Effect of Inert Venting on the Stability of Autorefrigerated Batch Reactors

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Removal of the exothermic heat of chemical reactions by autorefrigeration (vaporization of a liquid phase) is frequently used in continuous and batch chemical reactors. The vapor thus generated is usually liquified in a condenser and the condensate returned to the reactor.

This paper studies the effects of the formation of an inert gas by-product on the stability and control of batch autorefrigerated reactors.

Stability is shown to be strongly influenced by the production of these inerts because their buildup in the condenser reduces heat removal capacity. Inert buildup can be reduced by venting, but excessive venting results in a loss of not only inerts but also of the volatile components in the system. This leads to higher reactor temperatures, faster reaction rates and instability.

Digital simulation of a numerical example illustrates the effects of various parameters.

Previous papers (*4*, *5*) have considered the stability of perfectly and imperfectly mixed autorefrigerated reactors. The effects of removing the exothermic heat of reaction by evaporative cooling, instead of by conventional cooling jackets or coils, was studied for single reactions in a reactor/condenser system. The decrease in latent heat of vaporization near the critical temperature was shown to be a source of positive feedback. Incomplete mixing was shown to significantly influence reactor stability owing to the occurrence of spatial concentration and temperature gradients (that is, hot spots).

The purpose of this paper is to study the effects of the formation of an inert gas by-product on the stability and control of batch autorefrigerated reactors. These inerts can be formed by simultaneous or consecutive reactions. They accumulate in the condenser and reduce heat removal capacity by lowering the heat transfer film coefficient on the process side (due to the effect of the noncondensible gas on the simultaneous heat and mass transfer processes) and by lowering the differential temperature driving force (due to the lower dew point temperature).

The obvious strategy to prevent condenser blanketing is to vent off the inert as it is formed. It is not so obvious, however, that too much venting can also result in instability. If other volatile components are also lost in the vent stream, reactor temperatures will climb, in a constant pressure system, resulting in faster reaction rates and possible instability.

Hence there are upper and lower limits on the amount of venting that should be done. One approach to the problem would be to determine the best venting rate by using modern optimal control techniques such as Pontryagin's maximum principle.

In any real industrial batch reactor, however, there are batch to batch variations in parameters, feed stocks, and external disturbances that would require different optimum venting rates for many batches. Also, from an equipment standpoint, a flow controller and set point generator would be required in a conventional analogue control system.

A more practical and commonly used approach to the venting control problem is illustrated in Figure 1. A single feedback controller (on pressure control) is used. Its output actuates both the valve for coolant flow to the condenser and the valve for vent flow. The valves are split-ranged by use of positioners so that the coolant valve opens first, and then the vent valve if reactor pressure exceeds the set point, usually with some overlap (see Figure 1).

This split range valve setup is the control system considered in this paper.

There are, of course, other venting control schemes that could be considered: temperature control of the process side of the condenser, controlling y by direct measurement by using an analyzer, controlling y by computing y from measured pressure and temperature (if the system is truly binary), and controlling U by calculating U from measured heat fluxes and temperatures. All these have the disadvantage of increased hardware costs.

The condenser flow configuration will also influence the effect of inert formation on stability. Either the tube or shell sides can be used for condensation. The flows of vapor and liquid can be either concurrent (with downflow of vapor) or countercurrent (with upflow of vapor). The importance of the distributed nature of the condenser will

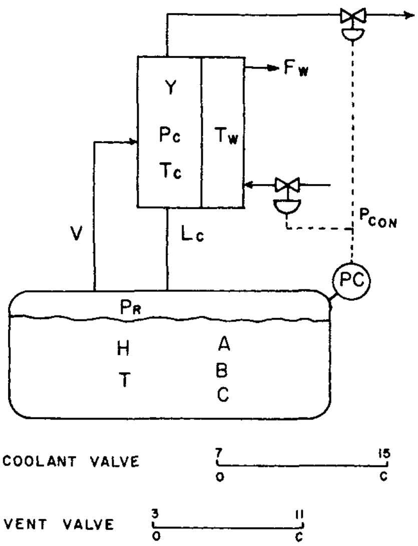

Fig. 1. Auto refrigerated batch reactor with split-range vent and coolant valves on pressure control.

