Detonation Cell Size Measurements in High-Temperature Hydrogen-Air-Steam Mixtures at the BNL High-Temperature Combustion Facility

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ABSTRACT

The High-Temperature Combustion Facility (HTCF) was designed and constructed with the objective of studying detonation phenomena in mixtures of hydrogen-air-steam at initially high temperatures. The central element of the HTCF is a 27-cm inner-diameter, 21.3-m long cylindrical test vessel capable of being heated to $700\text{K} \pm 14\text{K}$. A unique feature of the HTCF is the "diaphragmless" acetylene-oxygen gas driver which is used to initiate the detonation in the test gas.

Cell size measurements have shown that for any hydrogen-air-steam mixture, increasing the initial mixture temperature, in the range of 300K to 650K, while maintaining the initial pressure of 0.1 MPa, decreases the cell size and thus makes the mixture more detonable. The effect of steam dilution on cell size was tested in stoichiometric and off-stoichiometric (e.g., equivalence ratio of 0.5) hydrogen-air mixtures. Increasing the steam dilution in hydrogen-air mixtures at 0.1 MPa initial pressure increases the cell size, irrespective of initial temperature. It is also observed that the desensitizing effect of steam diminished with increased initial temperature. A 1-dimensional, steady-state Zel'dovich, von Neumann, Doring (ZND) model, with full chemical kinetics, has been used to predict cell size for hydrogen-air-steam mixtures at different initial conditions. Qualitatively the model predicts the overall trends observed in the measured cell size versus mixture composition and initial temperature and pressure. It was found that the proportionality constant used to predict detonation cell size from the calculated ZND model reaction zone varies between 10 and 100 depending on the mixture composition and initial temperature.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
LIST OF FIGURES	vii
EXECUTIVE SUMMARY	ix
ACKNOWLEDGMENTS	xi
 1 INTRODUCTION	 1-1
1.1 Background	1-1
1.2 Objectives	1-4
1.3 Organization of Report	1-4
 2 EXPERIMENTAL DETAILS	 2-1
2.1 Experimental Apparatus	2-1
2.1.1 Overview of the High Temperature Facility	2-1
2.1.2 Test Vessel	2-1
2.1.3 Gas Handling System	2-2
2.1.4 Gas Driver Detonation Initiation System	2-2
2.1.5 Heating System	2-3
2.1.6 Instrumentation	2-4
2.1.7 Data Acquisition and Control	2-5
2.2 Experimental Procedures	2-6
 3 EXPERIMENTAL RESULTS	 3-1
3.1 Gas Driver Characterization	3-1
3.1.1 Gas Driver Composition	3-1
3.1.2 Effect of Driver Length on Detonation Transmission	3-2
3.1.3 Gas Driver Energy	3-3
3.2 Detonation Cell Size Measurements	3-4
3.2.1 Baseline Experiment at 300K and 0.1 MPa	3-5
3.2.2 Hydrogen Oxidation at Elevated Temperature	3-7
3.2.3 Effect of Initial Mixture Temperature on Cell Size	3-8
3.2.4 Effect of Steam Dilution on Cell Size	3-8
3.2.5 Effect of Initial Mixture Pressure on Cell Size	3-9
3.3 Detonation Velocity	3-10
 4 DISCUSSION	 4-1
4.1 Cell Size Prediction	4-1
4.2 Use of Cell Size Data	4-2
4.3 Influence of Initial Temperature on Cell Regularity	4-3

TABLE OF CONTENTS

(Continued)

	<u>Page</u>
5 SUMMARY AND CONCLUSIONS	5-1
6 REFERENCES	6-1
APPENDIX A	A-1
APPENDIX B	B-1

LIST OF FIGURES

1.1	(a) Time evolution of detonation wave front and triple-point trajectories forming a fish-scale pattern, (b) labeling convention for a three wave interaction	1-5
1.2	Smoked foils obtained from detonations in a square channel for mixtures of hydrogen-oxygen-argon and hydrogen-air (Strehlow, 1969)	1-6
2.1	Schematic showing the High-Temperature Combustion Facility layout	2-7
2.2	Photograph showing the driver-end of the test vessel inside of the Tunnel	2-8
2.3	Schematic of the High-Temperature Combustion Facility gas handling system	2-9
2.4	Schematic showing the details of the driver gas handling system	2-10
2.5	Photograph of the heating system power control unit	2-11
2.6	Photograph of the heating pad and insulation distribution on the test vessel	2-12
2.7	Schematic showing the thermocouple positions on the test vessel for the temperature uniformity tests	2-13
2.8	Experimentally measured test vessel temperature distribution for a temperature set point of 500K	2-14
2.9	Experimentally measured test vessel temperature distribution for a temperature set point of 650K	2-15
2.10	Photograph of the control and data acquisition equipment located in the control room	2-16
3.1	Experimentally measured driver-gas ($C_2H_2+3O_2$) axial distribution in the test vessel at 1 second after driver-gas injection	3-11
3.2	Effect of driver partial pressure (or length) on detonation transmission in a 8 percent hydrogen and 92 percent air mixture at 650K and 0.1 MPa	3-12
3.3	Effect of driver partial pressure (or length) on detonation transmission in a 14.5 percent hydrogen and 85.5 percent air mixture at 300K and 0.1 MPa	3-13
3.4	Comparison of measured, BNL and Sandia National Lab (Tieszen et al., 1987), and calculated detonation cell size for hydrogen-air mixtures at 300K and 0.1 MPa	3-14
3.5	Proportionality constant (i.e., ratio of experimental cell size and calculated ZND reaction zone length) for hydrogen-air mixtures at 300K and 0.1 MPa	3-15
3.6	Hydrogen oxidation time history for a 15 percent hydrogen and 85 percent air mixture in the vessel at 650K and 0.1 MPa	3-16
3.7	Detonation cell size for hydrogen-air mixtures at 500K and 0.1 MPa	3-17
3.8	Detonation cell size for hydrogen-air mixtures at 650K and 0.1 MPa	3-18
3.9	Comparison of detonation cell size for hydrogen-air mixtures at 300K and 650K at 0.1 MPa	3-19

LIST OF FIGURES (Continued)

3.10	Proportionality constant (i.e., ratio of experimental cell size and calculated ZND reaction zone length) for hydrogen-air mixtures at 500K and 650K at 0.1 MPa	3-20
3.11	Detonation cell size as a function of temperature for stoichiometric hydrogen-air and steam mixtures at 0.1 MPa (symbols: open-SSDA, closed-HTCF, half closed-Sandia HDT, lines-ZND with $A=51$)	3-21
3.12	Detonation cell size as a function of temperature for stoichiometric and off-stoichiometric hydrogen-air and steam mixtures at 650K and 0.1 MPa (open symbols: SSDA, closed symbols: HTCF, lines: ZND model)	3-22
3.13	Detonation cell size as a function of the initial pressure for a 9 percent hydrogen and 91 percent air mixture at 650K	3-23
3.14	Detonation cell size as a function of the initial pressure for a stoichiometric hydrogen-air mixture with 30 percent dilution at 650K	3-24
3.15	Detonation cell size as a function of initial pressure for a 18 percent hydrogen - 82 percent air and 20 percent steam mixture at 650K	3-25
3.16	Comparison of measured and calculated detonation velocity for hydrogen-air mixtures at 300K and 0.1 MPa (vertical bars represent standard deviation in measured velocities)	3-26
3.17	Comparison of measured and calculated detonation velocity for hydrogen-air mixtures at 500K and 0.1 MPa (vertical bars represent standard deviation in measured velocities)	3-27
3.18	Comparison of measured and calculated detonation velocity for hydrogen-air mixtures at 650K and 0.1 MPa (vertical bars represent standard deviation in measured velocities)	3-28
4.1	Comparison of the ZND model predicted cell size ($\lambda = A\Delta$) using the maximum temperature gradient and the Mach Number 0.75 definitions for the reaction zone length	4-6
4.2	Calculated global activation energy for hydrogen-air mixtures at 300K and 0.1 MPa	4-7
4.3	Calculated global activation energy for hydrogen-air mixtures at 650K and 0.1 MPa	4-8
4.4	Comparison of dimensionless term (E/RT_n) for hydrogen-air mixtures at 300K and 650K at 0.1 MPa	4-9
4.5	Comparison of the ratio of cell size data standard deviation and average for hydrogen-air and steam mixtures at 300K and 650K and at 0.1 MPa	4-10

EXECUTIVE SUMMARY

The High-Temperature Hydrogen Combustion Research Program, jointly funded by the U.S. Nuclear Regulatory Commission (NRC) and the Japanese Nuclear Power Engineering Corporation (NUPEC) which is sponsored by the Ministry of International Trade and Industries (MITI), is a 5-year program at Brookhaven National Laboratory (BNL) with the objective of studying detonation phenomena in mixtures of hydrogen-air and steam under prototypical severe-accident conditions. The principal experimental facility used in research program is the High-Temperature Combustion Facility (HTCF). A smaller facility, i.e., the Small-Scale Development Apparatus (SSDA), was constructed to support the design of the larger HTCF and to obtain preliminary experimental data. Experiments in the SSDA are complete and the results are reported in NUREG/CR-6213. Both the SSDA and the HTCF were designed to study detonations in gaseous mixtures of hydrogen-air and steam at temperatures up to 700K. The actual maximum initial gas temperature employed in this program has been 650K.

The central element of the HTCF is a 27-cm inner-diameter and 21.3-m long cylindrical test vessel designed for a maximum allowable working pressure of 10.0 MPa at 700K. The test vessel is heated by electric heating blankets which are fastened to the test vessel. The blankets are constructed from cylindrical ceramic beads through which nichrome heating wire is threaded. Heating system calibration tests demonstrated that at temperature, i.e., up to 700K nominal, the vessel temperature is uniform to within ± 14 K. The facility is cleared of personnel during testing and the tests are remotely operated from a control room. Instrumentation is provided to measure properties of the detonation wave, including detonation velocity, pressure, and cell size.

In previous studies, high explosives were commonly used as the initiation source for experiments studying various detonation phenomenon. One of the unique features of both the SSDA and the HTCF is the use of a "diaphragmless" gas driver to initiate the detonation in the test gas. The driver gas is injected into one of the ends of the test vessels, and a detonation is initiated in the driver gas using an electrical spark discharge. The detonation propagates through the driver gas and is then transmitted into the test gas. After some initial shakedown tests, the gas driver has proven to be a very reliable and flexible component of both the SSDA and the HTCF. In order to limit driver effects on the detonation in the test gas, i.e., detonation overdrive, the amount of driver gas used in the HTCF was minimized.

The experimentally measured detonation velocities were all within a few percent of the theoretical Chapman-Jouguet (CJ) detonation velocity, including the 650K data, where in the SSDA the velocity was consistently about 5 percent below the CJ detonation velocity. This difference could be attributed to the much slower rate of pre-ignition hydrogen oxidation in the HTCF compared to the SSDA.

Detonation cell size was measured using the smoked foil technique. It is generally acknowledged that the detonation cell size of a mixture is inversely related to the sensitivity of that mixture to undergo detonation. For example, the smaller the cell size, the more sensitive the mixture. Cell size measurements have shown that for any hydrogen-air-steam mixture, increase of the initial mixture temperature, in the range of 300K to 650K, while maintaining the initial pressure at 0.1 MPa decreases the cell size and thus makes the mixture more sensitive.

The effect of steam dilution on cell size was tested in stoichiometric and off-stoichiometric (e.g., equivalence ratio of 0.5) hydrogen-air mixtures. Increasing the steam dilution in hydrogen-air mixtures at 0.1 MPa initial pressure increases the cell size and thus decreases the mixture sensitivity, irrespective of initial temperature. It was also observed that the desensitizing effect of steam diminished with increased initial temperature. The maximum steam dilution resulting in a detonation was 50 percent steam in a stoichiometric hydrogen-air mixture at 650K and 0.1 MPa.

A limited number of experiments were carried out to investigate the influence of initial mixture pressure on detonation cell size. There was very little effect observed in the pressure range tested, 0.1 MPa to 0.24 MPa, for relatively weak hydrogen-air-steam mixtures, i.e., cell size is weakly influenced by initial pressure.

A 1-dimensional, steady-state Zel'dovich, von Neumann, Doring (ZND) model, with full chemical kinetics, has been used to predict cell size for hydrogen-air-steam mixtures at different initial conditions. The cell size, λ , is taken to be proportional to the calculated ZND reaction zone length, Δ , (e.g., $\lambda = A\Delta$). Taking A to be a constant, the ZND model did a relatively good job at predicting the global trends in the cell size data as a function of mixture composition and initial conditions. However, a comprehensive comparison of the theoretical predictions with the experimentally measured cell size has demonstrated that the two parameters are not linked by a simple constant of proportionality. As Shepherd (1986) first demonstrated and this study corroborated, the proportionality constant is at least a function of the mixture equivalence ratio, ϕ , such that $\lambda = A(\phi)\Delta$. In this investigation, it has also been shown that A is also a function of the initial mixture temperature, such that $\lambda = A(\phi, T_0)\Delta$. It is clear from this study that in order to use the ZND model for scaling purposes, one must take great care in the choice of the proportionality constant.

An investigation was also performed to determine if the temperature has an effect on the regularity of the hydrogen-air mixtures. The data produced in the SSDA and the HTCF did not conclusively indicate that the initial temperature has any effect on the detonation cell regularity of these mixtures.

The data obtained from this investigation adds significantly to the existing data base on detonation cell size, thereby increasing our knowledge base on the effects of initial temperature, steam dilution, hydrogen concentration, and initial pressure. In particular, based on the detonation cell size data measured from the experiments in the HTCF and based on the range of parameters tested, the following conclusions were reached concerning the sensitivity of mixtures to undergo detonation:

1. Increase in the initial temperature of a hydrogen-air-steam mixture increases the mixture detonation sensitivity.
2. Increase in the steam dilution, at any initial temperature, results in a decrease in the mixture detonation sensitivity.
3. Increase in the hydrogen concentration up to stoichiometric conditions, at any initial temperature, increases the mixture detonation sensitivity.
4. For the limited initial pressure range tested in the HTCF, an increase in the initial pressure moderately increases the mixture detonation sensitivity.

To determine the likelihood of detonation, the HTCF detonation cell size data have direct applicability to containment local volumes with mixture compositions and initial conditions similar to those tested. For mixture compositions and initial conditions not tested in the HTCF, the likelihood of detonation initiation can be addressed using the HTCF data in conjunction with existing theoretical models.

