Ignition and Extinction of Surface and Homogeneous Oxidation of NH_3 and CH_4

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Ignition, extinction and autothermal behavior of surface and homogeneous oxidation reactions of CH_4, NH_3, and mixed NH_3/CH_4 fuel systems in air over resistively heated Pt foils was studied in an atmospheric pressure flow reactor. Also examined were the effects of varying fuel concentration on the ignition, extinction, and autothermal surface temperatures. Heterogeneous ignition occurred at ~200°C for NH_3 and at ~600°C for CH_4. The mixed fuel systems exhibited two surface ignitions (~200°C and ~600°C), implying a sequential ignition of the two fuels. The effects of removing one of the fuels during autothermal operation gave results consistent with this hypothesis.

In homogeneous ignition, two types of flames were observed: a boundary layer flame associated with NH_3 systems and an independent flame observed in all systems. Homogeneous ignition of the two fuels and the mixtures occurred at surface temperatures ranging from 1,100°C to 1,600°C and appeared to be dominated by CH_4 in the mixed systems. A generic behavior is proposed for homogenous-heterogeneous combustion of single and mixed fuels.

Introduction

Methane and ammonia oxidation are critically important reactions in the chemical industry. Heterogeneous oxidation of NH_3 over Pt-Rh gauzes yields NO via the Ostwald process (Lee and Farrauto, 1989), and CH_4 combustion is a major energy source (Bowen, 1982). Catalytic oxidation of NH_3/CH_4 mixtures, however, yields mostly HCN, an important precursor to nylon production (Hasenberg and Schmidt, 1986). The important stoichiometric reactions in the above processes are as follows:

$$NH_3 + \frac{5}{4} O_2 \rightarrow NO + \frac{3}{2} H_2O \quad \Delta H = -226 \text{ kJ/mol} \tag{1a}$$

$$NH_3 + \frac{3}{4} O_2 \rightarrow \frac{1}{2} N_2 + \frac{3}{2} H_2O \quad \Delta H = -318 \text{ kJ/mol} \tag{1b}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -803 \text{ kJ/mol} \tag{2a}$$

$$CH_4 + \frac{3}{2} O_2 \rightarrow CO + 2H_2O \quad \Delta H = -519 \text{ kJ/mol} \tag{2b}$$

$$NH_3 + CH_4 + \frac{3}{2} O_2 \rightarrow HCN + 3H_2O \quad \Delta H = -473 \text{ kJ/mol} \tag{3a}$$

$$NH_3 + CH_4 + \frac{11}{4} O_2 \rightarrow CO_2 + \frac{1}{2} N_2 + \frac{7}{2} H_20 \quad \Delta H = -1{,}121 \text{ kJ/mol} \tag{3b}$$

Reactions 1a and 3a give the desired selectivities into NO and HCN, respectively, and occur only heterogeneously. Thus, much research has been devoted to the heterogeneous oxidation of these fuels (Pignet and Schmidt, 1974; Flytzani-Stephanopoulos et al., 1980; Hasenberg and Schmidt, 1986; Waletzko and Schmidt, 1988). However, it is important for both safety and selectivity reasons to know the operating conditions that avoid the onset of homogeneous reaction.

In combustion applications, it usually is desired to convert a fuel, such as CH_4, into energy with high conversion rather than with high selectivity; since homogeneous reactions give higher conversions, research and existing technology in the combustion field focus on the homogeneous oxidation of fuels. However, the presence of a catalyst has been shown to lower preheating required for homogeneous ignition, and after ig-

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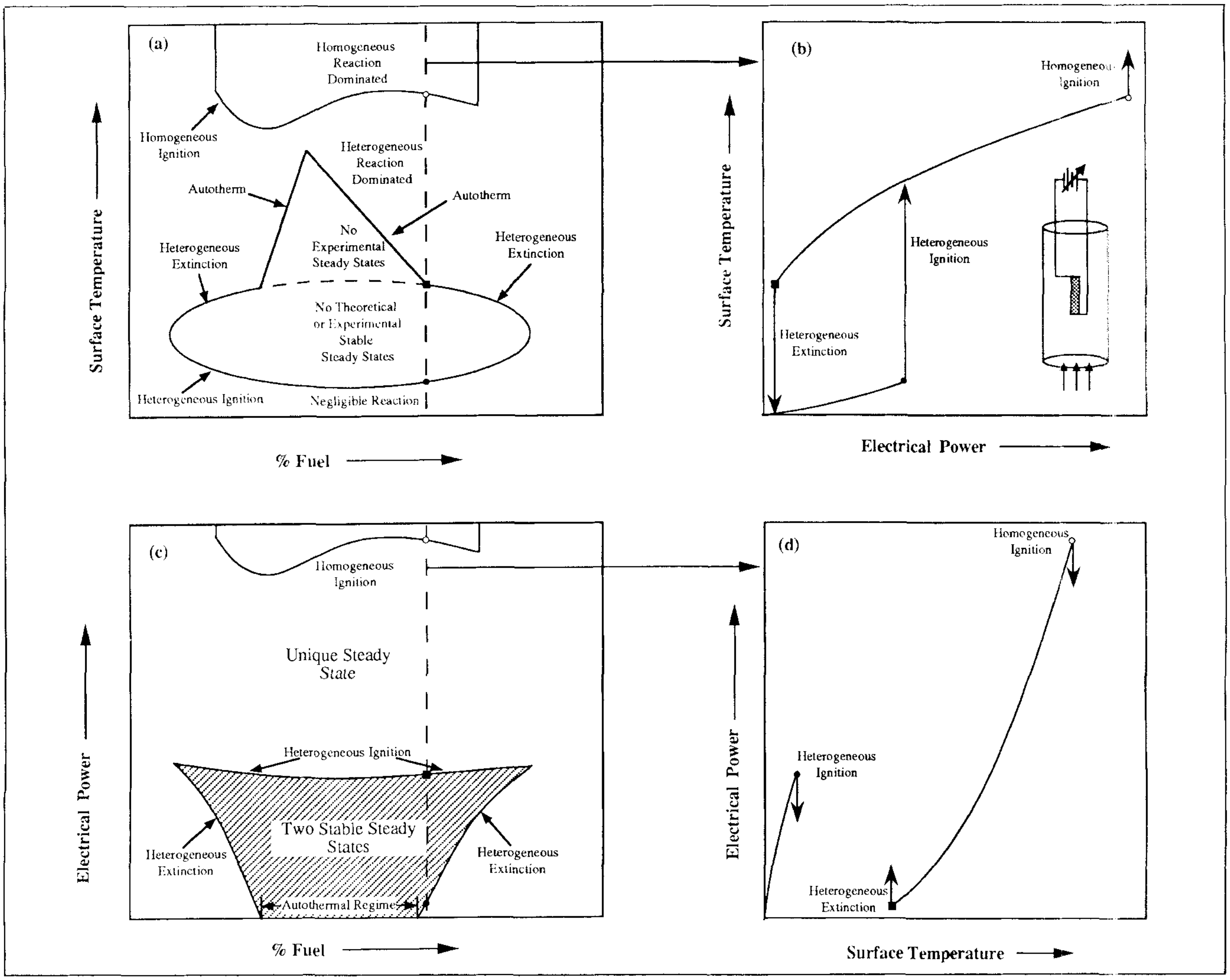