TABLE 1. NUMERICAL VALUES OF PARAMETERS

A_c = 500 sq. ft.
$C_{A1} = C_{B1} = -4883.39$ °R.
C_{A2} = 12.672
C_{B2} = 10.369
C_p = 0.75 B.t.u./(lb. °R.)
C_w = 1.0 B.t.u./(lb. °R.)
E = 30,000 B.t.u./lb.-mole
H = 2400 lb.
H_c = 50 cu. ft.
H_w = 240 lb.
ΔH_R = 600 B.t.u./lb. of A
ΔH_v = 274 B.t.u./lb.
K_c = 1 lb./sq.in./lb./sq.in.
K_{EQ} = 250 lb./(hr.) (lb./sq.in.)
K_w = 10,000 lb./hr.
M_c = 50 lb./lb.-mole
R_c = 0.549×10^{-6} (lb./sq.in.)(hr.^{2})/lb.^{2}
T_{w0} = 530°R.
U_0 = 150 B.t.u./(hr. sq.ft. °R.)
α_1 = 6.37×10^{10} hr.$^{-1}$

depend on what configuration is employed. In the author's experience, tube-side downflow of vapor is the most common arrangement because of better heat transfer film coefficients and higher flooding velocities. With this configuration, the assumption of a perfectly mixed process side appears to work well. The coolant side is usually of minor importance owing to high flows and high film coefficients and small temperature rises. Therefore, a perfectly mixed coolant side is assumed in this paper.

A digital simulation of a typical reactor/condenser system is used to explore the effects of the following parameters on stability and control:

1. Vent valve capacity (K_v).
2. Initial concentration of volatile reactant charged to the reactor (A_0).
3. Ratio of product reaction rate to inert reaction rate (r).
4. The inverse dependence of the condenser overall heat transfer coefficient U on the mole fraction of inert in the condenser, y (β).

To handle the last item rigorously, a detailed distributed model of the condenser would have to be developed to include the simultaneous heat and mass transfer processes occurring. Steady state models of these systems have been discussed in the literature (*1* to *3*). Apparently no dynamic models have been developed to describe these complex systems. In order to keep the condenser model simple, an approximate relationship was used giving an inverse dependence of the overall heat transfer coefficient on the amount of inert in the condenser y:

$$U = U_0 (1 - y)^{\beta} \tag{1}$$

SYSTEM

Simultaneous reactions are assumed in which reactants A and B form products C and D:

$$A + B \xrightarrow{k_1} C$$
$$A + B \xrightarrow{k_2} D$$

Overall reaction rates of both reactions are first order, with the same activation energies E and heats of reaction ΔH_R.

A is volatile and is the principal component vaporized out of the liquid and condensed in the condenser. B and C are higher boilers. Product D is the inert that collects in the condenser unless it is vented off. It is assumed that only a binary system of perfect gases of A and D are present in the condenser. Therefore, reactant A, which is the basic component needed for vaporization to remove heat from the reactor, will be lost from the condenser if the venting is too heavy. Liquid holdup in the condenser is neglected.

The reactor is assumed to be perfectly mixed with components A, B, and C present. Other assumptions are constant heat of vaporization of A and constant and equal heat capacities of all components. The equations describing the system are given below. Numerical values of parameters are given in Table 1.

Reactor:

$$\frac{dH}{dt} = -F_v \tag{3}$$

$$\frac{d}{dt}(H\,A) = -H\,(R_1 + R_2) - F_v\,(1 - y') \tag{4}$$

$$\frac{d}{dt}(H\,B) = -H\,(R_1 + R_2) \tag{5}$$

$$\frac{d}{dt}(H\,C) = 2H\,R_1 \tag{6}$$

$$C_p \frac{d}{dt}(H\,T) = \Delta H_R\,H\,(R_1 + R_2) + L_c\,C_p\,T_c - V\,(C_p\,T + \Delta H_v) \tag{7}$$

$$R_1 = A\,B\,\alpha_1 \exp\,(-E/R\,T) \tag{8}$$

$$R_2 = A\,B\,\alpha_2 \exp\,(-E/R\,T) \tag{9}$$

$$P = P^0{}_{A(T)}\,X_A + P^0{}_{B(T)}\,X_B + P^0{}_{C(T)}\,X_C \tag{10}$$

$$V = K_{EQ}\,(P - P_R) \tag{11}$$

Condenser:

