Stability of Autorefrigerated Chemical Reactors

WILLIAM L. LUYBEN

E. I. du Pont de Nemours and Company, Wilmington, Delaware

Stability of exothermic chemical reactors with cooling jackets or internal cooling coils has been extensively studied by steady state, phase plane, and linear analysis techniques. The purpose of this paper is to apply these techniques to the frequently encountered case of autorefrigerated or boiling liquid reactors. In these reactors the exothermic heat of reaction is removed, not by conductive and convective heat transfer, but by vaporization of a liquid phase or, more generally, by any kind of endothermic change in phase.

Open-loop and closed-loop stability of a continuous stirred-tank autorefrigerated reactor is studied. General equations are derived and illustrated by numerical examples.

Both constant and variable latent heats of vaporization are considered. A particularly interesting aspect of autorefrigerated reactor stability is operation near the critical temperature. Since the latent heat approaches zero, instability of the system is increased, representing a form of positive feedback in a chemical system.

Dynamics, stability, and control of chemical reactors have been studied extensively for many years. Exothermic and autocatalytic reactions have unstable, positive feedback characteristics that make their analysis both academically interesting and practically important for safe and efficient production of numerous chemicals.

Several types of reactors have been investigated: continuous stirred-tank reactors (*1, 6, 7, 19, 20, 22*), tubular reactors (*2, 3, 7, 15, 18, 20, 21, 27*), batch reactors (*14*), and combinations and recycle systems (*6, 10, 12*). State-of-the art reviews are given in references *11* and *26*.

Several techniques of analysis have been employed. Van Heerden (*22, 23*) proposed steady state analysis that judges stability by comparing slopes of heat generated curves Q_G and heat removal curves Q_R at points of intersection. For a continuous stirred-tank reactor, typical Q_G and Q_R curves are illustrated in Figure 1 for reversible and irreversible reactions. The effects of changing heat transfer coefficient U, area A, or cooling jacket temperature T_J are indicated.

Phase plane and linear analysis techniques have been used by Aris, Amundson, and co-workers in a host of publications which cover many types of reactors and systems (*1, 6, 12, 17* to *19*).

Application of Liapunov's direct method to chemical reactors has been discussed by Berger and Perlmutter (*5*) and by Warden, Aris, and Amundson (*24*). Root locus methods have been studied by Ellingsen and Ceaglske (*10a*) and by Fangel (*10b*). Feedforward control of chemical reactors has also been investigated (*16, 21*). Other stability techniques have recently been proposed (*16a* to *17a*).

Analog and digital computer simulations of specific reactor control and stability problems have been described in numerous papers (*4, 8* to *10, 13*).

In all these studies, heat is removed by two mechanisms: conductive and convective heat transfer to a cooling jacket or internal cooling coil usually described by an overall heat transfer coefficient $UA\ (T - T_J)$; and sensible heat required to warm up cold feed $FC_P\ (T - T_O)$. Thus the heat removal curve is a linear function of reactor temperature (see Figure 1).

The purpose of this paper is to study chemical reactor systems in which heat is removed by vaporization of a liquid phase. More generally, any kind of endothermic change in phase could be considered. Autorefrigerated or boiling liquid reactors are quite common and commercially important, for example C_4 alkylation, tetraethyl lead, and polyethylene (*25*).

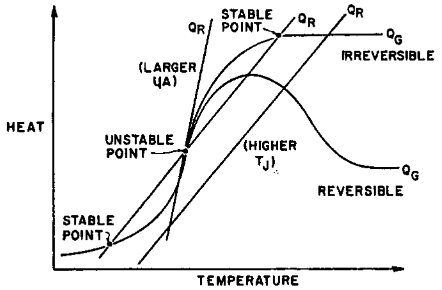

Fig. 1. Typical steady state analysis; continuous stirred-tank reactor; heat generated Q_G and heat removed Q_R.

Steady state, phase plane, and linear analysis techniques are used to examine open-loop and closed-loop stability of a continuous stirred-tank autorefrigerated reactor. General equations are derived and illustrated by specific numerical examples. Two equipment configurations are analyzed: a reactor isolated from its refrigeration system and an integrated reactor-condenser system.

Both constant and variable latent heats of vaporization are considered. A particularly interesting aspect of autorefrigerated reactor stability is operation near the critical temperature. Since the latent heat approaches zero, instability of the system is increased, representing a form of positive feedback in a chemical system.

SYSTEMS

A continuous stirred-tank reactor is considered in which a first-order irreversible reaction occurs

$$C \xrightarrow{k_{(T)}} \text{products}$$

Simple kinetics are chosen for purposes of illustration to make the analysis techniques clear and to facilitate comparison with previous work. Extension of the method to more complex reactions is straightforward.

Feed F enters the reactor with a composition C_O and temperature T_O. Heat is removed by the circulating autorefrigerant flow W. The following assumptions are made:

1. Reactor is perfectly mixed. This may be a gross simplification in many real systems.
2. Reactor is adiabatic except for the autorefrigerant stream.
3. Holdup in the reactor is constant.
4. Vapor is pure solvent with a latent heat of vaporization ΔH_V that may be constant or vary with temperature. (A parabolic function is assumed that approaches zero at the critical temperature of the solvent.)
5. Throughput F, holdup V, specific heat C_P, and heat of reaction ΔH_R are all constant.
6. Feedback controller dynamics are neglected.
7. Reaction is carried out in a solvent.

