Use of a Second Endothermic Reaction to Desensitize a Tubular Reactor

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Three parametric sensitivity criteria were examined for application to a pseudohomogeneous tubular reactor system, in which both methanol dehydration (exothermic) and methanol dissociation (endothermic) were catalyzed. The addition of the endothermic reaction was shown to lead to a desensitized reactor. It was illustrated, however, that the relative activities of the two catalysts should be somewhat similar to maintain the overall conversion of the resulting reactor for a given residence time.

The three criteria investigated tended to disagree with one another more, as the system was made less sensitive by the addition of more endothermic catalyst. A potential application of the resulting nonsensitive reactor design would be in methanol-fueled vehicles.

Introduction

A tubular reactor is decribed as sensitive when small changes in its operating conditions result in large changes in the reactor performance (e.g., maximum temperature). Although this qualitative definition of a sensitive reactor is quite clear, the way in which to establish quantitative criteria indicative of this behavior, which do not depend on an arbitrarily limited temperature maximum, is not so clear. The prediction of reactor sensitivity has been the subject of numerous studies (Bilous and Amundson, 1956; Barkelew, 1959; Adler and Enig, 1964; Froment, 1967; van Welsenaere and Froment, 1970; Oroskar and Stern, 1979; Morbidelli and Varma, 1982, 1985, 1988, 1989). A criterion that ideally characterizes reactor sensitivity is sought, from which, with a suitable reactor model, an explicit relationship may be derived that defines the region of parametric sensitivity for the given reactor system. The criteria used in the derivations of various parameter relationships were reviewed concisely by Morbidelli and Varma (1985).

Many of the quoted studies, using their various criteria, have derived expressions to characterize parametric sensitivity, but for only one or more exothermic reactions. In particular, the effect of adding a second endothermic reaction on the reactor sensitivity has not been discussed. While the addition of a second catalyst (in a heterogeneous reactor) to promote such a reaction should on intuitive grounds improve the resistance of a reactor to temperature runaway, no guidelines have been reported, such as for the choice of the ratio of the two catalysts in the reactor. Indeed, it has not been proven that the addition of a second endothermic reaction would desensitize the reactor. Therefore, this article will investigate the application of three different sensitivity criteria, first to the case of one (exothermic) reaction so that the use of the criteria can be illustrated (and a basis for comparison may be established) and second to a system in which a second (endothermic) reaction is possible so that a reasonable solution may be reached regarding its desensitization. To this end, kinetic data taken from microreactor studies of two such reactions (one endothermic and the other exothermic) were used.

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Parametric Sensitivity Criteria

From Morbidelli and Varma's (1985) review of a number of approaches to the definition of sensitivity guidelines for pseudohomogeneous reactors, it is evident that the majority of studies in both chemical reactors and combustion systems have taken the behavior of the second derivative either in the plane of the temperature (T) vs. reaction coordinate [time or axial distance (x)] or in the plane of temperature vs. concen-

tration (C) to be indicative of sensitivity. These two criteria are similar but lead to very different results for the present application as will be discussed later. Van Welsenaere and Froment (1970) studied two criteria: 1. a completely different criterion based on the behavior of the maxima of the system trajectories in the phase plane (T vs. C) and 2. one based on the behavior of the second derivative in the T vs. x plane (i.e., d^2T/dx^2). These two criteria will be analyzed here. A third criterion will also be investigated, namely one proposed by Adler and Enig (1964) which the second derivative of the reactor temperature in the phase plane (d^2T/dC^2).

To illustrate the application of these criteria, they will be applied to a system discussed by Kozole and Wallace (1988) designed to improve the cold-start problems of methanol-fueled automobiles. They discuss placing a tubular reactor on board of the vehicle which would convert part of the methanol fuel to a more volatile component. One reaction considered for this purpose is the dehydration of methanol to produce dimethyl ether (DME) by

$$2CH_3OH \rightleftharpoons H_2O + CH_3OCH_3 \qquad (1)$$

This reaction is exothermic (-3.1×10^5 J/kg) so that its use would reduce the burden of the battery in supplying the energy needed to vaporize the methanol and to raise the vapor temperature to the required reactor inlet temperature. In addition, it has been shown that reaction 1 proceeds readily over a variety of acidic catalysts with equilibrium conversions (>90%) of methanol possible at temperatures as low as 150°C depending on the space velocity of the system (see Supplementary Material). In a study of the methanol to gasoline process, Chang and Silvestri (1977) showed that the dehydration of methanol to DME is also the first step in the catalyzed reactions leading to the formation of gasoline components. They showed that these subsequent reactions (from DME to hydrocarbons) are more than three times as exothermic as the methanol dehydration reaction. How much DME continues to react to form light hydrocarbons depends on the catalyst, space velocity, and the reactor temperature used.

