Use of Sensitivity Analysis to Describe an Endothermic/Exothermic Reaction System

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A recent article by van der Vaart and van der Vaart (1991), to be referred to as V and V, described the use of an endothermic reaction to desensitize an otherwise (parametrically) sensitive tubular, pseudo-homogeneous reactor. Three sensitivity criteria used in the past were examined: I. using the relative behavior of the system trajectory and the zero isocline in the phase plane (T vs. C); II. defining a sensitive system as one for which $d^2T/dx^2 > 0$ at some point x (the axial distance along the reactor) before x_{max}, the point (hotspot) at which the reactor temperature attains its maximum T_{max}; and III. defining the system as sensitive when $d^2T/dC^2 > 0$ for some $x < x_{max}$. The third criterion was implemented by V and V (1991) using the curve of inflection points (CIP).

This work investigates the use of sensitivity analysis (SA) to characterize the presence or absence of temperature runaway in the same two-reaction system. SA has long played a role in the literature on control engineering and systems theory (for example, Mazer, 1960, p. 86, who uses normalized sensitivities and quotes a book as old as Bode, 1945). For a discussion of the mathematical foundation, see such textbooks by Pontryagin (1962, pp. 173, 180) and Hartman (1964, p. 95). As used in chemical kinetics and combustion by Dougherty and Rabitz (1980) and by Rabitz et al. (1983), who quote earlier references (in particular with respect to Green's function method for the computation of sensitivity functions), SA was proposed as a tool for the study of thermal runaway by Boddington et al. (1983) in homogeneous combustion and used for a similar purpose by Morbidelli and Varma in several articles (1986, 1988, 1989) on chemical reactors with one or two exothermic reactions. The present work applies this technique to V and V's system of one exothermic and one endothermic reaction, and compares this criterion directly with the above three as applied to this system.

It should be noted that the meaning of the term sensitivity as used by Boddington et al., by Morbidelli and Varma, and in the present work constitutes a specialization of the meaning of the term as used in the general control and systems literature. The general meaning refers to any variations of any feature of a system as a result of variations of some parameter. The special meaning refers to the (often unwanted) *large* variations (or runaway) of some output feature (temperature, usually) as a result of *small* variations of some input parameter.

Theory

With the same nomenclature and notation as in V and V (1991), the material and energy balances for the pseudohomogeneous reactor system are:

$$-u\frac{dC}{dx} = z_1 r_1 + z_2 r_2 \tag{1}$$

$$u\frac{dT}{dx} = -\frac{1}{\rho_g C_p}(z_1 r_1 \Delta H_1 + z_2 r_2 \Delta H_2) - \frac{2h}{\rho_g R C_p}(T - T_w), \tag{2}$$

where z_1 and z_2 denote the fractions of the total interstitial reactor volume associated with the catalysts for the exothermic (methanol dehydration) and endothermic (methanol dissociation) reactions, respectively; $z_1 + z_2 = 1$. The values of each parameter, as well as the rate expressions r_1 and r_2, are given in V and V (1991).

Boddington et al. (1983) defined the criticality of their reaction in terms of the maxima T_{max} of temperature (T) vs. time profiles or, equivalently, temperature vs. conversion profiles. Different profiles correspond to different values of the Semenov number ψ (the dimensionless ratio of the rate of heat generation to the rate of heat loss); so T_{max} is a function of ψ. Boddington et al. (1983) found that the gradient $(\partial T_{max})/(\partial\psi)$ exhibits a very sharp maximum as a function of ψ and proposed that the value ψ_{cr} of ψ at which this maximum occurs be the criterion for critical temperature runaway. Thus, ψ_{cr} is the value of ψ for which $(\partial^2 T_{max})/(\partial\psi^2) = 0$. They solved this equation by numerical methods after deriving their (rather cumbersome)

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expression for $(\partial^2 T_{max})/(\partial\psi^2)$. When describing their results, they used the phrase, T_{max} is "most sensitive" to small variations in ψ when ψ is close to ψ_{cr}.

