A Design Approach Based on Phase Plane Analysis: Countercurrent Reactor/Heat Exchanger with Parametric Sensitivity

A design approach based on a phase diagram of inlet temperatures is proposed for the countercurrent reactor/heat exchanger for highly exothermic reactions with inherent parametric sensitivities. The phase diagram shows the region of safe operation on a plane of feed and coolant inlet temperatures, free from runaway conditions. The boundaries surrounding the safe operation region are defined by design parameters. Simple procedures applicable to arbitrary expressions of global rate are developed for the phase diagram. The multi-pronged design problem of selecting the design parameters and operating conditions for the maximum possible conversion within the constraints due to the parametric sensitivities is condensed into and represented by a phase diagram and an analysis on the phase plane. A design alternative which eliminates the necessity of the preheater for highly exothermic reactions is discussed and the advantages are quantitatively illustrated to assert that this design should be seriously considered as a viable alternative.

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SCOPE

Chemical reactors, especially those in which highly exothermic reactions occur, are operated very carefully due to the existence of parametric sensitivities with respect to fluctuations in most of the operating variables. These reactors can be operated safely only within a narrow range of operating variables such as feed and coolant inlet temperatures due to the possibility of runaway as a result of this parametric sensitivity. For these highly exothermic reactions with the sensitivity problem, therefore, a liquid coolant instead of a gaseous coolant is used so that a better control of reactor temperature can lead to a wider range of safe operating conditions. Many studies have been reported in literature to predict the parametric sensitivity and establish runaway criteria for tubular reactors. Bilous and Amundson (1956) studied the parametric sensitivity with respect to feed concentrations and temperatures for quasi-isothermal tubular reactors and developed a method for prediction of such behavior based on transient response. Chambre (1956) and Barkelew (1959) used phase plane analysis for the general solution of the nonlinear equations for tubular reactors and established the boundary between stable and unstable regions. Oroskar and Stern (1979) extended the work of the above two investigators to obtain exact conditions leading to either stable or runaway reactor operation. Van Welsenaere and Froment (1970) took a different approach which requires comparatively less amount of computation to obtain conditions leading to runaway operation. All the above studies were confined to mostly first order kinetics and to some extent to n^{th} order kinetics. The temperature behavior in a countercurrent reactor/heat exchanger was investigated by Grens and McKean (1963).

Among those who studied new schemes of design for improved stability of reactors were Degnan and Wei (1979, 1980). They presented a theoretical analysis with experimental verification for cocurrent reactor/heat exchanger, which leads to a scheme that gives isothermal reactor conditions, decreased parametric sensitivity and improved stability, although this can be achieved only within narrow windows of operation. Somewhat less related is the work of Ampaya and Rinker (1977) among many others, who studied the effects of operating and design parameters for autothermal reactors with internal countercurrent heat exchange.

The runaway criteria presented so far in the literature were developed in such a way that some characteristic parameters of varying complexity need to be computed and compared in order to find out whether a given set of inlet conditions leads to runaway operation. The present study is undertaken with a different aim and a different approach so that for any given set of design parameters, flow rates and compositions, a phase diagram of feed and coolant inlet temperatures can be easily constructed using simple procedures. This diagram not only tells whether a set of inlet temperatures is safe from a runaway problem but also shows how safe it is. This phase diagram can also be used as a basis for the design of a countercurrent reactor/heat exchanger.

CONCLUSIONS AND SIGNIFICANCE

A convenient way of identifying the region of safe operation is to construct a phase diagram of inlet temperatures of the coolant (t_1) and the feed (T_o) on abscissa and ordinate respectively, for a given set of system parameters. A simple method is developed here to construct such a phase diagram which clearly delineates the regions of safe operation, negligible reaction and possible ignition. The boundary lines separating the safe operating region from the rest are defined exclusively as functions of system parameters. This enables one to possibly expand the boundaries of the safe operating region by proper selection of the system parameters. This, in turn, simplifies the design problem considerably.

The safe operating region consists of two distinct zones: an upper operating zone where $T_o \geq t_1$ and a lower operating zone where $T_o < t_1$. The reactor performance in the lower operating zone is generally very insensitive to even large fluctuation in feed temperature, while it is not so in the upper operating zone. Since the feed is relatively cold in the lower operating zone, reactor operation in this zone eliminates the need of a preheater of feed which is usually required in conventional operation

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using a hot feed. The exit conversion and hence the reactor preformance using a cold feed can be matched with that of a hot feed by extending the reactor; however this extension amounts to only a fraction of preheater on the basis of size and cost. Thus the design alternative with the cold feed operation can lead to a better and safer reactor operation.

The parametric sensitivity with respect to the fluctuations in coolant inlet temperature is more or less the same for the two operating zones. However this should not be a problem since one has always a better control on the coolant temperature. Nevertheless, one way of reducing the sensitivity is to independently increase the effectiveness of heat removal from the reactor by the coolant stream.

This phase plane analysis also serves as a tool to study the relative effect of various operational variables on the reactor stability and performance.

A highly exothermic vapor phase reaction is usually carried out in a fixed-bed reactor with countercurrent heat exchanger. The other cooling arrangement of using a constant-temperature bath is a limiting case of the countercurrent heat exchange. Typically, the ratio of reactor diameter to pellet size for such a reactor is set at a small value so as to avoid undesirable effects of radial dispersion. The radial gradients inside the reactor can be neglected under these conditions and a plug-flow model can be used to examine and design such reactors. Thus the steady state mass and energy balances can be written as:

$$\frac{1}{\pi R^2}\frac{dF_A}{dZ} = -R_A \tag{1}$$

$$\frac{1}{\pi R^2}\frac{d(\dot{M}C_{Pr}T)}{dZ} = R_A[-\Delta H] - \frac{2}{R}U(T-t) \tag{2}$$

$$\frac{-1}{\pi R^2}\frac{d(\dot{m}C_{Pc}t)}{dZ} = \frac{2}{R}U(T-t) \tag{3}$$

Here T and t are the reaction fluid and coolant temperatures respectively, and Z is the length coordinate along the direction of the flow of reaction fluid stream (Figure 1). For a given feed rate and composition, the global rate R_A can be expressed in terms of the conversion x of the key component A and temperature:

