DYNAMICS OF HETEROGENEOUS REACTION AT A STAGNATION POINT: NUMERICAL STUDY OF NONLINEAR TRANSIENT EFFECTS

R. C. LINDBERG* and R. A. SCHMITZ

Department of Chemical Engineering, University of Illinois, Urbana, Illinois 61801, U.S.A.

INTRODUCTION

IN AN earlier publication, Winegardner and Schmitz [1] reported results of a theoretical investigation into the transient nature of a chemical system reacting heterogeneously in the vicinity of a stagnation point. That study pointed out that some steady states were unstable to small disturbances and by means of a numerical example cited situations for which no stable state existed. The study was limited in scope because the analysis was based on linearized equations and as a result was capable of describing only the response to very small disturbances. It could not, for example, yield information concerning the amplitude or frequency of sustained oscillations, or of describing any other large-scale transient phenomena.

This paper presents numerical solutions of the nonlinear unsteady state equations describing the stagnation-flow problem considered in [1]. Because the numerical study necessitates fixing the values of parameters and kinetic constants and because some unrealistic assumptions are involved, general conclusions are not possible. Still the results should provide considerable insight into the unsteady state of systems involving diffusion of heat and mass coupled with an exothermic chemical reaction.

Most prior studies of nonlinear effects in stability considerations of chemically reacting systems have been devoted to perfectly-mixed or so-called "lumped-parameter" problems for which the transient state is described by ordinary differential equations. These have followed the early work of Aris and Amundson [2]. Similar studies of nonlinear effects in potentially unstable distributed or spatially-dependent reaction systems involving diffusive transport and finite-rate chemical kinetics are less common. Raymond and Amundson [3] have reported some computer simulations of such systems as have Kirkby and Schmitz [4]. Recently Lee and Luss [5] simulated the transient state of a

porous spherical catalyst particle with exothermic reaction proceeding in the pores and succeeded in illustrating a sustained oscillatory state for small values of the Lewis number.

Frequent reference will be made herein to equations and figures contained in [1]. For convenience in this regard, the symbol A will be attached to all numbers assigned to figures and equations in the present paper; numbers without the attached A refer to equations or figures in [1].

EQUATIONS AND ASSUMPTIONS

The assumptions employed in the numerical example of [1] were also invoked in all computations in the present study. In addition, the kinetic expression and the expression for heat losses from the surface were taken to be those in equations (49) and (50). The velocity field was assumed to be at its steady state at all times. Thus the dimensionless stream function $\varphi(\eta)$ was taken to be the tabulated solution of equations (1) and (2). In summary then, the unsteady state of the chemically reacting system of interest here is described by the following equations:

$$\frac{\partial c}{\partial \tau} - \varphi(\eta)\frac{\partial c}{\partial \eta} = \frac{\partial^2 c}{\partial \eta^2} \tag{1A}$$

$$\frac{\partial T}{\partial \tau} - \varphi(\eta)\frac{\partial T}{\partial \eta} = \frac{\partial^2 T}{\partial \eta^2} \tag{2A}$$

$$\eta = 0: \quad \left.\begin{aligned} \frac{\partial c}{\partial \eta} &= \frac{k}{\sqrt{(aD)}} c\, e^{-E/T} \\[2mm] \frac{\partial T}{\partial \eta} &= \frac{h(T - T_\infty)}{k_T \sqrt{(a/D)}} + \frac{(\Delta H)C_{A\infty}}{C_p}\frac{k}{\sqrt{(aD)}} c\, e^{-E/T} \end{aligned}\right\} \tag{3A}$$

$$\eta = \infty: \quad \left.\begin{aligned} c &= 1 \\ T &= T_\infty \end{aligned}\right\} \tag{4A}$$

where c is the reduced concentration, $C_A/C_{A\infty}$, of reactant A. All other symbols are as defined in [1].

The numerical values of the parameter groups $k/\sqrt{(aD)}$,

---

* R. C. Lindberg is presently with the Continental Oil Company, Ponca City, Oklahoma.

$(\Delta H)C_{A\infty}/C_p$, E and $k_T\sqrt{(a/D)}$ were taken to be those given in equation (51) in all cases reported here*.

