes to infinity, mixing is perfect and no gradients exist.

As more A reacts from stage to stage, the concentration of B increases for two reasons (a) consumption of A and production of B by reaction and (b) vaporization of mostly A to remove heat. The importance of the latter increases as the ratio of the heat of reaction to the heat of vaporization increases. Since B is a higher boiler, the temperature must increase from stage to stage, for a fixed system pressure, as the concentration of B increases. The higher temperature will tend to increase the reaction rate, consuming and vaporizing still more A.

Thus an inherent source of instability exists in imperfectly mixed evaporatively cooled systems. Runaways will occur if mixing is not sufficient to supply enough of component A for vaporization or to transport enough colder material to supply sensible heat removal.

It is interesting to note that a runaway will not be unbounded in the system being studied. The reaction rate will tend to increase as temperature increases. But the overall reaction rate, R, is a function of both temperature and the concentration of reactant A.

$$R_{(T)} = k_{(T)}\ A_{(T)} \tag{3}$$

The specific reaction rate, k, increases exponentially with temperature:

$$k = \alpha \exp\ (-E/RT) \tag{4}$$

The concentration of A however decreases with temperature at a fixed pressure as dictated by vapor-liquid equilibrium in this binary system. Therefore the product of these two effects, as shown in Figure 2, will be limited by k at low temperature and by A at high temperature. The reaction rate will of course be zero at the boiling point temperature of pure B when there is no A. A nonmonotonic curve results with a maximum reaction rate at some temperature. The location and magnitude of the maximum depends on the activation energy of the reaction, system pressure, and the relative vapor pressures of the components and their temperature dependence. In the region to the left of the maximum, increasing temperature increases the reaction rate. In the region to the right of the maximum, increasing temperature decreases the reaction rate. These regions could be considered the wet side (when reaction rate is limited by temperature) and the dry side (where reaction rate is limited by reactant A concentration).

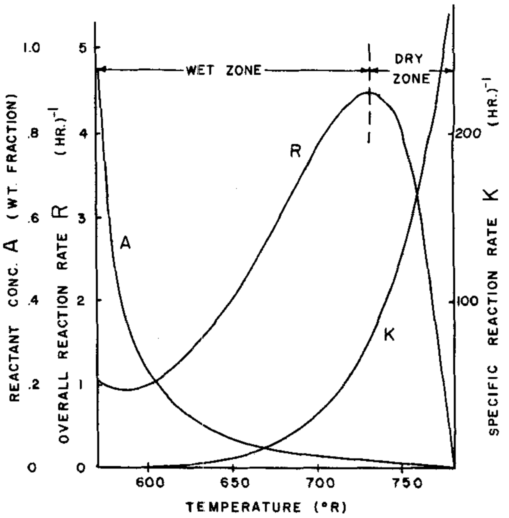

Fig. 2. Temperature dependence of reaction rates.

Autorefrigerated reactors can then be operated in either regime. Indeed it is possible in the imperfectly mixed case to have various stages operating in both regimes. However it is clear that the control systems must be quite different for these two cases. For operation on the wet side, a typical control system consists of a pressure (or temperature) controller manipulating coolant to the condenser. If pressure increases due to an increase in reaction rate, more coolant would be used to lower reactor temperature and slow down the reaction.

On the dry side, reaction rate is concentration limited. A typical control system would consist of a pressure controller manipulating reactant A feed rate, with coolant flow set at some desired rate. If pressure increases due to an increase in reaction rate, less reactant would be fed into the reactor to lower the concentration of A and slow down the reaction. The temperature in this case would increase.

Thus the control actions in the wet and dry regions are opposite. Severe control problems would be expected if one attempts to operate either of these systems at temperatures near the maximum in reaction rate curve. If during an upset the reactor goes over the peak, control action would be in the wrong direction. For example if a dry reactor goes over the maximum, the addition of more feed will decrease instead of increase reaction rate. Reaction rate is now temperature limited and more feed of A lowers the temperature.

