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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE Preprint 92-081	5. FUNDING NUMBERS
Dynamics of Homogeneous-Heterogeneous Reactors	DAAL03-89-C-0038

6. AUTHOR(S)

R. J. Olsen, W. R. Williams, X. Song, L. D. Schmidt, and
R. Aris

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Minnesota – School of Mathematics
127 Vincent Hall
Minneapolis, MN 55455

8. PERFORMING ORGANIZATION REPORT NUMBER

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OCT 20 1993
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARO 27747.246-MA-COE

11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
Approved for public release; distribution unlimited.	

13. ABSTRACT (Maximum 200 words)

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We have studied combustion reactions over catalytic foils and in catalytic monoliths for simple oxidations such as $CH_4 + O_2$, $NH_3 + O_2$, $C_3H_8 + O_2$, $CH_4 + NO$ and $NH_3 + NO$. For most reactions and geometries, we observe heterogeneous and homogeneous ignitions and extinctions and self-sustaining autothermal steady states. The range of compositions for which an autothermal state exists depends sensitively on the inlet gas velocity.

For stagnation point flow, reaction over a catalytic foil can be modeled by a one-dimensional boundary value problem in which saddle-node bifurcations correspond to ignitions and extinctions. Computations for a model with simplified kinetics reproduce the experimental dependence on input power to the foil and inlet gas composition. Calculations also show that the dynamics are affected strongly by the inlet gas velocity.

93-24867

93 10 18 165

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Dynamics of Homogeneous-Heterogeneous Reactors

R. J. Olsen, W. R. Williams, X. Song, L. D. Schmidt and R. Aris

Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455

Abstract—In many industrial processes both heterogeneous and homogeneous reactions can occur, and these reactions are strongly coupled through heat and mass transfer and reactive intermediates. Surface reactions can heat the boundary layer sufficiently to ignite homogeneous reaction, can deplete the boundary layer of a limiting reactant, and can act as a source or sink of free radicals.

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1. Introduction

Many processes of commercial importance, such as catalytic oxidation, involve simultaneous homogeneous and heterogeneous reaction pathways (Satterfield, 1980; Pfefferle and Pfefferle, 1987). Examples of catalytic oxidations include the production of syngas from methane, the air oxidation of NH_3 over platinum to produce NO, and the Andrussow process for the synthesis of HCN.

The nature of the coupling between the homogeneous and heterogeneous pathways must be understood if homogeneous-heterogeneous reactors are to be used effectively. The coupling occurs through heat and mass transfer between the catalyst and its surroundings and through reactive intermediates that are common to both pathways. The surface reaction can heat the boundary layer sufficiently to ignite homogeneous reaction, can deplete the boundary layer of a limiting reactant, and can act as a source or sink of free radicals. While surface reactions are frequently observed to exhibit ignition and extinction, such phenomena have received less attention in coupled systems. The determination of ignition and extinction points is an important step in characterizing the dynamical behavior of a reactor since these points provide information about operating limits of the process.

The catalytic combustion of premixed C_3H_8/air mixtures in stagnation point flow over platinum, which will be considered here, is a typical homogeneous-heterogeneous reaction system. The kinetic parameters for global, one-step rate expressions of Arrhenius form have been determined for both the homogeneous and the heterogeneous reactions (Westbrook and Dryer, 1981;

Hiam *et al.*, 1968). Using these rate expressions along with known values for the physical properties, we are able to compare experimental and calculated bifurcation behavior as a function of fuel/air ratio and power input to the catalyst. Based on the agreement between our calculated results and experimental data, we have extended our previous analysis (Song *et al.*, 1991) to study the effect of additional parameters on the behavior.

The momentum, energy and mass balance equations for plane stagnation point flow admit a change of variables that allows for the model equations to be written in terms of a single spatial coordinate. For steady state conditions, the model equation is a one-dimensional boundary value problem with $2n + 5$ variables where n is the number of chemical species. The use of global, one-step rate expressions retains all aspects of the coupling except for the role of radical intermediates.