Morbidelli and Varma (1986) expanded this method by investigating sensitivity functions $(\partial T_{max})/(\partial\phi_i)$ with respect to *any one* of a number of different parameters ϕ_i (such as heat of reaction, heat-transfer coefficient, and activation energy) as functions of one of them, say of the heat of reaction parameter $\alpha = \phi_1$, and observing that, when sufficiently high, the peaks of the various $(\partial T_{max})/(\partial\phi_i)$ vs. α curves ($i = 1, 2, 3, \ldots$) were reached at almost identical values of α, irrespective of whether the sensitivity was a derivative with respect to $\phi_1 = \alpha$, or any of the $\phi_i \neq \phi_1$. Furthermore, they preferred normalized sensitivities, $(\phi_i/T_{max})\,(\partial T_{max}/\partial\phi_i)$, to find $(\partial T_{max})/(\partial\phi_i)$, for which they first added a differential equation for $(\partial T/\partial\phi_i)$ to the equations describing their reactor system (cf. Hartman, 1964, or Pontryagin, 1962). [The equation for $(\partial T)/(\partial\phi_i)$ was obtained by taking the derivative, $\partial/(\partial\phi_i)$, of the differential equation for T and reversing the order of differentiation.] They used adjoint methods (another name for Green's function method used by Rabitz and coworkers, 1983) to solve the enlarged system. Next, having determined $(\partial T)/(\partial\phi_i)$ as a function of whichever is the independent variable, say x, in their differential equations, they used the equation:

$$\frac{\partial T_{max}}{\partial\phi_i} \overset{!}{=} \frac{\partial T}{\partial\phi_i}(x_{max}) \overset{\text{def}}{=} \left[\frac{\partial T}{\partial\phi_i}\right]_{x_{max}}, \tag{3}$$

to define their sensitivity function, where x_{max} is the x value at which the T vs. x profile reaches its maximum. We should observe at this point that x, the independent variable in the differential equations used by various authors, may well represent different quantities in different contexts (which does not affect the validity of the argument): Morbidelli and Varma (1989, in the beginning and the Appendix of their article) and V and V (1991) use the *axial distance* in the tubular reactor as the independent variable; Morbidelli and Varma (1989, in the rest of their article) and Morbidelli and Varma (1986) assign that role to the *conversion*.

Equation 3 raises a question. In view of Boddington's (l.c., p. 20) warning that:

$$\frac{\partial^2 T_{max}}{\partial\phi_i^2} \neq \frac{\partial^2 T}{\partial\phi_i^2}(x_{max}), \tag{4}$$

it is natural to wonder if either the first equality in Eq. 3 or the inequality in Eq. 4 might be false. This question may be approached by an elementary proof using the two-dimensional chain rule. This method, however, breaks down under certain conditions. Therefore, a more advanced approach using Newton-Puiseux's polygon method was then used, which identified the physical conditions under which the elementary proof is invalid. The same method proves that both the inequality in Eq. 4 and the equality in Eq. 3 are nevertheless valid under any physically plausible conditions. Upon request, we will provide the interested reader with a discussion of this method.

The central problem in V and V (1991) was to determine how much catalyst for (endothermic) methanol dissociation should be added to just desensitize the methanol dehydration reactor. In the present work, we have calculated the sensitivity as used by Morbidelli and Varma (1986, 1988, 1989) in an attempt to determine how this knowledge might contribute to finding the appropriate proportion of the two catalysts. Specifically, we have computed the normalized sensitivity with respect to T_0 according to the definition (cf. Eq. 3):

$$S^*_{T_0} \overset{\text{def}}{=} \frac{T_0}{T_{max}}\frac{\partial T_{max}}{\partial T_0} = \frac{T_0}{T_{max}}\left[\frac{\partial T}{\partial T_0}\right]_{x=x_{max}} \tag{8}$$