To operate these systems near the maximum point an adaptive identification technique would be required to make appropriate changes in control action.

To illustrate some of the above discussion quantitatively, let the overall reaction rate R be given by Equation (3) and the specific reaction rate k by Equation (4). The concentration of A can be found as a function of temperature for a given system pressure P by using Raoult's law

$$P = P_{A(T)}X_A + P_{B(T)}\ (1 - X_A) \tag{5}$$

TABLE 1. PARAMETERS USED IN NUMERICAL EXAMPLE

A_o = 0.5 wt. fraction
A_c = 500 sq.ft.
C_p = 0.75 B.t.u. (lb. — °R.)$^{-1}$
C_w = 1.0 B.t.u. (lb. — °R.)$^{-1}$
C_1 = —4883.39°R.
C_2 = 12.672
C_3 = —4883.39°R.
C_4 = 10.369
E = 30,000 B.t.u. (lb. — mole — °R.)$^{-1}$
F_o = 2,000 lb./hr.
ΔH_r = 600 B.t.u./lb.
ΔH_v = 274 B.t.u./lb.
H = 2,400 lb.
H_w = 240 lb.
K_{EQ} = 250 (lb./hr.)/lb./sq.in.
K_c = 2,000 (lb./hr.)/(°R.)
R = 1.99 B.t.u. (lb.mole — °R.)$^{-1}$
R_c = 0.549 × 10^{-6} lb./sq.in. (lb./hr.)$^{-2}$
T_o = 530°R.
T_{wo} = 530°R.
U = 150 B.t.u. (hr. — sq.ft. — °R.)$^{-1}$
α = 7.08 × 10^{10} hr.$^{-1}$

or

$$X_A = \frac{P - P_B}{P_A - P_B} \tag{6}$$

Assuming that the vapor pressure curves for A and B have the same temperature dependence

$$C_1 = C_3 \equiv R_T \tag{7}$$

the ratio of vapor pressures will be constant

$$\frac{P_A}{P_B} = \frac{\exp\,(R_T/T + C_2)}{\exp\,(R_T/T + C_4)} = e^{C_2 - C_4} \equiv R_p \tag{8}$$

Substituting into Equation (6) gives

$$X_A(T) = \frac{P \exp(-\,R_T/T_{-C_2}) - 1}{R_p - 1} \tag{9}$$

Now weight fraction A is related to mole fraction X_A by

$$A = \frac{X_A\,M_A}{X_A\,M_A + (1 - X_A)\,M_B} = \frac{X_A}{X_A + (1 - X_A)\,R_m} \tag{10}$$

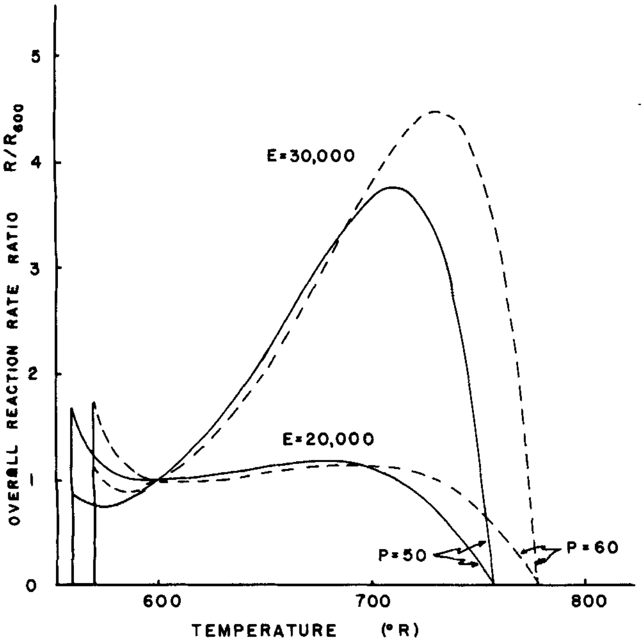

Fig. 3. Reaction rates.