2. Dynamical Behavior in Propane Oxidation over Pt

Schematic one-parameter bifurcation diagrams at four different feedstream compositions are shown in Fig. 1a. Each curve represents a typical experiment: the inlet gas temperature, mass flow rate, and inlet gas composition are fixed and the input power to the catalytic foil is varied, using an experimental apparatus shown in the inset of Fig. 2a. The measured response is the temperature of the surface at the stagnation point (T_S). At low and high power, curves are essentially linear due to simple resistive heating of the foil. For intermediate values of power, the response is nonlinear due to the exothermicity of the reaction, which has a self-accelerating effect on the rate. In this intermediate region a transition from a kinetic-limited reaction to a mass transfer-limited reaction occurs.
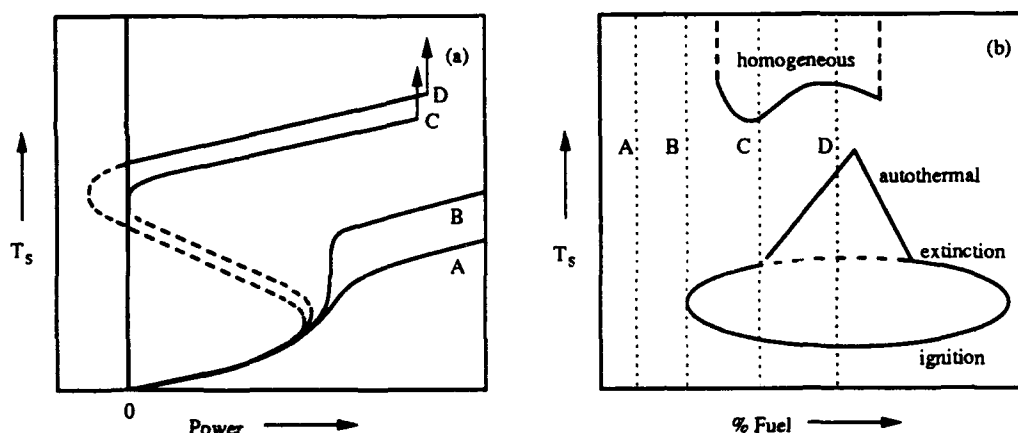

Figure 1: Schematic representations of one-parameter (power) and two-parameter (power and %fuel) bifurcation diagrams. Each curve of (a) is obtained by varying power with all remaining parameters fixed. A family of curves, of which four are shown, is generated by varying %fuel. The surface temperature at the bifurcation and autothermal points for each one-parameter curve is plotted as a function of %fuel to produce the two-parameter bifurcation diagram of (b).

At the lowest fuel/air ratio, T_S is a single-valued function of power (as illustrated by curve A) because the heat liberated by the reaction does not influence the system significantly. At a critical fuel/air ratio, the bifurcation diagram has a vertical tangent as shown in curve B. Further increases in the fuel/air ratio lead to multiple steady state behavior. An ignited state that sustains itself in the absence of input power is called an autotherm. The onset of autothermal behavior is shown in curve C, where the zero power line is tangent to the extinction point. Another feature shown by curve C is homogeneous ignition, indicated by the vertical arrow. Experimentally, homogeneous ignition typically results in a flame which flashes back to the

reactor inlet, although stable flames in the reacting boundary layer have been observed (Williams et al., 1991). Bifurcation diagram D exhibits a stable autothermal state and terminates in a homogeneous ignition point.

Ignition, extinction and autothermal behaviors are sketched as a function of inlet gas composition in Fig. 1b. This type of diagram is the result of projecting the ignition, extinction and autothermal points from each of the individual curves in Fig. 1a on the (%fuel,T_s)-plane. We have chosen this representation of the two-parameter behavior instead of the more familiar projection onto the (power,%fuel)-plane in order to emphasize the dependence of the surface temperature on the fuel/air ratio. The boundary of the oval region in Fig. 1b represents the ignition and extinction points for the heterogeneous reaction. The interior of the oval region corresponds to the unstable steady states. The piecewise linear representation of the autothermal surface temperature as a function of composition follows from the assumption that the kinetics in this state are limited by mass transfer. If a single stoichiometry describes the reaction, the autothermal temperature will attain its maximum value at the stoichiometric fuel/air ratio. The final feature of Fig. 1b is the curve of homogeneous ignition points, found at relatively high surface temperatures and over a fairly narrow range of composition.