Concentrations of reactant and product in the reactor are very small so that system pressure is determined by reactor temperature only. The response of a boiling liquid system to pressure changes should be very rapid because of the difference between sensible and latent heats. For example, if the reactor were subjected to a sudden decrease in pressure, only a small amount of liquid would have to be vaporized to drop the temperature of the bulk liquid to the new bubble point. Small vapor volumes would make this response even more rapid. Thus, little departure from phase equilibrium would be expected and none is assumed in this treatment.

Two equipment and control configurations are discussed with the use of steady state, linear, and phase plane techniques. In the first (Figure 2), refrigerant flow W is fixed by a flow controller and reset by temperature. Open-loop control in this system refers to no cascade temperature control but the flow controller still fixes W (regardless of system pressure). In this scheme it is assumed that the refrigerant stream removes latent heat only (no subcooling of liquid return).

The second system (Figure 3) is a more complex case in which the interaction between a condenser and the reactor is considered. The reactor temperature controller does not change refrigerant flow W directly but changes condenser coolant flow W_J. Therefore the dynamics of the condenser must be included. The hydraulics of vapor flow from reactor to condenser are also considered. The resulting pressure drop between the reactor and condenser makes T_C less than T and results in sensible heat effects. Variable latent heats are used. The condenser is assumed to consist of a single, perfectly mixed stage on both the process and coolant sides.

This should be a reasonable approximation if the overall temperature driving force is large at both ends of the condenser. For simplicity, heat capacity of the condenser metal is also neglected in this treatment, but could be easily included, if required, by including an energy equation for the metal, or more simply, by lumping the capacitance of the metal and coolant together. The latter technique should be adequate if the process-side film coefficients dominate heat transfer.

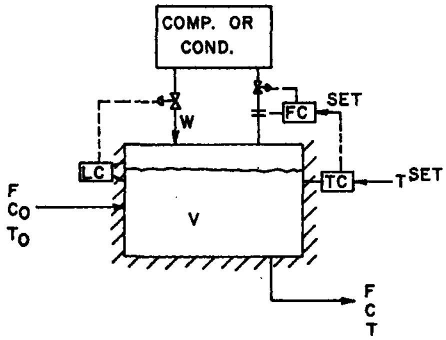

Fig. 2. Autorefrigerated reactor.

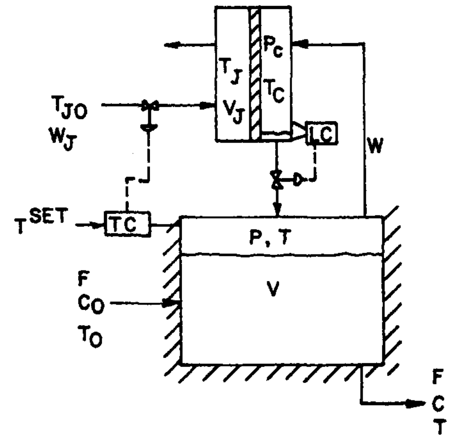

Fig. 3. Autorefrigerated reactor with condenser.

Holdup on the process side of the condenser is assumed negligible compared to the liquid holdup in the reactor (5 to 10% is a typical number in the author's experience). *This assumption results in the process-side energy equation being a simple algebraic relationship equating the rate of condensation to the rate of vaporization. If condenser holdup is not negligible, one must include a dynamic energy equation in the analysis, and if condenser holdup is not constant, one must include total continuity equations for both the condenser and the reactor.*

Although the second system is perhaps the one more commonly found in industrial applications, the first system is of some practical importance. Since the dynamic lags of the condenser are eliminated, faster and tighter control is possible. The first configuration is also particularly applicable to systems with several reactors and a central refrigerant recovery system.

AUTOREFRIGERATED REACTOR

Equations

The equations describing the system shown in Figure 2 are given below.

Component continuity equation:

$$V\,(dC/dt) = F\,(C_O - C) - V\,C\,k \tag{1}$$

Energy equation:

$$V C_P\,(dT/dt) = F C_P\,(T_O - T) + (-\Delta H_R)\,V\,C\,k - W\,\Delta H_V \tag{2}$$

Kinetic equation:

$$k = \alpha \exp\left[-E/R\,(T + 460)\right] \tag{3}$$

Latent heat (if variable):

$$\begin{aligned} \Delta H_V &= \Delta H_V^{O}\sqrt{1 - T/T_{CR}} \quad &\text{for} \quad T < T_{CR} \\ &= 0 \quad &\text{for} \quad T \geqq T_{CR} \end{aligned} \tag{4}$$

Controller ($k_P = 0$ for open loop):

$$W = W^O - k_P\,(T^{\text{Set}} - T) \tag{5}$$

Example

A specific numerical example based on Harriott's Example 15-1 (*14*, p. 317) is used in the following discussions to illustrate the methods. All figures are based on this example.

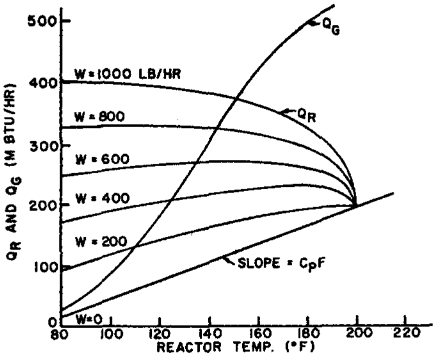

Fig. 4. Autorefrigerated reactor; steady state analysis; open-loop stability.