To this end, we have first enlarged the system of differential equations, Eqs. 1 and 2, for C and T, with two differential equations, Eqs. 9 and 12, for $(\partial C)/(\partial T_0)$ and $(\partial T)/(\partial T_0)$. These were obtained in the usual manner:

$$\frac{d}{dx}\frac{\partial C}{\partial T_0} = -\frac{1}{u}\left[\theta_C\frac{\partial C}{\partial T_0} + \theta_T\frac{\partial T}{\partial T_0}\right], \tag{9}$$

where

$$\theta_C = 2z_1k_1Ce^{-A_1/T} + z_2k_2e^{-A_2/T}, \tag{10}$$

$$\theta_T = \frac{z_1k_1A_1}{T^2}C^2e^{-A_1/T} + \frac{z_2k_2A_2}{T^2}Ce^{-A_2/T}, \tag{11}$$

and

$$\frac{d}{dx}\frac{\partial T}{\partial T_0} = -\frac{1}{u\rho_gC_p}\left[\theta'_C\frac{\partial C}{\partial T_0} + \theta'_T\frac{\partial T}{\partial T_0} + \frac{2h}{R}\frac{\partial T}{\partial T_0}\right], \tag{12}$$

where

$$\theta'_C = 2z_1k_1Ce^{-A_1/T}\Delta H_1 + z_2k_2e^{-A_2/T}\Delta H_2, \tag{13}$$

$$\theta'_T = \frac{z_1k_1A_1}{T^2}C^2e^{-A_1/T}\Delta H_1 + \frac{z_2k_2A_2}{T^2}Ce^{-A_2/T}\Delta H_2, \tag{14}$$

with the initial conditions,

$$\text{at } x=0,\ \frac{\partial C}{\partial T_0}=0,\ \frac{\partial T}{\partial T_0}=1. \tag{15}$$

We then calculated

$$\left[\frac{\partial T}{\partial T_0}\right]_{x=x_{max}}$$

straightforwardly by numerically integrating, from $x = 0$ to $x = x_{max}$, the system of Eqs. 1, 2, 9 and 12 by Gear's routine as given by IMSL in DIVPAG.

Results

As in V and V (1991), the simple one-reaction case was investigated first using the kinetic parameters corresponding to the more active dehydration catalyst (Union Carbide LZ-Y-72). The results are given in Figure 1, which plots $S^*_{T_0}$ against T_0, and should be compared with Figure 1 in V and V. Note that the present Figure 1 is the result of many integrations for

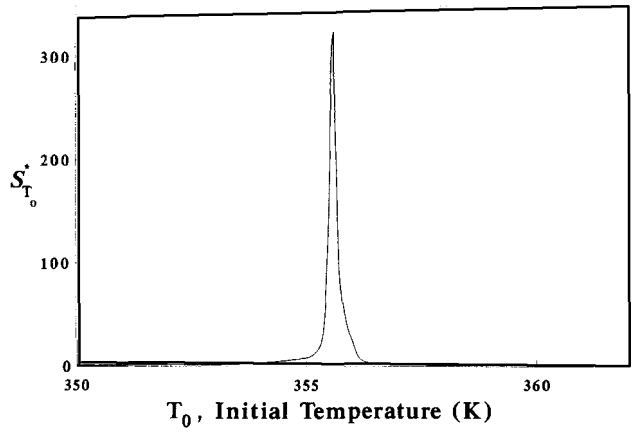

Figure 1. Normalized sensitivity with respect to T_0 for one-reaction (exothermic) system with constant wall temperature, T_w = 340 K.

various values of T_0, each integration yielding one point of the curve. The results indicate that the critical initial temperature for this system is approximately 355.6 K. Above this value, then, SA predicts that the behavior of the system will be sensitive to fluctuations in operating conditions. This result agrees especially well with the results of criterion III presented in V and V (1991).