3. Experiments and Calculations for Propane Oxidation

The experimental apparatus consists of an electrically heated platinum foil suspended in a Pyrex tube, as shown in the inset of Fig. 2a, through which the reactant gases flow upwards. The lower section of the tube is packed with glass beads to insure that the gas stream is well-mixed and is wrapped with heating tape so that the inlet gas temperature may be varied. Surface temperature is measured either by an optical pyrometer or a Chromel-Alumel thermocouple spot-welded to the surface. The ignition and extinction points for the surface reaction are determined by locating the limits of steady state multiplicity on the surface temperature vs. power curves. Homogeneous ignition is defined by the appearance of a flame. Ignition and extinction points are generally reproducible to within $\pm 20\,^\circ$C and are not very sensitive to the orientation of the foil with respect to the direction of gas flow.

The experimentally determined surface temperatures for heterogeneous ignition and extinction, autothermal behavior and homogeneous ignition are displayed in Fig. 2a. The abcissa R is defined as R = $\Phi/(\Phi + 1)$, where Φ is the fuel/air ratio divided by the fuel/air ratio for the stoichiometry of complete combustion to CO_2 and H_2O, which is 4% for propane in air. Except for fuel-lean compositions near the hysteresis point, the surface temperature at which heterogeneous ignition occurs is $\approx 200\,^\circ$C, essentially independent of composition. Heterogeneous extinctions take place at 400–500$\,^\circ$C. These occur over a restricted range of compositions due to the predominance of autothermal behavior in this system. To a good approximation, the autotherms are linear, indicating that the kinetics are mass-transfer limited. The discontinuity in the slope of the autotherm in the fuel-rich regime coincides with the visual observation of coke formation on the foil. Homogeneous ignition is observed for fuel/air mixtures between 2% and 8%, with a minimum surface temperature for ignition of about 1000$\,^\circ$C at $\approx 3\%$.

The equations for planar stagnation point flow (see the inset of Fig. 2b), written in dimensionless form, are

$$\frac{d^3f}{d\eta^3} + f\frac{d^2f}{d\eta^2} + \frac{1}{2}\left[\frac{\theta}{\theta_e} - \left(\frac{df}{d\eta}\right)^2\right] = 0 \tag{1a}$$

$$\frac{d^2\theta}{d\eta^2} + f\Pr\frac{d\theta}{d\eta} + \beta\Pr\mathbf{r} = 0 \tag{1b}$$

$$\frac{d^2m_1}{d\eta^2} + f\operatorname{Sc}\frac{dm_1}{d\eta} - \operatorname{Sc}\mathbf{r} = 0, \tag{1c}$$

subject to the boundary conditions

$$f = \frac{df}{d\eta} = 0 \quad , \quad \frac{d\theta}{d\eta} = -\beta r_S - \sqrt{\frac{\theta}{\theta_e}}\left[P_W - \kappa_r(\theta^4 - \theta_e^4) - h_L(\theta - \theta_e)\right] \quad , \quad \frac{dm_1}{d\eta} = r_S \text{ at } \eta = 0, \quad (2)$$

and

$$\frac{df}{d\eta} = 1 \quad , \quad \theta = \theta_e \quad , \quad m_1 = m_{1,e} \text{ at } \eta = \infty. \tag{3}$$