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This project was initiated in April 1991 with the help of Dr. Walter Y. Kato, who was the Chairman of the Department of Nuclear Energy at that time.

A number of individuals have provided technical assistance to this project. Mr. Joseph Curtiss and Mr. Joseph Jahelka, project engineers for the High-Temperature Combustion Facility (HTCF), provided their engineering advice and insights during the design and construction of the facility. Mr. Curtiss provided the integration of the interlock system, previously used by the Neutral Beam Test Facility, into the safety system for the HTCF. Recently retired, Dr. Costantino Economos, a team member since the start, helped in the planning and conceptualization of the project as well as in the design of some of the key elements of the HTCF. We acknowledge him for his contributions to the project and also wish him well in his retirement years. As DAT Safety Coordinator, Mr. Walter Becker has provided access to his broad technical experience in safety as well as many other technical issues. Mr. Steven Hoey has served as an advisor representing the Safety and Environmental Protection (S&EP) Division, and Mr. Patrick Sullivan has served as S&EP representative. They have both provided continual advice on safety-related issues, involving the operation of the HTCF.

The authors would especially like to thank Ms. Jean Frejka for her assistance in all administrative phases of this project. She is responsible for maintenance of all project records, for keeping our accounting of expenditures up to date and in reportable form, and is responsible for papers, presentations, and report manuscripts. We acknowledge her help in preparation of this manuscript for publication.

1. INTRODUCTION

The concern over the possibility of a combustion event occurring in a water-cooled nuclear reactor during a severe accident was heightened following the Three-Mile Island Unit 2 (TMI-2) accident. It is now generally acknowledged that a deflagration took place in the TMI-2 containment building during the progression of the accident (Henrie and Postma, 1983 and Toth, 1985). The ignited combustible gaseous mixture was made up of existing air in containment, steam released during the accident, and hydrogen produced by the reaction between the zirconium metal cladding and steam in the degraded core. As a result of TMI-2, combustion research focusing on hydrogen-air mixtures was intensified. Due to the high dynamic pressures associated with the detonation mode of combustion, one of the main goals of the research was to determine the necessary geometric and thermodynamic conditions required for detonation initiation. This knowledge is essential in order to help predict the possibility of such an event during a postulated severe accident and to estimate the associated loading on containment.

Under most severe accident scenarios, a containment atmosphere consisting of hydrogen, air, and steam at initial temperatures up to 373K and pressures up to roughly 3 atmospheres can prevail. For this reason, most of the detonation research was limited to these conditions (Tieszen et al., 1987). Calculations by Yang (1992) have shown that under certain accident scenarios local compartment temperatures in excess of 373K can occur. Since relevant data at such temperatures is limited and confidence in the modeling of detonations is not high, the need arose to perform further investigations into higher temperature detonation phenomenon.

The High-Temperature Hydrogen Combustion Research Program at Brookhaven National Laboratory is jointly funded by the U.S. Nuclear Regulatory Commission and the Japanese Nuclear Power Engineering Corporation. The overall objective is to extend the ability to assess potential detonation-type loads in containment during severe accidents, characterized by initial high-temperature and large steam fraction hydrogen-air-steam mixtures. This report presents the results from the first element of the High-Temperature Combustion Program, dealing with inherent detonability.

1.1 Background

A self-sustained detonation wave consists of a shock wave followed by a coupled exothermic reaction zone. The role of the shock is to adiabatically compress the unreacted mixture to a pressure and temperature such that chemical reactions progress very quickly. The detonation propagates at a supersonic velocity which depends on the chemical energy content of the mixture (e.g., kJ/kg). All the thermodynamic properties (e.g., pressure, temperature, density) at the end of the reaction zone can be calculated quite accurately via a Hugoniot analysis. In a Hugoniot analysis, a locus of solutions is obtained from the steady-state one-dimensional mass, momentum, energy equations, along with an equation of state. A unique solution can be identified if one imposes the so called Chapman-Jouguet (CJ) criteria which states that the relative fluid velocity downstream of the shock equals the local speed of sound. For a given mixture at a given initial condition, the CJ solution also corresponds to the detonation wave with the minimum propagation velocity.

It is quite surprising that the CJ velocity matches so closely the experimentally observed steady-state detonation velocity, considering a detonation is actually a highly 3-dimensional phenomenon and the CJ velocity is based on a strictly 1-dimensional analysis. It has been demonstrated that a detonation consists of a complex of shock waves propagating both in the direction of the detonation as well as transverse to the direction of propagation. Figure 1.1a shows the time evolution of the detonation front as it propagates from left to right. The corrugated detonation shock front consists of three distinct waves which are defined as the incident, mach, and transverse waves, as shown in Figure 1.1b. The point where the three waves intersect is referred to as the triple point. The "fish scale" pattern shown in Figure 1.1a represents the trajectories of the triple-points in the detonation front. The diamond shape pattern traced by two adjacent triple points is referred to as a detonation cell. Also shown in Figure 1.1a, as hatched lines, is the relative position of the

1. Introduction

exothermic portion of the reaction zone behind the various shock waves. As can be seen, the detonation wave front consists of a series of decaying blast waves which initiate chemical reaction in the mixture. As the blast wave propagates it decays and the reaction zone length increases only to be accelerated by the collision of the two converging transverse waves. During the cycle, the blast wave velocity can vary from 1.6 times the CJ velocity at the start of the cell down to 0.6 times the CJ velocity at the end of the cell, with the average close to the CJ velocity.

The detonation cellular pattern was first discovered experimentally by Denisov et al. (1960) using a "smoked foil" technique. In this technique, a plastic or metal foil is coated with carbon soot and placed on the inside wall of a detonation tube with the soot covered side facing the centerline of the tube. If the tube is then filled with a combustible gas mixture and a detonation is initiated such that it propagates over the foil, a characteristic fish-scale pattern similar to the one shown in the background of Figure 1.1a will be etched onto the foil. The precise reason why the triple points have the ability to write on the foils is not known, but it is believed that the high vorticity which exists in the shear layer which extends from the triple-point (not shown in Figure 1.1) plays an important role. The transverse width of the cell is referred to as the detonation cell size and is typically denoted by the Greek symbol λ . Shown in Figure 1.2 are photographs taken of three smoked foils obtained from detonations propagating in rectangular channels (Strelow, 1969). In all three foils, the mixture was stoichiometric hydrogen-oxygen with various diluents at room temperature and subatmospheric pressures. The center foil is from a stoichiometric mixture of hydrogen-oxygen with no dilution, and the left and right foils are from stoichiometric hydrogen-oxygen mixtures diluted with 50 percent nitrogen and 40 percent argon, respectively. Note that 50 percent nitrogen dilution of a stoichiometric hydrogen-oxygen yields a mixture which is very close to stoichiometric hydrogen-air which has a nitrogen mole fraction of 55 percent. The detonation cellular pattern in the nitrogen diluted mixture is very irregular; no single cell size can be identified and, therefore, one must report an average cell size. This irregularity in the cellular pattern is also typical in hydrocarbon-air mixtures. The cellular structure in the center foil, corresponding to a stoichiometric hydrogen-oxygen mixture with no dilution, shows a little more regularity, but it can also be considered fairly irregular. Diluting with argon (or any other monatomic gas) tends to make the cellular pattern more regular, as observed in the foil on the right in Figure 1.2.

It was later determined that several key detonation phenomena were governed by the mixture cell size. The "critical tube" phenomenon, which represents the minimum tube diameter, d_c , through which a detonation can successfully transmit into an unconfined space, for most common combustible mixtures, scaled with cell size according to $d_c = 13\lambda$ (Mitrofanov and Solouhkin, 1965). The minimum energy required to initiate a detonation directly, i.e., the "critical initiation energy," was also found to correlate with the detonation cell size (Lee, 1977). Finally, the "detonability limit" in a tube was found to depend on the detonation cell size (Dupre et al., 1985). The success in the scaling of these important dynamic parameters of detonation waves with the cell size has resulted in the use of the detonation cell size as the fundamental length scale of a detonation wave (Lee, 1984). However, it has been found that the scaling of the above mentioned dynamic parameters with cell size breaks down for mixtures which exhibit a regular detonation cellular structure similar to that observed in the foil on the right of Figure 1.2 (Moen et al., 1986; Shepherd et al., 1988; Desbordes et al., 1993).

Due to the importance of the cell size as a fundamental detonation length scale, Knystautas et al. (1984) headed a program to generate a data base of cell size for common fuel-air mixtures, including hydrogen, at atmospheric conditions. A 30-cm inner-diameter detonation tube was used to make these measurements. The data indicated that for all mixtures tested a plot of detonation cell size versus equivalence ratio resulted in a U-shaped curve where the minimum cell size corresponds roughly to the stoichiometric composition of the mixture. For lean mixtures, it was observed that the cell size is very sensitive to the mixture composition. In an extension to the work done by Knystautas, Tieszen et al. (1987), using a 45-cm diameter detonation tube, increased the cell size data base for hydrogen-air including the effect of steam dilution, initial pressure, and initial temperature. The maximum temperature investigated by Tieszen et al. (1987) was 373K, so no definite conclusions concerning the effect of temperature on cell size could

be reached. Since one is limited by the scale of the test apparatus used to acquire cell size data, it is very difficult to test very lean mixtures which are of the most interest in the evaluation of the likelihood of industrial accidents. Therefore, empirical relations are sought to extrapolate the data obtained in the laboratory scale to larger, more prototypic scales.

Two- and three-dimensional numerical simulations of detonation phenomena reproduce the cellular structure that has been observed experimentally (Oran et al., 1981; Fujiwara et al., 1989). Although encouraging, these codes have not yet been sufficiently refined to the point where they can be used as predictive tools. Much attention has been given to one-dimensional transient modeling of detonation waves. The instability in a true detonation wave, as manifested in the transverse waves, appears in a 1-dimensional simulation as a longitudinal instability. That is, the axial detonation wave velocity oscillates about the CJ steady-state solution. Although these transient, 1-dimensional models include all the proper physics (e.g., gasdynamic and full chemistry), they are of limited use in terms of quantitative prediction of 3-dimensional detonation phenomenon.

One-dimensional, steady-state detonation models, referred to as ZND models, have been used to study the structure of the detonation reaction zone (e.g., temperature, pressure, density spatial variation). These models assume that a non-reactive shock wave propagates into the mixture at the theoretical CJ velocity for the mixture. The steady-state conservation equations are then integrated over distance downstream from the shock wave, with the initial condition taken as that of the compressed gas just after the shock wave. With the knowledge of the details of reaction zone, a detonation reaction zone length which is a measure of the sensitivity of the detonation can be deduced, much like the cell size in a true three-dimensional detonation. One of the four definitions used in the past to describe the reaction zone length in a one-dimensional ZND detonation model is the distance between the shock wave and the point of maximum energy release, which corresponds to the location of maximum temperature gradient (Shepherd, 1986). With the availability of the complete description of the elementary chemical reactions and their rate constants, attempts have been made to correlate the reaction zone length calculated using the ZND model and the experimental cell size. Shchelkin and Troshin (1965) were the first to perform such an analysis and to propose a simple linear correlation between the two quantities. Westbrook et al. (1982) and Shepherd (1986) used detailed chemical kinetic schemes to look at the effect of mixture composition, dilution, and initial pressure and temperature on the reaction zone length for the hydrogen-air system. Both analyses showed that steam dilution increased the reaction zone length. Shepherd (1986) demonstrated that the ratio of the experimental cell size over the calculated reaction zone size is a function of the mixture composition, and in general takes on a value between 5 and 50. Recently, Stamps (1991) applied the ZND calculations to determine the effect of high initial temperature on hydrogen-air-steam mixtures. The calculations indicated that for off-stoichiometric hydrogen-air mixtures increasing the initial temperature initially reduced the reaction zone length reaching a minimum and then increased. Due to the lack of data above 373K, Stamps (1991) could not compare the calculated ZND reaction zone length with experimentally measured cell size.

The limited availability of cell size data has hampered our ability to assess the effect of temperature on the "sensitivity" of hydrogen-air-steam mixtures to undergo detonation for temperatures that are of interest for some severe accident conditions¹. This is especially relevant since the ZND calculations indicate that the capability of a mixture to detonate increases with temperature. While the ZND model has been shown to be applicable in correlating cell size data measurements, data are required over a larger range of temperature heretofore unavailable in order to help provide a more complete assessment. The experimental program described in the report has been directed towards providing some of this additional data.

¹The mixture "sensitivity" to detonation relates to the minimum energy required to initiate a detonation in a test mixture. Sensitive mixtures require relatively small quantities of energy to initiate a detonation. Additionally, sensitive mixtures are characterized by relatively small cell size.

1. Introduction

1.2 Objectives

The BNL High-Temperature Combustion Facility (HTCF) was constructed to investigate hydrogen combustion phenomena in gaseous mixtures of hydrogen-air and steam at temperatures up to 700K. The major component of the facility is a 27.3-cm inner-diameter, 21.3-m long heated detonation tube. The Small-Scale Development Apparatus (SSDA) was constructed to support the design of the HTCF and to augment the experimental data base. A detailed description of the SSDA can be found in NUREG/CR-6213.

The objectives of this phase of the experimental program are to:

- (1) Provide experimental data on the detonation cell size of hydrogen-air and steam mixtures as a function of initial mixture temperature, in order to determine the effect of temperature in the range of 300K to 650K on the sensitivity of the mixtures to undergo detonation. Note, mixtures of hydrogen-air introduced into the vessel preheated to 700K would burn immediately upon injection. The experiments performed to measure cell size also provide measurements of detonation velocity and pressure.
- (2) Evaluate the ability of the ZND model to predict the effect of temperature on the detonation cell size of mixtures of hydrogen-air and steam and to compare the measured detonation velocity with the prediction from the theoretical CJ theory.

The purpose for acquiring these data and for performing these evaluations has been to enhance our knowledge base in estimating the likelihood of mixtures, prototypical to nuclear power-plant severe accident conditions, to undergo a detonation or a high-speed combustion event.

1.3 Organization of Report

This report presents and discusses the results of an experimental program designed to investigate the intrinsic detonability characteristics of mixtures of hydrogen-air-steam at initially elevated temperatures. The information provided in this report comes from one programmatic element of the overall High-Temperature Combustion Program at BNL. Details of the overall program can be found in Ginsberg et al., 1991.