The same procedure was then used for V and V's two-reaction system, using the kinetic parameters for the less active dehydration catalyst (UCI, T-312). The results are shown in Figure 2, which again plots $S^*_{T_0}$ against T_0 (but now there are different curves for different z_1 values) and which should be compared with Figure 3 in V and V. It is seen that $T_{0,\text{crit}}$ increases as the proportion of endothermic reaction catalyst is increased (as the values of $z_2 = 1 - z_1$ increase). Note that the peaks become lower and more diffuse as the system becomes less sensitive (as z_2 becomes larger). A similar effect was observed by Morbidelli and Varma (1988) for their one-reaction system.

Finally, the sensitivity with respect to another parameter, z_1, was investigated:

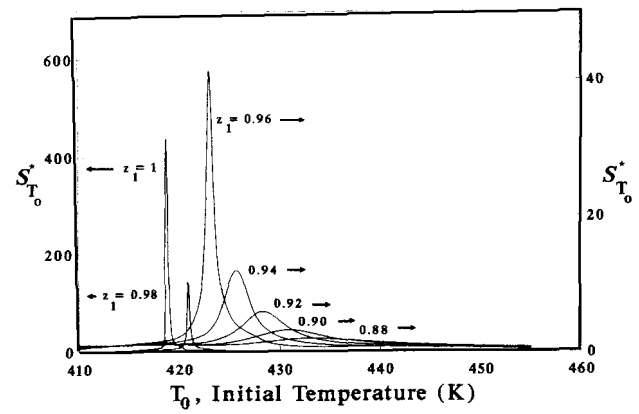

Figure 2. Normalized sensitivity with respect to T_0 for two-reaction system for various z_1 values, T_w = 405 K.

Note different ordinate scale for z_1 = 1 and 0.98.

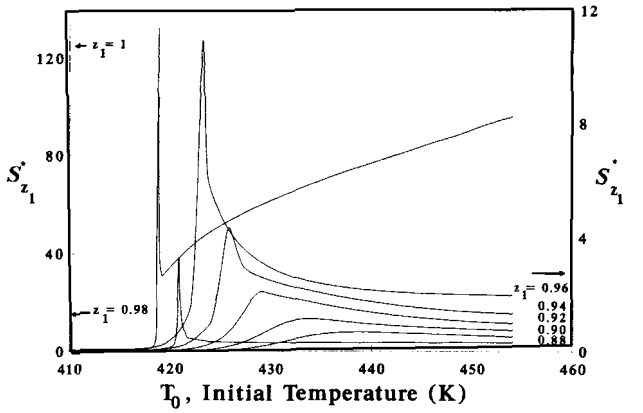

Figure 3. Normalized sensitivity with respect to z_1 for two-reaction system for various z_1 values, T_w = 405 K.

Note scale change.

$$S^*_{z_1} \overset{\text{def}}{=} \frac{z_1}{T_{\max}} \left[\frac{\partial T}{\partial z_1}\right]_{x=x_{\max}} \tag{16}$$

Of course, the differential equations for $(\partial C)/(\partial z_1)$ and $(\partial T)/(\partial z_1)$ that is, the analogues to Eqs. 9 and 12, will have two extra terms since z_1 appears explicitly in Eqs. 1 and 2, whereas T_0 was simply an initial condition. The results are given in Figure 3, which shows several plots of $S^*_{z_1}$ against T_0, for different z_1 values. The protracted tail of several curves results from a term which, due to the differentiation with respect to z_1, is independent of z_1. The relative importance of this term diminishes as the terms, which do depend on z_1, grow in importance, that is, as z_1 decreases and z_2 increases.

Discussion

Given a relatively sensitive system, such as the one represented by Figure 1, it is clear that the SA approach leads to a prediction of the boundary of the region of parametric sensitivity similar to that of the other techniques. Especially good, in the examples here discussed, is the agreement with criterion III, the analysis based on the CIP.