Simply using the relationship given by Barkelew (1959) with the parameter values given later in this article for the methanol dehydration reactor, the system was shown to be potentially sensitive so that slight variations in the inlet conditions could lead to a more severe temperature excursion. If a zeolitic catalyst is used, the maximum temperature resulting from such an excursion could be sufficient to trigger further reaction of the DME to form hydrocarbons and possibly leading to an autothermal scheme. Such an excursion could lead to (practically) irreversible deactivation of the catalyst or possibly excessively high maximum temperatures. Diluting the catalyst with inert solids which is often useful in such a case to mitigate the temperature excursion would lead to an overall increase in the reactor size and would therefore be unacceptable in this application.

In an effort to desensitize the reactor it was proposed to mix a second catalyst with the dehydration catalyst which would promote methanol dissociation:

$$CH_3OH \rightleftharpoons CO + 2H_2 \qquad (2)$$

This reaction is quite endothermic (2.8×10^6 J/kg) and could, therefore, act as a sink for the heat produced by the dehydration reaction. In addition, the CO and H_2 produced meet the criteria for both volatility and suitable combustion properties needed for cold starting. In this application, however, the available energy to be supplied by the automobile battery at 10°C is limited so that only the minimum proportion of dissociation catalyst needed to mitigate or desensitize the methanol conversion reactor should be added. This article decribes the parametric sensitivity of the two reaction system and a procedure based on a simplified reactor model whereby the proportion of the two catalysts could be calculated to provide insensitive reactor operation.

Reactor Model

The mathematical treatment of a tubular, catalytic reactor can follow a path of increasingly complex models. This path can begin with a one-dimensional, pseudohomogeneous reactor, in which gas-solid transports of heat and mass are much faster than the bulk transport rates and the chemical reaction rate. Using this approach near the region of parametric sensitivity, where the absolute rates of the chemical reactions increase dramatically, is not quantitatively valid. Nevertheless, this approach was used here to investigate the question if the addition of a second endothermic reaction could keep a reactor away from sensitive behavior. As long as the system is studied in parameter regions away from sensitive behavior, the assumptions of pseudohomogeneity should be reasonably accurate. In addition, the procedure used to investigate this question is valid for any one-dimensional reactor model.

Thus, the first approximation of the heterogeneous system is made using a one-dimensional pseudohomogeneous reactor model with constant fluid density. Data were taken from a study of a wide range of methanol dehydration catalysts (crushed to 60–80 mesh) using a dilute (1,000 ppm) stream of methanol in nitrogen at linear (interstitial) velocities greater than 0.6 m/s (see Supplemental Material). A second-order kinetic expression was found to fit the integral methanol dehydration data for a wide range of catalysts,

$$r_1 = k_1[C]^2 \exp(-A_1/T) \qquad (3)$$

where r_1 is the rate of methanol dehydration (mol methanol/m^3/s) based on the interstitial volume of the reactor. While the extent of the dehydration reaction is limited by equilibrium to 80 to 90% depending on the reaction temperature, the kinetic expression used here fits the data to >65% conversion. It is felt that since the issue of sensitivity will depend on reaction rates at concentrations well away from equilibrium, it is justified to assume that the reaction is irreversible. For a zeolitic catalyst (Union Carbide LZ-Y-72), k_1 was found by least squares estimate to be 1.1×10^{17} m^3/mol/s and A_1 was 14,196 K.

One dissociation catalyst (Palladium on alumina) developed by Wickham et al. (1990) was also tested under identical conditions as above (see Supplemental Material), for which a first-order expression was found to fit the data reasonably well,

$$r_2 = k_2[C]\exp(-A_2/T) \qquad (4)$$

For this catalyst, $k_2 = 2.3 \times 10^{24}$ s^{-1}, while A_2 was found to be 22,916 K. It should be noted that other studies have shown

that the dissociation kinetics are more complex than this (Karpuk, 1990) but published data are scarce.

Karpuk and Cowley (1988) also published methanol dehydration kinetic data using higher concentrations of methanol (85 to 100%) but with larger catalyst particles. The activation energy reported for the reaction was lower than that used here, implying that mass transfer resistances may have been significant. Nevertheless, the reactor model using their kinetics also predicted a region of sensitive behavior. Finally, a large number of dehydration catalysts are available for varying activities notably means that the relative activity of the two catalysts as described by the two kinetic expressions (Eqs. 3 and 4) is a design variable to an extent. More discussion concerning the effects of this relative activity will be given below.

Conceptually, the two reaction system to be investigated now may be thought of as being packed with two different catalysts otherwise identical in physical properties (i.e., surface area, particle size, and bulk density). This simplifying assumption does not affect the procedure presented here. The problem of how much the dehydration vs. the dissociation reaction should be promoted to operate an insensitive reactor is then simply one of determining, for the given kinetic values, what fraction of the total reactor volume should be occupied by the dehydration catalyst while the remainder remains the dissociation catalyst. It is likely, however, that a single catalyst could be manufactured which would be dual-functional, catalyzing both methanol dehydration and dissociation. This is not unreasonable since the catalyst support (e.g., activated alumina or zeolite) could act as the dehydration catalyst while the dissociation catalyst could be impregnated or deposited on the surface. Such a catalyst system would more nearly satisfy the assumptions of the pseudohomogeneous reactor model.