A description of the experimental facility used in this program, the test procedures followed, and the instrumentation/experimental techniques employed is contained in Section 2. Experimental results, largely in the form of cell size and wave speed, are presented in Section 3, which also includes discussions on the methods employed to characterize the gaseous driver. Wherever possible, the experimental observations are compared with simplified, heuristic theoretical models.

Implications in the overall trends in the data, the issue of geometric scale, the practicality of experimental data and existing correlations, the issue of cell regularity and wall effects on the hydrogen oxidation kinetics are discussed in Section 4.

Overall summary and conclusions are provided in Section 5. A summary of the experimental detonation cell size data is given in tabular form in Appendices A and B.

(a)

(b)

Figure 1.1: (a) Time evolution of detonation wave front and triple-point trajectories forming a fish-scale pattern, (b) labeling convention for a three wave interaction

Figure 1.2: Smoked foils obtained from detonations in a square channel for mixtures of hydrogen-oxygen-argon and hydrogen-air
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2. EXPERIMENTAL DETAILS

2.1 Experimental Apparatus

2.1.1 Overview of the High Temperature Facility

A schematic showing the overall site plan of the facility is given in Figure 2.1. The main component of the HTCF is a heated cylindrical detonation vessel located in a below-grade 100-meter-long tunnel. The tunnel is constructed from 3.05-meter diameter corrugated steel culvert tubes, backfilled with at least 3.05-meters of earth. One end of this tunnel is closed off; the other end is connected to the roughly 800-cu. meter Experimental Hall, which houses some of the heating system equipment and the Small-Scale Development Apparatus, described in Ciccarelli et al. (1994). The 100-meter-long tunnel is vented to prevent accumulation of hydrogen or other test gases due to accidental leaks in the gas handling system. Intake vents for tunnel air are located on the tunnel ceiling at tunnel stations just beyond both ends of the cylindrical detonation vessel, and a 3000-cfm exhaust blower is located above grade at a tunnel station mid span of the vessel. Also located at a tunnel station roughly at the mid point of the vessel are exhaust ports used for purging test-vessel gases to an elevated release point (i.e., stack) seven meters above grade.

During the operation of an experiment, all personnel are evacuated from the Experimental Hall and the tunnel. The experiments are performed remotely from a control room situated on the ground floor of the main building. As shown in Figure 2.1, the vacuum pump and electrical switching gear for the facility are housed in two separate small buildings adjacent to the main control room building. The compressed gas cylinders used in the experiments are located on a sheltered outdoor concrete pad.

In the following sections, the important features of the HTCF are described in more detail.

2.1.2 Test Vessel

The test vessel (or detonation tube) is composed of six identical 3.05-meter long, flanged tube sections and a 3.05-meter long, flanged driver section. A photograph of the assembled vessel inside the tunnel is shown in Figure 2.2. Each vessel section is mounted on its own mobile heavy-duty steel carriage. The carriage provides for some limited vertical and rotational positioning of the vessel for assembly purposes. All vessel sections were constructed according to the ASME Boiler and Pressure Vessel (B&PV) Code. Each vessel section is code stamped as complying with the B&PV Code Section VIII, Division II with a maximum operating pressure and temperature of 100 atm and 700K, respectively. The vessel has a 27.3-cm inner-diameter and is made of centrifugally-cast 304L stainless-steel. The seven tube sections are bolted together using stainless-steel studs and nuts. All vessels and their support structures were fabricated by Fluitron, Inc of Ivyland, Pennsylvania.

Instrumentation and gas connection ports are horizontally arranged with a uniform axial spacing of 0.61 m. At each axial position, ports are located on diametrically opposite sides of the vessel. This spacing allows for five port pairs per section, except for the driver section which only has ports on one side of the vessel. The spacing is maintained across the transition from one vessel section to the next. A standard port design, presenting a 6.35-cm diameter clear hole through the vessel wall and terminating in a standardized flange design, is utilized for all openings. Ports are plugged with retractable insert plugs designed to present a smooth gap-free surface on the inside of the vessel. Individual port plugs are customized to mount instrumentation or gas delivery piping to the vessel.

2. Experimental Details

2.1.3 Gas Handling System

A schematic of the gas handling system is given in Figure 2.3. All the gases are from gas cylinders (i.e., air, hydrogen, nitrogen, oxygen, and acetylene) of commercial grade. The air, hydrogen, and nitrogen are stored in standard 1A cylinders on the exterior gas pad. Acetylene and oxygen gas are stored in the tunnel, each in a smaller 40 cu. ft. bottle. A 100-psig commercial boiler is used as a source of steam for tests where steam is a test gas constituent. The tubing used throughout is 304 stainless steel, except for the tubing out of the steam generator which is 2.54-cm black iron pipe. The tubing connecting the exterior gas bottles to the first set of block valves in the tunnel is 2.54-cm-outer diameter. From the block valve to the mixing chamber, 1.27-cm-outer diameter tubing is used. Tubing which is actively heated is designated in Figure 2.3 by hatched lines. Stainless steel Swagelok fittings are used throughout. The valves are pneumatically actuated Jamesbury ball valves. The pneumatic actuators are controlled using 24 VDC solenoid valves.

The flow rates in the test gas lines (e.g. hydrogen, air, and steam) are determined by fixing the upstream pressure to a choked venturi. The upstream pressure is maintained during a fill via a PID pressure regulator whose feedback loop includes a pressure transducer placed upstream of the choked venturi, as shown in Figure 2.3. The test gas flow rates for hydrogen, air and steam are remotely set from the control room. Check valves are used when there is a potential for the backflow of one gas into the line of another. The hydrogen is first mixed with the steam and then mixed with the air in the mixing chamber. The mixing chamber consists of two flanged 5-cm, high-pressure pipe sections containing a turbulence enhancing device to aid in the mixing of the two input gases (e.g., hydrogen-steam and air or simply hydrogen and air). The turbulence generator is composed of several layers of corrugated plate, welded together to form a honeycomb geometry.

A large mechanical roughing pump is used to evacuate the vessel prior to each experiment. The vacuum pump is connected to a 10-cm copper pipe manifold that runs the length of the 100-meter-long tunnel. The vessel is connected to the manifold using 2.54-cm stainless steel tubing. Since the vessel length grows by over 15 cm when heated to 650K, flexible stainless steel hose is used to connect the vessel to any stationary plumbing, such as the vacuum manifold. Two large 100-HP blowers, each situated at the end of the vessel are used to blow air through the vessel and out the stack. These blowers serve two purposes: (1) to purge combustion products out of the vessel after each test and (2) to cool the vessel. Each blower is connected to the ends of the vessel via 15-cm diameter flexible hose. The two blower air outlets, at mid span of the vessel, are piped to the seven-meter exhaust stack using rigid aluminum ducting.

2.1.4 Gas Driver Detonation Initiation System

A gas driver system is used to initiate the detonation in the HTCF test vessel. The concept, similar to that used in the SSDA, is to produce a short slug of acetylene-oxygen mixture at one end of the vessel and initiate a detonation in this mixture using an "exploding wire." The detonation from the driver gas slug is then transmitted into the test gas. Since acetylene-oxygen is such a very reactive gas mixture, special attention must be paid in order to avoid thermal ignition at the heated vessel wall. In order to avoid this ignition problem, for experiments carried out at elevated temperature, the driver section (i.e., the first 3.05-m long test vessel section) into which the driver gas is injected, is not actively heated. As a result of heat conduction from the adjacent heated vessel, a temperature gradient is generated along the driver section. The ignition end of the driver section is at roughly room temperature and the other end is at the test temperature.

The driver gas plumbing and the high voltage trigger circuit used for the exploding wire can be seen in the foreground in the photograph in Figure 2.2, and the piping is shown schematically in Figure 2.4. The acetylene-oxygen mixture is injected into the vessel via a sparger system consisting of four equally spaced perforated tubes. As shown in Figure 2.4, the acetylene and oxygen gas bottles are connected to 1.27-cm diameter lines which include a shut-off ball

valve, a needle valve for throttling, and a flash arrestor. The driver gas composition can be varied either by the needle valves or by the bottle regulator delivery pressure. The acetylene delivery pressure was fixed at the maximum of 0.2 MPa absolute. The acetylene and oxygen are then mixed in a 1.9-cm line by flowing the two gases co-axially. The acetylene enters from a central 1.27-cm tube and the oxygen flows through the annular gap between the 1.90-cm tube and the 1.27-cm tube. The mixed acetylene-oxygen mixture then flows from the 1.90-cm diameter tube into a 1.27-cm diameter closed loop tube which acts as a manifold for four 1.27-cm diameter tubes which penetrate 10 cm into the vessel through the end plate. The four tubes enter the vessel at equally spaced radial positions just inside the vessel inner-wall, see Figure 2.2. The tube-ends are plugged, and each has a series of 1.6-mm holes which direct the flow inwards toward the vessel centerline.

The detonation in the acetylene-oxygen driver is initiated by the shock wave produced by an exploding wire. The exploding wire is a fine copper wire fastened between two electrodes which are mounted onto an instrumentation plug that protrudes into the center of test vessel through the driver endplate. The wire is made to explode by discharging a high voltage capacitor across it. The wire is made to explode by rapidly discharging approximately several hundred (theoretically about 560) joules of energy through a high-voltage capacitor circuit. The same high voltage circuit used on the SSDA was used for the present apparatus. The main circuit, consisting of a Maxwell 20 microfarad, 7.5 kV capacitor in series with an EG&G GP-85 spark gap is mounted inside a grounded metal cabinet as seen in Figure 2.2. The spark gap is triggered using an EG&G TM11A trigger module and the capacitor is charged using a 30 kV Hipotronics power supply. The trigger for the trigger module is a 24 VDC signal originating from the control software.

2.1.5 Heating System

The heating system was designed, manufactured and installed by Cooperheat Inc. of Piscataway, New Jersey. The assembled, insulated test vessels are each capable of being heated to the maximum operating temperature of 700K in four hours. The specification to the vendor for the temperature distribution of the vessel inner-wall required a spatial uniformity of $\pm 14K$. Temperature uniformity was verified at the vendor and checked again in greater detail at BNL. The maximum power consumption of the heating system is 650 kW.

The heating system is segmented into three major components, consisting of the heating elements, the power control unit, and a remote control unit. The remote control unit is located in the basement area directly below the control room. The remote control unit houses two multi-zone PID temperature controllers which are adjusted through a computer (RS-485 interfacing) located in the control room. This control unit is also the terminal for all the control zone thermocouples on the test vessel. The power control unit which distributes the power to the various heating zones on the vessel is located in the Experimental Hall, just beyond the tunnel exit. The power control unit, as shown in Figure 2.5, contains all the zone contactors as well as zone current monitoring devices. All interface signals between the power and remote control units are via 24 VDC signals. The power for the heating zones is derived from a 750 kW transformer, located outside the control building, which drops the laboratory 2200 VAC supply down to 480 VAC. The transformer is connected to a main disconnect in the electrical switch house and is then directed underground into the tunnel going through a 1200-amp safety disconnect switch located adjacent to the control power unit. The voltage is dropped to 120 VAC through a second transformer, and then enters the power control unit cabinet where it is distributed to the various heating zones. Each zone has two cables which originate at the power control unit and routed down the tunnel to the vessel through cable tray suspended from the tunnel wall. Each test vessel has a mounted junction box where the cables from the tray enter and are terminated at a power distribution block. The heater element leads hang below the vessel and are connected to the appropriate power distribution block.

The heating elements, which are mounted directly on the vessel outer wall, are shown in Figure 2.6. The resistance wire heating element is woven into a ceramic pad which is fastened to the vessel using stainless steel pipe clamps. The entire

2. Experimental Details

vessel is covered with two layers of 2.54-cm thick Kaowool insulation blankets. A typical 3.05-meter long vessel pipe section has three heating zones which can be controlled independently, and each flange pair also has its own heating zone yielding a total of 29 heating zones for the entire vessel. The heater pads were custom designed to give maximum heater coverage. The current draw from flange and pipe heaters is about 180 amps and 120 amps, respectively. Each zone has a K-type sheathed thermocouple strategically placed under a heating element which is used by the temperature controller to monitor the zone temperature. Each vessel section also has two additional monitoring thermocouples TAC-welded to the outer wall of the vessel. Each flange pair has one radial thermocouple well which allows for the measurement of the local metal temperature 2.54 cm from the vessel inner wall.

As depicted in Figure 2.3, some of the tubing is heated using trace heating, for those experiments performed at elevated temperature or when steam is a test mixture constituent. The steam exiting the boiler is superheated to roughly 375K in order to avoid condensation in the line. The black iron piping between the boiler and the steam PID pressure regulator is heated using an electric snake heating element. The heating element output is controlled by a temperature controller located in a cabinet adjacent to the remote control unit. The mixing chamber is also heated using the same type of heating element and is independently controlled. Standard trace heating tape is used on the tube sections between the steam PID pressure regulator and the mixing chamber and between the mixing chamber and the vessel. These two heating tapes are also independently regulated by temperature controllers.

As mentioned earlier, the temperature uniformity of the test vessel was verified at BNL by installing additional thermocouples and heating the vessel to 500K (440F) and 650K (710F). Unlike the previous heating tests where the thermocouples were evenly distributed throughout the entire test vessel, for this test the thermocouples were concentrated in the last three vessel sections. Figure 2.7 is a schematic indicating the positions of some of the thermocouples. In order to measure the inner-wall temperature a special rig was designed to hold the thermocouples up against the vessel inner-wall. The rig consisted of a high-tempered steel coil, shaped into a loop with a diameter roughly equal to the inner-diameter of the vessel, with thermocouples TAC-welded to the outside of the coil at four equally spaced circumferential positions. The coil is inserted into the vessel such that the four thermocouples end up in the 12, 3, 6, and 9 o'clock positions. Eight rigs were installed in the vessel at various axial locations, including under flanges and ports as shown in Figure 2.7. To measure the bulk gas temperature, one exposed junction sheathed thermocouple was placed into the mid instrumentation port of each of the seven vessel sections, with the junction at the tube centerline. The vessel outer-wall temperature was monitored using two TAC-welded thermocouples per vessel section which are not shown in Figure 2.7.