Figure 1. Examples of various types of bifurcation diagrams.

(a) Surface temperature vs. fuel composition bifurcation diagram with flammability limits indicated on the homogeneous ignition curve.
(b) Sample surface temperature vs. electrical power curve with experimental apparatus (inset).
(c) Electrical power vs. fuel composition for the same system.
(d) Diagram b is shown with the axes reversed to show the correspondence between the power vs. temperature curve and the power vs. fuel composition diagram.

nition the simultaneous gas-phase and catalytic reaction has been shown to minimize pollutant formation (Pfefferle and Pfefferle, 1987). Thus, much can be learned by studying the interaction of the two, although homogeneous and heterogeneous reactions are usually studied separately.

Among previous studies of the ignition of homogeneous and heterogeneous reaction systems are detailed investigations of the oxidations of C_2H_6 and CO/C_2H_6 mixtures over a Pt/Al_2O_3 pellet by Luss et al. (1987, 1985), and the study of the catalytic ignition of various fuels over a Pt wire by Cho and Law (1986). Also, Smith et al. (1971) studied the multiplicity of homogeneous combustion over a nonreacting hot surface. Homogeneous ignition over a hot catalytic surface was studied first by Coward and Guest (1927) with the focus on the ignition of natural gas over rods of various materials, including Pt. One of the major observations in the work was the existence of a sharp maximum in the homogeneous ignition temperature at stoichiometric feed over catalytic surfaces, while a minimum in the homogeneous ignition temperature was observed at the stoichiometric mixture over noncatalytic surfaces. Recently, Griffin and Pfefferle (1990) have followed up on this study and have provided some explanations for these results.

Other examinations of heterogeneous and homogeneous oxidations have used laser-induced fluorescence (LIF) to measure free radical concentrations. Many studies have examined the role of desorbing radicals in systems dominated by surface reactions (Ljungström et al., 1989; Selwyn and Lin, 1985; Marks and Schmidt, 1991). Also, Pfefferle and coworkers (Pfefferle et al., 1989; Griffin et al., 1989) and Cattolica and Schefer (1982) studied free radical concentration profiles during homogeneous ignition over catalytic and noncatalytic surfaces.

Here we present results from a continuing study of the bifurcation behavior of homogeneous/heterogeneous oxidation systems. The studies cited above provide an extensive framework for understanding these systems. However, unlike the studies cited above, we are more concerned with looking for generic behavior in these systems and with developing a general idea of the important mechanisms in these systems. Thus, rather than conducting detailed analyses of the types cited above, this work focuses on documenting behaviors in these systems and proposing possible explanations for the trends and observations.

In previous work, we have shown that any system, in which both homogeneous and heterogeneous reactions are significant, possesses a generic behavior (Williams et al., 1991). When graphed in the surface temperature vs. fuel composition parameter space, this behavior resembles a "witch's hat" corresponding to the heterogeneous reaction and a homogeneous curve above the witch's hat (Figure 1a). Although we did study the 1:1 NH_3/CH_4 system previously, the investigation focused primarily on single fuels. However, the mixed system exhibited two ignited heterogeneous steady states that did not fit into this generic pattern.

In the present study, we examine the effect of adding a second fuel on the homogeneous-heterogeneous oxidation bifurcation behavior and extend our knowledge of the generic behavior of single-fuel systems to multiple-fuel systems. In general, experimental bifurcation analysis is a powerful tool in understanding the dynamics of these types of reactors. Also, this analysis, coupled with theoretical bifurcation analysis, has been shown to provide valuable insight into the surface and gas-phase reaction kinetics as well as the interplay between surface and gas-phase reactions (Song et al., 1990). We chose to study the ignition, extinction, and autothermal behavior of the NH_3/CH_4 system, because it not only possesses interesting bifurcation characteristics but also the oxidation of NH_3/CH_4 mixtures to form HCN is an industrially important process.

Experimental Studies

Mixtures of air and NH_3, CH_4, or NH_3/CH_4 mixtures flowed upward in a 3.2-cm-dia. Pyrex reactor. The reactor consisted of a preheat section and a reactor section, each about 35-cm-long. The preheat section was packed with glass wool and beads and wrapped with heating tape so that the gases could be preheated to temperatures up to 450°C. However, in all experiments reported here, no preheat was used. The reactor section contained the catalyst sample attached to heating leads in a vertical orientation on a glass-joint seal and suspended about 10 cm above the preheat section. The catalyst was a 0.025-mm-thick, 2 cm × 0.5 cm platinum foil of 99.9% purity, which was spot-welded to nickel leads (inset, Figure 1b). The foil was heated resistively by a DC power supply, and the electrical power supplied to the foil was calculated from the known foil resistance vs. T_S curve of Pt.

Flow rates were controlled by mass flow controllers calibrated for each gas. The gas velocities, usually between 2 and 7 cm/s, were always in the laminar region, and the total flow rate had a small effect on the bifurcation behavior of any system studied. Temperatures were measured with a Chromel-Alumel thermocouple spot-welded to the surface and with an infrared optical pyrometer. Temperatures reported here are believed to be accurate to ±10°C at lower temperatures and ±30°C at temperatures above 1,000°C.