So finally the temperature dependence of the overall reaction rate can be found explicitly as a function of temperature.

$$R_{(T)} = [\alpha \exp\,(-\,E/RT)]$$
$$\left[\frac{P \exp(-\,R_T/T_{-C_2}) - 1}{R_m\,R_p - 1 + (P - R_m)\exp(-\,R_T/T_{-C_2})}\right] \tag{11}$$

Figure 3 gives curves of R, expressed as a ratio of the reaction rate at 600°R., versus temperature for several values of activation energy, E, and system pressure, P. These curves are based on the numerical example used in the simulation discussed below. Values of parameters are given in Table 1.

CONTINUOUS REACTOR

Mathematical Model

The equations describing the system shown in Figure 1 are:

1. n^{th} Stage in Reactor
total continuity:

$$F_{n-1} - F_n - V_n = 0 \tag{12}$$

component continuity:

$$H_n \frac{dA_n}{dt} = F_{n-1}\,A_{n-1} - F_nA_n - V_n\,Y_{wn} - H_n\,R_n + W\,(A_{n-1} - 2A_n + A_{n+1}) \tag{13}$$

energy:

$$H_nC_p \frac{dT_n}{dt} = C_p\,F_{n-1}\,T_{n-1} - C_p\,F_n\,T_n - (\Delta H_v + C_p\,T_n)\,V_n + \Delta H_r\,H_n\,R_n + W\,C_p\,(T_{n-1} - 2\,T_n + T_{n+1}) \tag{14}$$

kinetic: $$R_n = A_n\,\alpha \exp\,(-\,E/R\,T_n) \tag{15}$$

phase equilibrium:

$$P_n = P_{A(T_n)}\,X_n + P_{B(T_n)}(1 - X_n) \tag{16}$$

mass transfer: $$V_n = K_{EQ}\,(P_n - P_R) \tag{17}$$

2. Condenser
energy water side:

$$H_wC_w \frac{dT_w}{dt} = C_wF_w\,(T_{wo} - T_w) + U_cA_c\,(T_c - T_w) \tag{18}$$

energy process side:

$$L_c = U_cA_c\,(T_c - T_w)/(\Delta H_v + C_p\,(T_r - T_c)) \tag{19}$$

$$T_r = \frac{\sum_{n=1}^{N} V_n\,T_n}{\sum_{n=1}^{N} V_n} \tag{20}$$

$$X_c = \frac{\sum_{n=1}^{N} V_n\,Y_n}{\sum_{n=1}^{N} V_n} \tag{21}$$

phase equilibrium:

$$P_c = P_{A\,(T_c)}\,X_c + P_{B\,(T_c)}\,(1 - X_c) \tag{22}$$

hydraulic:

$$P_c = P_r - R_c \left[\sum_{n=1}^{N} V_n \right]^2 \tag{23}$$

3. Controller (Temperature or Pressure)

$$\begin{aligned} Fw &= Fwo - K_c\,(T_{\text{set}} - T_1) \\ Fw &= Fwo - K_C\,(P_{\text{set}} - P_R) \end{aligned} \tag{24}$$

The total, component, and energy equations for the first stage in the reactor ($n = 1$) must be modified to include the liquid stream Lc from the condenser.

STEADY STATE STABILITY ANALYSIS

Perfectly Mixed

Van Heerden's steady state technique was first applied to a perfectly mixed reactor. This technique does not yield necessary and sufficient information regarding stability but was employed because of its simplicity and the valuable insight into the process it provides. Heat generation curves Q_G and heat removal curves Q_R, for both temperature and pressure control, are given in Figure 4.

$$Q_G = \Delta H_r\,HA\,\alpha \exp\,(-E/RT)$$

$$\begin{aligned} Q_R &= (T - T_o)\,(C_pF_o) + Q_c = \\ &= (T - T_o)\,C_pF_o + V\,[\Delta H_r + C_p\,(T - T_c)] \end{aligned}$$

For a specified temperature, A is found from Equation (12) with the time derivative set equal to zero. Q_G can then be calculated.