This system of parabolic partial differential equations was solved numerically in the present work by an implicit finite-difference scheme. Advantage was taken of the fact that the partial differential equations themselves are linear, nonlinearities being confined to the boundary conditions in equation (3A). The solution method used closely parallels that described by Lindberg and Schmitz [6] in connection with a study of a surface reaction in nonsimilar laminar boundary-layer flows. The procedural details are omitted here since the application of the method to the particular problem at hand is straightforward. Details regarding increment sizes and tests of accuracy are available elsewhere [7]. Generally, at least three-figure accuracy in instantaneous temperatures was assured in all computations.

RESULTS AND DISCUSSIONS

Unique unstable state

Steady state solutions and the results of a linear stability study the problem at hand were conveniently summarized in Figs. 3 and 4. Among the more interesting and curious features of those results is the possibility of a system possessing no stable state at all. As can be seen from Fig. 4, this is the case for a range of values of h for $T_\infty = 1000°K$ and for $T_\infty = 920°K$. The result of a numerical simulation of the unsteady state for one such case ($T_\infty = 1000°K$; $h = 40.0$) is shown in Fig. 1A. The initial state was taken to be the
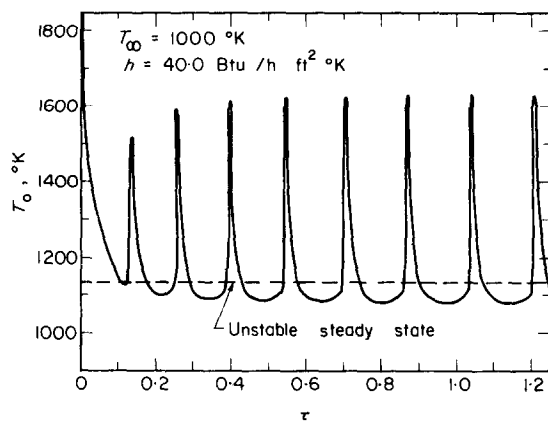
stable steady state for $h = 52.0$. (The units of h everywhere are Btu hft²°K). Figure 1A shows that oscillations about the unstable state set in and reach a constant amplitude and period within 2 or 3 cycles. The period of the steady oscillations is 0.177 in the dimensionless time units of τ. As shown in Fig. 1A, the maximum surface temperature encountered in the region of steady oscillations is about 1635°K. For comparison, the constant temperature of the surface corresponding to the unstable steady state is about 1135°K.

While Fig. 1A shows only the surface temperature variation with time, it follows that the concentration and temperature both approach periodic behavior at all values of the spatial variable η. At any fixed spatial position, including $\eta = 0$, the state of the system, once steady oscillations have been reached, follows a closed curve in the concentration-temperature plane, the curve shrinking to a point as η becomes large. The collection of these closed curves for all η values defines a "limit surface" in the three-dimensional space of c, T and η. The surface does not depend on the particular initial state of the system. The unsteady profiles generated in obtaining the results in Fig. 1A showed that the amplitude of the oscillations decreases sharply with increasing η. and for η values beyond 0.5 they are hardly

It should be noted that any appreciable extraneous heat capacities, such as that of the solid wall, would be expected to have a significant effect on the stability picture. In particular the effect would cause damping or reduction in the amplitude of oscillations. Such effects have been explored in a previous study of a similar problem [8].

FIG. 1A. Temperature oscillations for a case of a unique unstable steady state.

Simulation of extinction resulting from instabilities

If one traces the steady-state curve for $T_\infty = 900°K$ in Fig. 4 beginning at some low value of h, say $h = 10$, allowing a steady state to be achieved after each change, stable states of high chemical activity should be encountered up to $h = 17.2$. Beyond that value, the high-temperature states are unstable to small disturbances, but at the same time there exists a low temperature or "extinguished" stable state in which very little chemical reaction is taking place. The objective of the numerical solutions to be described here was to simulate such a procedure in which stepwise changes in h are made, and to observe the resulting unsteady state particularly when the unstable regime is encountered. Such changes in h may not correspond to an obvious experimental procedure, but similar behavior would be observed as well for other types of changes or for changes in other parameters. The effect of the parameter h is a convenient one to represent in connection with Fig. 1.