In a given run, the gas composition, flow rate, and inlet temperature were set to desired values, and the current was increased until heterogeneous ignition occurred. The current was then reduced until the heterogeneous reaction extinguished, or if the reaction remained ignited with no current, an autothermal T_S was recorded for that composition rather than an extinction T_S. Finally, for homogeneous ignition studies, the power to the ignited foil was then increased until a flame appeared or the T_S approached the foil melting point, (1,772°C).

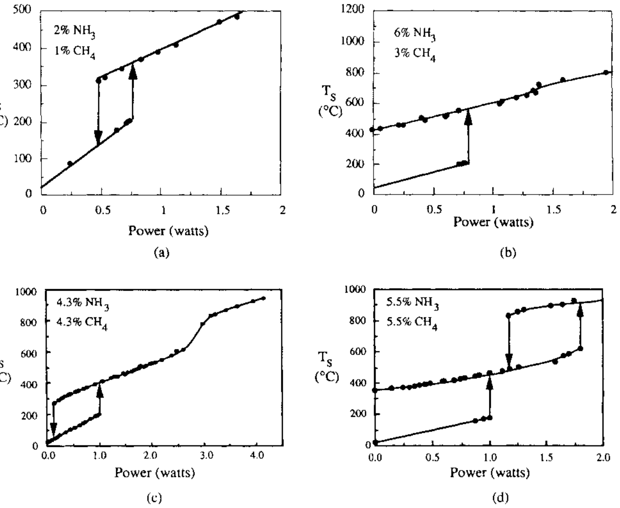

Figure 2. Sample surface temperature vs. electrical power for oxidation of fuel mixtures over *Pt*.

It shows: (a) a typical ignition/extinction hysteresis loop, (b) a hystersis loop possessing an autotherm, and the development of a second hysteresis loop in (d) from an abrupt increase in the upper curve in (c). In this and all figures shown here, gases entered the reactor at room temperature and 3.25 liters/min.

Such an experiment gives a graph similar to Figure 1b, where the control parameter (electrical power) is plotted vs. the dependent variable (surface temperature). These curves are generated at various fuel concentrations for all the NH_3/CH_4 ratios tested. The ignition, extinction, and autothermal behavior is then summarized in either a surface temperature vs. composition (Figure 1a) or a power vs. composition bifurcation diagram (Figure 1c). To show how these bifurcation diagrams are compiled, the composition corresponding to the curve in Figure 1b is indicated by a dashed line in Figure 1a as well as the location of the ignition and extinction points. To illustrate this for a power vs. composition diagram (Figure 1c), the axes of Figure 1b are reversed in Figure 1d, and a similar correspondence is shown. (A plot of the form in Figure 1d would result, if one used a constant surface temperature controller and monitored power requirements.)

Results

In Figure 2, typical surface temperature vs. power curves are shown which illustrate the major features observed in heterogeneous oxidation. The simplest behavior is the heterogeneous ignition/extinction hysteresis loop shown in Figure 2a. When the fuel concentration is increased toward the stoichiometric composition, extinction occurs for lower power inputs until the foil remains at an elevated temperature without any power (Figure 2b). This is referred to as the autotherm.

At some compositions, the mixed fuel systems exhibit an intermediate steady state. It is first observed as an abrupt, but continuous, temperature increase in the T_S vs. power curve

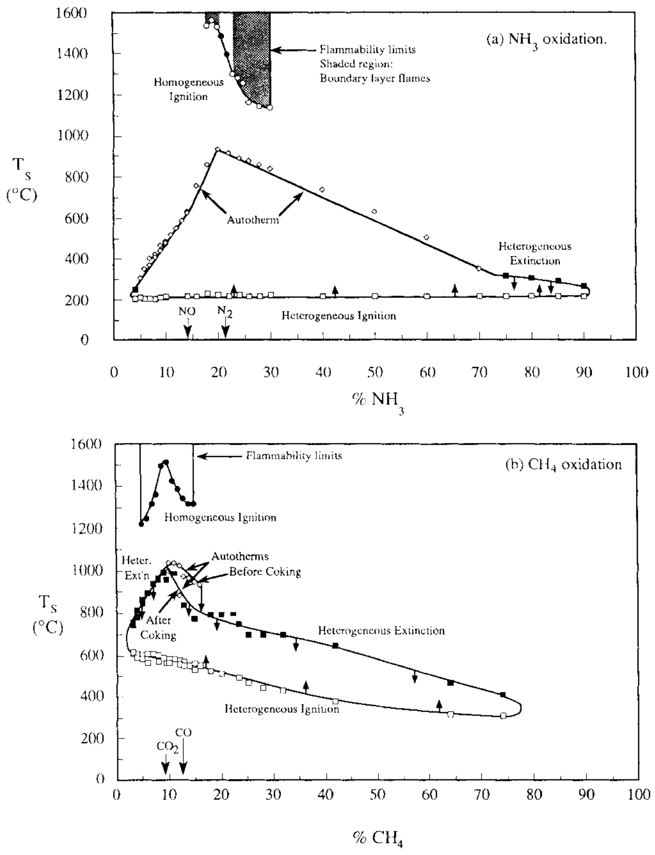

Figure 3. Homogeneous/heterogeneous bifurcation diagrams for the oxidation of (a) NH$_3$ and (b) CH$_4$ over *Pt*.

It shows surface temperatures where heterogeneous ignition (□), heterogeneous extinction (■), homogeneous independent flame ignition, (●), and homogeneous boundary layer flame ignition (○) occurred as well as the autothermal temperatures (◇).