Q_R is found by simultaneous solution of Equations (16) to (24) applied at steady state to find T_c and V.

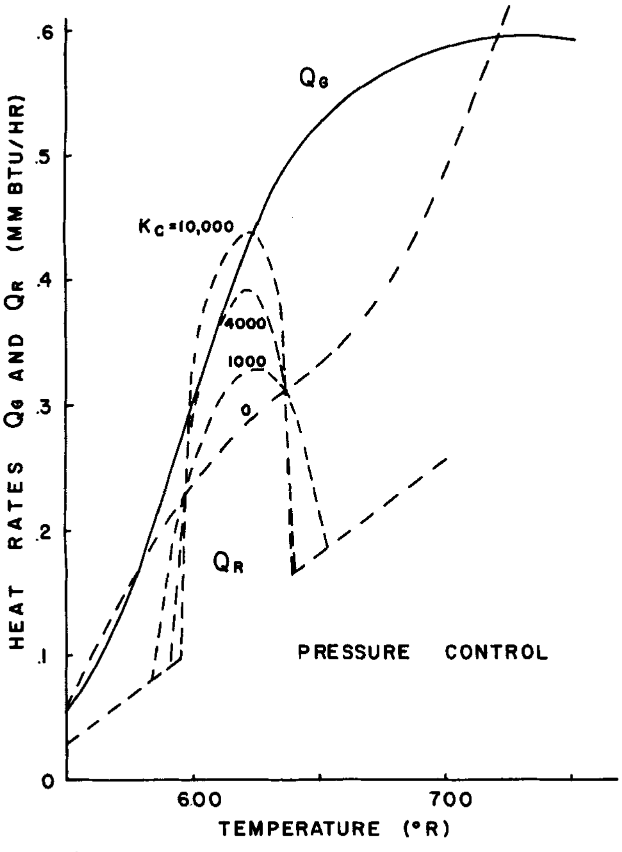

Fig. 4a. Steady state analysis: perfect mixing.

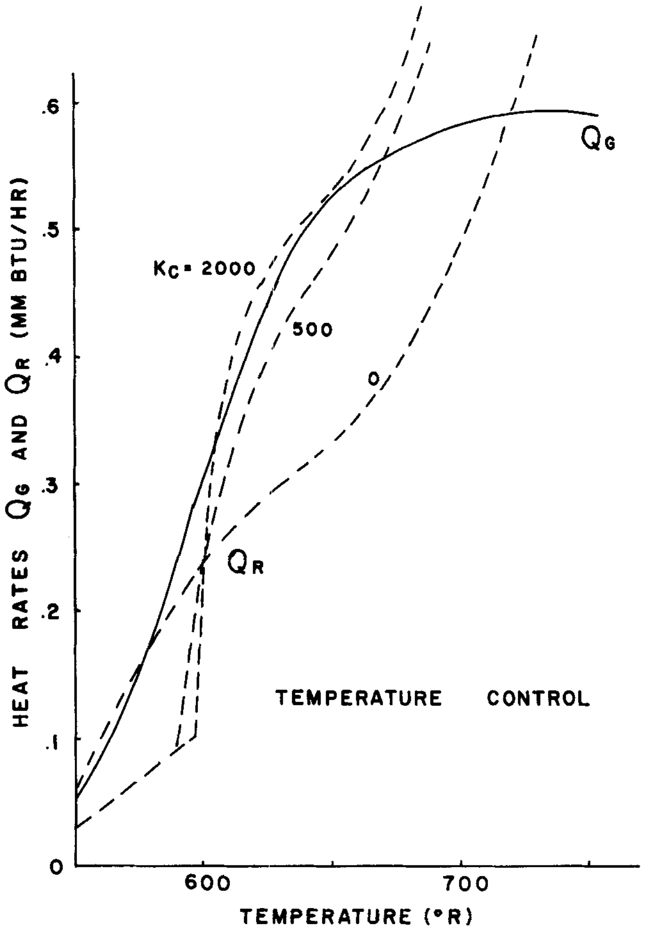

Fig. 4b. Steady state analysis: perfect mixing.