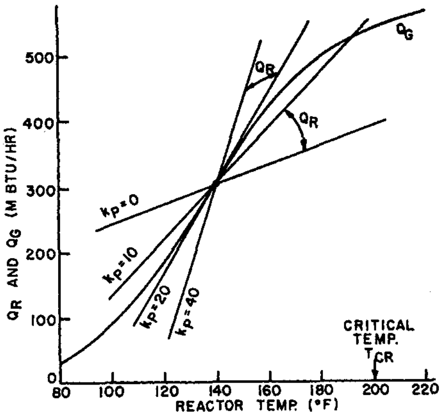

Fig. 5. Autorefrigerated reactor; steady state analysis; constant ΔH_v, closed-loop stability.

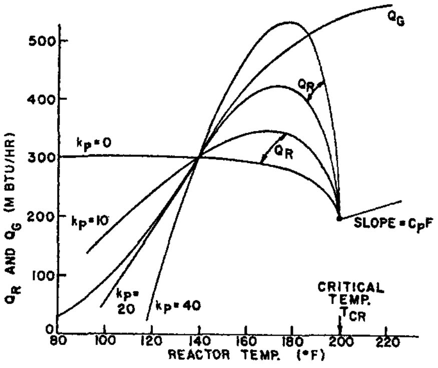

Fig. 6. Autorefrigerated reactor; steady state analysis; variable ΔH_v, closed-loop stability.

$F = 2{,}000$ lb./hr.
$C_O = 0.50$ lb./lb.
$T_O = 70$°F.
$C_P = 0.75$ B.t.u./(lb.)(°F.)
$V = 2{,}400$ lb.
$-\Delta H_R = 600$ B.t.u./lb.
$E = 30{,}000$ B.t.u./lb.-mole
$\alpha = 7.08 \times 10^{10}$ hr.$^{-1}$
$T_S = 140$°F.
$C_S = 0.246$ lb./lb.
$k_S = 0.868$ hr.$^{-1}$
$(Q_G)_S = 305{,}000$ B.t.u./hr.
$T^{\text{Set}} = 140$°F.

We choose

$\Delta H_V{}^O = 500$ B.t.u./lb. at 0°F. ($\Delta H_V = 274$ B.t.u/lb. if constant)
$T_{CR} = 200$°F.
$W^O = 729$ lb./hr.

Steady State Analysis

Following the methods described by Van Heerden (*22*, *23*), we can express the heat generated Q_G and heat removed Q_R in Equation (2) as:

$$Q_G = (-\Delta H_R)\, V\, C\, k$$

$$Q_R = FC_P\,(T - T_O) + W\,\Delta H_V$$

The $UA(T - T_J)$ term for a jacketed reactor is replaced by the $W\Delta H_V$ term in the autorefrigerated reactor.

Figure 4 gives Q_G and Q_R curves for the open-loop system with a latent heat that varies with temperature as given by Equation (4). Open-loop instability for any value of refrigerant flow W is indicated, since the slope of the Q_G curve is greater than the slope of the Q_R curve at points of intersection.

Figure 5 gives Q_G and Q_R curves for the closed-loop system with a constant latent heat of vaporization and various controller gains k_P. The heat generation curve Q_G is, of course, the same as in Figure 4. Heat removal is linear in reactor temperature as was the case with jacketed reactors. A k_P of about 40 is needed for stability.

Figure 6 gives Q_G and Q_R curves for the closed-loop system with a latent heat that varies with temperature. The heat removal curve is now highly nonlinear. At low temperatures the Q_R curves asymptotically approach the linear Q_R curves in Figure 5 for the constant latent heats because W goes to zero and the sensible heat of the feed becomes dominant. As the critical temperature of the refrigerant is approached, the Q_R curves begin to curve off, go through a maximum point, and drop to a common value $FC_P(T_{CR} - T_S)$ at the critical temperature. Above the critical temperature the curve is again linear (sensible heat of feed is only heat sink).

As expected, the slopes of all the Q_R curves for variable latent heat are less than the slopes for constant latent heat. This indicates a decrease in stability of the system.

An important point is revealed by the multiple points of intersection of the "$k_P = 40$" Q_R curve with the Q_G curve. The slope of the Q_R curve is greater than the Q_G at 140°F., indicating stability at that temperature with a controller gain of 40. However, if during some transient the reactor temperature ever approached the 187°F. level, the system would become unstable. This defines, of course, only an approximate region of stability.

Even with an infinite controller gain the system would become unstable if the temperature approached the critical temperature. This assumes $FC_P(T_{CR} - T_O) < Q_{G(T_{CR})}$. The system will not be unstable in the sense that the temperature goes to infinity. Eventually (about 450°F. in the example) the Q_R curve again crosses the Q_G curve.