The addition of the endothermic reaction, which was shown to desensitize the system, leads to more diffuse sensitivity curves with reduced maxima. Moreover, although for highly sensitive systems the T_0 values maximizing $S^*_{T_0}$ and $S^*_{z_1}$ agree, at least very closely [the property that caused Morbidelli and Varma (1988) to refer to the SA-based criticality criterion as intrinsic], these T_0 values diverge for low-sensitive systems (which destroys the intrinsic character of the SA criterion for low-sensitive systems); Figure 4 shows that the difference between these two T_0 values increases as z_1 decreases. Similar observations were made by Morbidelli and Varma (1988) for single-reaction systems with parameter values in a region of decreased sensitivity.

These facts concerning low-sensitive systems are related to another distinction between criterion III (using CIP) on the one hand and the SA technique and criterion I on the other: the former may declare a system to be insensitive for all physically meaningful values of T_0, whereas the latter two are unable

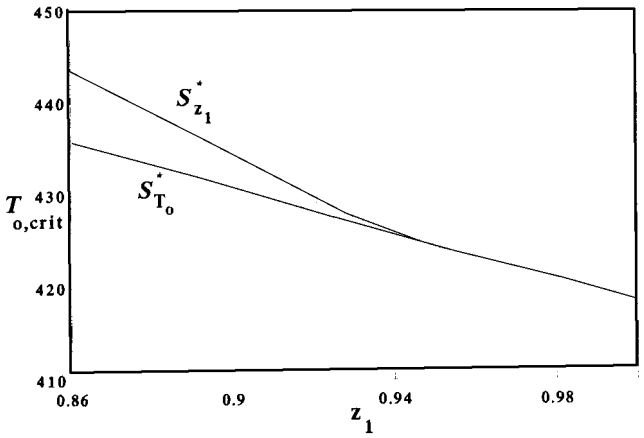

Figure 4. Critical T_0 values for calculated sensitivities with respect to z_1 and T_0 for two-reaction system.

to do so. From our experience, it appears that criterion II in this respect behaves like criterion I and SA. As an illustration, compare the results in Figures 2 and 3 of the present work with Figure 3 in V and V (1991). From the latter figure, it is clear that when $z_1 < 0.9$, the region bounded by the CIP lies entirely outside the physically realistic part of phase space (that is, to the right of $C = 1$). Thus, by criterion III, the system characterized by $z_1 = 0.9$ could *not* be sensitive for any value of T_0, since no trajectory could possibly intersect the CIP. However, the application of SA (cf. Figures 2 and 3 in the present work) will declare sensitive behavior to be present as long as the graphs of $S^*_{T_0}$ and $S^*_{z_1}$ as functions of T_0 show a maximum (which is the case for practically any z_1 value and certainly for $z_1 = 0.9$).

Although Morbidelli and Varma (1988) do mention that their system will gradually lose its sensitivity potential for certain parameter values, they still recommend to just use the (peak of) the (normalized) sensitivity as a function of the parameter of interest to determine critical sensitivity behavior. Returning to the objective of the present paper, that is, to determine how the SA method might contribute to finding the appropriate proportion of the two catalysts, we see that Morbidelli and Varma's (1988) recommended course of action can define appropriate (without temperature runaway) z_1 values *only* when *a priori* limits are imposed on T_0. The fact that criterion III opens the possibility under certain circumstances to make an insensitivity statement which need *not* be conditioned upon T_0 values is attractive from the point of view of the design engineer. Note that the SA method could probably be made to work toward the same end, if criticality could be expressed in terms of height or slope of the sensitivity curves. To date, no quantitative method of this type has been proposed.

Summarizing, the SA technique, as used by Boddington et al. (1983) and by Morbidelli and Varma (1986, 1988, 1989), is useful in determining the critical value of any particular parameter ϕ_i, for which the reaction system would become sensitive when one already knows that the system will be sensitive for some value of ϕ_i. The SA technique, however, is not equipped to decide whether such a value of ϕ_i exists in the first place. The intrinsic quality of SA, noted by Morbidelli and Varma (1986, 1988, 1989) and confirmed by Figure 4 for the rather different system studied in this work (though not proven by any physical or mathematical argument), is an important aspect of this method for highly sensitive systems, but breaks down and is therefore inappropriate for systems of lower sensitivity.