$$R_A = f(T,x) \tag{4}$$

Assuming that the mass flow rates $\dot{m}$ and $\dot{M}$, the specific heats, and the overall heat transfer coefficient U are constant, the above equations can be reduced to:

$$\frac{dx}{dz} = a_1 f \tag{5}$$

$$\frac{dT}{dz} = a_2 f - a_3(T-t) \tag{6}$$

$$\frac{dt}{dz} = -a_4(T-t) \tag{7}$$

where $z = Z/L$, $f = f(T,x)$, $x = (F_{Ao} - F_A)/F_{Ao}$

$$a_1 = \frac{\pi R^2 L}{F_{Ao}},\ a_2 = \frac{\pi R^2 L[-\Delta H]}{\dot{M}C_{Pr}},\ a_3 = \frac{2\pi RLU}{\dot{M}C_{Pr}},\ a_4 = \frac{2\pi RLU}{\dot{m}C_{pc}} \tag{7a}$$

Given a reaction, a designer has to choose the parameters involved in a_1 through a_4 and the reactant and coolant inlet temperatures that give the best possible performance of the reactor. The designer, however, is not free in these choices for highly exothermic reactions. The choices should be such that no runaway situation occurs, a situation in which spontaneous ignition of reaction can literally lead to explosion. It is therefore desirable to be able to tell from the reactor parameters and the inlet temperatures whether any particular choices will guarantee safe operation of the reactor. This paper concerns itself with the construction of a phase diagram of inlet temperatures (reactant and coolant) which clearly defines the safe operating ranges for arbitrary expression of global rate and with the utilization of the diagram for easy evaluation of design alternatives on the phase plane for the best possible choices of reactor parameters and operation conditions. Therefore, we first develop methods of constructing this diagram and illustrate the methods with a realistic problem. Simple runaway conditions are developed for this purpose. We then carry out an analysis on the phase plane to illustrate the utilization of the diagram and to propose a new design alternative to the conventional design practice, which appears to be obvious but has not yet been recognized for its full potential.

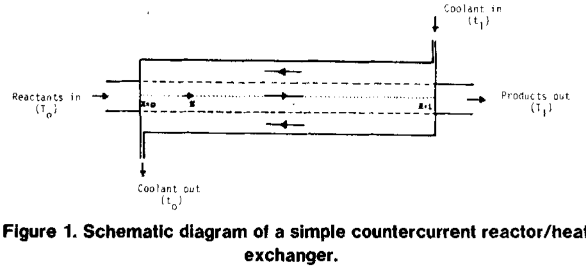

Figure 1. Schematic diagram of a simple countercurrent reactor/heat exchanger.

PHASE DIAGRAM OF INLET TEMPERATURES AND RUNAWAY CRITERIA

The question at hand for the phase diagram is to find "workable" or safe ranges of reactant (T_o) and coolant (t_1) inlet temperatures on a $T_o - t_1$ plane. For given reactor parameters, the inlet temperatures should be such that some appreciable amount of reaction should take place. On the other hand, the temperatures should be those which do not lead to runaway situation. Between these two extremes there lies the safe operating ranges, as shown in Figure 2. The phase diagram is therefore divided into three regions: the region of safe operation, that of negligible reaction and the ignition

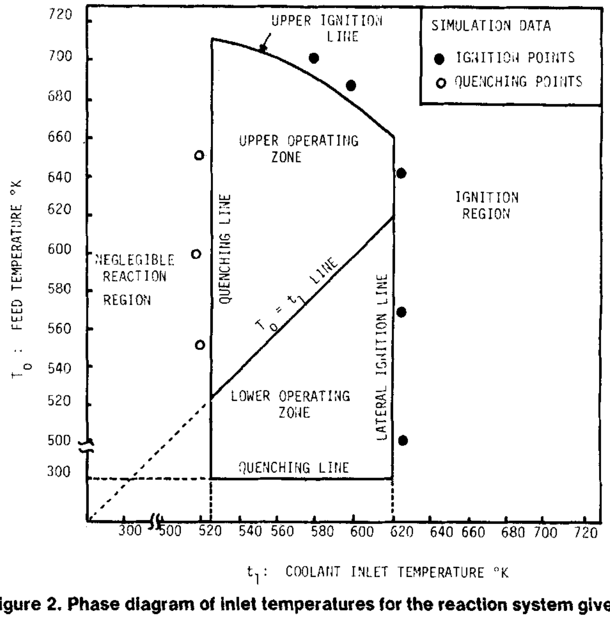

Figure 2. Phase diagram of inlet temperatures for the reaction system given in Table 1.

rating the safe region from the region of negligible reaction is to be called quenching line. The line separating the safe region from the ignition region is to be called *ignition line*. Referring to Figure 2, the ignition line in the region $T_o \geq t_1$ is to be called upper ignition line and that in the region $T_o < t_1$ the lateral ignition line for convenience. The task is then to develop expressions for these lines.

UPPER IGNITION LINE ($T_o \geq t_1$)

By definition, this line separates the upper operating zone ($T_o \geq t_1$) from the ignition region as shown in Figure 2. Suppose that ignition takes place at some point in the reactor. Let this point be z_i. Since the ignition is caused by a spontaneous, complete conversion of reactant at the point z_i, dT/dz at z_i is the highest in the reactor. When this ignition occurs, the heat generation term in Eq. 2 or 6 is much larger than the heat removal term. Therefore,

$$\left.\frac{dT}{dz}\right|_{z_i} > 0 \tag{8}$$

Furthermore, it follows from the fact that dT/dz at z_i is the highest in the reactor:

$$\left.\frac{dT}{dz}\right|_{z_i} \geq \left.\frac{dT}{dz}\right|_{z=0} \tag{9}$$

where the equality holds when $z_i = 0$. It can be deduced from Eq. 8 and 9 that

$$\left.\frac{d^2T}{dz^2}\right|_{z=0} > 0 \tag{10}$$

This condition will be satisfied if ignition takes place. Let us examine the sign of dT/dz when ignition takes place. Suppose $dT/dz|_{z=0} < 0$. Since $dT/dz|z = z_i > 0$, the derivative must change its sign between $z = 0$ and $z = z_i$ and therefore dT/dz must be zero somewhere between these two points. This point at which dT/dz is equal to zero is a minimum point since $dT/dz|_{z=0} < 0$ and $dT/dz|_{z=z_i} > 0$. The supposition $dT/dz|_{z=0} < 0$, therefore, contradicts the fact that any point satisfying $dT/dz = 0$ is a maximum point (see Appendix for the necessary and sufficient condition for a maximum). It follows then that $dT/dz|_{z=0} > 0$ if the ignition takes place. Combining this fact with Eq. 10, the following conditions will be satisfied if ignition takes place:

$$\left.\frac{dT}{dz}\right|_{z=0} \equiv T_o' > 0$$
$$\left.\frac{d^2T}{dz^2}\right|_{z=0} \equiv T_o'' > 0 \tag{11}$$