Linear Analysis

Closed-loop. The nonlinear differential and algebraic equations describing the closed-loop autorefrigerated reactor can be linearized around some steady state operating level to examine stability, as described by Aris and Amundson (*1*). Two linear, constant-coefficient ordinary differential equations result from Equations (1) to (5).

$$(dC/dt) = -\,a_{11}\,C - a_{12}\,T \tag{6}$$

$$(dT/dt) = -\,a_{21}\,C - a_{22}\,T \tag{7}$$

where

$$a_{11} = F/V + k_S$$

$$a_{12} = C_S k_S\, E/R\,(T_S + 460)^2$$

$$a_{21} = (-\,\Delta H_R)\,k_S/C_P$$

For constant latent heat

$$a_{22} = \frac{F}{V} - \frac{(-\Delta H_R) k_S C_S\, E}{C_P R(T_S + 460)^2} + \frac{\Delta H_V k_P}{C_P V}$$

For variable latent heat

$$a_{22} = \frac{F}{V} - \frac{(-\Delta H_R)\; k_S C_S\, E}{C_P R(T_S + 460)^2} + \frac{\Delta H_V{}^O[-\,W^O + 2\,k_P(T_{CR} - T_S)]}{2VC_P\, T_{CR}\sqrt{1 - T_S/T_{CR}}}\,, \text{for } T < T_{CR}$$

The S subscripts indicate steady state values. The stability requirements are

$$a_{11} + a_{22} > 0 \tag{8}$$

$$a_{11}\,a_{22} - a_{12}a_{21} > 0 \tag{9}$$

For constant latent heat Equation (8) becomes

$$2C_PF + k_SC_PV + \Delta H_V\, k_P > \frac{(-\Delta H_R)\, k_SC_SEV}{R(T_S + 460)^2} \quad (10)$$

For variable latent heat Equation (8) becomes

$$2C_PF + k_SC_PV + \frac{\Delta H_V{}^O[-W^O + 2\,k_P(T_{CR} - T_S)]}{2T_{CR}\sqrt{1 - T_S/T_{CR}}} > \frac{(-\Delta H_R)k_SC_SEV}{R(T_S + 460)^2}, \text{ for } T < T_{CR} \quad (11)$$

Equation (10) or (11) can be used to calculate the minimum controller gain for stability. For our example

for constant ΔH_V, $(k_P)_{\min} = 30$
for variable ΔH_V, $(k_P)_{\min} = 36$

Since a_{11}, a_{12}, and a_{21} are all positive, the stability criterion given by Equation (9) shows that a_{22} must at least be greater than zero.

For constant latent heat

$$C_PF + \Delta H_Vk_P > \frac{(-\Delta H_R)Vk_SC_SE}{R(T_S + 460)^2} \quad (12)$$

If sensible heat can be neglected

$$\Delta H_Vk_P > \frac{(Q_G)_SE}{R(T_S + 460)^2}$$

$$(k_P)_C > \frac{W_SE}{R(T_S + 460)^2} \quad (13)$$

Therefore for an autorefrigerated reactor we can define an approximate critical controller gain $(k_P)_C$ analogous to Wilson's critical ΔT for a jacketed reactor (27). For our example with constant ΔH_V, $(k_P)_C = 30$. $(k_P)_C$ is based on a more stringent stability criteria [Equation (12)] than $(k_P)_{\min}$ [Equation (10)] but neglects sensible heat effects. The two are about equivalent in our example.

Open-loop

If the open-loop system is considered

$$a_{22} = \frac{F}{V} - \frac{(-\Delta H_R)k_SC_SE}{C_PR(T_S + 460)^2}$$

For the system to be open-loop stable

$$C_PF > \frac{V(-\Delta H_R)k_SC_SE}{R(T_S + 460)^2} = \frac{(Q_G)_SE}{R(T_S + 460)^2}$$

Thus, autorefrigerated reactors must have only mildly exothermic reactions (small ΔH_R), small holdups (small $V/F = \tau$), or large specific heats to be open-loop stable.

Phase Plane Analysis (for the Variable Latent Heat Closed-Loop System)

Equations (1) to (5) can be combined to give

$$\frac{dC}{dt} = \frac{F}{V}(C_O - C) - C\,\alpha \exp\left[\frac{-E}{R(T + 460)}\right]$$

$$\frac{dT}{dt} = \frac{F}{V}(T_O - T) + \frac{(-\Delta H_R)C}{C_P}\,\alpha \exp\left[\frac{-E}{R(T + 460)}\right] - \left[\frac{W^O - k_P(T^{\text{Set}} - T)}{VC_P}\right][\Delta H_V{}^O\sqrt{1 - T/T_{CR}}]$$

These nonlinear ordinary differential equations are of the form

$$(dC/dt) = F_1\,(C, T) \quad (14)$$

$$(dT/dt) = F_2\,(C, T) \quad (15)$$

and are therefore nicely handled by phase plane methods of nonlinear mechanics (*1*). They can be readily solved by analog or digital methods, and plotting C vs. T as functions of time yields the phase plane or state space trajectories.

Figures 7, 8, and 9 show phase plane plots for the closed-loop example with variable latent heat and controller gains of 100, 75, and 50. Instability increases as k_P decreases. The system becomes unstable for any k_P if the temperature approaches the critical temperature during a transient.

Phase plane methods are probably the most useful of the techniques because they give rigorous answers that are not limited to evaluation of stability at a single point. Whole regions of stability can be determined; these regions are shown in Figures 7 to 9.

AUTOREFRIGERATED REACTOR WITH CONDENSER

Equations

The equations describing the combined reactor-condenser system shown in Figure 3 are given below.