Curve (a) in Fig. 2A shows the temperature history of $\eta = 0$ following the final step in h from 17.2 to 17.6. For this step the initial state was an apparently stable state arrived at by changing h from 16.8 to 17.2. The curve in Fig. 2A illustrates an exponential decrease in temperature from the high initial temperature and a damped oscillatory approach

---

* The quantity $k/\sqrt{(aD)}$ was printed erroneously as $k\sqrt{(aD)}$ in [1]. The value for $k/(aD)^{\frac{1}{2}}$ of 2.56×10^7 was employed in all computations here as well as in [1].
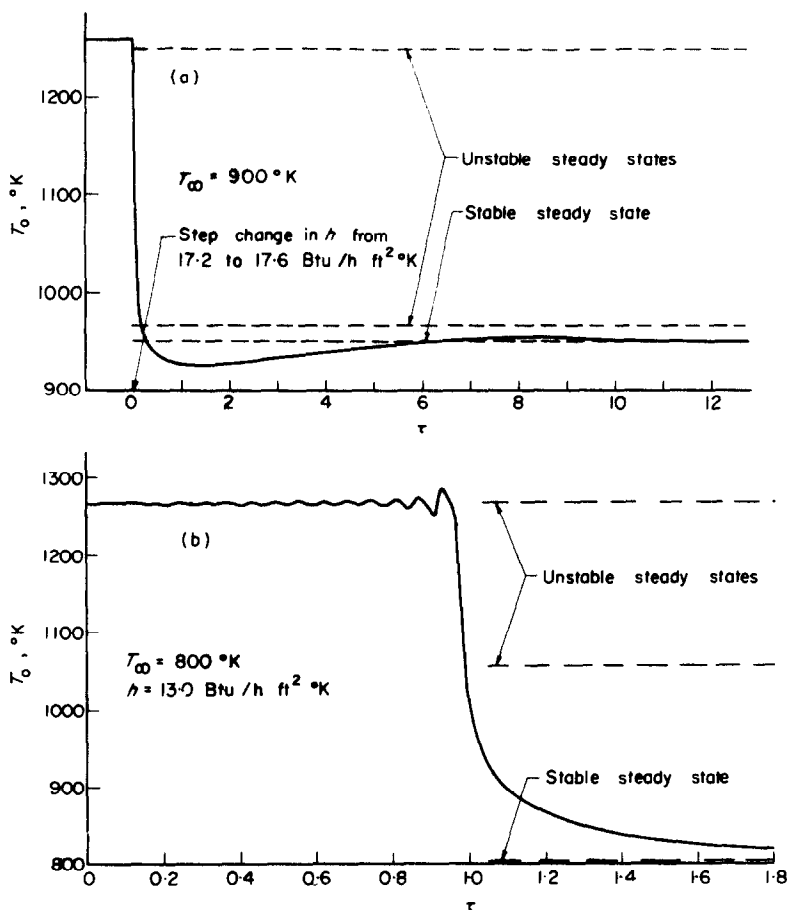
FIG. 2A. Extinction of a high-temperature steady state.

to the low-temperature or extinguished state. The oscillatory approach to the low stable state is as expected from the results of the linear study shown in Fig. 3. From those results one might also have expected the growth from the initial high temperature to be oscillatory since the high-temperature steady state corresponding to $h = 17.6$ lies in region V of Fig. 3. However, in most cases that were simulated, oscillations near a high-temperature state were, at best, barely observable. In particular, oscillatory growth of perturbations was observable only if the perturbation from the unstable profile was very small. For example, curve (b) of Fig. 2A represents a temperature transient for $T_\infty = 800°K$ and $h = 13.0$ for a situation in which the initial state was taken to be the unstable concentration and temperature profiles for $h = 13.0$ with accuracy to two decimal places. The result illustrates the expected unstable oscillatory character of the high-temperature state. However, when the initial state was

taken to be the high-temperature state at $h = 12.5$, the resulting transient following a step change to $h = 13.0$ showed an exponential temperature decrease. These results illustrate one of the shortcomings of a study of linearized equations. The linear equations probably describe correctly the nature of the behavior for small perturbations, but fail generally to yield information on how small the perturbations must be.

In the cases shown in Fig. 2A the transient behavior led to extinction of the chemical reaction. There may have been some question beforehand as to whether oscillations would be sustained about the unstable state just as if no stable state existed. There appears to be no obvious way to rule out that possibility a $priori$. However, in all simulations carried out in this study, the system was found to approach steady-state operation at a stable state whenever a stable state existed.