It also follows from the foregoing argument that the ignition cannot take place if

$$T_o' < 0$$

whenever $$T_o > t_1. \tag{12}$$

Typical temperature profiles for ignition and no ignition cases are shown in Figures 3A and 3B. Note that $d^2T/dz^2 > 0$ and $dT/dz < 0$ at $z = 0$ in Figure 3A which is for the no-ignition case.

In order to draw the upper ignition line based on Eq. 11, the coolant temperature at $z = 0$ (t_o) has to be known. An approximate expression for t_o in terms of T_o and t_1 is obtained under ignition conditions. If ignition occurs, the conversion is complete and the overall energy balance gives:

$$\dot{m}C_{pc}(t_o - t_1) = F_{Ao}[-\Delta H] - \dot{M}C_{pr}(T_1 - T_o) \tag{13}$$

Since a liquid coolant is used for highly exothermic reactions with sensitivity problem, the coolant sensible heat is much greater than the reactant sensible heat, i.e., $\dot{m}C_{pc} \gg \dot{M}C_{pr}$. Furthermore, the ignition point is usually near the reactor inlet when $T_o > t_1$, leaving the most part of the reactor for simple heat exchange. Under these

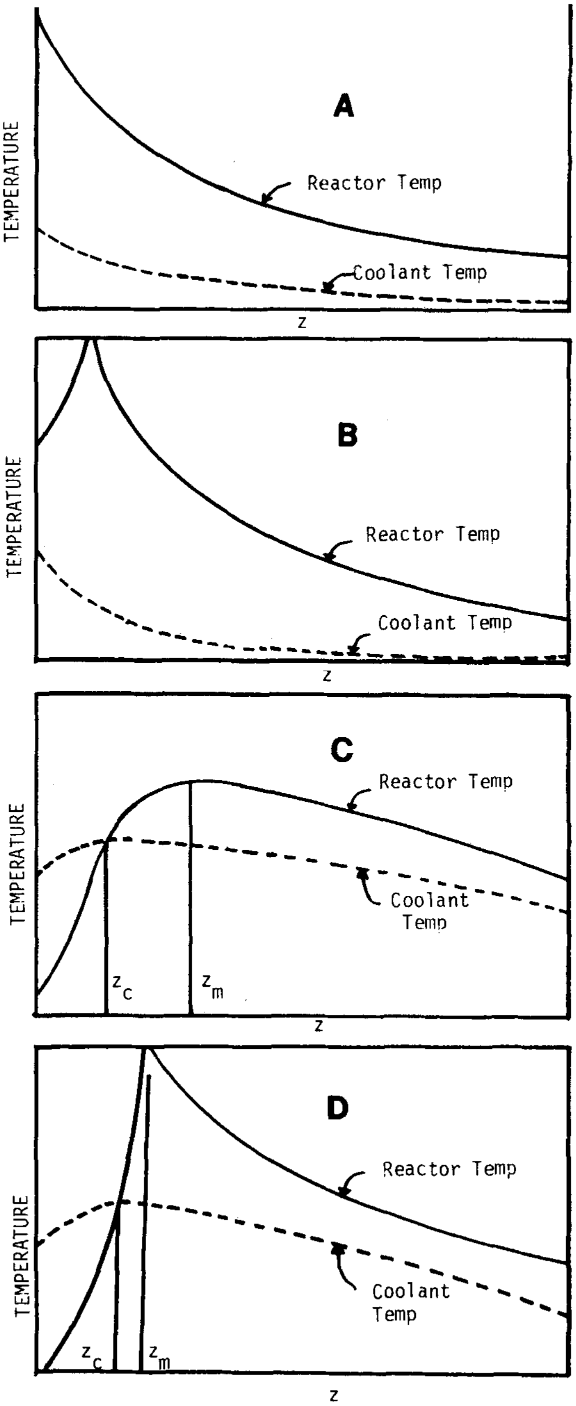

Figure 3. (A) Typical temperature profiles for ignition when $T_o > t_1$; (B) typical temperature profiles for ignition when $t_o > t_1$; (C) typical temperature profiles for safe operation when $T_o < t_1$; (D) typical temperature profiles for ignition when $T_o < t_1$.

conditions and with typical heat transfer coefficients, T_1 can be approximately by t_1. With this approximation, Eq. 13 becomes

$$t_o = t_1 + C_1 + C_2(T_o - t_1) \tag{14}$$

where

$$C_1 = F_{Ao}[-\Delta H]/\dot{m}C_{pc}$$
$$C_2 = \frac{\dot{M}C_{pr}}{\dot{m}C_{pc}} \tag{15}$$

Equation 14 gives a reasonably good value of t_o corresponding to a set of $T_o - t_1$ values that lead to ignition. Thus, the upper ignition line can be drawn as the locus of the lowest (T_o, t_1) values satisfying Eqs. 11 and 14. Note that Eq. 11 is just a sufficient condition for ignition and not a necessary and sufficient condition.

LATERAL IGNITION LINE ($T_o < t_1$)

By definition this line separates the lower operating zone ($T_o < t_1$) and the ignition region as shown in Figure 2. An important characteristic of the region in which $T_o < t_1$ is that the reactants and coolant temperatures always intersect each other as shown in Figures 3c and 3d, provided that an appreciable reaction takes place. A consequence of this behavior is that the part of the reactor with $0 \le z \le z_c$ (where z_c is the point of intersection of the temperature profiles or simply the crossover point) is equivalent to a preheater since in this section the coolant actually heats up the feed with very little reaction taking place. The rest of the reactor ($z_c < z \le 1$) acts as a normal reactor heat exchanger.