Reactor

Component continuity equation:

$$V\,(dC/dt) = F\,(C_o - C) - VCk \quad (16)$$

Energy equation:

$$VC_P\,(dT/dt) = F\,C_P\,(T_o - T) + (-\Delta H_R)\,VCk - W[\Delta H_V + C_P\,(T - T_C)] \quad (17)$$

Kinetic equation:

$$k = \alpha \exp\,[-E/R\,(T + 460)] \quad (18)$$

Latent heat:

$$\Delta H_V = \Delta H_V{}^o\sqrt{1 - T/T_{CR}} \text{ for } T < T_{CR} \quad (19)$$

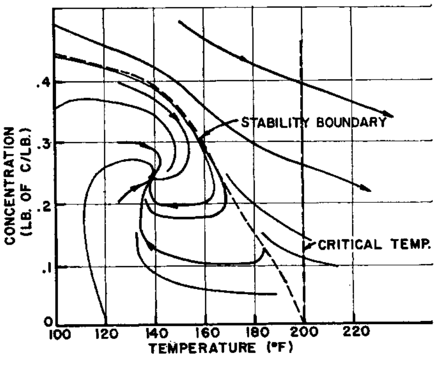

Fig. 7. Autorefrigerated reactor; phase plane; $k_P = 100$.

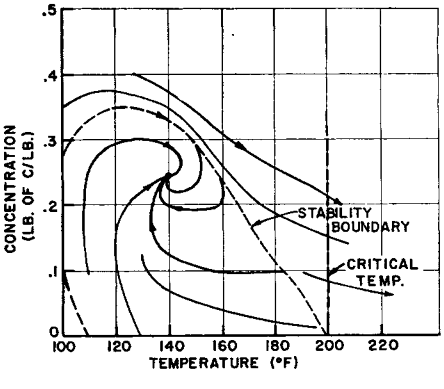

Fig. 8. Autorefrigerated reactor; phase plane; $k_P = 75$.

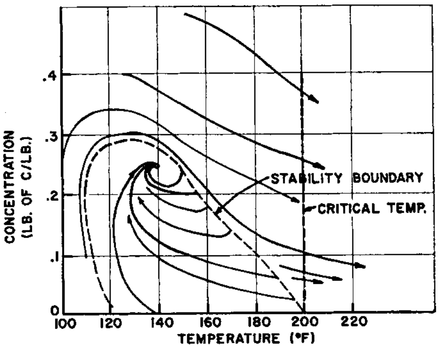

Fig. 9. Autorefrigerated reactor; phase plane; $k_P = 50$.

Vapor pressure:

$$P = \phi_{(T)} \tag{20}$$

Condenser

Hydraulics:

$$P - P_C = R_C W^2 \tag{21}$$

Vapor pressure:

$$P_C = \phi_{(T_C)} \tag{22}$$

Energy equation (coolant side):

$$V_J C_J \frac{dT_J}{dt} = W_J C_J (T_{JO} - T_J) + UA (T_C - T_J) \tag{23}$$

Energy equation (process side):

$$W = \frac{UA (T_C - T_J)}{\Delta H_V + C_P (T - T_C)} \tag{24}$$

Controller

$$W_J = W_J{}^o - k_P (T^{\text{Set}} - T) \tag{25}$$

Example

The same example is used with the following modifications and additions:

T_S = 140°F.
P_S = 2.89 lb./sq. in. abs.
T_{CS} = 136°F.
P_{CS} = 2.60 lb./sq. in. abs.
R_C = 0.549×10^{-6} (lb./sq. in.) (hr.^{2})/lb.^{2}
W = 719 lb./hr.
V_J = 240 lb.
C_J = 1 B.t.u./(lb.) (°F.)
U = 150 B.t.u./(hr.) (°F.) (sq. ft.)
A = 50 sq. ft.
T_{JO} = 70°F.
T_{JS} = 109.3°F.
$W_J{}^o$ = 5,080 lb./hr.

Note that less refrigerant flow is required at steady state due to the lower liquid return temperature. However, exactly the same amount of heat must be taken out of the condenser as in the other system. An arbitrary vapor pressure curve is used.

Steady State Analysis

The heat generation curve for the reactor-condenser system is exactly the same as with the other system. However, the heat removal curve will be quite different because, for any choice of T, coolant flow W_J is fixed, not refrigerant flow W.

$$\begin{aligned} Q_R &= FC_P (T - T_O) + W [\Delta H_V + C_P (T - T_C)] \\ &= FC_P (T - T_O) + UA (T_C - T_J) \end{aligned} \tag{26}$$

where W and T_C are found (along with T_J and W_J) for a given k_P by simultaneous solution of Equations (21) to (25), with the time derivative in Equation (23) set equal to zero.

Figure 10 gives Q_R and Q_G curves for various k_P values. The reactor-condenser system is seen to be open-loop unstable. A controller gain of about 125 is required for stability. Heat removal curves drop off as the critical temperature is approached. Their values at T_{CR} vary with k_P because of sensible heat effects of the refrigerant flow W.

The heat removal curves intersect the heat generated curve at three temperatures: 140°, 199°, and 214°F. for a k_P of 750. The second is an unstable point, but the first and third are stable. This means that the reactor could be operated at 214°F., a temperature above its critical temperature, with a k_P of 750, because of sensible heat effects. The second stable operating temperature increases as k_P decreases.

Figure 11 shows the destabilizing effect of increasing the resistance to flow (R_C) between the reactor and the condenser for a fixed controller gain k_P = 750. The Q_G and Q_R curves do not even intersect if R_C is increased by a factor of about 3, indicating that the reactor could not be operated with a flow resistance this large. There is some maximum R_C permissible even with an infinite controller gain, for a fixed T_{JO}.

Steady state analysis, of course, gives no indication of the effect of condenser holdup on stability.