It is of interest to note than an analysis of steady state

results alone (from Fig. 4 with the assumption that all high-temperature states are stable) would have indicated extinction of the chemical reaction for $T_\infty = 900°K$ when h exceeded a value of $22\cdot8$.

Two stable states

In the final case to be described here, T_∞ was taken to be at $800°K$ and h was fixed at a value of 10. Under these conditions, there are two stable steady states, as shown in Fig. 4. The purpose of numerical computations for this case was to illustrate the effect of the initial state on the ultimate performance of the system. In all solutions, the initial value of c was set to equal to unity everywhere, and the temperature profile was the steady temperature profile for chosen values of the surface temperature with reactivity at the surface equal to zero; i.e. either $k = 0$ or $c(\eta) = 0$ for $\tau < 0$. Different initial profiles were generated by various choices of the initial surface temperature T_s. The question asked is: What is that value of T_s above which all transients lead to the high-temperature steady state? This might be considered equivalent to asking: What is the *ignition* temperature of the heterogeneous reaction system? Interpreted in this manner and in certain other ways, which may be more meaningful as far an actual experimental situation is concerned, the ignition condition is not predictable from steady state solutions or from a linear analysis.

Results of transient solution are shown in the form of a phase plane representation of the state at $\eta = 0$ in Fig. 3A.

The trajectories in that figure clearly show that ignition of the reaction is attained for $T_s > 986°K$.

REFERENCES

1. D. K. WINEGARDNER and R. A. SCHMITZ, Dynamics of heterogeneous reaction at a stagnation point, *AIAA Jl* 5, 1589–1595 (1967).
2. R. ARIS and N. R. AMUNDSON, An analysis of chemical reactor stability and control, *Chem. Engng Sci.* 7, 121–
3. L. R. RAYMOND and N. R. AMUNDSON, Some observations on tubular reactor stability, *Can. J. Chem. Engng* 42, 173–177 (1964).
4. L. L. KIRKBY and R. A. SCHMITZ, An analytical study of the stability of a laminar diffusion flame, *Combustion and Flame* 10, 205–220 (1966).
5. J. C. M. LEE and DAN LUSS, The effect of Lewis number on the stability of a catalytic reaction, *A.I.Ch.E. Jl* 16, 620–625 (1970).
6. R. C. LINDBERG and R. C. SCHMITZ, On the multiplicity of steady states in boundary layer problems with surface reaction, *Chem. Engng Sci.* 24, 1113–1129 (1969).
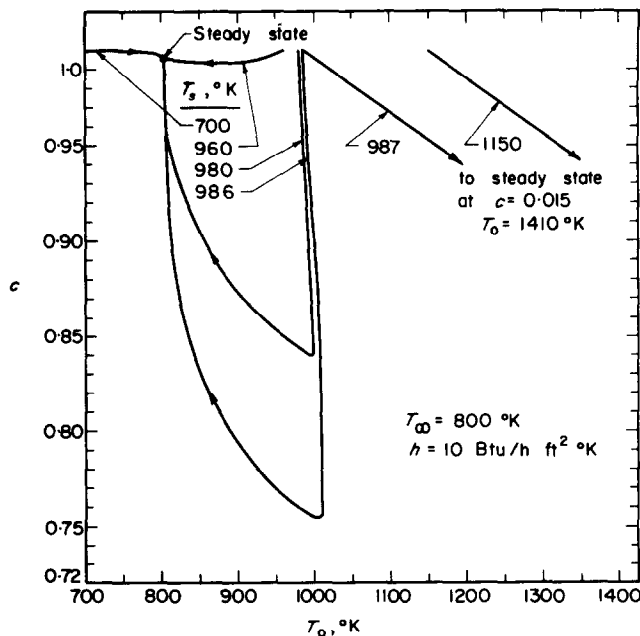

FIG. 3A. Phase plane at $\eta = 0$.

7. R. C. LINDBERG, The nature of solutions to boundary layer problems with surface reaction, Ph.D. Thesis,

8. D. K. WINEGARDNER and R. A. SCHMITZ, Stability of reaction on a spherical particle, *A.I.Ch.E. Jl* **14**, 301-310 (1968).