$$H_c \frac{d}{dt}(\rho_c\,y') = 2\,H\,R_2 - F_v\,y' \tag{12}$$

$$H_c \frac{d\rho_c}{dt} = V - L_c - F_v \tag{13}$$

$$P_c = P - R_c\,V^2 \tag{14}$$

$$\rho_c = M_c\,P_c/R\,T_c \tag{15}$$

$$Q_c = U\,A_c\,(T_c - T_w) \tag{16}$$

$$U = U_0\,(1 - y)^{\beta} \tag{17}$$

$$L_c = \frac{Q_c - F_v\,C_p\,(T - T_c)}{\Delta H_v + C_p\,(T - T_c)} \tag{18}$$

$$P^0{}_{A(TC)} = (1 - y)\,P_c \tag{19}$$

$$H_w\,C_w \frac{dT_w}{dt} = C_w\,F_w\,(T_{w0} - T_w) + Q_c \tag{20}$$

$$F_w = K_w\,X_w \tag{21}$$

$$F_v = K_v\,X_v \tag{22}$$

Controller and valves:

$$P_{\text{con}} = P^0{}_{\text{con}} - K_c\,(P^{\text{set}} - P) \tag{23}$$

$$X_w = (15 - P_{\text{con}})/8 \tag{24}$$

$$X_v = (11 - P_{\text{con}})/8 \tag{25}$$

Vapor pressures:

$$\left.\begin{aligned} \ln P^0{}_A &= C_{A1}/T + C_{A2} \\ \ln P^0{}_B = \ln P^0{}_C &= C_{B1}/T + C_{B2} \end{aligned}\right. \tag{26}$$

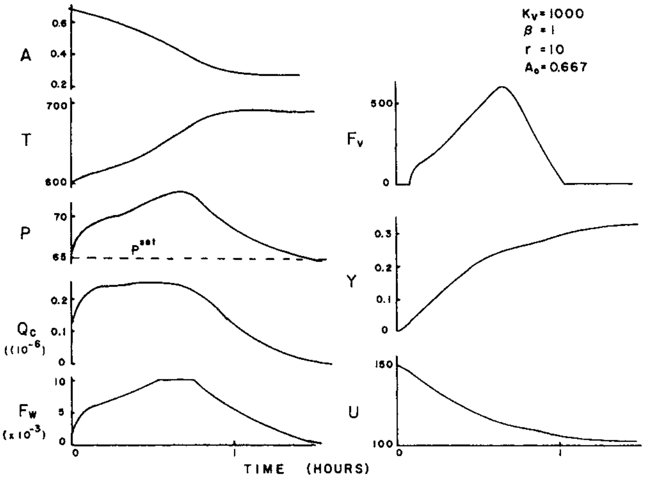

Fig. 2. Base case changes in variables with time over a batch cycle.

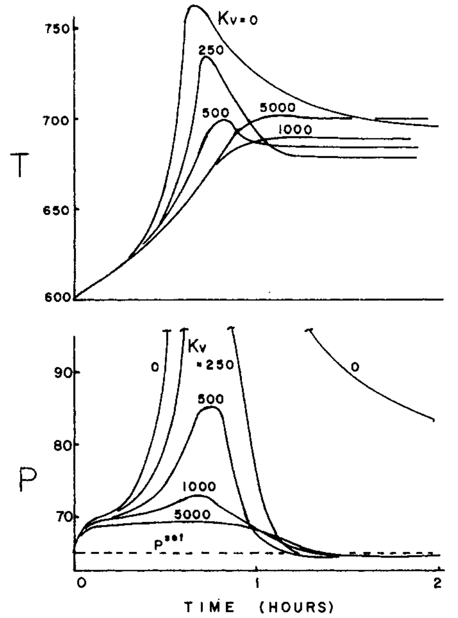

Fig. 3. Effect of vent valve size.

RESULTS AND DISCUSSION

Results of digital simulation of Equations (3) to (26) for various values of the parameters K_v, β, r, and A_0 are given in Figures 2 to 6. Batch profiles of several variables are shown in Figure 2 for the base case with

1. $K_v = 1{,}000$ lb./hr. The maximum vent flow rate, with the vent valve wide open, would be 1,000 lb./hr.
2. $\beta = 1$. Heat transfer coefficient U is linearly dependent on inert concentration in the condenser y.
3. $r = 10$. Inert formation rate is one-tenth the product formation rate.
4. $A_0 = 0.667$. Feed charged to the reactor consists of two parts of A to one part B; that is, there is a stoichiometric excess of A of 100%.