Linear Analysis

Linearization and simplification of the nonlinear differential and algebraic equations describing the closed-loop, variable latent heat, autorefrigerated reactor-condenser system [Equations (16) to (25)] give these constant-coefficient linear differential equations

$$\left.\begin{aligned} (dC/dt) &= -a_{11}\, C - a_{12}\, T - a_{13}\, T_J \\ (dT/dt) &= -a_{21}\, C - a_{22}\, T - a_{23}\, T_J \\ (dT_J/dt) &= -a_{31}\, C - a_{32}\, T - a_{33}\, T_J \end{aligned}\right\} \tag{27}$$

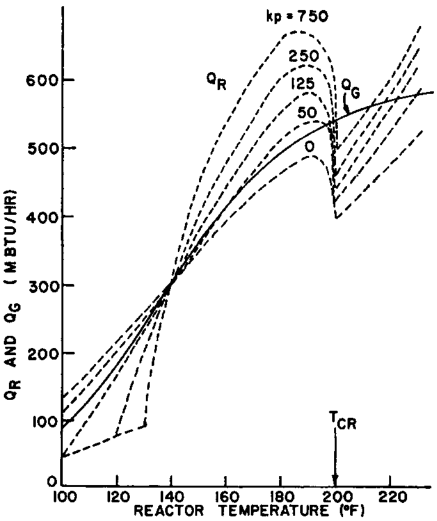

Fig. 10. Autorefrigerated reactor with condenser; steady state analysis.

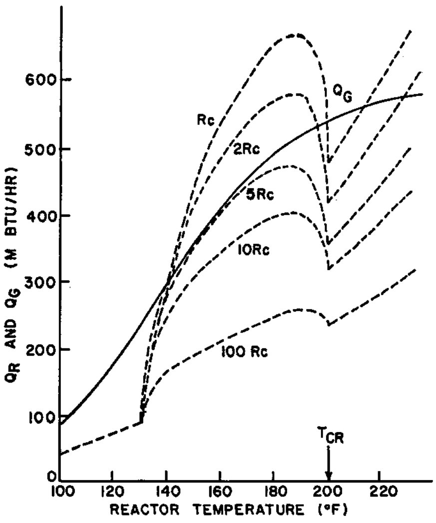

Fig. 11. Autorefrigerated reactor with condenser; steady state analysis; effect of hydraulics.

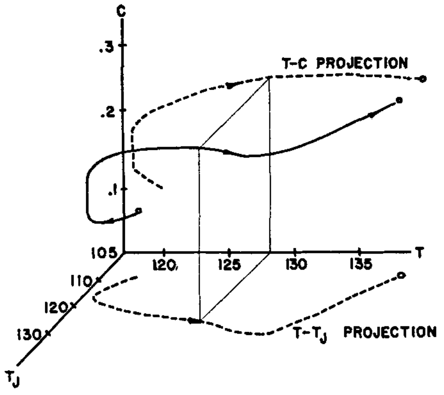

Fig. 12. Autorefrigerated reactor with condenser, state space.

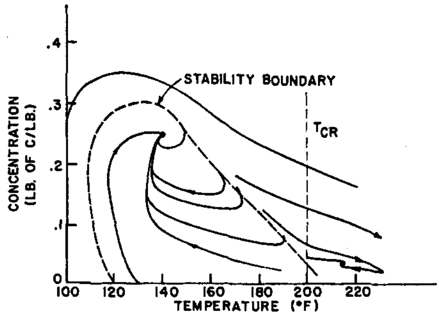

Fig. 13. Autorefrigerated reactor with condenser, phase plane, $k_P = 750$.

where

$$a_{11} = F/V + k_S$$

$$a_{12} = C_S k_S E/R\,(T_S + 460)^2$$

$$a_{13} = 0$$

$$a_{21} = (-\Delta H_R)\,k_S/C_P$$

$$a_{22} = F/V + (UA/C_P V) - \frac{(-\Delta H_R)\ C_S k_S E}{R\,C_P(T_S + 460)^2} - g_1$$

$$a_{23} = (UA/VC_P)\,(g_2 - 1)$$

$$a_{31} = 0$$

$$a_{32} = \frac{(T_{JS} - T_J{}^o)\,k_P}{V_J} + \frac{UA}{C_J V_J}\,(g_1 - 1)$$

$$a_{33} = \frac{W_J{}^o}{V_J} + \frac{UA}{C_J V_J}\,(1 - g_2)$$

$$g_1 = \frac{2\,R_C\,UA\,W_S}{C_P V\,\phi'_S} \left[\frac{UA + T_{CS}\,C_P + W_S\,H_V{}^o/2\,\sqrt{1 - T_S/T_{CR}}}{C_P T_S + \Delta H_{VS} + 2\,R_C W_S(UA + W_S C_P)/\phi'_S}\right]$$

$$g_2 = \frac{2\,W_S\,R_C\,UA/\phi'_S}{C_P T_S + \Delta H_{VS} + 2\,R_C W_S\,(UA + W_S C_P)/\phi'_S}$$

The Routh stability criteria require that

$$a_{11} + a_{22} + a_{33} > 0 \tag{28}$$

$$a_{11}\,a_{22}\,a_{33} > a_{12}\,a_{22}\,a_{33} + a_{11}\,a_{23}\,a_{32} \tag{29}$$

$$a_{11}\,a_{22} + a_{11}\,a_{23} + a_{22}\,a_{33} > a_{12}\,a_{22} + a_{23}\,a_{32} + \frac{a_{11}a_{22}a_{33} - a_{12}a_{22}a_{23} - a_{11}a_{23}a_{32}}{a_{11} + a_{22} + a_{33}} \tag{30}$$