The perfectly mixed reactor is seen to have two stable open loop ($K_c = 0$) operating levels, one at a high temperature (720°R.) and one a low temperature (<550°R.). A controller gain of about 2,000 is required to operate the reactor close to the desired 600°R. level using temperature control.

The heat removal curves with pressure control show that a high gain would be required to operate at the 600°R. level and that a slight temperature upset will cause the reactor to runaway to the high temperature equilibrium point. This was precisely the behavior experienced when pressure control was attempted in the computer simulation. The explanation of this phenomenon is the nonunique relationship between temperature and pressure in this binary system. As temperature increases, pressure would increase if compositions remained constant. But higher temperatures increase the reaction rate and reduce the amount of the more volatile reactant A. Therefore, pressure will increase with temperature over the lower range but will decrease as the reactor becomes richer in component B.

Imperfectly Mixed

A modified version of Van Heerden's steady state stability technique can be used to study the effects of interstage mixing W on the stability of imperfectly mixed autorefrigerated reactors. A simple two-stage reactor is studied with the first stage at some fixed temperature T_1. A fixed first stage temperature simplifies the analysis and gives some insight into the process. Actually T_1 cannot be fixed since it is a dependent variable in the problem. Therefore several values of T_1 are used. Pressure is assumed constant and equal in both stages.

Consider the heat generation and heat removal in the second stage at various temperatures T_2. Heat generation curves can be calculated directly; fixing pressure P and

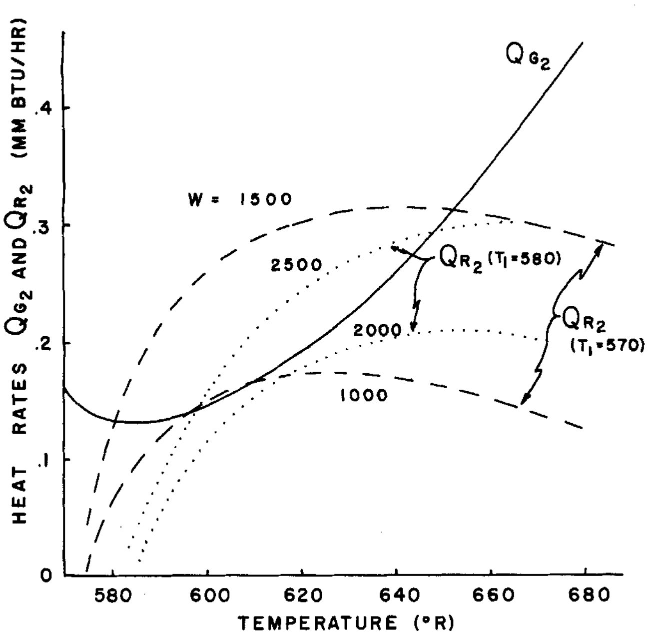

Fig. 5. Steady state analysis: imperfect mixing.

temperature T_2, fixes A_2 and k_2, thus

$$Q_{G2} = H_2 A_2 k_2 \Delta H_R \tag{25}$$

Heat is removed from the second stage by sensible heat of the material circulating between the two stages

$$(Q_{R2}) \text{ sensible} = W\, C_p\, (T_2 - T_1) \tag{26}$$

and by vaporization of liquid. Assuming the reactor is operating at the 600°R. level so that the vapor is essentially pure A, the vaporization rate will be limited by the net amount of A being transported into the second stage (the amount entering less the amount reacting). Therefore the heat removed by vaporization will be:

$$(Q_{R2}) \text{ vaporization} = [W(A_1 - A_2) - H_2 k_2 A_2]\, \Delta H_v \tag{27}$$