It can be seen in Figure 2 that reactant A is consumed at a variable rate during the batch, hitting a maximum between 0.5 and 0.7 hr., despite the fact that the concentrations of A and B are lower at this time than initially. This is due to the increase in temperature, as more volatile A is consumed and high boiler C is produced, having more effect on the overall reaction rate at this stage in the reaction than the reactant concentrations.

The offset in the proportional-only pressure controller is about 7 lb./sq.in. during this period of peak reactivity. The water valve goes wide open, giving 10,000 lb./hr. of coolant flow. Venting rate peaks at about 600 lb./hr. Inert concentration in the condenser builds up to about $y = 0.25$, holding fairly steady during the period of heavy venting, and finally reaches 0.35 by the end of the batch. The overall heat transfer coefficient U drops off as y increases.

Figure 3 shows the effect of various vent valve capacities on temperature and pressure profiles. Increasing the vent valve size ($K_v = 5{,}000$) gives better pressure control but also higher temperatures at the end of the batch due to the increased loss of A. These higher temperatures, which would be undesirable with a temperature-sensitive product, would be even higher if the initial amount of reactant A charged to the reactor were less. Control deteriorates rapidly with smaller vent valves. Note, however, that final temperatures are lower because less A is lost.

Figure 4 shows the effect of the dependence (β) of the overall heat transfer coefficient U on the inert concentration in the condenser gas, y. It appears that U must be

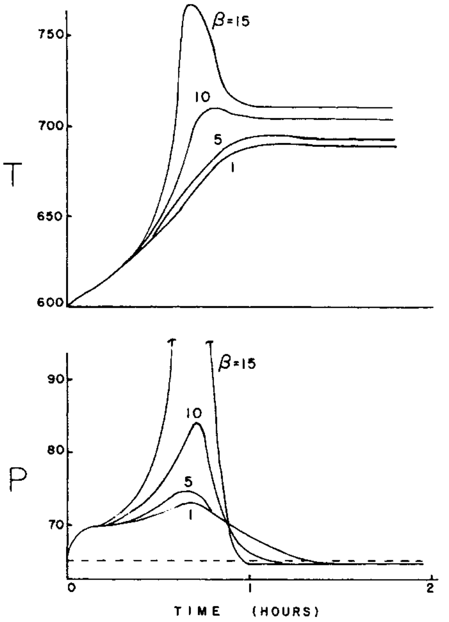

Fig. 4. Effect of dependence of U on inerts.

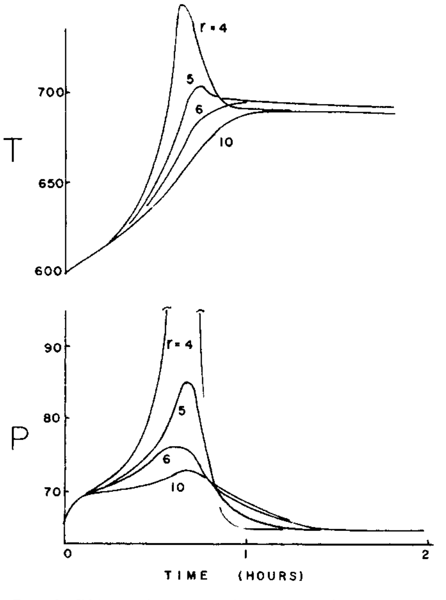

Fig. 5. Effect of product/inert reaction rates.

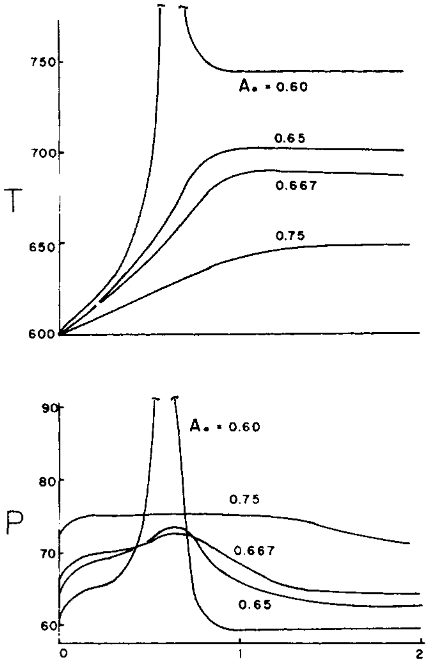

Fig. 6. Effect of initial concentration of *A*.

lowered rapidly by inert, for the numerical case studied, for the effect on control to be significant.