Another characteristic of this region is that regardless of safe operation or ignition, both the temperatures T and t show maxima. The maximum coolant temperature t_m should naturally occur at z_c since Eq. 7 for $z = z_c$ is obviously the necessary and sufficient condition for t_m. The maximum reactor temperature T_m occurs at a point z_m between $z = z_c$ and $z = 1$.

It is conceivable that a prediction can be made as to whether a set of inlet temperatures leads to ignition by estimating the magnitude of T_m since if ignition is to occur, it should be at z_m. Recalling that $dT/dz = 0$ is the necessary and sufficient condition for T_m, Eq. 6 results in

$$a_2 f\,(T_m, x_{zm}) - a_3\,(T_m - t_{zm}) = 0 \tag{16}$$

An approximate estimation of T_m can be made from the above equation with the assumption that: (a) $(T_m - t_{zm})$ can be approximated to $(T_m - t_1)$; and (b) x_{zm} can be approximated to zero. The former assumption is justified since: (i) T_m will be much larger than any coolant temperature generally and especially under ignition; and (ii) under the usual shell-side conditions of operation, the coolant temperature will be relatively flat. The second assumption is reasonable since normally z_m will be very close to z_c and x_{zc} as mentioned earlier is nearly zero. Applying the above two assumptions, Eq. 16 can be rewritten as

$$a_2 f\,(T_m, 0) - a_3\,(T_m - t_1) = 0 \tag{17}$$

Given the inlet conditions and the system parameters, T_m can be estimated from Eq. 17.

There are two interesting features of Eq. 17 which directly lead to the condition of ignition in the lower operating zone. First, according to Eq. 17, T_m depends on the coolant inlet temperature (t_1) only and not the feed temperature (T_o). This is reasonable since T_o is always less than t_1 in this region where regardless of the value of T_o, the reactor temperature rises to the level of coolant temperature at z_c. Usually the value of z_c is small. In other words, Eq. 17 tells that in the lower operating zone, the coolant inlet temperature is largely responsible for ignition.

The second feature can be better understood when Eq. 17 is expressed explicitly in t_1 as

$$t_1 = T_m - \frac{a_2}{a_3} f(T_m, 0) \tag{18}$$

Now let us analyze Eq. 18. The function $f(T_m)$, it should be recognized, is an exponential function of Arrhenius type. Therefore at low values of T_m, the first term in the right hand side of Eq. 18 dominates the second term while the opposite is true at higher values of T_m. Thus as the value of T_m is increased from a low value to high value, t_1 initially increases and then starts decreasing. Consequently, t_1 in Eq. 18 has a maximum with respect to T_m. Mathematically

$$\frac{dt_1}{dT_m} = 0 \text{ at a certain value of } T_m \tag{19}$$

This, however can be shown as contradictory to the physical nature of the system. Consider a physical situation where T_o is held constant and t_1 is increased progressively. It is apparent under these conditions that T_m should increase. In other words, progressively increasing values of T_m should imply progressively increased values of t_1 and at no point consistently increasing values of T_m result from or imply decreased values of t_1. Hence, Eq. 18 is a clear violation of this physical reality at higher temperatures. The anomalous behavior of Eq. 18 at higher values of T_m can be directly attributed to the failure of the assumption $X_{zm} = 0$. Actually, when the temperatures are high, appreciable amount of reaction takes place between $z = z_c$ and $z = z_m$ and thus $x_{zm} > 0$. Significant magnitudes of x_{zm} are in fact indicative of escalating reaction towards possible runaway.

Therefore we can state that the condition for possible ignition in the region where $T_o < t_1$, is the serious violation of Eq. 18. Stated differently, ignition will possibly occur for coolant inlet temperatures above the critical value of t_1 given by

$$t_1 = T_m - \frac{a_2}{a_3} f(T_m, 0) \tag{20}$$

$$\text{such that } \frac{dt_1}{dT_m} = 0$$

Thus the lateral ignition line is defined by a vertical line at the value of t_1 satisfying Eq. 20.

QUENCHING LINE

By definition, almost no reaction takes place at temperatures below the quenching line. Then the heat generation due to reaction is negligible and the reactor system is equivalent to a simple countercurrent heat exchanger. Therefore, Eqs. 6 and 7 can be reduced to

$$\frac{dT}{dz} = -a_3(T - t) \tag{21}$$

$$\frac{dt}{dz} = -a_4(T - t) \tag{22}$$

The solution for T_1 is:

$$T_1 = \frac{T_o e^{-a_3(1-a_4/a_3)} + \dfrac{t_1}{1 - a_4/a_3}\left(1 - e^{-a_3(1-a_4/a_3)}\right)}{1 + \dfrac{a_4/a_3}{1 - a_4/a_3}\left(1 - e^{-a_3(1-a_4/a_3)}\right)} \tag{23}$$

In order to develop an equation for the quenching line, one can impose as a practical matter the condition that exit conversion in the quenching region should be less than 1% if the reactor were to behave isothermally at T_1. The reason for selecting T_1 to represent the isothermal temperature is that T_1 will be the highest of T_1, t_1 and T_o if there is any appreciable reaction. Under such conditions, the concentrations will be practically unchanged and hence the rate of reaction is only a function of T_1. Using this condition in Eq. 5, the condition for the quencing region will be

$$x_1 = \int_0^1 \frac{dx}{dz}\,dz = a_1 f(T_1, 0) < 0.01 \tag{24}$$

Therefore, the equation for the quenching line is:

$$a_1 f(T_1, 0) = 0.01 \tag{25}$$

where T_1 is given by Eq. 23.

CONSTRUCTION OF THE PHASE DIAGRAM AND AN EXAMPLE

In summary, the phase diagram of inlet temperatures can be constructed based on the following steps:

(1) The phase diagram is plotted on $T_o - t_1$ plane with t_1 on abscissa and T_o on ordinate.

(2) The phase diagram is divided diagonally along $T_o = t_1$ line.