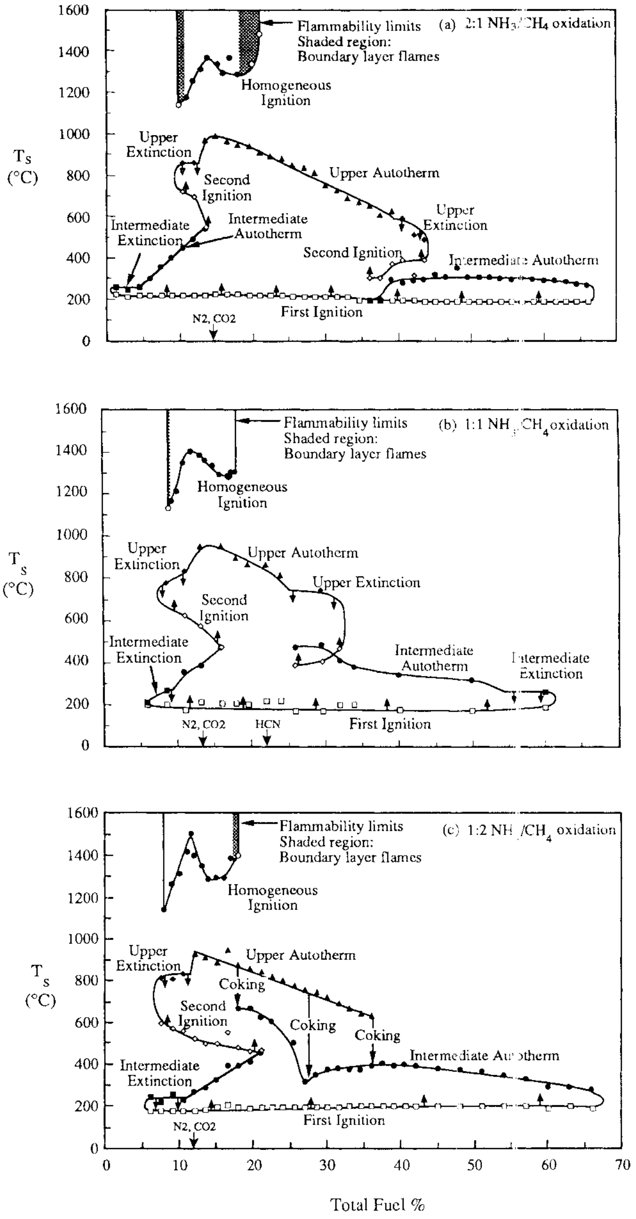

Figure 4. Homogeneous/heterogeneous bifurcation diagram for the oxidation of a (a) 2:1, a (b) 1:1, and a (c) 1:2 NH$_3$/CH$_4$ mixture over *Pt*.

It shows surface temperatures where the bifurcations and autotherms occurred in the lower steady states (first heterogeneous ignition, □), the intermediate steady states (second heterogeneous ignition, ◇; intermediate autotherm, ●, intermediate extinction, ■), and the upper steady states (homogeneous boundary layer flame ignition, ○; homogeneous independent flame ignition, ●; upper autotherm, ▲; upper extinction, ◆).

(Figures 2b and c). A further increase in fuel toward the stoichiometric composition causes this continuous increase to become a second hysteresis loop (Figure 2d). In this case, there are no more than two stable steady states for a fixed power. However, if the upper curve extinction power becomes less than the lower curve ignition power, three stable steady states are observed for the same power. For some compositions, two elevated temperature autotherms were observed.

Finally, for systems within the flammability region, a further power increase results in the ignition of a flame. Two types of flames were observed. The first type is the independent flame that burns throughout the reactor and generally propagates downward to the preheat packing. The term "independent flame" is used because this flame cannot be extinguished by turning off the electrical power to the foil. In systems containing NH$_3$, a second type of flame is observed at some compositions that will be referred to as the "boundary layer flame." This flame only burned in the boundary layer of the foil and extinguished as soon as the electrical power was reduced below the electrical power required to ignite the flame (i.e., no hysteresis). Also, for all boundary layer flames studied, further heating of the surface did not give independent ignition, and the boundary layer and independent flame ignition temperatures appeared to lie on the same curve. Therefore, in all bifurcation diagrams, one curve will be drawn through both the boundary layer and independent flame ignition points with vertical lines separating the regions where boundary layer flames and independent flames were observed.

Bifurcation diagrams from these T_S vs. power studies are summarized in Figures 3 and 4 where the homogeneous ignition and heterogeneous bifurcation points and autotherms observed in these experiments are graphed in bifurcation diagrams. In these diagrams, the total fuel concentration for a fixed ammonia to methane ratio is graphed as the abscissa and either surface temperature or electrical power is graphed as the ordinate. For a bifurcation diagram, it would be more appropriate to graph power because one can directly see the multiplicity of steady states and because electrical power is the control parameter. However, we have chosen to use surface temperature in these diagrams because the behavior at various surface temperatures is similar for other related systems such as gauzes and monoliths where resistive heating is difficult or impossible and thus electrical power would be irrelevant.

Ammonia oxidation

Figure 3a shows the ammonia oxidation system. The heterogeneous oxidation of ammonia was by far the simplest system studied. Because the system does not form carbon to deactivate the surface, stable and precisely reproducible steady states were observed for virtually all compositions studied, and the autotherm gives the expected straight line functionality of a mass-transfer-limited reaction with breaks in the lines at the NO and N_2 stoichiometric compositions (Williams et al., 1991). Ammonia oxidation ignites at ~200°C regardless of composition and, once ignited, cannot be extinguished between 3% and 70% NH_3 in air except by removing NH_3 or O_2. In fuel-rich or -lean mixtures, the surface temperature must be lowered to around 300°C to extinguish the reaction, again fairly independent of composition. The practical effect of this is a remarkably large range of compositions for which autothermal operation is possible.

The homogeneous oxidation of ammonia in air occurs between 15% and 31% NH_3 over the Pt surface, which is a slightly wider range than reported in the literature (15-28%, Lewis and von Elbe, 1987). These flames are dominated by boundary layer flames with only the compositions near stoichiometry exhibiting an independent flame (20-23%). In ammonia oxidation, the fuel-rich boundary layer flames ignite at lower surface temperatures than the independent flame at the stoichiometric point.