The temperature data taken when steady-state conditions were reached at the two test temperatures are shown in Figures 2.8 and 2.9. The two horizontal lines shown in each figure represent the minimum and maximum temperatures required to meet the $\pm 14\text{K}$ ($\pm 25^\circ\text{F}$) specification. In general, all of the measured temperatures fall within this band except for the thermocouples at 19.2 m (63 ft) and 20.4 m (67 ft) from the driver flange. The thermocouple at 19.2 m (63 ft) is next to the inner-surface of an instrument plug; and since the instrument ports and plugs represent a heat sink, it is not surprising that a slightly lower temperature would be measured at this location. This observation is true even in the inner-wall thermocouples which are close to a port. The low temperature at 20.4 m (67 ft) cannot be explained, especially since all four thermocouples on a rig at the same axial location give excellent results. In most cases, the rig thermocouples indicated higher temperatures on the top inner-surface as compared to the bottom. The side thermocouples measured temperatures between those located at the top and bottom.

2.1.6 Instrumentation

The instrumentation used in the present experiments are identical to those used in the SSDA (Ciccarelli, 1994). Test gas thermodynamic conditions such as temperature, pressure and mixture composition are all monitored and logged

2. Experimental Details

before a detonation is initiated. Standard K-type, exposed junction probe thermocouples with an accuracy of 1.2K are used to monitor the gas temperature. The vessel pressure is monitored using a strain gage Wika pressure transducers with an operating range of 0 to 0.34 MPa absolute with an accuracy of 0.1 percent of full scale. These gauges are used in a current loop so as to minimize electrical noise. The gauge is isolated from the vessel by a ball valve just before detonation initiation. The test mixture composition is set by the user by varying the mass flow rates through each of the constituent choked venturi. The Fox venturis have a manufacturer's quoted accuracy of 2 percent. Three gas samples are taken from the vessel, using pre-evacuated 150-ml gas cylinders, before each test. After the test, the samples are then analyzed as a further check on hydrogen content using a gas chromatograph (Carle Model 311H). The gas chromatograph is periodically calibrated using hydrogen gas standards with an accuracy of 2 percent. For tests with steam, the venturi mass flow rate is used to back out the steam content.

Detonation pressure is measured using fast-response PCB 113A24 quartz piezoelectric pressure transducers. Due to the high temperature environment, the transducers are housed in special water-cooled adaptors. These transducers have a maximum pressure range of 6.8 MPa with a rise time of 1 μ s. The accuracy of the transducer is less than 1 percent of full scale. Detonation time-of-arrival is measured using ionization probes. These probes consist of two electrodes which penetrate about 1.27 cm into the vessel. The electrodes are connected to a simple circuit which outputs a voltage signal when the electrodes are shorted by the passage of the detonation reaction zone. The time-of-arrival is used in conjunction with probe spacing to determine the average detonation velocity. As described in Ciccarelli et al. (1994), the accuracy of the velocity measured this way is 0.4 percent of the measured value.

Detonation cell size is measured using the "smoked-foil" technique. Aluminum foils are used, typically 2-meter long, 0.5-mm thick, which when shaped into a cylinder covers almost the entire circumference of the vessel inner-wall. The foil ends were riveted to 3-mm thick, 5-cm wide steel rings placed on the inside of the foil for added strength. The inside of the foil is smoked after the rings are mounted. The cylindrically shaped foil is placed upright on one end, and a kerosene lamp is burned inside. The foil is sooted incrementally from the bottom to the top in sections roughly 30-cm high. As discovered from the SSDA tests, for experiments at elevated temperature, the best results were obtained when the foil was first coated with a very thin layer of silicone fluid before smoking.

2.1.7 Data Acquisition and Control

All data acquisition and control equipment is located in the control room. A photograph of the control room layout is shown in Figure 2.10. A 486 Gateway PC equipped with several commercially available Strawberry Tree data acquisition and control cards and software are used to run the experiments from the control room. Three ACPC 12-bit analog input cards (16 channels each) are used for monitoring pressure transducer and thermocouple signals. One ACPC digital input/output card (40 channels) is used for actuating valves and monitoring limit switches. One ACAO 12-bit analog output card (6 channels) is used to feed the set points to the three PID pressure regulators. A Personal 488 card is also installed to provide GPIB capabilities to the system. The cards are driven by an icon-based Strawberry Tree program called Workbench.

Two 100-MHZ, 4-channel LeCroy 314L digital oscilloscopes are used to capture the high speed output signals from the piezoelectric pressure transducers and the ionization probes. Hard copies of the oscilloscope signals were made after each experiment.

Two additional computers not shown in Figure 2.10 are used to input the temperature set points for the vessel heating system and for various trace heat zones.

2. Experimental Details

2.2 Experimental Procedures

The following is a brief description of the steps taken to execute a detonation experiment at elevated initial temperature. Before the vessel heating system is started, a smoked foil is prepared as described in Section 2.1.6. The end cover and associated heater and insulation components of the last vessel section are removed and the smoked foil is inserted. The endcover is then put back in place, and the heating system is turned on at the remote control unit. The temperature set points for the vessel and the trace heaters are then entered into the computers in the control room. Typically, the flanges, because of their mass, are initially set to a temperature above the test temperature in order to speed up the heating process. Since the driver is not heated, the exploding wire can be put into place at any time during the vessel heat up. After the wire is in place, the vessel vacuum can be started. When all the temperature set points have been achieved, all personnel are cleared from the tunnel and the Experimental Hall. The final step in the clearing of these areas is the closure of a large plug door which satisfies the facility interlock system and permits the flow of combustible gases (i.e., releases instrument air to the valves) and the charging of the trigger system high voltage capacitor.

With combustible gas flow enabled, the respective PID pressure regulator settings and the various chart and log parameters are input at the computer terminal in the control room. The high-voltage capacitor for the triggering device is charged and the scopes are armed. The operator then starts a program which takes control of the gas filling and firing sequence. The first operation performed by the program is to start the flow of the constituent gases. Before injection into the vessel is initiated, the mixture flow bypasses the test vessel out the exhaust stack, until steady-state flow conditions are achieved. This bypass phase takes 20 seconds, after which the gas is directed into the vessel. The vessel is filled to a pressure just below the test pressure. After the test gas has been loaded: three gas samples are taken, the sample bottles valved out, and the driver gas is injected raising the vessel pressure to the test pressure (e.g., one atmosphere). Note, the larger the driver partial pressure, the longer is the driver slug. Once the driver gas is injected, there is a 2-second delay, allowing the valves to close, and the exploding wire is triggered and the detonation is initiated. The combustion products in the vessel are then flushed out through the stack using the two blowers located at each end of the test vessel. Only after purging has been completed are personnel allowed by the interlock to enter the tunnel to remove the smoked foil and perform other duties in preparation for the next test.

Figure 2.1: Schematic showing the High-Temperature Combustion Facility layout

2 Experimental Details

Figure 2.2: Photograph showing the driver-end of the test vessel inside of the Tunnel

Figure 2.3: Schematic of the High-Temperature Combustion Facility gas handling system

2. Experimental Details

Figure 2.4: Schematic showing the details of the driver gas handling system

Figure 2.5: Photograph of the heating system power control unit

Figure 2.6: Photograph of the heating pad and insulation distribution on the test vessel

Figure 2.7: Schematic showing the thermocouple positions on the test vessel for the temperature uniformity tests

2. Experimental Details

Figure 2.8: Experimentally measured test vessel temperature distribution for a temperature set point of 500K

Figure 2.9: Experimentally measured test vessel temperature distribution for a temperature set point of 650K

2. Experimental Details

Figure 2.10: Photograph of the control and data acquisition equipment located in the control room

3. EXPERIMENTAL RESULTS

3.1 Gas Driver Characterization

One of the unique features of the HTCF is the use of a "diaphragmless" gas driver (i.e., no physical boundary between driver and test gas) to initiate detonations in the test gas. This is an important feature since it avoids the time-consuming process of disconnecting the vessel after each experiment to insert a new diaphragm. One also has the ability to vary the driver slug length by simply changing the amount of driver gas injected into the test vessel. The disadvantage is that the driver gas slug is not as well defined as could be by a diaphragm separating the test gas from the driver gas. As the driver gas is injected into the test vessel, it mixes with pre-loaded test gas. The degree of mixing and the extent of driver gas convection down the vessel cannot easily be controlled. In the next three sections, results from experiments on the characterization of the axial driver gas composition, the transmission of the detonation from the driver to the test gas, and an estimate of the driver energy are presented.

3.1.1 Gas Driver Composition

A series of calibration tests were performed in order to determine the driver gas composition (i.e., acetylene-oxygen composition) before injection into the vessel and the driver gas distribution inside the test vessel just after injection. With the needle valves that control each driver gas constituent fully open, it was determined that both the acetylene and oxygen flows were choked at their respective flash arrestor. Since the opening in both flash arrestor are identical and the molecular mass of acetylene (26 gm/mole) and oxygen (32 gm/mole) are about the same, the ratio of the acetylene/oxygen volumetric flow rates is equal to the ratio of their respective delivery pressures. The acetylene delivery pressure was set to its maximum of 0.2 MPa, and the driver composition was set by varying the oxygen delivery pressure. As a result of the constraint on the maximum acetylene delivery pressure (i.e., flow rate), the driver composition and driver injection time are directly related, since the driver injection time is simply the driver volume in the vessel divided by the driver flow rate. For example, for a given driver gas composition, there is a corresponding injection time. If the driver is made leaner, the oxygen pressure is raised resulting in an increase in the overall driver gas flow rate and a reduced injection time. The opposite is true for a richer driver. The driver injection time is an important parameter since it determines the extent to which the driver gas will convect down the vessel during the injection period.

The first test was designed to verify that the setting of the acetylene and oxygen delivery pressure resulted in the expected driver gas composition. Since the gas chromatograph was set up for detecting only hydrogen, it could not be used to verify the driver composition. The approach taken was to fill the test vessel with driver gas to a subatmospheric pressure and then to initiate a detonation in the mixture and measure the detonation velocity. By knowing the detonation velocity, one can back out the mixture composition analytically. It should be noted that this approach was meant as a check and not intended to give an accurate measure of the driver composition. The oxygen delivery pressure was set at 0.8 MPa absolute, and the acetylene was set at 0.2 MPa which translates to a 20 percent acetylene - 80 percent oxygen mixture. The vessel was evacuated, filled with driver gas to a vessel pressure of 0.05 MPa absolute, and then detonated. The measured detonation velocity down the entire length of the vessel was 2100 ± 9 m/s. Using the chemical equilibrium code STANJAN (Reynolds, 1986), the CJ detonation velocity for a 20 percent acetylene mixture was calculated to be 2160 m/s, which is only 3 percent higher than the measured velocity.

The next series of tests was performed to determine the extent of mixing between the driver gas and the test gas in the vessel during the driver gas loading. Recall that the driver gas is injected radially inwards towards the vessel centerline from four perforated tubes located just inside the vessel inner wall at the driver end. Therefore, the driver gas volume fraction would be expected to be a maximum at the driver endplate and decrease with axial distance from the endplate. The driver gas distribution in the vessel was measured by taking gas samples at various axial locations after driver

3. Experimental Results

injection. The vessel was filled with an equimolar mixture of hydrogen-air to a pressure just below one atmosphere followed by driver gas injection bringing the vessel pressure to one atmosphere. Gas samples were then taken one second after the end of driver gas injection, which would correspond to the time of ignition in a detonation experiment. Based on the amount of hydrogen detected in a sample, the fraction of the sample consisting of driver gas could be inferred. For example, if the sample consisted of 50 percent hydrogen, this would correspond to zero driver gas present; if no hydrogen was detected, this would correspond to 100 percent driver gas at the sample location.

Three "driver partial pressures" were used in the tests with a driver gas composition of 25 percent acetylene and 75 percent oxygen. The driver partial pressure refers to the increase in vessel pressure resulting from driver gas injection and, therefore, is a measure of the volume of driver gas added to the vessel. The measured axial distribution of the driver gas is given in Figure 3.1, where the ratio of the driver gas volume to the total gas volume (i.e., driver plus test gas) is plotted versus axial distance from the driver section endplate. Each symbol in Figure 3.1 represents a gas sample, where three samples were taken per calibration test run. The symbols shown on the figure at an axial distance of zero represent samples taken through the endplate at the exploding wire location. The driver injection time for a 1-psi driver is 16.5 seconds which yields a driver gas flow rate of 10.7 CFM. Note that the driver gas constitutes between 30 and 40 percent of the gas at the exploding wire location. The driver fraction then drops off asymptotically with distance. These tests also show that the driver gas migrates a substantial distance down the vessel, e.g., 6.10-m (20-ft) for a driver partial pressure of 1 psi. Since the driver gas fraction profiles appear similar in shape and since the values at the endplate are roughly the same, the effective driver length (defined as the maximum distance away from the endplate where driver gas is detected) should scale with the driver volume, or partial pressure. For example, the effective driver length for a driver partial pressure of 0.25 psi is 1.52-m (5-ft), doubling the driver pressure to 0.5 psi roughly doubles the effective driver length to 3.35-m (11-ft), and quadrupling the driver pressure to 1 psi roughly quadruples the effective driver length to about 6.10-m (20-ft). It is also interesting to note that the ratio of the effective driver length to the ideal driver length, assuming a homogeneous slug of driver gas, is roughly four.

To some extent, dilution of the acetylene-oxygen driver gas with test gas is advantageous since the detonation pressure in the driver gas will match more closely the detonation pressure in the test gas. The transient phase that the detonation undergoes during the transition from the driver to the test gas is thereby shortened. However, with the dilution of the driver gas: (1) the acetylene-oxygen is convected further down the test vessel and, therefore, the driver effects will also be translated further down the tube and (2) a diluted driver requires more energy for direct initiation (e.g., critical initiation energy for acetylene-air is an order of magnitude higher than that for acetylene-oxygen). However, no problem with insufficient energy for direct initiation of the acetylene-oxygen driver gas was encountered in any of the reported experiments conducted.