The equations describing the material and energy balances under these simplifying assumptions are:

$$-u\frac{dC}{dx}=z_1r_1+z_2r_2 \tag{5}$$

$$u\frac{dT}{dx}=-\frac{1}{\rho_gC_p}(z_1r_1\Delta H_1+z_2r_2\Delta H_2)-2\frac{h}{\rho_gRC_p}(T-T_w) \tag{6}$$

Here z_1 and z_2 denote the fractions of the total interstitial volume associated with the dehydration and dissociation catalysts, respectively, and u is the linear velocity. The initial conditions will be denoted as C_0 and T_0 for the concentration of methanol (mol/m^3) and temperature (K). The remainder of the parameter values calculated at a mean temperature of 350 K are:

$$u=0.74 \text{ m/s}$$
$$C_p=1{,}496 \text{ J/kg/K}$$
$$\Delta H_1=-2.98\times10^5 \text{ J/kg}$$
$$\Delta H_2=2.90\times10^6 \text{ J/kg}$$
$$h=290 \text{ W/m}^2\text{/K}$$
$$R=0.002 \text{ m}$$

One-Reaction System

To understand the significant differences introduced by adding the endothermic reaction, it is useful to first discuss the simple, one-reaction case. For this case, $z_2=0$ in Eq. 5 and 6.

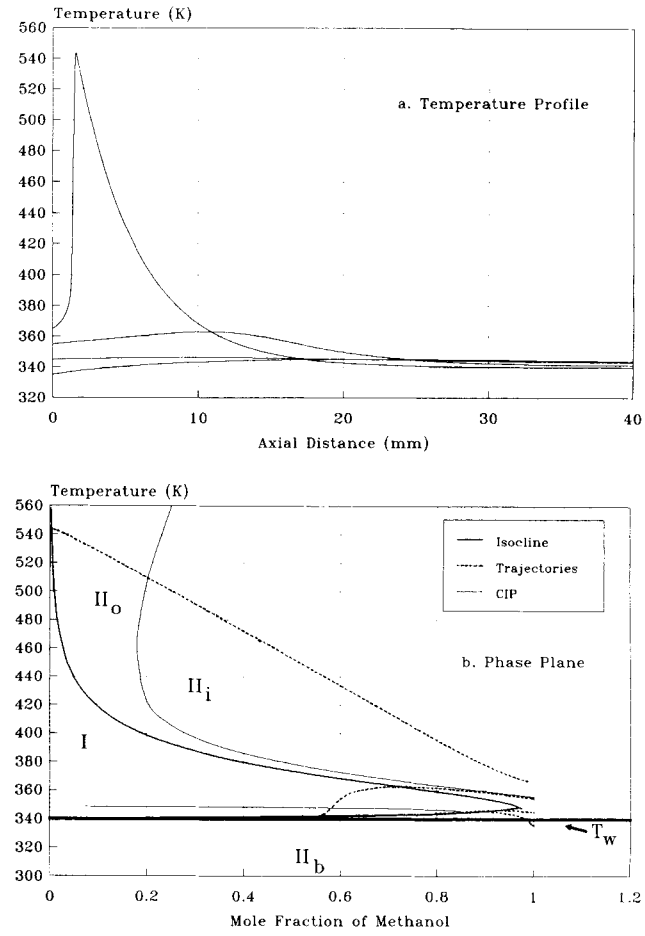

Figure 1. Tubular methanol dehydration reactor with constant wall temperature, $T_w=340$ K.

Note the regions of the phase plane as defined in the text.

The model can now be integrated numerically assuming a pure methanol feed at 1 atm. The results are shown in Figure 1a for $T_w=340$ K and four values of T_0. Clearly, the change in inlet temperature from 355 K to 365 K has a much more pronounced effect on the maximum temperature within the reactor than does the change from 345 K to 355 K. Changes in other parameter values would also lead to sensitive behavior. In any event, if a zeolitic catalyst were used as methanol dehydration catalyst, this maximum temperature could lead to further reaction of the dimethyl ether to form hydrocarbons via reactions which are significantly more exothermic thus possibly leading to an autothermal reaction scheme.

The first criterion proposed by van Welsenaere and Froment (1970) defines the region of parametric sensitivity by means of the relative behavior of the trajectories and the zero isocline of the system. The trajectories consist simply of the points $[C(x), T(x)]$ plotted in the phase plane (T vs. C) for all the values of x. The zero isocline is the curve consisting of all points (C,T), at which these trajectories have a zero slope in the phase plane (i.e., $dT/dC=0$). The zero isocline is calculated by setting dT/dx, as given by Eq. 6, equal to zero; indeed, since dC/dx is never zero for finite x (except at the singular point), the slope in the phase plane, dT/dC, is zero whenever $dT/dx=0$. It should be noted that the isocline is independent

of the initial conditions of the system, while trajectories will, of course, begin at the initial conditions. Both the trajectories and the corresponding zero isocline of the cases described in Figure 1a are given in Figure 1b. Note that each trajectory crosses the isocline with zero slope as required. Note also that each trajectory starts at the respective initial temperature (T_0), and $C/C_0 = 1$ and moves to the left. Because the reactor temperature is of paramount importance in this application, the temperature axis has been chosen to be vertical in the phase plane. This is opposite to the convention followed by van Welsenaere and Froment (1970). Their maximum (with respect to C) of the maxima curve corresponds to the right most point of the zero isocline.