Methane oxidation

Methane oxidation (Figure 3b) is somewhat more complicated than ammonia oxidation. This is due primarily to carbon formation on the surface in excess CH_4 that was visually observed at all fuel-rich compositions. This prevented autothermal operation for all but a very narrow range of compositions (10-12% CH_4 in air). Autotherms were observed initially for compositions between 12% and 18% CH_4; but, typically after about five minutes the temperature would drop and the foil would extinguish. This coincided with a visual observation of carbon formation. Both the initial and final autothermal or extinction temperatures are shown in Figure 3b. Methane oxidation had a much higher heterogeneous ignition T_S than ammonia (~600°C compared to ~200°C for ammonia), although the ignition range for CH_4 was quite large (3-75%). The ignition T_S exhibited a much stronger dependence on fuel composition than ammonia. While ammonia oxidation on the surface ignited around 200°C for all compositions, the surface ignition temperature for methane oxidation decreased with increasing fuel composition so that at the fuel-rich limit of surface ignition the ignition temperature was just above 300°C.

The homogeneous ignition of methane yielded only independent flames with a flammability range of 5-15% CH_4 in air. Consistent with previous work cited above (Griffin and Pfefferle, 1990; Coward and Guest, 1927), the maximum surface temperature required to ignite the methane flame occurred at the stoichiometric composition for CO_2 formation (9.5% CH_4 in air).

Heterogeneous oxidation of the mixed fuels

In Figure 4, the bifurcation diagrams of 2:1, 1:1 and 1:2 NH_3/CH_4 mixed fuel oxidation are shown. The mixed fuels all exhibit multiple heterogeneous ignition temperatures at some compositions, and the 1:1 (Figure 4b), and 1:2 NH_3/CH_4 (Figure 4c) mixtures also have multiple autotherms at some compositions. There are always two regions of fuel compositions with multiple ignition temperatures: one region near the stoichiometric point for N_2 and CO_2 production and the other for very fuel-rich mixtures. In the region of slightly fuel-rich mixtures, there is only one ignition to the upper steady state. In the 1:1 mixture, this occurs near the stoichiometric composition for HCN formation (22% total fuel in air).

The first heterogeneous ignition occurred around 200°C for all compositions and fuel ratios studied, and the second heterogeneous ignition occurred between 400 and 800°C and was relatively independent of fuel ratio. The upper autotherm was observed over the widest range of compositions for the 2:1 NH_3/CH_4 mixture (Figure 4a). The 1:2 NH_3/CH_4 mixture had the smallest upper autothermal range, because, similar to methane alone, carbon formation caused a drop in temperature after about five minutes, which resulted in a drop to the intermediate autotherm. In all but the 1:1 mixture, intermediate extinction could not be observed in the fuel-rich regime. This state should exist as shown theoretically by Song et al. (1991), which implies that it occurs only over a very narrow range of compositions and at very low power inputs.

In the 1:1 mixture, the second ignition in the 28-32% fuel range occurred at a lower temperature than the intermediate autotherm. When power was applied to the surface at the intermediate autotherm, the surface temperature decreased and then began to oscillate. Finally, at a lower temperature than the autotherm but at a greater power input, the second ignition occurred. This behavior is discussed in more detail in a previous article (Williams et al., 1991).

Homogeneous oxidation of mixed fuels

The progression of the homogeneous ignition profiles from NH_3 through the 4:1, 2:1, 1:1, 1:2 and 1:4 NH_3/CH_4 mixtures to CH_4 is shown in Figures 5a-5g and summarized in Figure 5h. The progression shows that the boundary layer flame seems to be closely associated with ammonia oxidation, because a boundary layer flame is observed for almost all flammable compositions in ammonia and occurs over a progressively narrow region of compositions as the ammonia becomes a smaller portion of the fuel mixture, and finally CH_4 oxidation alone exhibits no boundary layer flames.

Figure 5h summarizes some important features of the qualitative behavior of the profiles. First, for most methane containing mixtures the maximum ignition T_S occurs at or near the stoichiometric mixture. Only at 4:1, NH_3/CH_4 does the maximum move off the stoichiometric mixture toward the fuel-

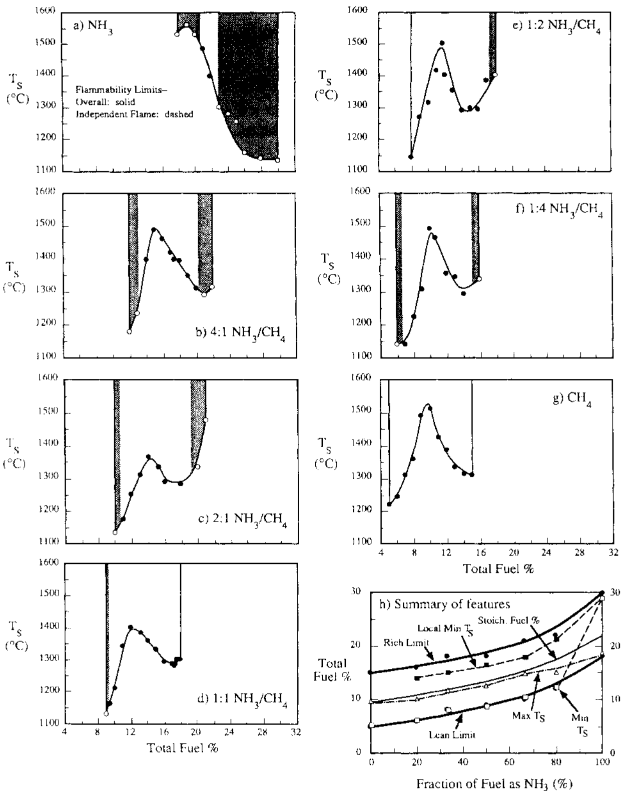

Figure 5. Surface temperatures required for homogeneous boundary layer (○) and independent (●) flame ignition over *Pt*.

In the oxidation of: (a) NH_3, (b) 4:1 NH_3/CH_4, (c) 2:1 NH_3/CH_4, (d) 1:1 NH_3/CH_4, (e) 1:2 NH_3/CH_4, (f) 1:4 NH_3/CH_4, (g) CH_4, and summary of features (h). (Total fuel percentage vs. the fraction of fuel as NH_3)-flammability limits (●), local and global minimum ignition temperature (■, □), maximum ignition temperature (△), stoichiometric composition (–).

lean limit, where ammonia oxidation has its maximum. For all methane-containing mixtures, the minimum ignition T_S occurs at the fuel-lean limit, whereas the minimum ignition T_S for ammonia oxidation occurs near the fuel-rich limit. However, all the mixtures exhibited a local minimum in fuel-rich mixtures similar to the minimum in ammonia oxidation, as shown in Figure 5h.