The use of Equation (28) requires that

$$\frac{2F}{V} + k_S + UA\left(\frac{1}{C_P V} + \frac{1}{C_J V_J}\right) + \frac{W_J{}^o}{V_J} > \frac{(-\Delta H_R)C_S k_S E}{C_P R\,(T_S + 460)^2} + g_1 + \left(\frac{UA}{C_J V_J}\right) g_2 \tag{31}$$

Equation (31) shows that stability is increased by increasing U, A, $W_J{}^o$, and ϕ'_S and by decreasing V_J and R_C. Since k_P does not appear in Equation (31), this stability criterion cannot be satisfied by increasing gain; that is, the systems cannot be made closed-loop stable if Equation (31) is not satisfied. The maximum value of the ratio of the flow resistance to the vapor pressure slope, R_C/ϕ'_S can be estimated from Equation (31). For our example

$$\left[\frac{R_C}{\phi'_S}\right]_{\max} = 11.5 \times 10^6 \frac{(\text{lb./sq. in.})\,(\text{hr.}^2)/\text{lb.}^2}{(\text{lb./sq. in})\,(°\text{F.})}$$

or for $\phi'_S = 0.116$ lb./sq. in./°F. at 140°F.

$$[R_C]_{\max} = 2.5\,[R_C]_{\text{base}}$$

This agrees with the steady state analysis (Figure 11) which indicated that a resistance greater than about 3 $(R_C)_{\text{base}}$ would cause instability.

Maximum values of V_J or minimum values of U or A could be similarly estimated.

Phase Plane Analysis

Equations (16) to (25) can be combined and put in the form

$$\left.\begin{aligned} (dC/dt &= F_1\,(C, T, T_J) \\ (dT/dt) &= F_2\,(C, T, T_J) \\ (dT_J/dt) &= F_3\,(C, T, T_J) \end{aligned}\right\} \tag{32}$$

Three-dimensional phase plane or state space plots can be constructed from Equations (32) (see Figure 12). Since we are primarily concerned with C and T, only the C-T projections are shown in Figures 13 and 14 for different k_P's. All the curves start from their initial conditions with $T_J = 109.3$°F. With small condenser holdup V_J, stability is not very sensitive to T_J. However, these C-T projections are not unique; they depend upon the initial value of T_J. To be rigorous, a three-dimensional volume of stability should be defined. Approximate regions of stability and the existence of two stable operating temperatures are shown.

Figures 15 and 16 show the destabilizing effects of increasing hydraulic pressure drop ($R_C \times 2$) or increasing condenser coolant holdup ($V_J \times 10$). The latter case leads to particularly oscillatory behavior and a small region of stability.

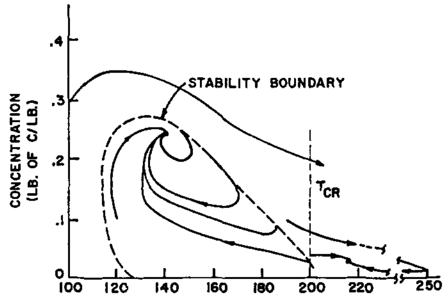

Fig. 14. Autorefrigerated reactor with condenser, phase plane, $k_P = 500$.

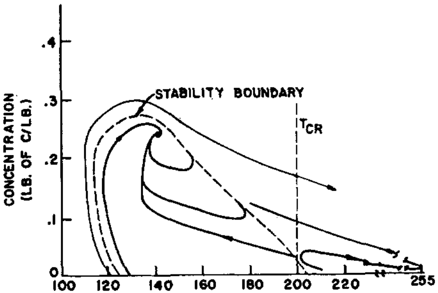

Fig. 15. Autorefrigerated reactor with condenser; phase plane with $2R_C$; $k_P = 750$.

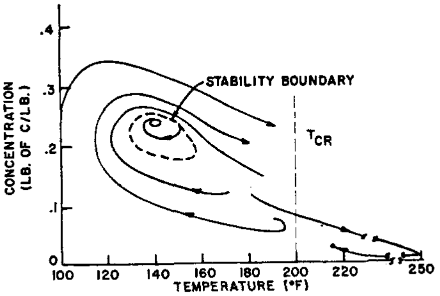

Fig. 16. Autorefrigerated reactor with condenser; phase plane with 10 V_J; $k_P = 750$.

CONCLUSIONS

1. Steady state, phase plane, and linear analysis techniques can be extended to autorefrigerated reactors to examine the effect of system parameters on stability. Phase plane analysis is particularly useful in defining regions of stability.
2. Autorefrigerated reactors with variable latent heats of vaporization operating near the critical temperature show marked instability.
3. Autorefrigerated reactors will usually be open-loop unstable. Minimum controller gains can be estimated from steady state or linear analysis.
4. Stability of an autorefrigerated reactor-condenser system is increased by keeping condenser holdup small and by reducing hydraulic pressure drop.