The zero isocline serves to divide the phase plane into two distinct regions (I and II), as shown in Figure 1b corresponding to the inside and outside of the zero isocline. As the trajectories in Figure 1b demonstrate, those in region II rise (indicating that $dT/dx > 0$) before reaching their maxima on the zero isocline. Once they are in region I, the trajectories must drop eventually reaching the singular point $(0, T_w)$.

In their study of a similar system, van Welsenaere and Froment (1970) noted that the trajectories showing more pronounced temperature rises, i.e., which correspond to sensitive behavior, cross the zero isocline at a point above the curve's right most point. This led them to propose that this characteristic was indicative of sensitive behavior and that the trajectory which actually passed through the right most point of its corresponding zero isocline defined the critical initial conditions for a system with otherwise identical parameter values. In Figure 1b it is evident that the trajectories with inlet conditions $T_0 = 355$ and 365 K and $C/C_0 = 1$ would, under this criterion, be considered sensitive. Although the temperature profiles given in Figure 1a for these two cases do show a temperature increase, only the higher temperature case ($T_0 = 365$ K, $C/C_0 = 1$) actually appears to be sensitive in a common sense. This first criterion then appears to be somewhat conservative (cautious) although such a judgment implies that an *a priori* maximum reactor temperature has been identified. It is the intention of any of these criteria to define sensitive behavior intrinsically, without defining such a maximum temperature.

The second criterion reported by van Welsenaere and Froment (1970) involved evaluating the second derivative of $T(x)$ with respect to x to determine if an inflection point in $T(x)$ existed at a point in the reactor before x_{max} where the maximum temperature, T_{max}, is reached. This is more intuitive than the previous criterion in that if the second derivative, d^2T/dx^2, is positive at a point in the reactor before the temperature has reached its maximum, it is plausible to expect that the approach to T_{max} will be more sudden and that the value of T_{max} will be greater than if $T(x)$ were concave down from the reactor inlet to T_{max}.

The second derivative of T with respect to x for the one-reaction case is simply the first derivative of the righthand side of Eq. 6 with $z_2 = 0$ and is a function of both temperature and concentration. To apply the criterion completely, the second derivative in the T vs. x plane, d^2T/dx^2, must be evaluated for all the values of C and T along a trajectory before the point (C_{max}, T_{max}). In every case examined in this study, however, it was found that evaluating the second derivative at the initial condition was sufficient in determining the existence of an inflection point in $T(x)$ before T_{max}. That is, no instance was encountered in which the second derivative began negative at the inlet of the reactor and subsequently turned positive before x_{max}. This generally is not the case (e.g., Figure 3 in van Welsenaere and Froment, 1970), and this observation is not a recommendation of simply calculating d^2T/dx^2 for the initial conditions to determine sensitivity.

Using this criterion (along the entire trajectory) for the conditions illustrated in Figure 1, the system was calculated to be sensitive when $T_0 > 350$ K. That is, for values of $T_0 > 350$ K the second derivative of $T(x)$ in the T vs. X plane was positive for some values of $x < x_{max}$. This result is in agreement with that obtained using the first criterion.

The third criterion investigated (proposed by Adler and Enig, 1964) is similar to the latter one, but uses d^2T/dC^2 rather than d^2T/dx^2. This second derivative, which is somewhat more cumbersome to compute than the former, can be used to give the inflection point of a trajectory in the phase plane. The curve of these inflection points which will be denoted as the CIP curve, is given in Figure 1b and serves to divide region II into two subregions.

Trajectories in region II_i are concave upward which, for the values of $x < x_{max}$, represents an accelerating increase in the reactor temperature. Note that this criterion does distinguish between the $T_0 = 355$ K and the $T_0 = 365$ K cases, defining only the latter to be sensitive which is more plausible on common sense grounds as shown in Figure 1a. Thus, this criterion seems to be less conservative (cautious) than the two former definitions. This observation has also been made by Morbidelli and Varma (1985).

The question is then how the above criteria may provide a tool to determine: a. whether the addition of an endothermic reaction can desensitize a reactor and b. if so, if the appropriate proportion of that reaction, z_2 is needed to desensitize the reactor.

Two-Reaction System

It is apparent that all of these criteria indicate that a region of parametric sensitivity exists for the tubular methanol dehydration reactor. The addition of an endothermic reaction catalyst such as, in this case, one promoting methanol dissociation, might provide a heat sink while still converting methanol to a product (CO and H_2) with high volatility and good combustion properties. As was stated earlier, however, no more dissociation catalyst should be mixed (either physically or in the formulation of a single-catalyst pellet) with the dehydration catalyst than is needed to prevent temperature runaway. Using more than this minimum amount would overtax the vehicle battery.