Transients upon fuel removal in mixed oxidation autotherms

The ignition behavior in the mixed fuels suggests that the intermediate steady state could be a result of sequential oxidation where the ammonia ignites at lower temperatures followed by methane ignition at higher surface temperatures. To test this hypothesis, the effect of removing each of the two fuels on the autothermal operation of the reactor was studied. This was done by allowing the reactor to come to its steady autothermal state, removing one of the fuels and recording the resulting surface temperature. Where carbon formation occurred, the measurement was made for the autotherm that existed before the onset of carbon formation.

The results of this study in Figure 6 show the autothermal temperatures from Figure 4. The autothermal surface temperatures resulting from turning off one of the fuels are graphed at the initial fuel % (not at the steady-state fuel %). While this fuel percentage is not strictly proper, presenting the results in this manner has the benefit of seeing the effects directly on the graph as vertical displacements. With multiple autotherms, usually the results of removing the fuels were identical regardless of which autotherm was used as the original steady state. The exception was in the 1:2 NH_3/CH_4 system where ammonia removal caused the intermediate steady state to extinguish for all compositions. For clarity, this is not shown in Figure 6c.

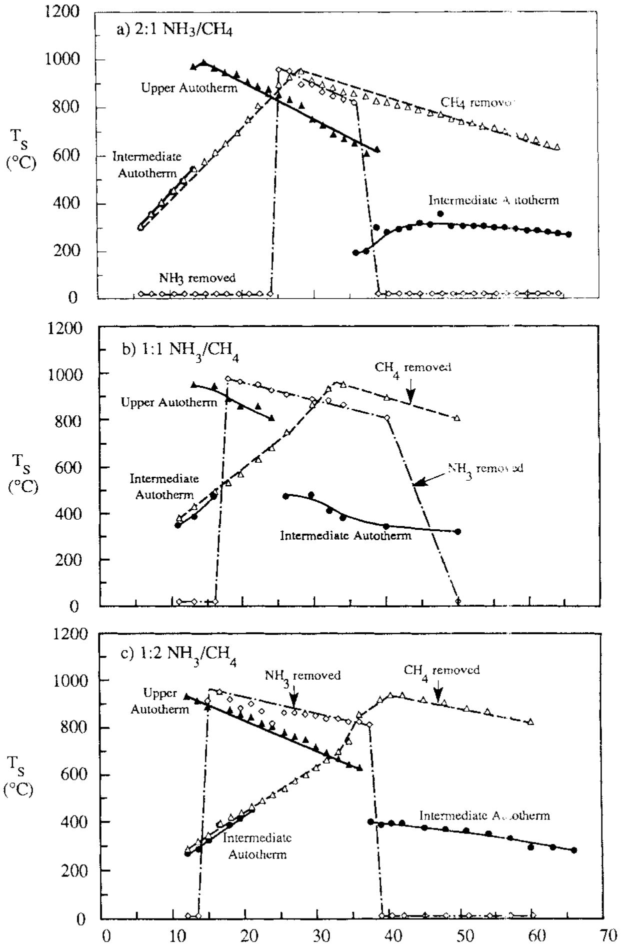

Figure 6. Effects of removing one fuel from mixed fuel autotherms in the heterogeneous oxidation of (a) 2:1, (b) 1:1, and (c) 1:2 NH_3/CH_4 mixtures.

Original autotherms are shown from Figure 4, with the resulting autothermal T_S on removing either CH_4 (△), or NH_3 (◇, •—•—) overlaid.

For all the mixed-fuel oxidations studied, there was no effect on the intermediate autotherm near the N_2/CO_2 stoichiometric composition when the methane was removed, but in all cases ammonia removal caused extinction of the foil. In fact, in the 2:1 NH_3/CH_4 system, the methane removal curve looks almost identical to the ammonia oxidation autotherm.

Generally, removal of ammonia always resulted either in extinction or in an increase in temperature; there were no cases where the temperature simply decreased. Removal of methane never caused extinction, but it always caused the temperature in near stoichiometric mixtures of the upper autotherm to drop to the intermediate autotherm. Finally, for all the mixtures studied there was a regime where removing either fuel caused an increase in temperature. The regime was the largest for 2:1 NH_3/CH_4 and the smallest for 1:2 NH_3/CH_4. In the 1:1 mixture, this corresponded to the industrial operation of the Andrussow process (28-30% total fuel).

Discussion

In these experiments, we have investigated the effect of adding a second fuel to the system on the generic behavior of homogeneous-heterogeneous oxidation of single fuels (Williams et al., 1991). We have observed that systems containing two fuels can exhibit three stable steady states but that many of the features of both the heterogeneous and homogeneous oxidation of the individual fuels are preserved in the mixed systems. The probable causes of these observations are discussed below.

Heterogeneous oxidation of the mixed fuels

The emergence of the intermediate steady state appears to be due to initial oxidation of ammonia at low T_S followed by ignition of methane at higher T_S. This is supported by the fact that the first ignition occurs around 200°C and is relatively independent of compositions for all the mixtures (Figure 4), which is qualitatively similar to ammonia oxidation (Figure 3a). Further, the second ignition occurs near 600°C, which corresponds to the ignition of pure methane oxidation (Figure 3b). The most compelling evidence for the sequential oxidation of the two fuels comes from the experiments where one of the fuels was removed (Figure 6). Removal of methane had no effect on all the intermediate autotherms near the stoichiometric point, but removal of ammonia caused the reaction to extinguish. The fuel-rich intermediate autotherms, however, appear to be more complicated. For the 2:1 and 1:2 ammonia/methane mixtures, ammonia removal still caused extinction, but methane removal caused an increase in temperature from ~300°C to ~700°C. This increase and the observation of carbon formation on the surface imply that in the fuel-rich autotherm, some methane may be decomposing and forming carbon on the surface, which would lower the autothermal temperature.