The upper section where $T_o \geq t_1$ has an upper operating zone and the lower section where $T_o < t_1$ has a lower operating zone.

(3) The upper operating zone is bounded on the left by the quenching line, on the top by the upper ignition line, and by the diagonal (Figure 1).

(4) The lower operating zone is bounded on the right by the lateral ignition line, at the bottom by the quenching line, and by the diagonal.

(5) The upper ignition line is defined as the locus of the lowest values of (T_o, t_1) satisfying the conditions.

$$T_o' > 0 \text{ and } T_o'' > 0 \tag{26}$$

with $$t_o = t_1 + C_1 + C_2(T_o - t_1)$$

(6) The lateral ignition line is the vertical line at t_1 defined by

$$t_1 = T_m - \frac{a_2}{a_3} f(T_m, 0) \tag{27}$$

such that $$\frac{dt_1}{dT_m} = 0. \tag{28}$$

(7) The quenching line is defined by

$$a_1 f(T_1, 0) = 0.01 \tag{29}$$

where T_1 is as given by Eq. 23.

In order to illustrate the construction method, a realistic problem involving a general hydrocarbon oxidation process is considered. The reaction system similar to the one treated by Froment and Bischoff (1979) and Van Welsenaere and Froment (1970) is summarized in Table 1. A vapor-phase hydrocarbon mixed with oxygen and inerts is fed to a fixed-bed catalytic reactor with countercurrent heat exchanger. The reactor consists of 2,500 tubes of 3 m long and 2.5 cm diameter. The hydrocarbon concentration in the feed is 1.5 mol% in excess oxygen. Under these conditions a single, pseudo first-order irreversible reaction is assumed to take place:

$$R_A = r_A \rho_B = 8.5(10^7) \exp(-13{,}636/T) P_A \rho_B$$

Since the concentration of the key reactant is very low (1.5 mol%), the total number of moles in the reactor gas stream can be assumed constant and the rate expression can be written as

$$R_A = r_A \rho_B = 8.5(10^7) \exp(-13{,}636/T) P y_{Ao}(1 - x) \rho_B \tag{30}$$

where P is total pressure and y_{Ao} is feed mole fraction of the hydrocarbon. It follows from Eqs. 4 and 30, that f for the system is given by

$$f = k_o \exp(-13{,}636/T) P y_{Ao}(1 - x) \rho_B \tag{31}$$

TABLE 1. REACTION SYSTEM OF HYDROCARBON OXIDATION

Reactor: 2,500 packed tubes of 3 m long and 2.5 cm diameter

Parameters	
Reactor Length (L)	3m
Reactor Radius (R)	1.25 cm
Mole Fraction of Hydrocarbons in Feed (y_{Ao})	0.015
Molecular Weight of Feed (MW)	29.5 kg/kmol
Feed Mass Velocity or Mass Flow Rate per Area ($\overline{M}$ or $\dot{M}/N\pi R^2$)	5,000 kg/m²·h
Number of Tubes (N)	2,500
Coolant Mass Rate ($\dot{m}$)	1.0(10⁶) kg/h
Heat of Reaction ($-\Delta H$)	1.28(10⁶) kJ/kmol
Average Specific Heat of Gas Mixture (C_{pr})	1.0 kJ/kg·K
Average Specific Heat of Coolant (C_{pc})	4.0 kJ/kg·K
Overall Heat Transfer Coefficient (U)	3.5(10²) kJ/m²·h·K
Pre-Exponential Factor (k_o)	8.5(10⁷) kmol/kg·h
Activation Energy Divided by Gas Constraint (G)	1.3636(10⁴) K
Catalyst Bed Density (ρ_B)	1.3 (10³) kg/m³
Total Pressure (P)	1 atm
Pellet Diameter (d_p)	3 mm
Feed Temperature (T_o)	Variable (≥ 300 K)
Coolant Inlet Temperature (t_1)	Variable

Since the reactor consists of 2,500 tubes, a_1 through a_4 in Eqs. 5 through 7 should be written appropriately for the system as

$$a_1 = \frac{L[MW]}{\overline{M} y_{Ao}}, \quad a_2 = \frac{L[-\Delta H]}{\overline{M} C_{pr}}, \quad a_3 = \frac{2LU}{\overline{M} C_{pr} R}, \quad a_4 = \frac{2N\pi RLU}{\dot{m} C_{pc}} \tag{32}$$

where $\overline{M}$ and $[MW]$ are the mass velocity and average molecular weight of the reaction fluid and N is the number of tubes. We will follow the procedure summarized above to construct the phase diagram in Figure 1 for the reaction system given in Table 1.

Quenching Line

According to the item (7) mentioned earlier, it is defined by

$$T_1 \simeq t_1 + (T_o - t_1) \exp(-33.6)$$

and $$1.956(10^9) \exp(-13{,}636/T_1) = 0.01 \tag{33}$$

Since $e^{-33.6}$ is negligibly small, $T_1 = t_1$ practically and hence the quenching line is given by a straight line parallel to ordinate at t_1 such that $1.956(10^9)\exp(-13{,}636/t_1) = 0.01$, or $t_1 = 525$ K. Consequently, the quenching line for the upper operating zone is given by $t_1 = 525$ K. The quenching line for the lower operating zone is given by T_o = minimum available feed temperature. In this case it is assumed that $T_o = 300$ K (room temperature) is the quenching line for the lower operating zone. These lines are shown in Figure 2.

Upper Ignition Line

According to the item (5) mentioned earlier, this line is obtained from:

$$0 < T_o' = 1.27(10^{12}) \exp(-13{,}636/T_o) - 33.6(T_o - t_o) \tag{34A}$$

$$0 < T_o'' = \exp(-27{,}272/T_o)\{2.21(10^{28})/T_o^2 - 2.49(10^{21})\} - \exp(-13{,}636/T_o)\{5.83(10^{17})(T_o - t_o)/T_o^2 + 4.28(10^{13})\} + 1.11(10^3)(T_o - t_o) \tag{34B}$$

and $$t_o = t_1 + 13.31 + 0.015(T_o - t_1) \tag{34C}$$

For a given value of t_1, Eq. 34C gives t_o in terms of T_o, which can be substituted into Eqs. 34A and 34B. Then, the lowest value of T_o which satisfies Eqs. 34A and 34B can be calculated. Since the quenching line is given by $t_1 = 525$ K, the T_o values corresponding to t_1 = 525, 550, 575, 600, 625, etc. have been calculated. A continuous curve drawn through these (T_o, t_1) points is the upper ignition line as shown in Figure 2.