Heat removal will vary with W and with T_1, the value of the first stage temperature chosen. Heat generation curves [from Equation (25)] and total heat removal curves [from the sum of Equation (26) and (27)] for the second stage can be plotted versus second stage temperature as shown in Figure 5. Points of intersection are steady state solutions, and Figure 5 indicates multiple steady state solutions are possible. The steady states will tend to be stable if the slope of the heat removal curve is greater than the slope of the heat generation curve. For example, to operate T_2 at 600°R. with T_1 at 570°R. or with a 30°R. temperature gradient, an interstage mixing rate of about 1,000 is required. To operate T_2 at 600°R. with T_1 at 580°R., with a 20°R. temperature gradient, a mixing rate of about 2,500 is required.

SIMULATION

Equations (12) to (24) were simulated on the Lehigh University GE 225 digital computer. Values of parameters are given in Table 1. Steady state conditions for 2 and 4 staged reactors and for various mixing rates are given in Table 2. High interstage mixing rates are required to prevent large temperature gradients. This effect increases as the number of stages increases.

Transient responses to changes in feed composition A_o from 0.5 to 0.7 wt. fraction are given in Figure 6. Variations in last stage temperature (T_2 or T_4) are seen to be more rapid and larger than first stage temperature T_1. Lower mixing rates decrease the speed of response and increase the magnitude of the disturbance. The temperature sensitivity of the reactor increases with the number of stages or as the reactor becomes more distributed. Notice that the 4 stage reactor with a 10,000 mixing rate shows a temperature runaway or hot spot in the last stage. Reactant concentration in the last stage, A_4, is seen to decrease despite the increase in feed concentration A. Thus the degree of mixing can drastically change the transfer function between inlet and outlet concentrations, both the time constant and the gain.

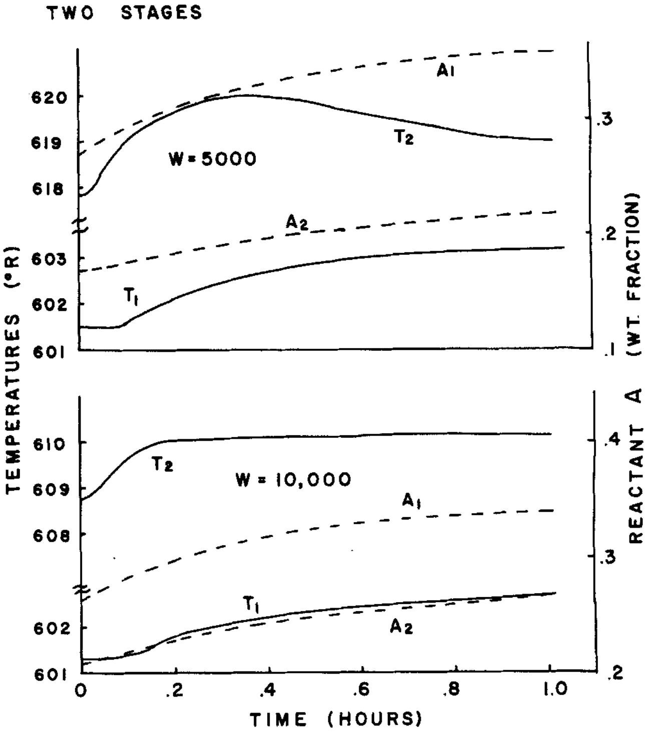

Fig. 6a. Transient response.