To compare the behavior of the one-reaction system and the two-reaction system, it is instructive to examine the singular point and the zero isocline of the system of Eqs. 5 and 6. Together, they determine a good deal of the behavior of the system trajectories. The singular point is defined as the point in the phase plane where both dC/dx and dT/dx equal zero. Hence, the isocline must contain the singular point which for this system is obviously $(C, T) = (0, T_w)$. Note that Eqs. 5 and 6 represent both the one-reaction system ($z_2 = 0$) and the two-reaction system ($z_2 > 0$). These two cases have a number of features in common.

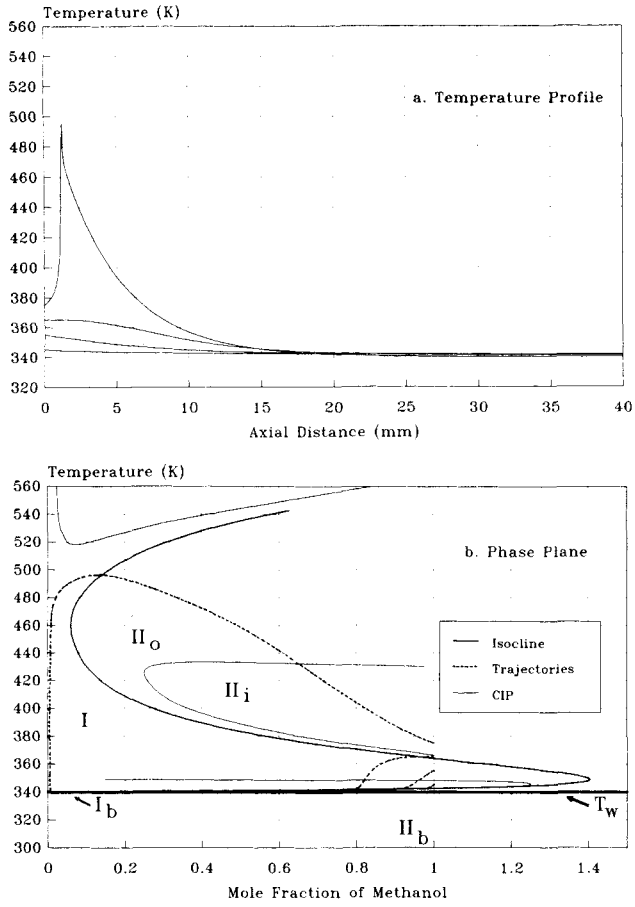

Figure 2. Tubular reactor with two reactions; zeolite dehydration catalyst with dissociation catalyst ($z_2 = 0.5$), $T_w = 340$ K.

• $dC/dx < 0$ everywhere in the first quadrant of the phase plane so that every trajectory must travel from the initial point (C_0, T_0) to the left. This should be kept in mind when examining Figures 1b, 2b and 3b.

• $(0, T_w)$ is the unique singular point.

• The singular point can be shown to be a global attractor (i.e., all trajectories approach it as $x \to \infty$).

However, the two cases differ in the shape of their zero isocline.

In accordance with the features given above, the first quadrant of the phase plane can be divided into two regions, *viz.*, I and II, as shown in Figure 1b in which dT/dx must be either positive or negative, respectively. By evaluating Eq. 6 for the point $(0, T)$ where $T > T_w$ it is easy to see that region I is where $dT/dx < 0$ and therefore $dT/dx > 0$ in region II (i or o). Region II is of particular interest here, since any temperature excursions must occur there. On an intuitive basis, it is apparent that increasing the size of region I should reduce the chance of sensitive behavior. It is obvious that if region I were expanded to the extent that it included the entire trajectory the reaction would be quenched, since $T(x)$ would have a negative slope from the reactor inlet. Consequently, changes in system parameter values, which cause region I to expand, should serve to desensitize the reactor.

Consider, first, the zero isocline for the one-reaction system shown in Figure 1b. The equation for this curve can be found by setting the righthand side of Eq. 6 equal to zero with $z_2 = 0$ and solving the resulting equation for C;

$$C = \sqrt{\frac{2h}{k_1 z_1 \Delta H_1 R}(T_w - T)e^{A_1/T}} \tag{7}$$

Note that, except for the point $(C, T) = (0, T_w)$, this isocline is entirely above the line $T = T_w$ (as shown in Figure 1b). Region II is further subdivided by the CIP curve into regions II_i and II_o. The region under the line $T = T_w$ will be denoted as II_b. For many realistic parameter values, region II is large enough to allow trajectories to exhibit sensitive behavior (such as moving rapidly toward high temperatures) before reaching the isocline and begin their descent.