Lateral Ignition Line

According to the item (6) presented previously, this line is given by

$$t_1 = T_m - 3.79(10^{10}) \exp(-13{,}636/T_m)$$

$$\text{such that} \quad \frac{dt_1}{dT_m} = 0 \tag{35}$$

Therefore the lateral ignition line is the vertical line at $t_1 = 621$ K. This line is shown in Figure 2.

Using all the above equations and following the stepwise procedures given earlier [items (1) through (4)], the phase diagram of inlet temperatures is plotted as shown in Figure 2 for the present problem. In order to check the reliability of the procedures, the temperatures corresponding to the onset of ignition and the quenching region are calculated numerically using the original system equations and plotted in Figure 2 for comparison. It is seen that the phase diagram predicts the true nature of the reactor behavior very closely.

PHASE PLANE ANALYSIS

The design problem for a reactor/heat exchanger is to choose reactor length (L), reactor diameter (R), overall heat transfer coefficient (U), coolant flow rate ($\dot{m}$), feed rate ($\dot{M}$), feed composition (y_{Ao}) and inlet temperatures (T_o and t_1) in such a way that desired (optimum) output of the product is achieved, yet safe from any possible runaway due to uncontrollable fluctuation in the operating variables. If the reaction is diffusion-affected, the catalyst pellet size will be an additional parameter to be considered. Due to the large number of design and operation variables involved, the design problem is generally very complicated and there is always a need for a systematic approach to tackle this multifaceted design problem.

It will be shown in this section how the phase diagram can be utilized to develop a systematic scheme to simplify the design problem considerably. First of all it should be realized that two of the most important operation variables are T_o and t_1 in the sense these are the most susceptible to unexpected fluctuations during the reactor operation. This is the main reason to select T_o and t_1 as the bases of the phase diagram. All the other operation variables along with the design variables are lumped into and represented by the system parameters a_1 through a_4. It should be recalled that the parameters a_1 through a_4 are the coefficients involved in the general conservation equations of the reactor.

For any given set of system parameters, the phase diagram of inlet temperatures can be easily constructed by following the procedures developed earlier. As stated earlier the quenching and ignition lines of the safe operating region are defined exclusively by the parameters a_1 through a_4. One of the main thrusts of the design problem is the proper choice of these parameters such that the reactor can be operated safely over a wider range of temperature, since this allows to achieve higher levels of conversion. Thus the design problem can be condensed into a single problem of expanding the boundaries of safe operating region by moving the quenching and ignition lines outward or upward. However it should be realized that this should not be done at the expense of augmenting the reactor size or lowering the throughput considerably.

Consider the illustrative example of hydrocarbon oxidation. In order to see how the boundaries of the phase diagram can be expanded by proper selection of the design and operational variables, the Eqs. 33, 34 and 35 defining the quenching the ignition lines should be rewritten as the following:

$$\text{Quenching line:} \quad a_1' e^{-G/t_1} = 0.01$$

$$\text{Upper ignition line:} \quad a_2' e^{-G/T_o} - a_3(T_o - t_o) > 0$$

$$\left[(a_2')\frac{G}{T_o^2} - a_1'a_2'\right] e^{-2G/T_o} - \left[a_2'a_3\left\{1 + \frac{G}{T_o^2}(T_o - t_o)\right\}\right] e^{-G/T_o} + a_3(a_3 - a_4)(T_o - t_o) > 0$$

$$\text{Lower ignition line:} \quad t_1 = T_m - \frac{a_2'}{a_3} e^{-G/T_m}$$

$$\frac{dt_1}{dT_m} = 0$$

where

$$G = \text{activation energy/gas constant}$$
$$a_1' = k_o PL(MW)/\overline{M}$$
$$a_2' = k_o P y_{Ao} L(-\Delta H)/\overline{M} C_{Pr}$$
$$a_3 = 2LU/\overline{M} C_{Pr} R$$
$$a_4 = 2N\pi RLU/\dot{m} C_{Pc}$$

From the above equations, it is obvious that the quenching line can be pushed to the left of the phase diagram by increasing a_1'. In the case of the upper ignition line, decreasing a_2' requires higher feed temperatures for T_o' and T_o'' to be positive and thus pushes this line upward. The lateral ignition line can be pushed to the right by decreasing a_2'/a_3. Thus the best design policy is to

$$\text{Maximize } a_1' \text{ or } PL/\overline{M}$$
$$\text{Minimize } a_2' \text{ or } P y_{Ao} L/\overline{M}$$
$$\text{and} \quad \text{Maximize } a_3 \text{ or } LU/\overline{M}R$$

Since these parameters are interlinked by the design variables, the best policy requires an optimal search. Nevertheless, it can be readily seen that low y_{Ao} and R and high U irrespective of the values of the other variables lead to the best policy, though low y_{Ao} and R values result in decreased throughput. In this context, it is interesting to note that the reactor operation in the lower operating zone simplifies the design policy since maximization of both a_1' and a_3' is sought. In fact, operation in the lower operating zone leads to a more stable and economical reactor performance, which is discussed in the immediately following text.

REACTOR CONFIGURATION WITHOUT PREHEATER

The phase diagram of Figure 2 reveals an important point. For a given coolant inlet temperature, any point in the upper operating zone is more sensitive to temperature fluctuations than a point in the lower operating zone. This sensitivity problem is shown in Figure 4. As evident from Figure 4 it is always better to operate the reactor in the lower operating zone than the upper operating zone from the sensitivity viewpoint. This fact leads to an interesting design alternative: a countercurrent reactor/heat exchanger without preheater. In this regard, it is notable that the feed temperatures are usually chosen from the upper operating zone in conventional operation.