The state variables are the dimensionless stream function f, the dimensionless temperature θ and the mass fraction of propane m_1. The subscript s refers to the surface and the subscript e refers to ambient conditions. The homogeneous reaction rate r appears in the energy balance (Eq. 1b) and the mass balance (Eq. 1c). The heterogeneous reaction rate r_S appears in the boundary conditions specifying the energy and mass flux to the surface (Eq. 2). For the details of the derivation of the equations and the method of solution, see (Song *et al.*, 1991).
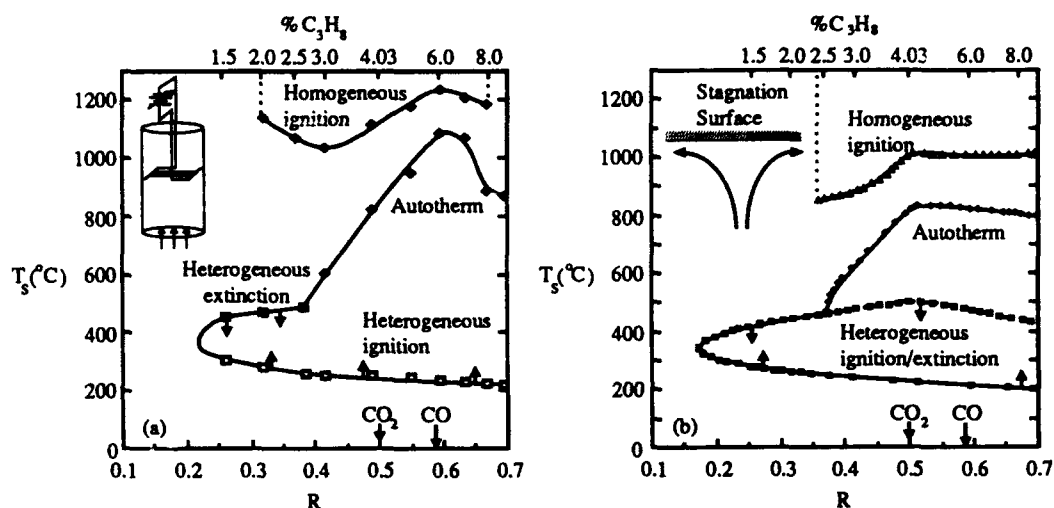

Figure 2: Homogeneous-heterogeneous ignition and extinction curves for C_3H_8 oxidation over Pt. The experimental data are shown in (a) and the calculated curves in (b). The experimental apparatus is sketched in the inset of (a), and the geometry used to derive the model equations is shown in the inset of (b). The model accurately reproduces the compositions corresponding to the onset of multiple steady state behavior, autothermal behavior and homogeneous ignition.

The results obtained for the model are given in Fig. 2b. The qualitative agreement with the experimental data is remarkably good in excess O_2 where the rate parameters for the heterogeneous reaction are reliable. The surface temperature for heterogeneous ignition is reproduced accurately, as are the inlet gas compositions for the onset of steady state multiplicity, autothermal behavior and homogeneous ignition. The maximum autothermal temperature and homogeneous ignition temperature occur at the stoichiometric composition for complete combustion, reflecting the underlying global rate expressions incorporated in the model.

4.   The Effect of Inlet Gas Velocity

Given the success of the model in reproducing the system behavior as a function of input power and composition, we continued our study of the model behavior by examining the effect of varying other parameters. We describe here the bifurcation behavior with respect to inlet gas velocity, retaining input power as the primary bifurcation parameter. κ_r, h_L, P_W and the dimensionless reaction rates r and r_S all depend on the inlet gas velocity.
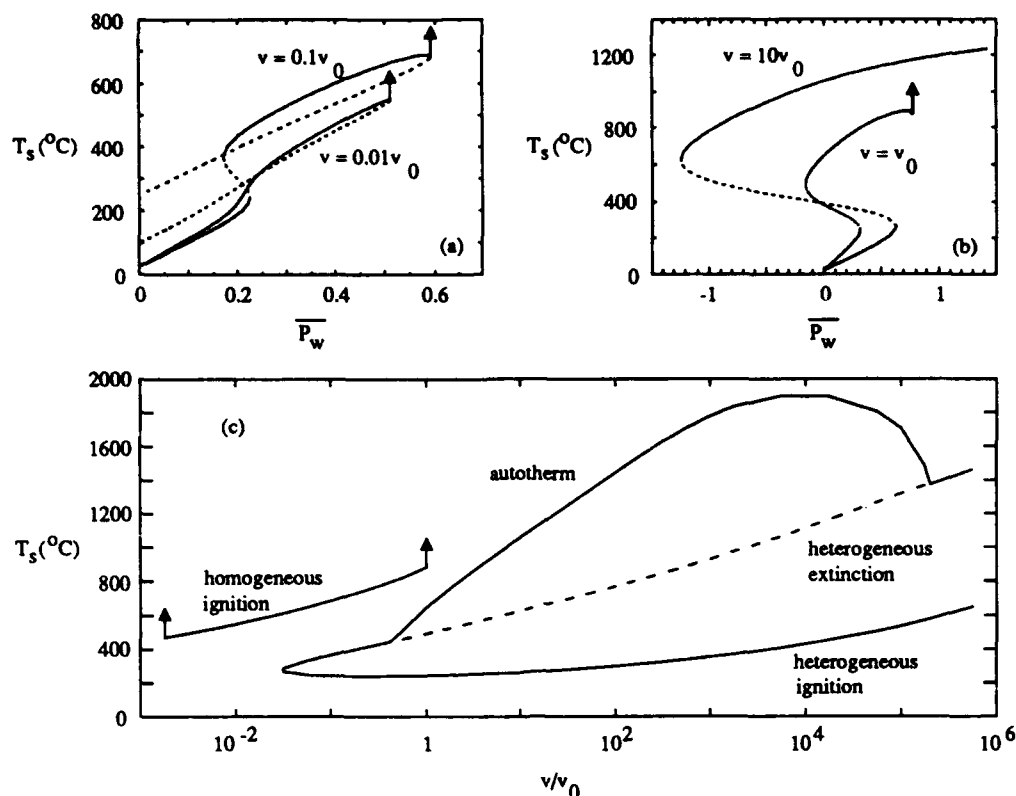
Figure 3: The effect of inlet velocity on the homogeneous-heterogeneous ignition and extinction of C_3H_8 oxidation over Pt for a composition of 3% propane in air and a reference velocity v_0 of 5 cm/s. Curves in (a) and (b) show T_S as a function of normalized power $(\overline{P_W} = (v/v_0)P_W)$ at the indicated velocities. The curves in (c) show the dependence of T_S on velocity. Homogeneous ignition occurs in the absence of heterogeneous ignition at sufficiently low velocities. As the velocity is increased, the homogeneous ignition is suppressed, and at very high velocities, the autothermal state also disappears.