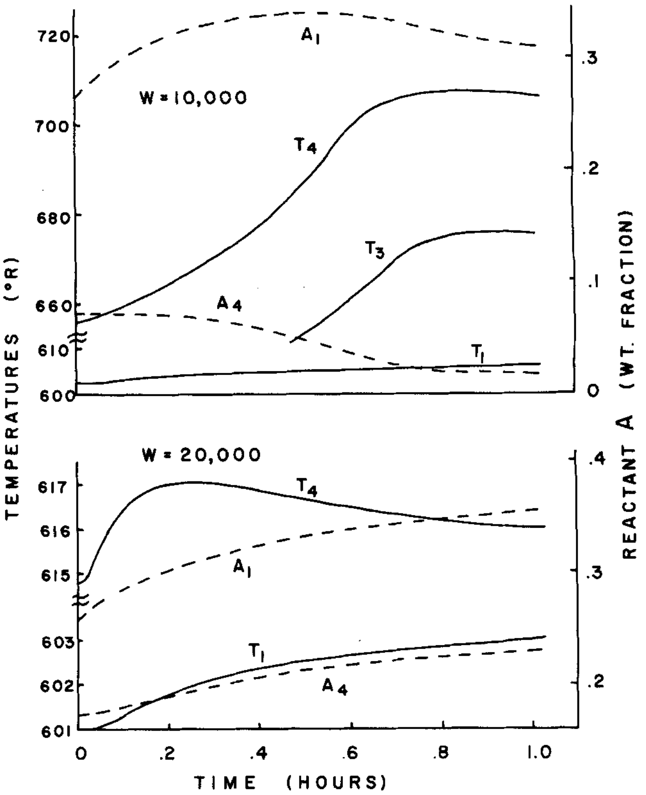

Fig. 6b. Transient response.

TABLE 2. STEADY STATE CONDITIONS FOR N STAGES WITH TEMPERATURE CONTROL

N	Interstage Mixing (lb.)/(hr.) W	n	Temperature T_n (°R.)	Reactant Composition A_n (wt.fraction)	Vapor Rate V_n (lb./hr.)
2	5,000	1	601	0.268	424
		2	618	0.168	460
	10,000	1	601	0.263	387
		2	609	0.211	434
	50,000	1	601	0.247	358
		2	603	0.237	384
4	10,000	1	602	0.263	296
		2	618	0.170	417
		3	639	0.102	300
		4	656	0.070	100
	20,000	1	601	0.256	179
		2	607	0.216	232
		3	612	0.187	210
		4	615	0.173	184

BATCH REACTOR

Mixing can have a pronounced effect on the stability of batch autorefrigerated reactors. Figure 7 gives results of a simulation of a batch reactor for various values of W. The same equations were used but with no feed or product withdrawal. A four stage reactor was considered with all stages initially at 580°R. and $A = 0.5$. Temperature controller setpoint was ramped from 580 to 680°R. in 1 hr.

High mixing rates are required to prevent large temperature gradients. The last temperature stage, T_4, goes through a maximum before being cooled back down. Notice that the condenser heat duty is affected by the degree of mixing and therefore, mixing should be considered in condenser design.