3.1.2 Effect of Driver Length on Detonation Transmission

In order to obtain reliable cell size data, the detonation wave must be self-sustained when it passes over the smoked foil and thus the detonation velocity over the smoked foils should steady at, or just under, the theoretical CJ value for the test mixture. In direct initiation of a detonation either using high explosives or a gas driver, the shock wave which is transmitted from the ignition source into the test gas has a higher pressure and velocity than the test gas CJ values. As a result, the detonation in the test gas is initially overdriven and subsequently decays to a CJ detonation. The overdriven detonation decays because the flow leaving the reaction zone is subsonic relative to the front and thus an expansion wave in the reaction products can weaken the detonation. The distance required for the detonation to decay depends on the energy release characteristics of the ignition source. For high-explosives, the transmitted shock has a very high peak pressure, but the positive pressure duration is very short due to the small size of the source. In a gas driver, the transmitted shock pressure is much lower than that in the high-explosive, but the pressure pulse duration is significantly longer than that for the high-explosive due to the length of the driver slug. The expanding combustion products from

the driver act like a piston partially supporting the overdriven detonation in the test gas. The shorter the driver length, the faster the overdriven detonation will decay to the local CJ conditions. However, if the driver length is too short, the transmitted shock from the driver will not result in the successful transmission (i.e., initiation) of the detonation into the test gas. Due to the finite length of the test vessel, the shortest driver possible is desired to assure that recorded cell patterns are from self-sustained detonations.

A series of experiments was performed where the driver partial pressure, and thus the effective driver length, was varied and the detonation velocity was measured down the length of vessel. The results from these experiments are given in Figure 3.2. The driver composition for all the tests was 25 percent acetylene and 75 percent oxygen and the driver gas partial pressure was varied from 0.2 psi to 1 psi. The test gas was 8 percent hydrogen and 92 percent air at 650K and 0.1 MPa. This test mixture was chosen because of its very low detonation velocity and pressure which would result in the longest distance for the overdriven detonation to decay to a steady-state CJ detonation. The theoretical CJ detonation velocity and pressure for this test gas is 1233 m/s and 0.377 MPa, respectively. As observed in Figure 3.2, the detonation is initiated immediately in the driver where the propagation velocity is of the order of 2200 m/s. When the detonation emerges from acetylene-oxygen driver into the test gas, the detonation velocity quickly decays to a velocity just under the test gas CJ velocity. The final velocity is below the CJ value because of losses to the vessel wall from the reaction zone, which for this mixture is substantial due to its long reaction zone. There is a clear correlation between the distance where the detonation velocity falls off in Figure 3.2, and the effective driver length as given in Figure 3.1. Following a rapid decay, the detonation velocity fluctuates about the test gas CJ detonation velocity. The average terminal velocity for the different driver pressures is similar except for the largest driver (e.g., 1.0 psi) where the average velocity is somewhat higher. For a driver partial pressure of less than 0.2 psi, a detonation was not initiated in the test gas. Thus, the 0.2 psi driver appears to be the critical driver partial pressure since after the detonation emerges from the driver it drops to a velocity below CJ and then recovers. This type of behavior is typical of point source initiation from high explosives at the critical initiation energy (Lee, 1977).

A similar series of experiments was carried out in a test gas of 14.5 percent hydrogen and 85.5 percent air at 300K, which has a theoretical CJ detonation velocity of 1500 m/s. The results from these tests are given in Figure 3.3. The driver composition for this series of experiments is 30 percent acetylene and 70 percent air. This test mixture has a CJ detonation pressure of about 1.1 MPa, which is about three times that of the 8 percent hydrogen-air mixture at 650K, and thus the overdrive of the detonation emerging from the driver is less for this mixture. As a result, one would expect better driver performance under these conditions. This effect is observed. A driver as small as 0.1 psi is sufficient for a successful detonation transmission, and the average steady-state velocities for all the drivers, including the 1.1-psi driver, are similar. For a 30 percent acetylene driver, the effective driver lengths are slightly longer than the 25 percent acetylene drivers since, as noted in Section 3.1.1, the driver injection time is longer.

It can be concluded from the experimental results presented in Figures 3.2 and 3.3 that in all cases, as the detonation emerges from the driver section it quickly decays to the test gas CJ velocity. For the test gases at 300K, all the driver lengths performed satisfactorily. For the very weak mixtures at 650K, the longer driver did not perform as well. Based on these experimental findings on the effect of driver length on the transmitted detonation, it was decided that the optimum driver would be a 0.25 psi driver with a composition of 25 percent acetylene and 75 percent oxygen. The majority of the experiments discussed in the following sections were performed with these gas driver characteristics.

3.1.3 Gas Driver Energy

The driver energy is additional energy which is deposited into the combustible medium for the sole purpose of detonation initiation of the test gas. Once the detonation is formed, it is maintained by the chemical energy released from the combustible medium itself. This added energy has an impact on how quickly the detonation can adjust to the

3. Experimental Results

steady-state condition for the particular combustible mixture. Therefore, one would like to minimize this energy. In the past, high explosives have been used to initiate detonations in hydrogen-air mixtures. For example, in the Heated Detonation Tube (HDT), Tieszen et al. (1987) typically used 40 gm of explosives for most hydrogen-air mixtures and up to 80 gm for very lean mixtures. We can compare driver energetics with previous work that employed high-explosive initiators by measuring the amount of energy released by the HTCF gas driver.

The amount of available chemical energy in the driver gas based on the mass of acetylene can be calculated knowing the number of moles of acetylene and the heat of combustion of acetylene. For a typical 0.25-psi driver, the volume occupied by the driver gas is 0.021 m³. At room temperature and pressure, this corresponds to 0.85 moles of gas. For this number of moles of a 25 percent acetylene and 75 percent oxygen mixture, there are 0.21 moles of acetylene. Based on a heat of combustion of 1256 kJ/mole for acetylene (Baker et al., 1983), 267 kJ of energy are released if all the acetylene is consumed. This amount of energy is equivalent to 46 gm of PETN high-explosive. This must be considered an upper bound for the energy released by the driver gas because not all the energy goes into the detonation.

To obtain a measurement of the actual energy released from the driver gas, the blast wave pressure generated by the detonation of the driver gas in air was measured at a distance of 22.3 meters from the ignition source. For a 1-dimensional geometry, the following expression (Thibault et al., 1987)

$$\frac{\Delta P}{P_o} = \frac{4\gamma/(\gamma+1)}{\left[1 + \left(\frac{4\gamma}{\gamma^2-1}\right) \cdot \left(\frac{xP_o}{E}\right)\right]^{1/2}} - 1 \quad (3.1)$$

relating the blast overpressure, ΔP , with the source energy, E , can be used to determine the energy released by the driver gas. For a 0.25 psi driver with a 30 percent acetylene and 70 percent oxygen composition and an initial pressure, P_o , of 0.1 MPa, the blast overpressure, ΔP , measured at a distance of 22.3 meters was 0.133 MPa. Taking the ratio of the specific heats, γ , to be 1.4, the above expression yields an energy density of 1900 kJ/m², which for a 27.3-cm diameter gives a total energy of 111 kJ or 19 gm of PETN high-explosive. Therefore, the actual energy yield for a typical HTCF gas driver is anywhere from one half to one quarter of the high-explosive initiator energy used in the HDT at Sandia.

3.2 Detonation Cell Size Measurements

In this section, detonation cell size measurements from smoked foils are reported for hydrogen-air-steam mixtures over a range of initial temperatures and pressures. As discussed in the Section 1.1, the cellular pattern inscribed on the smoked foil by the detonation in hydrogen-air mixtures is fairly irregular. Therefore, the reported cell size data is an average value from a sample taken from each foil. The cell size is determined by the "dominant mode method" (Moen et al., 1982), whereby the cell size is based on the average spacing between the diagonal parallel lines (e.g., triple-point trajectory) on the foil. In general, the longest lines with the most contrast are selected. After the smoked foil is extracted from the vessel, it is sprayed with a clear lacquer to protect the tracks on the foil. The dominant lines are then traced onto a clear mylar sheet where the average line spacing is measured. The cell size data reported in the following sections are only for detonations which resulted in more than three cells across the foil. For detonations generating less than three cells, it is possible that the detonation cellular structure is being influenced by the vessel confinement. However, this is not to say that these detonations are not self-sustained.

A code, developed by Shepherd (1986), based on the 1-dimensional ZND model of detonation, was used to calculate the reaction zone structure. The gas pressure, density, and composition are simultaneously integrated as a function of

distance behind the incident shock wave. Clearly the model for the chemical reactions plays an important role in determining the reaction zone length. There have been various different sets of reaction mechanisms and rate constants proposed by various investigators. The reaction mechanisms and their respective rate constants used in this code were obtained from Miller et al. (1982). The set of 23 elementary reactions, containing 11 species, used in the kinetic model for hydrogen oxidation are given in Table 3.1. The input required by the ZND code is the initial mixture composition and thermodynamic conditions along with the mixture CJ detonation velocity, which is obtained from the equilibrium code STANJAN (Reynolds, 1986). The code outputs four different reaction zone lengths based on different criteria. We have chosen the reaction zone length to be defined as the distance between the shock wave and the point downstream where the temperature gradient is maximum (i.e., location of maximum energy release rate). The experimentally measured cell size is compared to the predicted cell size derived from the calculated ZND detonation reaction zone length, Δ . The predicted cell size is taken to be proportional to the reaction zone length (i.e., $\lambda = A \Delta$). The dependence of the proportionality constant A on various parameters has been investigated and will be discussed in the following sections. The test conditions and experimental results are presented in graphical form within the text and in tabular form in Appendix A.

3.2.1 Baseline Experiment at 300K and 0.1 MPa

Figure 3.4 presents the experimental detonation cell size data from the HTCF as a function of the hydrogen mole fraction at 300K. The data covers the hydrogen-air composition range from 15 percent to 55 percent hydrogen. Also included in the figure are experimental data from the SSDA (Ciccarelli et al., 1994) and from Sandia's HDT (Tieszen et al., 1987). The plot of cell size versus hydrogen mole fraction results in the classical "U"-shaped curve where the minimum corresponds to the stoichiometric composition. The vertical bars on some of the SSDA results indicate the standard deviation in the cell size measurements from the smoked foil. Detailed analysis of the smoked foils from the SSDA has been performed since the SSDA report (Ciccarelli et al., 1994) was issued. The data from this analysis of the SSDA smoked foils is given in Appendix B in tabular form. In general, the standard deviation in the measured cell size data for each foil is about ± 25 percent of the average value, which is consistent with the findings of Tieszen et al. (1987). A detailed analysis of the HTCF foils was not performed; however, a similar ± 25 percent standard deviation would be expected. Figure 3.4 indicates that the data from the HTCF is consistent with the cell size data from the SSDA and compares well with the HDT data, concentrated near the lean limit.

The ZND model prediction of cell size, using a proportionality constant of 51 for all the mixtures, is shown in Figure 3.4 as a solid line. The line is a curve fit of several points calculated covering the range of experimental conditions tested. The scaling factor of 51 was arbitrarily chosen by anchoring the SSDA experimental cell size data to the ZND model prediction at the stoichiometric composition (i.e., 30 percent hydrogen). However, the apparent agreement between the experimental and the model predictions is deceiving because of the logarithmic scale. In Figure 3.5, the ratio between the experimental cell size (from both the SSDA and the HTCF) and the calculated ZND reaction zone length ($A = \lambda/\Delta$) is plotted versus hydrogen mole fraction. The horizontal line represents the assumption of a constant value of 51 for the proportionality constant, A , used for the ZND model predictions in Figure 3.4. The results indicate that for mixture concentrations above 20 percent hydrogen, a value between 40 and 50 for this ratio is typical. However, for mixtures below 20 percent hydrogen, the ratio quickly drops to a minimum value of about 5, for a 16 percent hydrogen mixture. This variation in the proportionality "constant," A , as a function of the hydrogen concentration was also observed by Shepherd (1986). The actual trend in A as a function of hydrogen mole fraction, or equivalence ratio as shown in Shepherd (1986), is different from that shown in Figure 3.5 because the value of Δ used by Shepherd to obtain A is based on a different definition for the reaction zone length.

3. Experimental Results

Table 3.1 Hydrogen oxidation mechanism and rate constants*

Reaction	A	β	E
1. $\text{H}_2 + \text{O}_2 \rightleftharpoons \text{OH} + \text{OH}$	1.70×10^{13}	0.00	47780
2. $\text{OH} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}$	1.17×10^9	1.30	3626
3. $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$	5.13×10^{16}	-0.82	16507
4. $\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$	1.80×10^{10}	1.00	8826
5. $\text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2 + \text{M}$	2.10×10^{18}	-1.00	0
6. $\text{H} + \text{O}_2 + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{O}_2$	6.70×10^{19}	-1.42	0
7. $\text{H} + \text{O}_2 + \text{N}_2 \rightleftharpoons \text{HO}_2 + \text{N}_2$	6.70×10^{19}	-1.42	0
8. $\text{OH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	5.00×10^{13}	0.00	1000
9. $\text{H} + \text{HO}_2 \rightleftharpoons \text{OH} + \text{OH}$	2.50×10^{14}	0.00	1900
10. $\text{O} + \text{HO}_2 \rightleftharpoons \text{O}_2 + \text{OH}$	4.80×10^{13}	0.00	1000
11. $\text{OH} + \text{CH} \rightleftharpoons \text{O} + \text{H}_2\text{O}$	6.00×10^8	1.30	0
12. $\text{H}_2 + \text{M} \rightleftharpoons \text{H} + \text{H} + \text{M}$	2.23×10^{12}	0.50	92600
13. $\text{O}_2 + \text{M} \rightleftharpoons \text{O} + \text{O} + \text{M}$	1.85×10^{11}	0.50	95560
14. $\text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M}$	7.50×10^{23}	-2.60	0
15. $\text{H} + \text{HO}_2 \rightleftharpoons \text{H}_2 + \text{O}_2$	2.50×10^{13}	0.00	700
16. $\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$	2.00×10^{12}	0.00	0
17. $\text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \text{OH} + \text{OH} + \text{M}$	1.30×10^{17}	0.00	45500
18. $\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{HO}_2 + \text{H}_2$	1.60×10^{12}	0.00	3800
19. $\text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2$	1.00×10^{13}	0.00	1800
20. $\text{HO}_2 + \text{CO} \rightleftharpoons \text{CO}_2 + \text{OH}$	1.51×10^{13}	0.00	22934
21. $\text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2 + \text{M}$	3.20×10^{13}	0.00	-4200
22. $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	1.51×10^7	1.30	-758
23. $\text{CO} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{O}$	1.60×10^{13}	0.00	41000

*Reaction rate coefficients are in the form $k_f = AT^n \exp(-E/RT)$. Units are moles, cubic centimeters, seconds, Kelvins, and calories/mole.