Second, using the kinetic values given for Eq. 4 the endothermic (dissociation) reaction, Eqs. 6 and 7 were integrated for $z_1 = 0.5$. The results are given in Figure 2a. The behavior of this system in the phase plane along with the zero isocline and the CIP curve is given in Figure 2b. In general, the zero isocline for the two-reaction system is derived from Eq. 6 in the same way as above but now with $z_2 > 0$,

$$\Phi(C, T; z_2, T_w, \Delta H_1, \Delta H_2, k_1, k_2, A_1, A_2, h, R) =$$

$$-z_1 \Delta H_1 k_1 C^2 e^{-A_1/T} - z_2 \Delta H_2 k_2 C e^{-A_2/T} - \frac{2h}{R}(T - T_w) = 0 \tag{8}$$

This isocline is not entirely above the line $T = T_w$. It intersects this line twice; once for $C = 0$, and again for $C = C_w$,

$$C_w = -\frac{z_2 \Delta H_2 k_2}{z_1 \Delta H_1 k_1} e^{\frac{A_1 - A_2}{T_w}} \tag{9}$$

An additional subregion is thus defined by the area between the $T = T_w$ line from above and the zero isocline from below (I_b), although in the case shown in Figure 2b this area is very small. From Figure 2b as compared with Figure 1b it is also seen that the addition of dissociation catalyst moves the zero isocline to the right in the phase plane thereby expanding region I at the expense of region II. Note also that for both the one- and two-reaction cases, the isocline eventually tends toward higher values of C as T increases meaning that T_{max} occurs at lower conversions. This can be shown from Eqs. 7 and 8 but occurs only for absurdly high temperatures in the one-reaction system (while unrealistic, it is predicted from Eq. 7 because of the anomalous behavior of the Arrhenius term at temperatures $> A_1/2$). However, this doubling back of the zero isocline occurs for the two-reaction case at realistic values of T. For the latter case, this corresponds to the temperature region where the second reaction begins to play a role.

Equation 8 will now be used to generalize this observation. It will be shown that when any nine of the ten parameters, on which Φ depends, are held constant and the remaining one is allowed to increase, then the zero isoclines corresponding to the various values of that increasing parameter constitute a family of nested curves in the C-T plane, both above the $T = T_w$ line and below it. More precisely, let the parameter that is allowed to vary be denoted as Θ and drop the other parameters from the notation, so that the equation of the isocline is $g(C, T; \Theta) = 0$. It should be remembered that $g(C, T; \Theta) > 0$ if

and only if $dT/dx>0$. Following the nomenclature given in the figures, let I and I_b denote the regions above and below the line $T=T_w$, respectively, where $g(C,T;\Theta)<0$ and II and II_b to denote the analogous regions where $g(C,T;\Theta)>0$. The isocline defined by $g(C,T;\Theta)=0$ will be denoted by isocl_Θ and contains the boundary between I_Θ and II_Θ as well as between $I_{b\Theta}$ and $II_{b\Theta}$. The latter two regions are of minor importance since temperature excursions there are unlikely.

Now let (C_Θ^*, T_Θ^*) be one particular point on isocl_Θ so $g(C_\Theta^*, T_\Theta^*)=0$. Now suppose that $\partial g(C_\Theta^*, T_\Theta^*)/\partial\Theta<0$ for all the relevant values of Θ, for all $C_\Theta^*>0$ and for all $T_\Theta^*>T_w$. It follows that if Θ' is "close to" Θ and $\Theta'>\Theta$, then $g(C_\Theta^*, T_\Theta^*;\Theta)<0$. Hence, the point ($C_\Theta^*$, T_Θ^*) on isocl_Θ (on the boundary between regions I_Θ and II_Θ) does belong to the region $I_{\Theta'}$: $I_\Theta \subset I_{\Theta'}$. The same argument applies for all the points of isocl_Θ. In summary, if $\partial g(C,T;\Theta)/\partial\Theta<0$, then the region I_Θ [defined by $g(C,T;\Theta)<0$] expands with increasing Θ and, on the intuitive grounds given above, the system tends to grow less sensitive as Θ increases. Similarly, if $\partial g(C,T;\Theta)/\partial\Theta>0$, then the region II_Θ expands with increasing Θ creating a system which is more sensitive. Similar results hold for the growth of regions $I_{b\Theta}$ and $II_{b\Theta}$, but without the conclusions regarding sensitivity.

From Eq. 8 it can be easily verified that the parameters z_2, A_1, ΔH_2, k_2 and h belong to the first category, $\partial g/\partial\Theta<0$. So their increase will promote desensitization. The parameters A_2, $|\Delta H_1|$, k_1, R and T_w belong to the second category, $\partial g/\partial\Theta>0$: their increase will tend to make the system more sensitive.

It is now clear how the position of the zero isocline can be used to predict the behavior of the trajectories. A trajectory starting in region I will fall (decreasing temperature) continually while one beginning in region II will rise (increasing temperature) until it reaches the zero isocline. Here there is a chance for the reactor to be sensitive to small changes in the system parameter values. Again, the third criterion simply states that this will be the case when the trajectory passes through region II_i at any point before it crosses the zero isocline. A test of the second criterion cannot be so easily made using the phase plane. Indeed, a case is given below, for which $d^2T/dx^2>0$ for some values of $x<x_{\max}$ and yet the trajectory never enters region II_i.