Fixing the composition at 3% propane in air and the inlet gas temperature at 300 K, we obtain the bifurcation diagrams of Fig. 3. The quantity v/v_0 is the ratio of the inlet velocity to a reference velocity of 5 cm/s, which was the velocity used in Fig. 2b. In Fig. 3c the bifurcation sets and autothermal curves have been projected on the $(T_S, v/v_0)$-plane. Six different bifurcation diagrams are observed as the inlet velocity is varied. Of these, the diagram at very low velocity exhibits no bifurcations and the diagram at very high velocity exhibits a simple hysteresis loop resulting from heterogeneous ignition and extinction only. Bifurcation diagrams at intermediate velocities are displayed in Figs. 3a and 3b. For the lowest velocity shown in Fig. 3a, there is homogeneous ignition in the absence of heterogeneous ignition. For a velocity one order of magnitude larger, a narrow range of hysteresis arising from the heterogeneous reaction is visible along with the homogeneous ignition. Homogeneous ignition without heterogeneous ignition and autothermal behavior was not found in the variation of inlet composition discussed above. The bifurcation diagram of Fig. 3b for $v = v_0$ is common to Fig. 2b (R = 3/7). Increasing the velocity one order of magnitude further, we find that homogeneous ignition is suppressed while heterogeneous ignition and an autotherm persist. The range of velocities shown in Fig. 3c cannot be realized in any single experimental apparatus. Additionally, effects due to free convection and flow in the sonic regime are not included in Eqs. 1-3. However, it is the trend in qualitative

behavior shown in Figs. 3a and 3b which is of primary interest, and the model is reasonably accurate for this range of velocities.

5. Conclusions and Summary

We have shown that a model for homogeneous-heterogeneous combustion of C_3H_8 based on simplified rate expressions reproduces many of the interesting features of the observed experimental dynamics as inlet composition is varied. Having verified the qualitative accuracy of the model, we are able to simulate the dynamics in regions of parameter space that are difficult to probe experimentally. For example, by varying inlet gas velocity over several orders of magnitude, the sensitivity of the model to this parameter is obtained. Both the experimental and computational results illustrate that the presence of the catalyst has a marked effect on homogeneous ignition behavior.

Notation

All quantities listed are dimensionless

f = stream function
θ = temperature
β = heat of reaction
m_1 = fuel mass fraction
r_S = heterogeneous reaction rate
κ_r = radiative heat transfer coefficient

η = distance
Pr = Prandtl number
r = homogeneous reaction rate
Sc = Schmidt number
P_W = input power
h_L = conductive heat transfer coefficient

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