Third body efficiencies: $k_5(\text{H}_2\text{O}) = 21k_5(\text{Ar})$; $k_5(\text{H}_2) = 3.3k_5(\text{Ar})$; $k_5(\text{CO}_2) = 5k_5(\text{Ar})$; $k_5(\text{CO}) = 2k_5(\text{Ar})$; $k_{12}(\text{H}_2\text{O}) = 6k_{12}(\text{Ar})$; $k_{12}(\text{H}) = 2k_{12}(\text{Ar})$; $k_{12}(\text{H}_2) = 3k_{12}(\text{Ar})$; $k_{14}(\text{H}_2\text{O}) = 20k_{14}(\text{Ar})$.

3.2.2 Hydrogen Oxidation at Elevated Temperature

Before detonation tests were conducted at elevated temperature, a series of tests was performed at 650K to investigate the degree of hydrogen oxidation in the vessel. This is a follow-up series to experiments performed on the SSDA (Ciccarelli et al., 1994) that indicated a substantial amount of hydrogen oxidation had occurred during and following mixture injection into the vessel at 650K and at an initial pressure of 0.1 MPa. Based on grab samples at various times, the SSDA tests revealed that a nominal 15 percent hydrogen-air mixture drops to about 10.5 percent hydrogen-air in roughly five minutes after injection (see Figure 3.6). This experimental result disagrees with the hydrogen depletion predicted by the overall reaction rate proposed by DeSoete (1975). The DeSoete correlation predicts almost no hydrogen depletion for a 15 percent hydrogen air mixture at 650K and 0.1 MPa.

The oxidation tests were repeated in the HTCF using the same 15 percent hydrogen mixture and initial conditions. The hydrogen depletion over time is also given in Figure 3.6. Note that the HTCF vessel fill time is on the order of 30 seconds. The first grab sample in the HTCF was at 60 seconds and the subsequent samples were taken at 180 seconds and 300 seconds. It is clear from Figure 3.6 that the overall hydrogen depletion rate in the HTCF is much lower than that in the SSDA. In four minutes, the hydrogen mole fraction drops to 14.5 percent in the HTCF as opposed to 10.5 percent in the SSDA. This finding is more in line with the DeSoete prediction.

Hydrogen oxidation in a hot vessel is due to slow chemical reactions within the bulk of the gas mixture and catalytic reactions occurring between the gas and the vessel wall. The oxidation rates observed in the SSDA cannot be accounted for solely by the reactions occurring in the bulk of the gas (Ciccarelli, 1994). Therefore, the difference between the oxidation rates observed in the HTCF and the SSDA must be largely due to surface effects. The vessel material determines the rate at which surface reactions proceed. The SSDA and the HTCF are constructed of two different types of stainless steel (SS). The SSDA vessel material is 316L SS and the HTCF material is 304L SS. The main difference in the two types of stainless steel is that 304L has slightly less carbon and nickel and slightly more chromium than the 316L. It is highly unlikely that these small differences in the metal composition can account for the observed difference in oxidation rates. The vessel surface area to volume ratio doesn't effect the surface reaction rate itself, but it does determine the rate at which the average hydrogen concentration drops in the vessel. For a cylinder, the surface area to volume ratio varies like the inverse of the diameter. Therefore, one would expect less of a drop in the hydrogen concentration in the HTCF compared to the SSDA since the surface area to volume ratio is less. This scaling argument does not hold in the case of DeSoete's experimental results which show very slow oxidation rates at 650K even though the stainless-steel vessel used was very small (i.e., inner diameter of 32 mm and length of 90 mm).

In both the SSDA and the HTCF oxidation tests, the mixture was rapidly injected into the test vessel through an orifice located in the side instrument port such that the jet of test gas laterally impinged on the vessel wall opposite the injection port². The jet velocity and the distance between the orifice and the jet-impingement point are both different for the SSDA and HTCF. However, the influence on hydrogen oxidation by the jet impingement on the hot inner-vessel surface is not known and was not studied in the present investigation. The data indicates that the hydrogen depletion in the HTCF was very small, and initial temperature or injection mode had no measurable influence on the test gas initial composition. The mechanism of hydrogen oxidation at elevated temperature is, however, not fully understood and requires additional research.

²In the HTCF, this mode of injection was later changed to an axial injection from the endplate; however, no oxidation tests were performed in this configuration.

3. Experimental Results

3.2.3 Effect of Initial Mixture Temperature on Cell Size

Detonation tests were performed at 0.1 MPa with initial temperatures up to 650K in order to determine the effect of initial mixture temperature on cell size. The measured detonation cell size for these tests are given in Figures 3.7 and 3.8 for initial mixture temperatures of 500K and 650K, respectively. Also shown are the SSDA results and the ZND model prediction using $A = 51$, which was also used in the 300K tests shown in Figure 3.4. As in the case of the 300K data, only those detonations with more than three cells across the vessel circumference are included. At both temperatures, the cell size measurements made in the HTCF reproduce very well with the data obtained for the more sensitive mixtures tested in the SSDA. At 650K, reproducible detonation cell size data was obtained down to a lean mixture of roughly 8 percent hydrogen in air. The data is deemed reliable based on several factors: (1) similar cell size was measured for two different driver partial pressures and (2) the detonation velocity in the last half of the vessel was constant. The vertical bars in the SSDA data at 650K in Figure 3.8 correspond to the standard deviation in the measured cell size data. As in the 300K data, the standard deviation obtained for the 650K data is about ± 25 percent of the average cell size.

The effect of temperature on cell size is best illustrated in Figure 3.9, where the 300K data from Figure 3.4 and the 650K data from Figure 3.8 are superimposed. The general trend in the data (i.e., U-shaped curve) at both temperatures is about the same; the only difference is that the 650K curve is much broader than the 300K curve. This plot clearly shows that for a given hydrogen-air mixture, increasing the initial mixture temperature decreases the detonation cell size, especially for lean mixtures. For example, for a 15 percent hydrogen-air mixture, the cell size at 300K is 18.7 cm; and at 650K, the cell size is an order of magnitude smaller (e.g., 1.6 cm). For a 30 percent hydrogen mixture, the effect of raising the temperature from 300K to 650K is to roughly halve the cell size. The other important observation from Figure 3.9 is that increasing the temperature has the effect of widening the detonability limit, i.e., lowering the lean detonability limit.

From Figures 3.7 and 3.8, it can be seen that the ZND model predicts the general trends in the experimental data. Employing $A = 51$, the ZND model, however, over predicts the data for the sensitive mixtures and under predicts the data for the leaner mixtures. The actual proportionality constant (i.e., ratio of the measured cell size and the calculated ZND reaction zone length) for the 500K and 650K data is plotted in Figure 3.10. At 500K, mixtures containing greater than about 20 percent hydrogen result in a value for A of about 30. At 650K, a proportionality constant of about 20 is obtained for mixtures with more than 10 percent hydrogen. At both temperatures, the value of A increases substantially as the lean limit is approached. It should be noted that this trend in the value of A with hydrogen mole fraction is opposite to the trends observed in Figure 3.5 for the 300K data.

3.2.4 Effect of Steam Dilution on Cell Size

Most postulated severe accident scenarios where hydrogen is released into containment also involves the release of steam. The presence of steam in containment is very important since it has been shown in the past to have a mitigating effect on detonability. Due to the scale of the SSDA, test conditions were limited to very sensitive, nonprototypic hydrogen-air mixtures with steam as a diluent. This SSDA data was extended in the HTCF where sensitive hydrogen-air mixtures could be tested but with higher steam dilutions. The HTCF data in conjunction with the SSDA data are shown in Figure 3.11. The data indicates that for a given mixture temperature, increasing the steam dilution increases the cell size and thus decreases the mixture sensitivity. However, as the mixture temperature is increased, the mitigating effect of steam addition is diminished. For example, at 400K, the maximum mixture steam content that could be tested was 20 percent; and at 650K, mixtures containing up to 40 percent steam resulted in detonations. The experimental data shows reasonably good agreement with ZND model predictions with $A = 51$.

The HTCF enabled testing of much weaker and more prototypic hydrogen-air mixtures, e.g., 10 and 17.3 percent hydrogen (i.e., equivalence ratio of 0.5), with steam dilution. For these leaner hydrogen-air mixtures, the tests were restricted to an initial temperature of 650K. Cell size measurements for these weaker mixtures are given in Figure 3.12 for various steam dilutions along with the stoichiometric results at 650K from Figure 3.11. It is interesting to note that for all three hydrogen mixtures tested, for a given hydrogen concentration an Arrhenius type of relationship between cell size and steam dilution is observed. That is increasing the steam dilution initially has little effect on the cell size until a critical value after which the cell size increases exponentially. This critical steam dilution is observed to increase with increasing hydrogen concentration. The cell size data given in Figure 3.12 also shows that for a given steam dilution, decreasing the hydrogen mole fraction increases the cell size. This trend is expected based on the observed influence of hydrogen mole fraction on cell size from Figure 3.8. The experimental detonation cell size data for 17.3 and 30 percent hydrogen can be correlated fairly well using the ZND model and a proportionality constant of 25 and 50, respectively. There is insufficient data for 10 percent hydrogen to comment on the ZND correlation, however, the ZND model does predict the experimentally observed dramatic increase in cell size at roughly 10 percent steam dilution.

3.2.5 Effect of Initial Mixture Pressure on Cell Size

In a severe accident, the containment pressure increases above atmospheric due to the production of hydrogen and steam. The containment pressure at any time is the sum of the air, hydrogen, and steam partial pressures. The partial air pressure in containment remains constant as the accident progresses since no additional air is generated. The steam partial pressure depends on whether the steam is saturated or superheated. Under saturated conditions, the partial pressure of steam is fixed by the average containment temperature, which can vary over time. The hydrogen partial pressure is independent of temperature and only depends on the volume of hydrogen produced. During an accident, a spatial variation in the hydrogen-air-steam composition would ensue as a result of local phenomena. However, due to the relatively slow rate at which the hydrogen/steam are produced, the pressure would be nearly uniform throughout containment. Therefore, combustion could occur over a range of pressures and mixture composition depending on where ignition occurs in containment. For a given hydrogen-air-steam mixture, the maximum pressure is determined by taking the air partial pressure to be 0.1 MPa at 300K (i.e., "constant air density") and adding the partial pressures of each of the constituents and then compensating for any increase in initial temperature above 300K.

A series of experiments with hydrogen-air-steam mixtures at 650K was carried out to investigate the effect of initial pressure on detonation sensitivity or cell size. Recall that in performing a detonation experiment, the amount of driver gas injected into the vessel just before ignition raises the vessel pressure to the desired test pressure. However, the limited (by ASME code) delivery pressure of acetylene restricts the maximum initial test gas pressure. To extend the range of initial test gas pressure, the acetylene in the driver gas mixture was replaced with hydrogen. The hydrogen-oxygen driver was successful in detonating hydrogen-air test mixtures but was unsuccessful in detonating hydrogen-air-steam mixtures. Therefore, for hydrogen-air-steam mixtures, the initial pressure was limited to 0.2 MPa so that the acetylene could be used in the driver gas.

Cell size data for a 9 percent hydrogen-air mixture at 650K with initial pressures up to 0.24 MPa is shown in Figure 3.13. Note, this corresponds to the maximum mixture pressure, assuming constant air density. The detonation for this highest pressure data point was initiated using a hydrogen-oxygen driver. Both the ZND model prediction and the experimental data at 650K indicate little effect of initial pressure on the detonation cell size between 0.1 MPa and 0.24 MPa. The scatter in the data is all within the ± 25 percent uncertainty associated with the cell size measurements.

The effect of initial mixture pressure on hydrogen-air-steam mixtures at 650K was also investigated. Cell size was measured in a stoichiometric hydrogen-air mixture with 30 percent dilution and an 18 percent hydrogen-air mixture with 20 percent steam added. The results are shown in Figures 3.14 and 3.15. The constant air density pressure for both

3. Experimental Results

these mixtures is about 0.35 MPa. However, the maximum initial pressure that could be tested was 0.2 MPa because of limitations imposed on the gas driver delivery pressure and the ineffectiveness of a hydrogen-oxygen driver at these conditions. For both hydrogen-air-steam mixtures, the ZND model predicts very little effect of pressure on cell size. As shown in Figures 3.14 and 3.15, the experimentally measured cell size also indicates that the cell size is fairly insensitive to initial pressure between 0.1 MPa and 0.2 MPa. Although sparse, this series of tests generally show the relative insensitivity of cell size with initial pressure above 0.1 MPa. To extend the observation to "constant air density" conditions for hydrogen-air-steam mixtures would require a more elaborate high pressure driver system.

3.3 Detonation Velocity

The detonation wave which is transmitted from the driver gas into the test gas is initially overdriven relative to the test gas CJ velocity. As the overdriven detonation wave propagates down the vessel it decays to a CJ detonation wave corresponding to the test mixture composition and temperature. Typically, this transient phase occurs over the first 3 to 6 meters of the 21-meter long vessel. From this distance to the end of the vessel, the detonation velocity fluctuates about the theoretical CJ velocity. The *average* detonation velocities, typically measured over the last 10 to 15 meters of the vessel, for hydrogen-air mixtures at 300K, 500K and 650K are given in Figures 3.16, 3.17, and 3.18, respectively. The solid line denoting the theoretical CJ detonation velocity was calculated using the equilibrium code STANJAN (Reynolds, 1986). The standard deviation in the measured velocities from each experiment is indicated by vertical bars. The comparison of the measured detonation velocity with the theoretical CJ value is an important factor in determining whether the detonation has achieved steady-state conditions. Typically, the measured velocity deviates by no more than 2 percent from the theoretical CJ detonation velocity. The agreement between the theoretical CJ detonation velocity and the measured velocity is excellent at all three initial temperatures. For the leaner mixtures, the measured velocity tends to be below the CJ velocity because of heat and momentum losses within the relatively long reaction zone. Also, the standard deviation in the velocity measurements tends to increase as mixtures become leaner.

In the detonation experiments carried out in the SSDA, the reported average detonation velocities, measured in hydrogen-air mixtures at 650K, were consistently below the CJ velocities (Cicarelli, 1994). Slow hydrogen oxidation, occurring during the 60 seconds from the start of the vessel fill to the time of ignition, was speculated, changing the initial mixture composition. As a result of the oxidation, the actual mixture had less hydrogen and some steam present, which would decrease the CJ velocity. However, in the HTCF for detonations in hydrogen-air mixtures at 650K (see Figure 3.18), the measured average detonation velocity is in good agreement with the CJ velocity. This difference between the SSDA and HTCF in the agreement with the CJ velocity, as discussed in Section 3.2.2., is due to the higher rate of oxidation prior to ignition observed in the SSDA, as compared to the HTCF.