NOTATION

A = condenser area, sq. ft.
C = concentration, lb. of component C/lb.
C_P = specific heat process, B.t.u./(lb.) (°F.)
C_J = specific heat coolant, B.t.u./(lb.) (°F.)
E = activation energy, B.t.u./lb.-mole
F = feed rate, lb./hr.
ΔH_V = latent heat of vaporization, B.t.u./lb.
$-\Delta H_R$ = exothermic heat of reaction, B.t.u./lb.
J = jacket
k = first-order reaction rate, hr.$^{-1}$
k_P = feedback controller gain, lb./(hr.) (°F.)
O = feed conditions
P = reactor pressure, lb./sq. in. abs.
P_C = condenser pressure, lb./sq. in. abs.
Q_G = rate of heat generation, B.t.u./hr.
Q_R = rate of heat removal, B.t.u./hr.
Q_S = steady state heat load, B.t.u./hr.
R = perfect gas constant, B.t.u./(lb.-mole) (°R.)
R_C = vapor flow resistance, (lb./sq. in.) (hr.^{2})/lb.^{2}
S = steady state
T = reactor temperature, °F.
T_C = condenser temperature, °F.
T^{Set} = controller setpoint, °F.
T_J = jacket temperature, °F.
T_{CR} = critical temperature, °F.
U = overall heat transfer coefficient, B.t.u./(hr.) (sq. ft.) (°F.)
V = reactor holdup, lb.
V_J = condenser coolant holdup, lb.
W = refrigerant flow rate, lb./hr.
W_J = coolant flow, lb./hr.
α = pre-exponential factor, hr.$^{-1}$
ϕ = vapor pressure function, lb./sq. in. abs.
τ = time constant, hr.

LITERATURE CITED

1. Aris, Rutherford, and N. R. Amundson, *Chem. Eng. Sci.*, **7**, No. 3, 121 (1958).
2. Baddour, R. F., et al., *ibid.*, **20**, 281, 297 (1965).
3. Barkelew, C. H., *Chem. Eng. Progr. Symposium Ser. No. 25*, **55**, 37 (1959).
4. Batke, T. L., et al., *ISAJ*, 14 (January, 1957).
5. Berger, J. S., and D. D. Perlmutter, *A.I.Ch.E. J.*, **10**, No. 2, 233 (1964).
6. Bilous, O., and N. R. Amundson, *ibid.*, **1**, 4, 513 (Dec. 1955).
7. Boynton, D. E., et al., *Ind. Eng. Chem.*, **51**, No. 4, 489 (April, 1959).
8. Cowley, P. E. A., and D. E. Johnson, *ISA Conf. Preprint 5.3-2-64* (October, 1964).
9. Dassau, W. J., and G. H. Wolfgang, *Chem. Eng. Progr.*, **59**, No. 4, 43 (April, 1963).
10. Douglass, J. M., et al., *Ind. Eng. Chem. Fundamentals*, **1**, No. 4, 253 (November, 1962).

10*a*. Ellingsen, W. R., and N. H. Ceaglske, *A.I.Ch.E. J.*, **5**, No. 1, 30 (March, 1959).

10*b*. Fangel, P., *Chem. Eng. Sci.*, **21**, 49 (1966).

11. Foss, A. S., *Chem. Eng. Progr. Symposium Ser. No. 25*, **55**, 47 (1959).
12. Gall, C. E., and Rutherford Aris, *Can. J. Chem. Eng.*, 16 (February, 1965).
13. Gee, R. E., et al., *Chem. Eng. Progr.*, **50**, 497 (1954).
14. Harriott, Peter, "Process Control," McGraw-Hill, New York (1964).
15. ———, *Chem. Eng.*, **68**, 165 (May 15, 1961); 81 (May 29, 1961).
16. Harris, J. T., and R. S. Schecter, *Ind. Eng. Chem. Proc. Res. Develop.*, **2**, No. 3, 245 (July, 1963).

16*a*. Leathram, J. F., et al., *A.I.Ch.E. J.*, **10**, 16 (1964).

16*b*. Luus, R., and Leon Lapidus, *Chem. Eng. Sci.*, **21**, 159 (1966).

17. Nemanic, D. J., et al., *Chem. Eng. Sci.*, **11**, 199 (1959).

17*a*. Paradis, W. D., and D. D. Perlmutter, *A.I.Ch.E. J.*, **12**, No. 1, 130 (1966).

18. Raymond, L. R., and N. R. Amundson, *Can. J. Chem. Eng.*, 173 (August, 1964).
19. Schmitz, R. A., and N. R. Amundson, *Chem. Eng. Sci.*, **18**, 265, 391, 415, 447 (1963).
20. Solheim, O. A., *Chr. Michelsen Inst. Rept. No. 56.2/OAS 1 and 2* (1959).
21. Tinkler, J. D., and D. E. Lamb, *Chem. Eng. Progr. Symposium Ser. No. 55*, **61**, 155 (1965).
22. Van Heerden, C., *Ind. Eng. Chem.*, **45**, No. 6, 1242 (June, 1953).
23. ———, *Chem. Eng. Sci.*, **8**, 133 (1958).
24. Warden, R. B., et al., *ibid.*, **19**, 149, 173 (1964).
25. Weisser, E. P., *Chem. Eng. Progr.*, **61**, No. 4, 86 (April, 1965).
26. Williams, T. J., *Control Eng.*, 100 (July, 1958).
27. Wilson, K. B., *Trans. Inst. Chem. Eng.*, **24**, 77 (1946).

Manuscript received August 5, 1965; revision received December 1, 1965; paper accepted January 14, 1966. Paper presented at A.I.Ch.E. Philadelphia meeting.