The potential advantages, at least in some cases, of not using a preheater for highly exothermic reactions have not been fully recognized. In short, the advantages of not using a preheater are twofold: elimination of the sensitivity problem with respect to changes in reactant inlet temperature and a reduction in fixed costs due to the elimination of the preheater. Suppose for the example considered that the coolant inlet temperature is chosen to be 600 K. Also suppose that the feed is available at room temperature or 300 K. For a feed of 600 K, the conversion is about 30%. The feed without preheating (300 K) results in a 27.5% conversion. If we were to tolerate a decrease of 2.5 percentage points in conversion, the preheater could be eliminated from the reactor configuration. An alternate comparison can be based on the same conversion, which requires a longer reactor for the configuration without preheater. For the example being considered, an increase of 15% in reactor length is required to attain 30% conversion: a tradeoff between the cost of a preheater and the additional reactor cost corresponding to the 15% increase. This tradeoff is summarized in Table 2 for various levels of conversion. The preheater length is calculated assuming that the exit stream from the reactor is used to exchange heat with the cold feed in a preheater (heat exchanger) geometrically and thermally similar to the main reactor/exchanger system. The mean temperature difference across the heat ex-

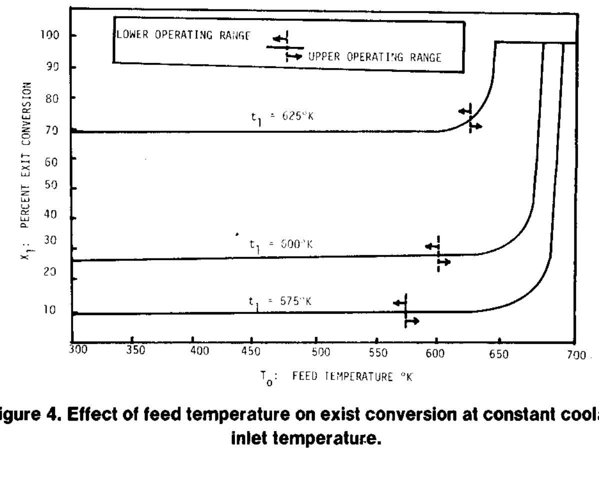

Figure 4. Effect of feed temperature on exist conversion at constant coolant inlet temperature.

TABLE 2. COMPARISON OF NEW DESIGN WITH CONVENTIONAL DESIGN

Scheme	Coolant Inlet Temperature (t_1), K	Exit conversion (x_1) in percentage	Reactor Length, m	Preheater Length, m	Total Length, m
Conventional Design with 600 K Feed	575	11.0	3.00	2.65	5.65
New Design with 300 K Feed	575	11.0	3.45	0.00	3.45
Conventional Design with 600 K feed	600	29.5	3.00	2.65	5.65
New Design with 300 K Feed	600	29.5	3.25	0.00	3.25
Conventional Design with 600 K Feed	625	71.5	3.00	2.65	5.65
New Design with 300 K Feed	625	71.5	3.20	0.00	3.20

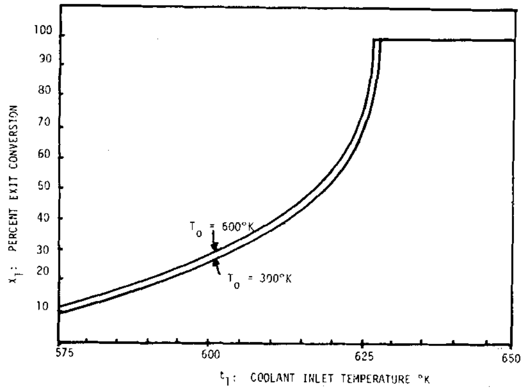

Figure 5. Effect of coolant inlet temperature on exit conversion at constant feed temperature.

changer is assumed to be 10 K. It is apparent from the table that the equipment cost required for such an increase in reactor volume is far less than that of a preheater. It is seen then that the preheater can be eliminated at a minimal cost, resulting in less overall fixed costs.

The sensitivity with respect to coolant inlet temperature remains almost the same for both configurations, Figure 5. The sensitivity problem with respect to coolant inlet temperature is much less of a problem than that with respect to feed temperature since one has a much better control over the coolant temperature. However, this precludes the attainment of exist conversions in excess of 60% since around this region even a small positive deviation in the coolant temperature leads to runaway, as shown in Figure 4, no matter what the feed temperature is. One way of circumventing this predicament is to realize that faster heat removal from the reactor flattens the reactor temperature profiles and thus the reactor becomes operable even at coolant temperatures higher than 625°K. This can be accomplished by increasing the value of a_3. This parameter can be varied independently of the other a's. The results of a_3 increased by 50% to 150% are shown in Figures 6 and 7. It is

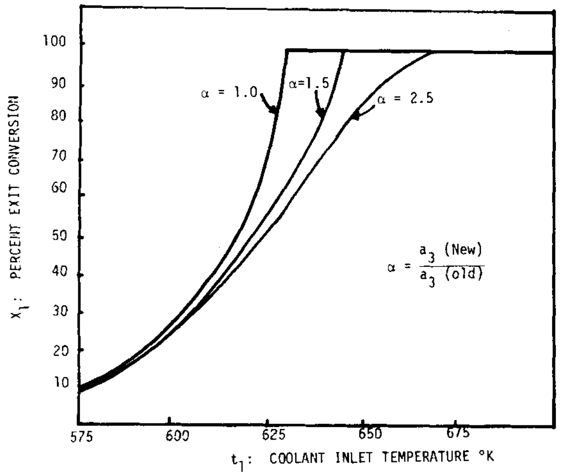

Figure 6. Effect of increasing a_3 on coolant inlet temperature sensitivity for hot feed.

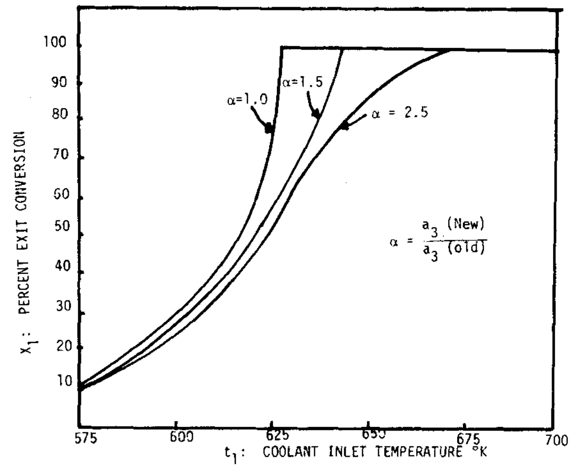

Figure 7. Effect of increasing a_3 on coolant inlet temperature sensitivity for cold feed.

seen that the degree of insensitivity with respect to the coolant temperature is slightly better with the configuration with no preheater than with preheater.