Further support for the intuition that increasing or decreasing region I, as described above for all the system parameters, should lead to a reduced or enhanced sensitivity can be derived from the third criterion. Specifically, it is easy to prove that the CIP curve never intersects the zero isocline. Thus, any changes in system parameters which are shown by the above method to increase region I must cause the CIP curve to also move farther to the right in the phase plane. As will be shown below, this definitely reduces the sensitivity of the system (as defined by the third criterion), since the intersection of the area where $d^2T/dC_2>0$ and the area where (C,T) are physically possible is reduced.

In the two-reaction case (one exothermic and one endothermic), there are five possibilities (see Figure 2):

1. If the trajectory begins in I_b, it will drop until it crosses the zero isocline where it will begin to rise eventually reaching T_w for $C=0$. It will never rise above T_w. This corresponds to the formation of a "cool spot" in the reactor.

2. If the trajectory begins in I, it will drop to either T_w directly or into region I_b where it will behave as in possibility 1. In any event, the temperature will never rise to above T_0.

3. If the trajectory begins in region II_0, it will rise with a negative second derivative (d^2T/dC^2) until it crosses the isocline after which it enters I (see 2).

4. If the trajectory begins in II_i, it will rise with a positive second derivative until it crosses the $d^2T/dC^2=0$ line. It is very likely that this temperature rise will be sudden (i.e., it accelerates). However, the absolute magnitude of the temperature ($T_{\max}$) will depend on where the trajectory crosses this curve as well as the relative position of the zero isocline to the trajectory.

5. If the trajectory begins in region II_b, it may rise into II (see 3) only if the zero isocline's right most point is to the left of the $C=1$ line or into I_b (see 1).

Yet another branch of the CIP curve is shown to exist above the entire zero isocline. Trajectories above this branch must be concave upward but are well above the region of physical interest.

From Figure 2a, it is clear that the addition of dissociation (endothermic) catalyst will reduce the chances of the reactor exhibiting sensitive behavior for a given T_0. The definition of this sensitivity is still somewhat unclear, however. It is clear from Figure 2b that the zero isocline is important in determining the behavior of a system's performance as given by its trajectory. However, region II is not simply the parametric region of sensitivity. The application of the three sensitivity criteria discussed here also lead to ambiguous results. With reference to the cases shown in Figure 2, the trajectories for $T_0=345$ and 355 K are insensitive by all three criteria. The trajectory starting at $T_0=365$ K, however, is defined to be sensitive according to the first criterion described above: it crosses its zero isocline above the right most point of that curve. This trajectory, however, is not sensitive according to the second or the third criterion. That is, neither the second derivative in the $T-x$ plane d^2T/dx^2, nor is d^2T/dC^2 positive for any $x<x_{\max}$. Finally, the trajectory starting at $T_0=375$ K is sensitive according to all three criteria.

Thus the methanol dehydration/dissociation reactor represented by the results given in Figure 2 appears to be less sensitive. It is also seen from Figure 2 that the overall conversion for the reactor operated in the nonsensitive region is less than the analogous cases shown in Figure 1b [note that the conversion essentially drops to zero when $T(x)\simeq T_w$]. In addition, the reactor can still run away as is indicated by the trajectory with $T_0=375$ K. In fact, the conversions for the nonsensitive trajectories were shown to be identical to those when the second reaction was removed from the model ($z_1=0.5$, but $z_2=0$). This indicates that the dissociation catalyst is not active enough. Essentially, the reactor has been filled with an inert solid diluent. While the region of sensitivity has been reduced, the reactor residence time must be increased to maintain the same conversion. Only when the temperature does shoot up, are the effects of the dissociation reaction felt as manifested by the lower $T_{\max}$ in Figure 2a *vis-a-vis* Figure 1a. Thus, to minimize the size of the reactor, which must be placed under the hood of an automobile, the relative activity of the two reactions must be more similar.

Since the kinetic data of only one dissociation catalyst were available, a slightly less active metal oxide on γ-alumina dehydration catalyst was chosen (United Catalyst Inc. T-312) (see