Figure 3.1: Experimentally measured driver-gas ($C_2H_2+3O_2$) axial distribution in the test vessel at 1 second after driver-gas injection

3 Experimental Results

Figure 3.2: Effect of driver partial pressure (or length) on detonation transmission in a 8 percent hydrogen and 92 percent air mixture at 650K and 0.1 MPa

Figure 3.3: Effect of driver partial pressure (or length) on detonation transmission in a 14.5 percent hydrogen and 85.5 percent air mixture at 300K and 0.1 MPa

3 Experimental Results

Figure 3.4: Comparison of measured, BNL and Sandia National Lab (Tieszen et al., 1987), and calculated detonation cell size for hydrogen-air mixtures at 300K and 0.1 MPa

ZND proportionality constant, A, for hydrogen-air mixtures at 300K and 1 atm

Figure 3.5: Proportionality constant (i.e., ratio of experimental cell size and calculated ZND reaction zone length) for hydrogen-air mixtures at 300K at 0.1 MPa

3 Experimental Results

Figure 3.6: Hydrogen oxidation time history for a 15 percent hydrogen and 85 percent air mixture in the vessel at 650K and 0.1 MPa

Figure 3.7: Detonation cell size for hydrogen-air mixtures at 500K and 0.1 MPa

3 Experimental Results

Figure 3.8: Detonation cell size for hydrogen-air mixtures at 650K and 0.1 MPa

Figure 3.9: Comparison of detonation cell size for hydrogen-air mixtures at 300K, 650K and 0.1 MPa

3 Experimental Results

Figure 3.10: Proportionality constant (i.e., ratio of experimental cell size and calculated ZND reaction zone length) for hydrogen-air mixtures at 500K, 650K and 0.1 MPa

Figure 3.11: Detonation cell size as a function of temperature for stoichiometric hydrogen-air and steam mixtures at 0.1 MPa (symbols: open-SSDA, closed-HTCF, half closed-Sandia HDT, lines-ZND with A-51)

Figure 3.12: Detonation cell size as a function of temperature for stoichiometric and off-stoichiometric hydrogen-air and steam mixtures at 650K and 0.1 MPa (open symbols: SSDA, closed symbols: HTCF, lines: ZND model)

Figure 3.13: Detonation cell size as a function of initial pressure for a 9 percent hydrogen and 91 percent air mixture at 650K

3 Experimental Results

Figure 3.14: Detonation cell size as a function of the initial pressure for a stoichiometric hydrogen-air mixture with 30 percent dilution at 650K

Figure 3.15: Detonation cell size as a function of initial pressure for a 18 percent hydrogen - 82 percent air and 20 percent steam mixture at 650K

Figure 3.16: Comparison of measured and calculated detonation velocity for hydrogen-air mixtures at 300K and 0.1 MPa (vertical bars represent standard deviation in measured velocities)

Figure 3.17: Comparison of measured and calculated detonation velocity for hydrogen-air mixtures at 500K and 0.1 MPa (vertical bars represent standard deviation in measured velocities)

Figure 3.18: Comparison of measured and calculated detonation velocity for hydrogen-air mixtures at 650K and 0.1MPa (vertical bars represent standard deviation in measured velocities)

4. DISCUSSION

4.1 Cell Size Prediction

For practical reasons, it is not feasible to obtain cell size data at a scale comparable to a reactor containment, i.e., scales on the order of meters to tens of meters. The largest apparatus used to measure detonation cell size in hydrogen-air-steam mixtures is the HDT at Sandia National Laboratories. At 43 cm in diameter, this facility is roughly one or more orders of magnitude smaller than prototypic scales. To make predictions at prototypic scales, one must extrapolate from the limited cell size data available. The best method to extrapolate existing cell size data is to use the ZND model. The constant of proportionality ($A = \lambda/\Delta$), can be deduced by anchoring the ZND model prediction at the largest measured cell size. For a prescribed test-mixture concentration where the largest cell size was measured (say λ_{meas}), the ZND model yields the chemical induction length (say Δ_{calc}). The ratio of these two values is the recommended constant of proportionality. However, there still remains the uncertainty in the dependence of the constant A with mixture composition and initial temperature. As demonstrated in Figures 3.5 and 3.10, the value of A varies significantly over the range of test conditions investigated. The largest variation occurs in the lean mixtures, where at 300K the value of A decreases by roughly a factor of five, and at 500K and 650K where A rapidly rises with decreasing hydrogen mole fraction. At 300K, the factor, A , drops off for the leaner mixtures because, as observed in Figure 3.4, the slope of ZND cell size versus hydrogen mole fraction curve is steeper than the experimental curve. The opposite is true at 650K (see Figure 3.8) and thus A increases for lower hydrogen mole fractions. It is not clear whether this behavior is due to inaccuracies in the ZND model kinetics or is simply due to the 3-dimensional gasdynamics in the reaction zone which are not considered in the ZND model.

In a study using a similar ZND model, Stamps et al. (1991) calculated the cell size for hydrogen-air mixtures as a function of initial mixture temperature. In that investigation, the ZND reaction zone length, Δ , was defined as the distance from the shock to the point in the reaction zone where the flow reaches Mach 0.75. This definition results in a length that extends through the induction zone and into the final phase of the heat release zone. Therefore, the calculated reaction zone using the Mach 0.75 definition is longer than that obtained by using the maximum temperature gradient definition employed in this study. Stamps found that for a given hydrogen-air mixture, increasing the initial temperature from 300K initially reduces the reaction zone length up to a certain critical temperature, at which point any further increase in the initial mixture temperature results in an increase in the reaction zone length. It was postulated that the minimum in the reaction zone length was due to a change in the rate-limiting, chemical-kinetic mechanism corresponding to the extended classical second-limit criterion, as first described by Shepherd (1986). That is, there is a change in the rate-limiting mechanism between the ordinary chain-branching mechanism (e.g., Reaction 3 in Table 3.1) and the so-called 3-body recombination mechanism (e.g., Reactions 5-7, 12, 14, and 17 in Table 3.1). The minimum in the reaction zone length (i.e., predicted cell size) is a result of the difference in the effective activation energies for these two types of reaction mechanisms.

Shown in Figure 4.1 is the experimentally measured cell size versus initial mixture temperature for a 17.5 percent hydrogen-air mixture at 0.1 MPa. Also shown in Figure 4.1 is the ZND model predictions using both the maximum temperature gradient and the Mach 0.75 definitions for the reaction zone length. As the figure indicates, both ZND predictions were anchored at the experimental data point at 500K. The experimental data indicates that cell size decreases monotonically with temperature, as is predicted by the ZND model using the dT/dx maximum definition for the reaction zone length. The experimental cell size data does not exhibit the trend with temperature predicted by the ZND model using the $M=0.75$ definition. The same trend in cell size is observed for other hydrogen-air mixtures (Ciccarelli et al., 1994b). This is an indication of the trend in cell size data versus temperature observed by Stamps et al. (1991) is an artifact of their choice for the definition of the reaction zone length. As mentioned by Stamps et al. (1991), the reaction zone length based on the Mach 0.75 definition extends into the later phase of the heat release where the three body reactions, such as Reactions 5-7 in Table 3.1, are important. Noting that there is, as yet, no justifiable reason

4. Discussion

(other than dimensional analysis) as to why cell size should correlate with the 1-dimensional ZND model reaction zone length, the present results at least indicate that the maximum temperature gradient should be used to define the reaction zone length.

4.2 Use of Cell Size Data

A primary objective of the hydrogen program is to acquire additional information to augment the present capability for assessing the likelihood for detonations to occur during a postulated severe accident in a nuclear reactor. Assuming that one can predict the progression of the accident in terms of the local hydrogen-air-steam concentrations and mixture temperature and pressure, cell size data alone cannot predict whether or not a detonation is possible. Cell size data can be used to give qualitative information to help make informed decisions on the likelihood of a gas mixture, at given initial and boundary conditions, to detonate. For example, if one compartment has a mixture with a large steam fraction compared to another, everything else being the same, one can assume that the likelihood of a detonation in the compartment with more steam is less because the corresponding cell size is larger. In order to predict quantitatively the conditions for a mixture to detonate, in the absence of reliable numerical modeling, one must use available cell size data in conjunction with correlations linking cell size with different detonation phenomenon.

Correlations relating detonation phenomenon to detonation cell size include: detonability limits ($d = \lambda/\pi$; d is the tube inner-diameter), critical tube diameter ($d = 13\lambda$), and critical initiation energy ($E \propto \lambda^3$) (Lee, 1984). If it is assumed that the cell size scaling provided by the detonation correlations apply for hydrogen-air-steam mixtures at elevated temperature, one can conclude, based on the cell size data, that the sensitivity of a mixture increases with increased initial temperature. For example, the data indicates that for a given hydrogen-air-steam mixture at 0.1 MPa, the cell size decreases with increasing initial mixture temperature. Furthermore, if we relate mixture sensitivity to critical initiation energy, mixtures with smaller cell size require smaller initiation energy. Also, since the detonability limit is characterized by cell size, a mixture with smaller detonation cell size can sustain detonations in more confined spaces. A detonation in, for example, an 8 percent hydrogen-air mixture at 650K could propagate in roughly a 30-cm diameter vessel, which is more than an order of magnitude smaller than the length scales which would exist in a typical reactor containment. However, during a typical accident scenario a large amount of steam is released into the reactor containment and it has been shown that steam dilution reduces the detonability of the mixture, especially for off-stoichiometric hydrogen-air mixtures. However, the desensitizing effect of steam dilution is diminished with increased mixture temperature. For initial mixture pressures below 0.1 MPa, pre-existing cell size data typically indicate that the cell size decreases with increasing pressure (Desbordes et al., 1993). The present data shows that for hydrogen-air-steam mixtures in the pressure range of 0.1 MPa to 0.24 MPa, typical of reactor accident conditions, cell size is relatively unaffected by mixture initial pressure. Hence, mixture sensitivity is more strongly affected by initial temperature than by initial pressure.

The above-mentioned empirical detonation phenomenon correlations imply that the detonation cell size, λ , is the sole dependent parameter describing the various detonation phenomenon. The correlations are based on experimental data obtained using various fuel-air mixtures (e.g., hydrogen-oxygen-nitrogen) at 300K which display an irregular cellular structure, as shown in Figure 1.2. It is well known that these correlations break down for mixtures displaying a regular detonation cellular structure, as found in heavily argon-diluted, hydrogen-oxygen mixtures (Shepherd et al., 1988; Desbordes et al., 1993). As a result of the investigation of detonation instability (Fickett and Davies, 1979), it has been proposed that the regularity of the detonation cellular structure decreases with the global activation energy, E_A . This is in qualitative agreement with the experimental observation that the detonation cell irregularity increases with the value of the dimensionless group, E_A/RT , where R is the universal gas constant, and T is the postshock gas temperature (Ul'yanitskii, 1981; Moen et al., 1986). This dimensionless group gives a measure of the sensitivity of the chemical

induction time to small changes in the detonation Mach number (Moen et al., 1986). Shepherd et al. (1988) demonstrated that this parameter alone cannot account for the observed cell regularity for all mixtures.

4.3 Influence of Initial Temperature on Cell Regularity

If one adopts the dimensionless group E_A/RT as the governing parameter for cell regularity (Ul'yanitskii, 1991), the influence of initial mixture temperature on the global activation energy and the postshock temperature must be investigated. To date, there has been no investigation into the effect of initial mixture temperature on cell regularity and thus on the applicability of the cell size correlations cited above. Therefore, in order to make use of the detonation cell size data reported here in conjunction with the various detonation correlations, the question of the influence of initial temperature on cell regularity must be addressed. It has been suggested that the regularity of the detonation cellular structure in hydrogen-air mixtures increases with increasing initial temperature, and thus the established correlations do not apply (Lee and Berman, 1996). This claim is based on the fact that the postshock temperature for hydrogen-air mixtures increases with increasing initial mixture temperature and thus the value of E_A/RT decreases. For example, for stoichiometric hydrogen-air, the postshock temperature is 1537K and 1770K for initial mixture temperatures of 300K and 650K, respectively.

The global activation energy for hydrogen-air mixtures at 300K and 650K was calculated using a constant-volume model approximation for the reaction zone similar to the approach taken by Shepherd (1986). The hydrogen oxidation mechanisms and rate constants are identical to those used in the ZND model (Table 3.1). The global activation energy is calculated assuming that the induction time, τ , can be described by a single-step reaction of the form

$$\tau = \frac{k}{\rho} \exp \left(\frac{E_A}{RT} \right) \quad (4.1)$$

where k is the kinetic rate factor and ρ is the postshock density (Moen et al., 1986 and Shepherd et al., 1988). Taking the global activation energy to be a constant in the above equation, one can calculate E_A knowing the induction time, τ , at two different post-shock temperatures. Rearranging Equation (4.1) yields

$$\frac{E_A}{R} = \frac{\ln(\tau^+) - \ln(\tau^-)}{\frac{1}{T^+} - \frac{1}{T^-}} \quad (4.2)$$

where the "+" and "-" terms refer to conditions calculated at $(1+\delta)Mc_j$ and $(1-\delta)Mc_j$, respectively, where δ is simply a constant which perturbs the detonation Mach number and thus the post-shock temperature. Figure 4.2 plots the calculated global activation energy as a function of hydrogen mole fraction in hydrogen-air mixtures at 300K, taking δ equal to 0.02 and 0.05. The two calculations show very similar trends, the only difference is that the peaks are slightly higher for the case where $\delta=0.05$. The activation energy for the usual rate limiting step, Reaction 3 in Table 3.1, is 16.5 kcal/mole, and the calculations indicate that near stoichiometric conditions the global activation energy is about 25 kcal/mole. The higher global activation energy is due to the competition for H atoms by the 3-body Reactions 5-7 from Table 3.1 (Westbrook and Urtiew, 1982 and Shepherd, 1986). The global activation energy increases with decreasing hydrogen fraction and is between 50 and 60 kcal/mole for the weak mixture which is consistent with the 3-body reconfiguration reaction 17 ($E=45.5$ kcal/mole) being the rate limiting step. The global activation energy as

4. Discussion

a function of hydrogen mole fraction for hydrogen-air mixtures at 650K is shown in Figure 4.3, again taking δ equal to 0.02 and 0.05. At 650K, the activation energies calculated using the two different values for δ are almost indistinguishable. Comparing Figures 4.1 and 4.2, one can see that the activation energy for mixtures at 650K is consistently above that at 300K. At 650K, the activation energy is independent of the hydrogen mole fraction over a very wide range (i.e., between 8 percent and 70 percent hydrogen) and rises very sharply between 7 and 10 percent hydrogen.