For virtually all compositions of the fuel-rich intermediate autotherm in the 1:1 mixture and for some compositions in the upper autotherms of the other mixtures, removal of either fuel causes an increase in temperature. In the 1:1 mixture, this composition corresponds to the operation composition of the Andrussow process for HCN synthesis. Since HCN production is endothermic with respect to N_2 and CO_2 production (Eqs. 3a and 3b), the increase in temperature with removal of either fuel could be due to a shift from HCN production with both fuels present to N_2 or CO_2 production when only one fuel is present.

Therefore, it appears that the intermediate autotherm near the stoichiometric point is strictly ammonia oxidation, but some methane may be participating in the reaction in the fuel-rich intermediate autotherm. The effect of a second fuel on the generic witch's hat behavior is, to a reasonable approximation, simply a superposition of two witches' hats (Figure 7). This suggests three steady states for fuel-rich and -lean mixtures. However, for compositions near the stoichiometric mixture, only two steady states exist because the intermediate autotherm exceeds the second ignition temperature. In principle, this could be observed in any oxidation system where the two fuels ignite at disparate temperatures. In fact, a similar behavior was observed by Harold and Luss (1985) in the simultaneous oxidation of CO and C_2H_6 mixtures where the individual surface ignition temperatures of the two fuels differed only by 100°C.

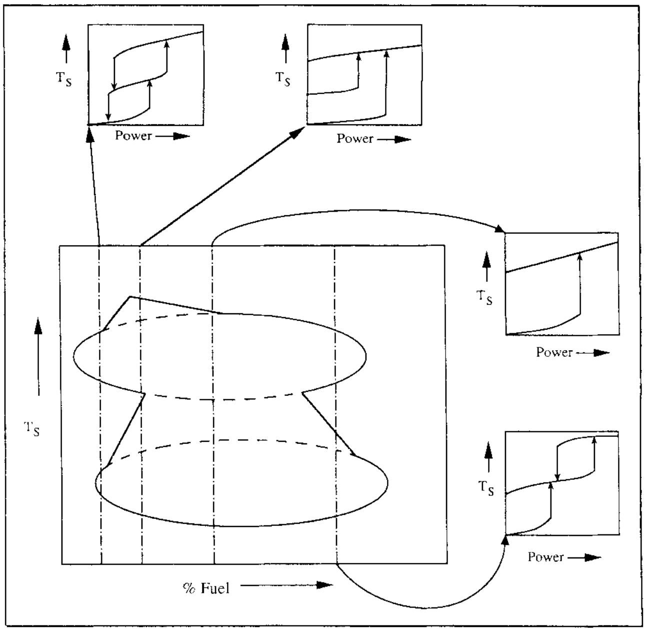

Figure 7. Double witch's hat behavior expected when two fuels with disparate heterogeneous ignition temperatures are oxidized on a catalyst.

Expected witch's hats from individual fuels are shown superimposed with features not observable experimentally (- - - -). Corresponding T_S vs. electrical power curves are shown at the indicated compositions.

Homogeneous oxidation of the mixed fuels

The progression of the mixed fuels in Figure 5 illustrates that methane appears to control much of the homogeneous behavior. The major features of pure methane oxidation can be seen even in the 4:1 NH_3/CH_4 system. Already, the composition range of the independent flame has been increased from only 20-22% for NH_3 oxidation (Figure 5a) to 14-20% in the 4:1 NH_3/CH_4 system, with only mixtures near the flammability limits giving boundary layer flames (Figure 5b). This is probably because the methane tends to burn more vigorously so that even if a boundary layer flame ignited, it would become independent once the flammable methane mixture was exposed to it. Methane also appears to control other major features such as the minimum and maximum T_S for homogeneous ignition (Figure 5h), although a local minimum apparently corresponding to NH_3 oxidation exists for all the mixtures. Therefore, methane and ammonia appear to have reversed their roles in homogeneous ignition compared to heterogeneous ignition.

Finally, it should be noted that for all mixtures, the minimum homogeneous ignition T_S never occurs for the stoichiometric mixture for N_2 and CO_2 production. This seems counterintuitive because in the stoichiometric mixture, the combustion is most efficient with no excess reactants acting as diluents. It was proposed (Lewis and von Elbe, 1987) that this was caused by the fact that the surface temperature is higher for a given heat input (electrical power or preheat) at the stoichiometric mixture than all other mixtures. Thus, although the stoichiometric mixture ignited at the highest T_S, it actually occurred at the minimum heat input.

Griffin and Pfefferle (1990) recently suggested that the sharp maximum observed in the homogeneous ignition T_S could not be caused by the linear dependency of a mass-transfer-limited heterogeneous reaction. Indeed, when we monitored power required to ignite the homogeneous reaction (not shown), we found that the maximum homogeneous ignition power input occurred at the same composition as the maximum homogeneous ignition T_S for all mixtures studied. Griffin and Pfefferle (1990) then proposed that this sharp maximum in the methane profile was due to a transient heating effect on the surface. In an experiment designed to decouple the transient effect, they further showed that the actual ignition profile did not possess the sharp maximum observed by Coward and Guest (1927). We feel that this is an important consideration, but we were careful in our studies to assure that we had indeed attained steady state. Further, even in their decoupled experiments, the minimum homogeneous ignition T_S still did not occur at the stoichiometric feed.

As a result of the decoupled experiments of Griffin and Pfefferle (1990), our results shown here on CH_4 and NH_3 oxidation, and previous results obtained for C_3H_8 oxidation (Williams et al., 1990), we feel it should not be expected that minimum homogeneous ignition T_S should occur at stoichiometric composition over a catalytic surface. In fact, this is supported by the results of Song et al. (1991), where the theoretical ignition T_S profiles in homogeneous CH_4 and C_3H_8 oxidation showed no minima at stoichiometric composition over a catalytic surface. The model used only standard transport equations but still yielded this counterintuitive result. Therefore, this effect is real, and it reflects a heat and mass transfer coupling that cannot be understood with simple approximations.