Figure 5 shows how instability increases as more and more inerts are formed relative to product. Larger vent valves and probably a bigger initial charge of *A* would be required to achieve good control at higher inert production rates.

Figure 6 illustrates the very pronounced effect of the initial amount of volatile reactant *A* charged to the reactor. This appears to be the parameter to which stability is most sensitive. A relatively small change in A_0 from 0.65 to 0.60 leads to a runaway reaction. Therefore, any source of variation in the amount of *A* in the reactor, for example errors in charging or losses of *A* due to leaks, can have a very pronounced effect on reactor stability. The pressure setpoints have been varied with A_0 to maintain an initial temperature of 600°R.

Although control can be improved by higher values of A_0, the use of too much *A* results in a loss of capacity for a given size reactor. It also means a raw material loss or requires additional recovery and recycle facilities. Therefore, a balance must be made between stability and process operating costs.

Control could be improved by using a larger condenser that would provide more heat transfer area. However, there is some economic optimum for this design parameter also, since capital cost increases with condenser size.

CONCLUSIONS

The formation of inerts and the strategy of venting off these inerts to prevent condenser blanketing strongly affect the stability of batch autorefrigerated reactors. The amount of inert produced, the amount of venting, and the adverse effect of inerts on heat transfer coefficients all influence the control of these systems. Stability appears to be most sensitive to the amount of volatile component initially charged to the reactor. Digital simulation of mathematical models can be conveniently employed to elucidate the complex interacting effects of both design and operating parameters on control and stability.

NOTATION

A = volatile reactant concentration, wt. fraction
A_0 = initial reactant concentration, wt. fraction
A_c = condenser heat transfer area, sq.ft.
B = nonvolatile reactant concentration, wt. fraction
C = product concentration, wt. fraction
C_{A1}, C_{B1} = vapor pressure constants temperature dependence, °R.
C_{A2}, C_{B2} = vapor pressure constants
C_p = specific heat of all components, B.t.u./lb. °R.
C_w = specific heat of coolant, B.t.u./lb. °R.
D = inert by-product component
E = reaction activation energy, B.t.u./lb.-mole
F_v = vent flow rate, lb./hr.
F_w = coolant flow rate, lb./hr.
H = reactor holdup, lb.
H_c = condenser process-side volume, cu.ft.
H_w = condenser coolant-side holdup, lb.
ΔH_R = exothermic heat of reaction, B.t.u./lb. of *A*
ΔH_v = latent heat of vaporization of *A*, B.t.u./lb.
K_{EQ} = mass transfer coefficient, lb./(hr.)(lb./sq.in.)
K_c = feedback controller gain, lb./sq.in./lb./sq.in.
K_v = vent valve coefficient, lb./hr.
K_w = coolant valve coefficient, lb./hr.
k = specific reaction rate, lb./(hr.)(cu.ft.)
L_c = liquid flow rate from condenser to reactor, lb./hr.
M_c = molecular weight condenser gas, lb./mole
P = total vapor pressure reactor liquid, lb./sq.in.
P_i^0 = vapor pressure of i^{th} component, lb./sq.in.
P_R = pressure of reactor vapor, lb./sq.in.
P^{set} = set point to pressure controller, lb./sq.in.
Q_c = heat transfer rate in condenser, B.t.u./hr.
r = ratio of product reaction rate to inert reaction rate
R = perfect gas constant, B.t.u./lb.-mole °R., or lb./sq.in./cu.ft./lb.-mole °R.
R_1, R_2 = overall reaction rate, lb./hr.
R_c = hydraulic constant for vapor flow from reactor to condenser, (lb./sq.in.)(hr.^{2})/lb.^{2}
T = reactor temperature, °R.
T_c = process-side condenser temperature, °R.
T_w = coolant-side condenser temperature, °R.
T_{w0} = inlet coolant temperature, °R.
U = condenser heat transfer coefficient, B.t.u./(hr.)(sq.ft.)(°R.)
U_0 = condenser heat transfer coefficient with no inert, B.t.u./(hr.)(sq.ft.)(°R.)
V = vapor rate from reactor to condenser, lb./hr.
X_i = mole fraction i^{th} component in reactor liquid
X_v = vent valve position
X_w = coolant valve position
y = mole fraction inert in condenser
y' = weight fraction inert in condenser
α = preexponential factor, hr.$^{-1}$
β = factor giving dependence of U on y
ρ_c = density gas in condenser, lb./cu.ft.

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