Criterion III, employed by V and V (1991), combining phase plane analysis and the CIP, has been shown to identify cases where sensitivity is absent over the entire range of certain individual parameters and has the additional advantage of conveniently providing a more complete picture of other interesting aspects of system behavior, such as overall conversion.

As for the numerical labor, the SA technique doubles the number of differential equations to be solved as compared to criterion III. On the other hand, if one is interested in sensitivity functions with respect to a number of parameters, however, the adjoint method provides some relief, whereas the other criteria do require some additional effort: zero isocline for I, $(d^2T)/(dx^2)$ for II, CIP for III. Table 1 summarizes the most important features of the four methods that have been compared here.

Finally, some general comments should be made regarding the accuracy of using the one-dimensional pseudo-homogeneous reactor model for identifying sensitive behavior. It is a characteristic of tubular reactors that (for exothermic reactions) a temperature maximum will form along the axial coordinate. The transition to sensitive behavior is characterized by a rapid increase in T_{max} as system parameters are gradually

Table 1. Important Features of the Four Methods Compared

Method	Must Traj. be Computed?	Other Needed Mathematical Expressions	Procedure	Criterion
I	Yes	Zero Isocline	Plot traj. and zero isocline in phase plane	Trajectory passing through right-most point of isocline defines $\phi_{i,crit}$
II	Yes	d^2T/dx^2	Evaluate d^2T/dx^2 for each point along the trajectory	Trajectory for which $d^2T/dx^2 = 0$ for $x < x_{max}$ defines $\phi_{i,crit}$
III	Yes	d^2T/dC^2	Plot trajectories and CIP in phase plane	Trajectory which is tangent to CIP for $x < x_{max}$ defines $\phi_{i,crit}$
SA	Yes, up to $x = x_{max}$	S_{ϕ_i}	Plot S_{ϕ_j} vs. ϕ_i for any j	$\phi_{i,crit}$ is defined at max. of $S_{\phi j}$ in $S_{\phi j} - \phi_i$ plane (not necessarily $j = i$)

changed. Clearly, a pseudo-homogeneous representation of such a reactor, which has been designed (and fitted) to accurately describe the system at or near T_0, is most accurate when $(T_{max} - T_0)$ is small and least accurate when $(T_{max} - T_0)$ becomes large. Each of the four criteria discussed above, including the first one and SA, both of which explicitly use T_{max} in their definition, defines sensitivity by evaluating the model at some point in the $(T_{max} - T_0)$ vs. ϕ_i plane well before the largest values of $(T_{max} - T_0)$ are reached. For each of the three earlier criteria, this can be seen from V and V (1991). With regard to the SA criterion, we note that maximum sensitivity by definition occurs at the inflection point of the $(T_{max} - T_0)$ curve in the $(T_{max} - T_0)$ vs. ϕ_i plane, and hence is reached well before the largest value of $(T_{max} - T_0)$. Therefore, it should be expected that the pseudo-homogeneous model can be successfully used to identify the *transition* of the system to the sensitive region, even though it may be inadequate to describe the system behavior *within* the sensitive region.

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 i, 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
S_{ϕ_i} = sensitivity with respect to parameter ϕ_i
S^* = normalized sensitivity
T = temperature, K
u = gas velocity, m/s
x = independent variable
z_i = fraction of reactor volume associated with catalyst i
ρ_g = density of gas, kg/m^3

Greek letters

ϕ_i = general symbol for parameter i
α = dimensionless heat of reaction parameter

Subscripts

0 = initial condition
1 = methanol dehydration (exothermic) reaction
2 = methanol dissociation (endothermic) reaction
max = point in the reactor at which $T(x)$ is at a maximum
w = reactor wall

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