Summary

This work has demonstrated the importance of experimental bifurcation analysis in understanding complicated reaction systems (Eqs. 1-3). From the systematic study of the NH_3/CH_4 system, we have identified many important considerations in an important industrial process and have been able to infer some information on selectivity without any species analysis. We also have been able to arrive at several generalizations:

- In any system where exothermic homogeneous and heterogeneous reactions occur, one can expect a generic surface temperature vs. composition diagram similar to the one shown in Figure 1a.
- Adding a second fuel to such a system can cause added multiplicity (such as in NH_3/CH_4 and CO/C_2H_6 oxidations). At least in the case of NH_3/CH_4, this appears to be due to a sequential ignition of the two fuels caused by a disparity in heterogeneous ignition temperatures. Graphically, this can be understood as a superposition of the witch's hats of the individual fuels. Since CO and C_2H_6 have heterogeneous ignition temperatures differing by 100°C (Harold and Luss, 1985), it is quite possible that this is the cause of the multiplicity in this system as well. Thus, other multiple fuel systems where the two fuels have disparate ignition temperatures would be possible candidates to possess this added multiplicity. This multiplicity could be observed experimentally only if the autotherm of the more easily ignited fuel does not exceed the ignition point of the other fuel because this would hide the ignition behavior of the other fuel (Figure 7).
- Finally, this superposition of the witch's hats can be complicated by selectivity changes and consequent heat release, such as the shift from NO, N_2, CO and CO_2 production in the separate oxidations of NH_3 and CH_4 to the production of HCN in the mixed fuel system. Our experiments show this effect, although it was not so pronounced that the superposition of the bifurcation diagrams of the two individual fuels was not obvious.

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Literature Cited

Bowen, W. J., "Supplies of Methane in the United States," *Methane-Fuel for the Future*, P. L. McGeer and E. J. Dubin, eds., Plenum Press, New York, 1 (1982).

Cattolica, R. J., and R. W. Schefer, "The Effect of Surface Chemistry on the Development of the [OH] in a Combustion Boundary Layer," *Int. Symp. on Combustion*, Combustion Institute, Pittsburgh, 311 (1982).

Cho, P., and C. K. Law, "Catalytic Ignition of Fuel/Oxygen/Nitrogen Mixtures over Pt," *Combustion and Flame*, **66**, 159 (1986).

Coward, H. F., and P. G. Guest, "Ignition of Natural Gas-Air Mixtures by Heated Metal Bars," *ACS J.*, **49**, 2479 (1927).

Flytzani-Stephanopoulus, M., L. D. Schmidt, and R. Caretta, "Steady State and Transient Oscillations in Ammonia Oxidation on Platinum," *J. Catal.*, **64**, 346 (1980).

Griffin, T. A., and L. D. Pfefferle, "Gas Phase and Catalytic Ignition of Methane and Ethane in Air over Pt," *AIChE J.*, **77**, 861 (1990).

Griffin, T. A., L. D. Pfefferle, M. J. Dyer, and D. R. Crosley, "The Ignition of Methane/Ethane Boundary Layer Flows by Heated Catalytic Surfaces," *Combust. Sci. and Tech.*, **65**, 19 (1989).

Harold, M. P., and D. Luss, "An Experimental Study of Steady State Multiplicity Features of Two Parallel Catalytic Reactions," *Chem. Eng. Sci.*, **40**, 39 (1985).

Harold, M. P., M. Sheintuch, and D. Luss, "Analysis and Modelling of Multiplicity Features. 2. Isothermal Experiments," *Ind. Eng. Chem. Res.*, **26**, 794 (1987).

Hasenberg, D., and L. D. Schmidt, "HCN Synthesis from CH_4 and NH_3 on Pt," *J. Cat.*, **97**, 156 (1986).

Lee, H. C., and R. J. Farrauto, "Catalyst Deactivation Due to Transient Behavior in Nitric Acid Production," *Ind. Eng. Chem. Res.*, **28**, 1 (1989).

Lewis, B., and G. von Elbe, *Combustion, Flames, and Explosions of Gases*, 3rd ed., Academic Press, Orlando, FL (1987)

Ljungström, S., B. Kasemo, A. Rosén, and T. Wahnström, "An Experimental Study of the Kinetics of OH and H_2O Formation on Pt in the $H_2 + O_2$ Reaction," *Surface Sci.*, **216**, 63 (1989).

Marks, C. M., and L. D. Schmidt, "Hydroxyl Radical Desorption in Catalytic Combustion," *Chem. Phys. Lett.*, in press (1991).

Pfefferle, L. D., T. A. Griffin, M. Winter, D. R. Crosley, and M. J. Dyer, "The Influence of Catalytic Activity on the Ignition of Boundary Layer Flows," *Combustion and Flame*, **76**, 325 (1989).

Pfefferle, L. D., and W. C. Pfefferle, "Catalysis in Combustion," *Cat. Rev.-Sci. Eng.*, **29**, 219 (1987).

Pignet, T., and L. D. Schmidt, "Selectivity of Ammonia Oxidation on Platinum," *Chem. Eng. Sci.*, **29**, 1123 (1974).

Selwyn, G. S., and M. C. Lin, "Free Radical Formation in the Catalytic Oxidation of NH_3 over a Polycrystalline Pt Surface at High Temperatures," *Langmuir*, **1**, 212 (1985).

Smith, H. W., R. A. Schmitz, and R. G. Ladd, "Combustion of a Premixed System in Stagnation Flow," *Comb. Sci. and Tech.*, **4**, 131 (1971).

Song, X., W. R. Williams, L. D. Schmidt, and R. Aris, "Bifurcation Behavior of Homogeneous-Heterogeneous Combustion: II. Theoretical Analysis for Stagnation Flow," *Combustion and Flame*, in press (1991).

Song, X., W. R. Williams, L. D. Schmidt, and R. Aris, "Ignition and Extinction of Homogeneous-Heterogeneous Combustion: Methane and Propane Oxidation on Platinum," *Int. Symp. on Combustion*, Combustion Institute, Pittsburgh, in press (1991).

Waletzko, N., and L. D. Schmidt, "Modeling Catalytic Gauze Reactors: HCN Synthesis," *AIChE J.*, **34**, 1146 (1988).

Williams, W. R., M. T. Stenzel, X. Song, and L. D. Schmidt, "Bifurcation Behavior of Homogeneous-Heterogeneous Combustion: I. Experimental Results over Platinum," *Combustion and Flame*, in press (1991).

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