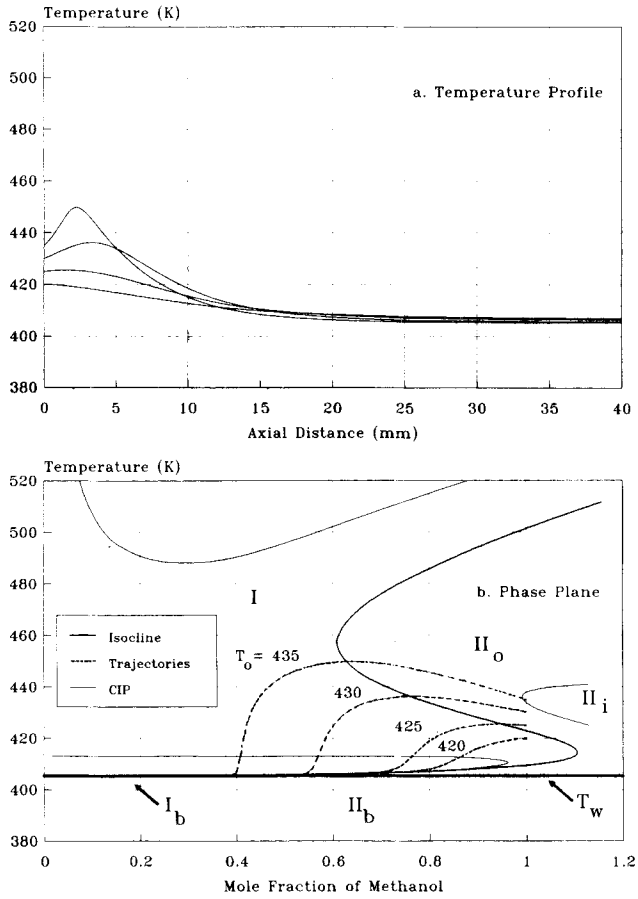

Figure 3. Tubular reactor with two reactions; less active γ-alumina dehydration catalyst with same dissociation catalyst ($z_2 = 0.1$), $T_w = 405$ K.

Supplementary Material), whose k_1 was calculated to be 5.6×10^{19} m^3/mol/s while A_1 was 19,230 K. The results of a reactor using 90% of this catalyst with the same dissociation catalyst as above are given in Figures 3a and 3b. Note that in Figure 3b (the scale has been expanded for clarity) region II_i is practically inaccessible so that no physically realistic trajectory can exhibit the concave upward shape with the concomitant rapid temperature increase. Now the second reaction plays a role at all temperatures. Consequently, the reactor has been desensitized, according to the third criterion, for all reasonable initial conditions. Again, while the first criterion defines the upper three trajectories to be sensitive, only the upper two were shown to be sensitive according to the second criterion. The ordering of these two criteria is in agreement with that noted by van Welsenaere and Froment (1970) in spite of the fact that this system was very different. If a (subjective) value of T_{max} were considered, the results given in Figure 3a would indicate that none of the trajectories were severe so that the third criterion would be suitable in this case. Equally important for this application, however, is that the overall conversion for this case is much higher so that the reactor size is minimized which is in contrast to the case given in Figure 2. Hence a reactor suitable for on-board installation is feasible, for which fluctuations in the operating conditions would not lead to temperature excursions with the concomitant catalyst deactivation caused by secondary reactions.

Conclusions

Using a simplified reactor model, three commonly employed criteria for the identification of a sensitive system were applied to an on-board methanol dehydration reactor. The first criterion is defined by the relative behavior of the system trajectories and the zero isocline in the phase plane. Specifically, a set of parameters was said to define sensitive behavior when the corresponding trajectory crossed the zero isocline at that curve's right most point. The second criterion investigated the sign of the second derivative, d^2T/dx^2, from the reactor inlet to x_{max} along the system trajectory. Similarly, the third criterion defines a system to be sensitive if the system trajectory is concave up in the T-C plane before reaching T_{max}. While all the three criteria defined a sensitive parametric region for the example system discussed, the region defined by the first and second criteria was larger than that defined by the third.

To mitigate this sensitivity, it is proposed that adding a second catalyst to the system which would catalyze a strongly endothermic reaction such as methanol dissociation would provide the system with an internal heat sink. All the three criteria indicated that the two-reaction (dehydration and dissociation) system would reduce the region of sensitivity relative to the one-reaction system alone. However, the difference between the two catalysts' activities must be moderate to maintain the overall conversion without increasing the size of the reactor. In any event, all the three criteria predicted different initial conditions to be sensitive with the first being most cautious (predicting the largest parametric region of sensitivity) while the third was the least cautious.

The definitions of sensitivity thus appear to disagree as the system becomes less sensitive. That is, when a system is considered which is extremely sensitive, the various criteria which have been proposed to define sensitivity can agree in large part as to what the actual parametric region of sensitivity is. As a system's sensitivity is reduced, however, as can clearly be achieved in this case by simply adding dissociation catalyst, the various definitions agree less as to where in the parametric space the system is actually sensitive. In a similar vein, Morbidelli and Varma (1989) report that a definition of sensitivity based on the sensitivity analysis also produces less clear results, as the system parameters are changed to produce a less dramatically sensitive reactor (which corresponds to an expansion of region I).

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Notation

A_i = activation energy of reaction i/gas constant, K
C = concentration of methanol (MeOH), mol MeOH/m^3 free volume
C_p = specific heat, J/kg/K
h = overall heat transfer coefficient, W/m^2/K
ΔH_i = heat of reaction, J/kg
k_i = pre-exponential factor of reaction i, (m^3/mol MeOH)$^{n-1}$/s (n = reaction order)
R = radius of reactor, m

r_i = reaction rate, mol MeOH/m^3 free space/s
T = temperature, K
u = gas velocity, m/s
x = axial coordinate, m
z_i = fraction of volume associated with catalyst i
ρ_g = density of gas, kg/m^3

Subscripts

1 = methanol dehydration reaction
2 = methanol dissociation reaction
max = point in reactor at which $T(x)$ is at a maximum
w = reactor wall

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