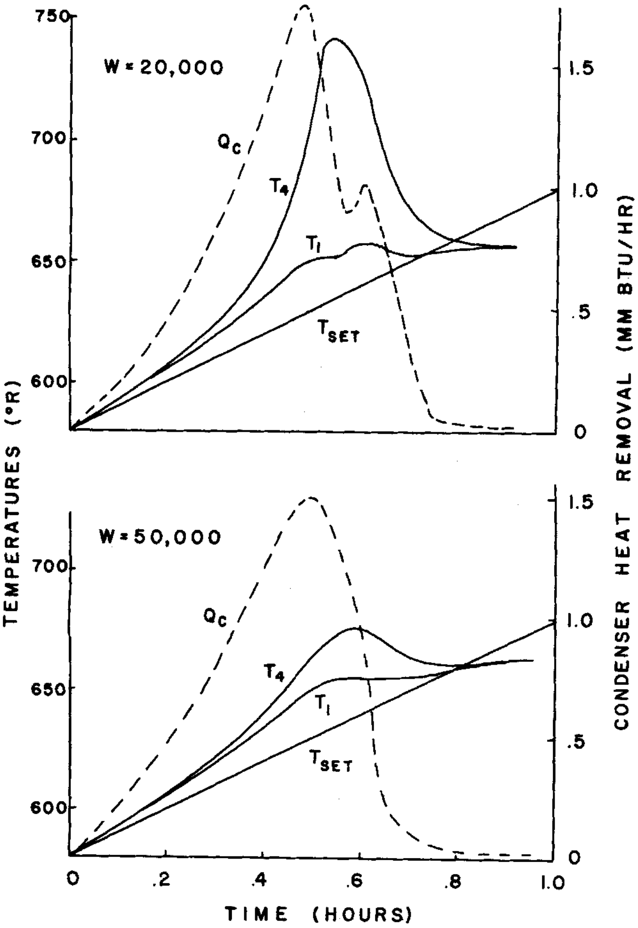

Fig. 7. Batch autorefrigerated reactor.

CONCLUSION

Mixing has a pronounced effect on the stability and performance of both continuous and batch autorefrigerated reactors. Hot spots, runaways, and large temperature gradients can occur unless mixing rates are high. These effects become more pronounced as the system becomes more distributed, affecting reactor steady state and dynamic performance. Autorefrigerated reactors can be operated wet or dry with reaction rate increasing or decreasing with temperature. A control problem can be expected at the transition point.

NOTATION

A = reactant concentration—wt. fraction
A_c = condenser area, sq.ft.
C_p = specific heat reactant and product, B.t.u. (lb.-°R.)$^{-1}$
C_1 = vapor pressure of A temperature dependence, °R.
C_2 = vapor pressure constant for A
C_3 = vapor pressure of B temperature dependence, °R.
C_4 = vapor pressure constant for B
C_w = specific heat condenser water, B.t.u. (lb.-°R.)$^{-1}$
E = activaiton energy, B.t.u./lb.-mole
F = flow rate, lb./hr.
F_w = water flow rate, lb./hr.
H = holdup, lb.
ΔH_v = heat of vaporization, B.t.u./lb.
ΔH_R = heat of reaction, B.t.u./lb.
H_w = holdup of water in condenser, lb.
K_c = feedback controller gain, lb. (hr.-°R.)$^{-1}$
K_{EQ} = mass transfer coefficient, lb. (hr.-lb./sq.in.)$^{-1}$
k = specific reaction rate, hr.$^{-1}$
M = molecular weight, lb. (lb.-mole)$^{-1}$
N = total number of stages
P = pressure, lb./sq.in.abs.
P_A = vapor pressure A, lb./sq.in.abs.
P_B = vapor pressure B, lb./sq.in.abs.
P_c = condenser pressure, lb./sq.in.abs.
P_R = reactor pressure, lb./sq.in.abs.
R = overall reaction rate, hr.$^{-1}$
R = perfect gas constant, B.t.u. (lb.-mole °R.)$^{-1}$
R_c = vapor flow resistance between reactor and condenser, lb./sq.in. (lb./hr.)$^{-2}$
R_m = ratio molecular weights
R_p = ratio of vapor pressures
R_T = $C_1 = C_3$, °R.
T = temperature, °R.
t = time, hours
T_c = condenser process temperature, °R.
T_r = reactor vapor temperature, °R.
T_w = condenser water temperature, °R.
T_{wo} = inlet water temperature, °R.
U_c = condenser heat transfer coefficient, B.t.u. (hr.-sq.ft.-°R.)$^{-1}$
V = vapor rate, lb./hr.
W = interstage mixing rate, lb./hr.
X = mole fraction A in reactor liquid
X_c = mole fraction A in condenser liquid
Y = mole fraction A in vapor
Y^w = weight fraction A in vapor
α = pre-exponential factor, hr.$^{-1}$

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