The potential advantages of eliminating a preheater therefore are: 1) elimination of sensitivity problem with respect to large variations in feed temperature; 2) a reduction in fixed costs; and 3) improved insensitivity with respect to changes in coolant temperature even though the improvement is only slight. In view of these potential advantages, the reactor configuration with no preheater should be considered as an alternative in any design of a countercurrent reactor/heat exchanger.

IN CONCLUSION

(1) The phase plane analysis proposed here presents a clear and convenient way to identify the regions of safe operation for any given set of system parameters, which considerably simplifies the design problem for the reactor systems under consideration.

(2) Even though a relatively simple example is considered here, the analysis can be extended to a variety of systems including those involving parallel and consecutive reactions. However in those cases the procedure becomes somewhat complicated since the reactor performance is a function of selectivity in addition to conversion.

(3) The design alternative considered here may find its usefulness for systems involving highly exothermic reactions. However for moderately exothermic reactions, the alternative may not necessarily be advantageous.

(4) A potential application of this work lies with the reactors which experience decay of catalytic activity with time due to catalyst deactivation. Since the operation of such reactors requires an optimal temperature progression, the design alternative may simplify the process of optimal study for such cases.

(5) In the case of a constant-temperature bath for cooling, simply set $a_4 = 0$ and all the results obtained were valid. Furthermore, the approximation regarding t_1 and T_1 is not necessary. Note that $t_1 = t_o$ = constant when the constant-temperature bath is used.

(6) If a reactor is designed in such a way that there exist signif-

icant radial gradients, the effects are to narrow the range of safe operating conditions. The effects of axial dispersion, although negligible at typical operating conditions, are to widen the range somewhat.

NOTATION

a_j = a coefficient in the conservation equations with j = 1,2,3,4
c_j = a coefficient in the ignition line equations with j = 1,2
C_p = specific heat
d_p = particle diameter of the catalyst
F_j = molar flow rate of species j
f = a function of temperature and conversion
G = activation energy divided by gas constant
k_o = pre-exponential factor of rate constant
L = length of the reactor
$\overline{M}$ = mass velocity of the reaction fluid stream
$\dot{M}$ = mass flow rate of the reaction fluid stream
$[MW]$ = average molecular weight of the reaction fluid stream
$\dot{m}$ = mass flow rate of the coolant stream
N = total number of tubes of the reactor
P = total pressure inside the reactor
P_j = partial pressure of species j
R = radius of the reactor tube
R_j = reaction rate of species based on unit reactor volume
r_j = reaction rate of species j based on unit mass of catalyst bed.
T = temperature of the reaction fluid stream
t = temperature of the coolant stream
U = overall heat transfer coefficient for the reactor/heat exchanger.
x = conversion of the key component
x_{zm} = x at $z = z_m$
x_{zc} = x at $z = z_c$
y_j = mole fraction of species j
Z = length coordinate
z = normalized Z coordinate
z_i = z at the point of onset of ignition
z_c = z at the crossover point of the reactor and coolant temperature profiles
z_m = z at the point of maximum reactor temperature

Greek Letters

α = a_3 (new)/a_3 (old)
$[-\Delta H]$ = molar exothermic heat of reaction
ρ_B = average bed density

Superscripts

$'$ = first derivative with respect to z
$''$ = second derivative with respect to z

Subscripts

0 = value at $z = 0$
1 = value at $z = 1$
A = one of the reactant species, usually the key component
C = value for the coolant stream
m = maximum value
r = value for the reaction fluid stream

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APPENDIX A: MAXIMUM REACTOR TEMPERATURE—NECESSARY AND SUFFICIENT CONDITION

In general, the necessary and sufficient conditions for maximum in T with respect to z are $dT/dz = 0$ and $d^2T/dz^2 < 0$ at $T = T_m$ or $z = z_m$. Expressing in terms of Eq. 6

$$\left.\frac{dT}{dz}\right|_{zm} = a_2 f|_{zm} - a_3(T - t)|_{zm} = 0$$

or

$$a_2 f|_{zm} = a_3(T - t)|_{zm} \tag{A1}$$

and

$$\left.\frac{d^2T}{dz^2}\right|_{zm} = a_2 \left.\frac{df}{dz}\right|_{zm} - a_3 \left.\frac{dT}{dz}\right|_{zm} + a_3 \left.\frac{dt}{dz}\right|_{zm} < 0 \tag{A2}$$

Since

$$f = f(T,x)$$

$$\frac{df}{dz} = \frac{\partial f}{\partial x}\cdot\frac{dx}{dz} + \frac{\partial f}{\partial T}\cdot\frac{dT}{dz}$$

Using Eqs. 5 and 7, we obtain that

$$\left.\frac{dx}{dz}\right|_{zm} = a_1 f|_{zm} \tag{A3}$$

$$\left.\frac{dt}{dz}\right|_{zm} = a_4(T_m - t_{zm}) \tag{A4}$$

Substituting Eqs. A1, A3 and A4 in Eq. A2, we get

$$\left.\frac{d^2T}{dz^2}\right|_{zm} = a_2 f|_{zm}\left\{a_1 \left.\frac{\partial f}{\partial x}\right|_{zm} - a_4\right\} \tag{A5}$$

Note that in Eq. A5,

$$a_1 > 0$$
$$a_2 > 0$$
$$a_4 > 0$$
$$\text{and } f|_{zm} > 0$$

Except for negative order type reactions, $\partial f/\partial x$ is always negative. For example, if the reaction is of first-order kinetics

$$f = k_o e^{-G/T}\rho_{Ao}(1 - x)$$

$$\frac{\partial}{\partial x} = -k_o e^{-G/T}\rho_{Ao} \text{ which is always negative.}$$

Therefore, for most of the reactions, the condition for the maximum reactor temperature is that given by Eq. A1.

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