Using the global activation energies from Figures 4.2 and 4.3, for $\delta = 0.02$, the dimensionless parameter E_A/RT was determined as a function of hydrogen mole fraction, see Figure 4.4. Note these curves resemble the ZND reaction zone length predictions since the reaction zone length is given by $\Delta = u\tau$, where u is the relative postshock particle velocity, which is a fairly insensitive parameter, and τ is a function of E_A/RT via Equation (4.1). Based on the results in Figure 4.4, if we consider cell regularity to be linked with the dimensionless parameter E_A/RT , as described above, one would expect that the cellular structure would be more regular at 650K compared to 300K, especially for the leaner mixtures. Furthermore, the fact that the activation energy is very insensitive to δ at 650K means that the reaction (or induction) time is insensitive to fluctuations in the shock Mach number. This is characteristic of stable mixtures, which have been found to display a more regular cellular structure.

Theoretically, one should be able to determine whether cell regularity is influenced by initial mixture temperature by simply inspecting the cellular structure recorded at various temperatures. Unfortunately, this approach only works when comparing irregular and very regular cellular structures as in Figure 1.2. However, for the present situation where only minor differences are expected, one must use a more rigorous approach. As mentioned earlier in this report, a detailed analysis of the cell size variation was performed on a selection of foils obtained from the SSDA. The cellular pattern was manually traced onto a Mylar sheet and the distance between adjacent parallel lines (i.e., cell size) was recorded. The average and standard deviation of the cell size data was obtained using standard PC software. The ratio of the standard deviation and the average cell size, sdv/ave , can be used as an indicator of the regularity of the cell pattern from the foil. The higher the ratio, the more irregular the pattern. Figure 4.5 plots the value of sdv/ave from the cell size data as a function of hydrogen mole fraction, for hydrogen-air mixtures at 300K and 650K, and steam dilution for stoichiometric hydrogen-air and steam mixtures at 650K. The bulk of the data is bounded by sdv/ave values of 0.2 and 0.3 with an average value of 0.25. Based on the results in Figure 4.5, there appears to be no clear correlation between cell regularity (i.e., sdv/ave) and mixture composition, initial temperature or steam dilution.

Since only the dominant diagonal lines are selected from the cellular pattern the person tracing the lines, in effect, preprocesses the data available on the foil. This preprocessing of the data can be very subjective, and important data pertinent to the assessment of cell regularity could have been filtered. As a result, one cannot treat the findings from Figure 4.5 as conclusive. A more scientific, unbiased, approach for measuring cell size distribution is required before one can come to some conclusion concerning cell regularity. Such an investigation was undertaken by Shepherd and Tieszen (1986) where the actual foil imprint was digitized and analyzed using a 2-dimensional Fourier Transform technique to extract pertinent statistical data on the cell size distribution. This approach is much less subjective than that taken here; however, even in the more automated approach, some manipulation (i.e., filtering, enhancing, etc.) of the digitized image was required to bring out the triple-point tracks. We believe a more definitive test of the effect of elevated initial temperature on the regularity of the cellular structure would be to measure the critical tube or critical initiation energy at high temperatures and compare the results to the well-established correlations for irregular mixtures (e.g., $d_c = 13\lambda$).

The calculations presented above suggest that as the temperature of hydrogen-air mixtures increases, the cellular pattern should become more regular. If these predictions were demonstrated experimentally to be valid, then the implication would be that the detonation correlations are not applicable to hydrogen-air systems at high temperature. Other means

4. Discussion

of correlation would have to be sought. As of this time, the available data for the effect of temperature on the regularity of hydrogen-air mixtures are inconclusive and as a result, it cannot be determined whether or not the regularity of these mixtures either increases or decreases with temperature. The applicability of the correlations to high-temperature mixtures of hydrogen and air is uncertain. As mentioned above, critical tube or critical initiation energy experiments would provide data to help resolve the uncertainty. We consider these tests to be crucial because of the present reliance on existing correlations for extrapolating results from experiments.

Figure 4.1: Comparison of the ZND model predicted cell size ($\lambda = A\Delta$) using the maximum temperature gradient and the Mach Number 0.75 definitions for the reaction zone length

Figure 4.2: Calculated global activation energy for hydrogen-air mixtures at 300K and 0.1 MPa

Figure 4.3: Calculated global activation energy for hydrogen-air mixtures at 650K and 0.1 MPa

Figure 4.4: Comparison of dimensionless term (E/RT_{vn}) for hydrogen-air mixtures at 300K and 650K at 0.1 MPa

Figure 4.5: Comparison of the ratio of cell size data standard deviation and average for hydrogen-air and steam mixtures at 300K and 650K and at 0.1 MPa

5. SUMMARY AND CONCLUSIONS

The SSDA and HTCF have been built at BNL to investigate high-speed, high-temperature hydrogen combustion phenomenon. Both vessels have been successfully implemented, and this report presents cell size data obtained from both the SSDA (Cicarelli et al., 1994) and the HTCF.

In previous studies, high explosives were commonly used as the initiation source for experiments studying various detonation phenomena. One of the unique features of both the SSDA and the HTCF is in the use of a "diaphragmless" driver to initiate the detonation in the test gas. After some initial shakedown in both test chambers, the gas driver has proven to be a very reliable and flexible component. In order to minimize driver effects on the detonation in the test gas, the amount of driver gas used in the HTCF was constrained to about 1 percent of the total vessel volume (i.e., driver partial pressure of 0.25 psia). It has been shown that the yield of the gas driver is equivalent to 19 grams of high explosives and that as a result of the short driver, detonation overdrive in the test gas was very localized.

The experimentally measured detonation velocities were all within a few percent of the theoretical CJ detonation velocity, including the 650K data wherein the SSDA the velocity was consistently about 5 percent below the CJ detonation velocity. This difference could be attributed to the much slower rate of pre-ignition hydrogen oxidation in the HTCF compared to the SSDA. The velocities in the HTCF were constant, typically within ± 1 percent, over the last half of the vessel. This is a good indication of stable detonation waves.

It is generally acknowledged that the size of the detonation cell of a mixture is inversely proportional to the sensitivity of that mixture to undergo detonation. For example, the smaller the cell size, the more sensitive the mixture. Detonation cell size was measured in the HTCF using the smoked foil technique. The following observations have been made, using data from the HTCF, on the influence of various mixture parameters on the measured cell size.

Cell size measurements from the HTCF have shown that for any hydrogen-air-steam mixture increasing the initial mixture temperature, in the range of 300K to 650K, while maintaining the initial pressure of 0.1 MPa decreases the cell size and thus makes the mixture more sensitive. This does not support the predictions by Stamps and Tieszen (1991) that with increasing initial temperature, the cell size initially decreases to a minimum and then increases. Associated with the observed decrease in the cell size with increasing initial mixture temperature is the apparent widening of the detonability range.

In the HTCF, the effect of steam dilution on cell size was tested in stoichiometric and off-stoichiometric (e.g., equivalence ratio of 0.5) hydrogen-air mixtures. Increasing the steam concentration (or partial pressure) in hydrogen-air mixtures at 0.1 MPa initial pressure increases the cell size and thus decreases the mixture sensitivity, irrespective of initial temperature. It was also observed that the desensitizing effect of steam on hydrogen-air detonability diminished with increased initial temperature. The maximum steam dilution resulting in a detonation was 50 percent steam in a stoichiometric hydrogen-air mixture at 650K and 0.1 MPa.

A limited number of experiments were carried out to investigate the influence of initial mixture pressure on detonation cell size. There was very little effect observed in the pressure range tested, 0.1 MPa to 0.24 MPa, for relatively weak hydrogen-air-steam mixtures. The minimal sensitivity to pressure is also predicted by the ZND model.

Detailed cell measurements from a limited number of SSDA foils and a qualitative evaluation of HTCF data were used to investigate the effect of temperature on detonation cell regularity. The measurements revealed that the deviation in the reported average cell size was about ± 25 percent of the average value. These measurements revealed no correlation between the standard deviation in the cell data and the initial mixture temperature as would be expected if the cell regularity would increase. It is believed that measuring critical tube diameter at elevated temperature will provide valued information on this issue of the effect of initial temperature on cell regularity.

5. Summary and Conclusions

A 1-dimensional steady-state ZND model, with full chemical kinetics, has been used to predict cell size for hydrogen-air-steam mixtures at different initial conditions. The cell size is taken to be proportional to the calculated ZND reaction zone length ($\lambda = A\Delta$). Taking A to be a constant, the ZND model did a relatively good job at predicting the overall trends in the cell size data as a function of mixture composition and initial conditions. However, a comprehensive comparison of the theoretical predictions with the experimentally measured cell size have demonstrated that the two are not linked by a simple constant of proportionality, A . Shepherd (1986) first demonstrated, and corroborated in this study, that the proportionality constant is a function of the mixture equivalence ratio, ϕ , such that $\lambda = A(\phi)\Delta$. In this investigation, it has also been shown that A is also a function of the initial mixture temperature, such that $\lambda = A(\phi, T_0)\Delta$.

Due to the large disparity in the scale of a typical experimental apparatus and a nuclear reactor containment, experimental detonation cell size data cannot be used directly in the analysis of severe accidents. The ZND model provides a vehicle to extrapolate detonation cell size data to a more prototypic scale. However, as pointed out above and previously by Shepherd (1986), the proportionality constant between the measured detonation cell size and the calculated ZND reaction zone length is not a universal constant. In this report, the value of the proportionality constant was chosen by anchoring the ZND model predictions to the measured cell size for the most sensitive hydrogen-air mixture. During a postulated severe accident, the hydrogen mixtures of interest may not be as sensitive as those used in the study. Thus, for a severe accident analysis, one must choose a value for the constant which results in the best fit to the experimental cell size data in the hydrogen concentration range of interest.

The data obtained in this investigation enhances the existing detonation cell size data base by including the added parameters of mixture temperatures and steam dilution. This extended data base allows one to make a more confident choice of the proportionality constant to be used in conjunction with the ZND model for accident scenarios characterized by hydrogen-air-steam mixtures at elevated temperatures.

The data obtained from this investigation adds significantly to the existing data base on detonation cell size, thereby increasing our knowledge base on the effects of initial temperature, steam dilution, hydrogen concentration, and initial pressure. In particular, based on the detonation cell size data measured from the experiments in the HTCF and based on the range of parameters tested, the following conclusions were reached concerning the sensitivity of mixtures to undergo detonation:

1. Increase in the initial temperature of a hydrogen-air-steam mixture increases the mixture detonation sensitivity.
2. Increase in the steam dilution, at any initial temperature, results in a decrease in the mixture detonation sensitivity.
3. Increase in the hydrogen concentration up to stoichiometric conditions, at any initial temperature, increases the mixture detonation sensitivity.
4. For the limited initial pressure range tested in the HTCF, an increase in the initial pressure moderately increases the mixture detonation sensitivity.

To determine the likelihood of detonation, the HTCF detonation cell size data have direct applicability to containment local volumes with mixture compositions and initial conditions similar to those tested. For mixture compositions and initial conditions not tested in the HTCF, the likelihood of detonation initiation can be addressed using the HTCF data in conjunction with existing theoretical models.

6. REFERENCES

- Baker, W. E. et al., Explosion Hazards and Evaluation, Elsevier Scientific Publishing Co., New York, 1983.
- Ciccarelli, G. et al., "High-Temperature Hydrogen-Air-Steam Detonation Experiments in the BNL SSDA," NUREG/CR-6213, BNL-NUREG-52414, 1994.
- Ciccarelli, G. et al., "Detonation Cell Size Measurements and Predictions in Hydrogen-Air-Steam Mixtures at Elevated Temperatures," *Combustion and Flame*, 99, pp. 212-220, 1994b.
- Denisov, Yu. H. and Ya. K. Troshin, *Phys. Chem. Sect.*, Vol. 125, p. 217, 1960.
- Desbordes, D. et al., "Failure of Classical Dynamic Parameters Relationships in Highly Regular Cellular Detonation Systems," Progress in Astronautics and Aeronautics, 153, Dynamics of Explosions, J. R. Bowen et al., 1993.
- DeSoete, G. G., "The Flammability of Hydrogen-Oxygen-Nitrogen Mixtures at High Temperature," presented at the Italian Flame Days, Sanremo, Italy, April 10-11, 1975.
- Dupre, G., R. Knystautas, J. Lee, *Prog. In Astro. and Aero.*, Vol. 106, p. 244, 1985.
- Fujiwara, T., and K. V. Reddy, "Propagation Mechanism of Detonation - Three-Dimensional Phenomenon," *Memoirs of the Faculty of Engineering, Nagoya University*, Vol. 41, No. 1, 1989.
- Ginsberg, T., J. Boccio, and C. Economos, "Conceptual Design Specification of the BNL High-Temperature, High-Speed Combustion Research Program," BNL Technical Report L-1924, January 1992.
- Henrie, J. O and A. K. Postma, "Analysis of the Three Mile Island (TMI-2) Hydrogen Burn," 2nd International Topical Meeting on Nuclear Reactor Thermal-Hydraulics, Santa Barbara, CA, January 1983. Published as *Thermal Hydraulics of Nuclear Reactors*, Vol. 2, ANS Order No. 700081, 1983.
- Knystantas, R. et al., "Measurement of Cell Size in Hydrocarbon-Air Mixtures and Predictions of Critical Tube Diameter, Critical Initiation Energy, and Detonability Limits," Progress in Astronautics and Aeronautics, 94, 1984.
- Lee, J. H. S. and M. Berman, "Hydrogen Combustion and its Application to Nuclear Reactor Safety," Advances in Heat Transfer in Nuclear Reactor Safety, Vol. 29, Academic Press, Inc., G. A. Greene, Editor, January 1997.
- Lee, J. H.S., "Initiation of Gaseous Detonations," *Annual Review Phys. Chem.*, Vol. 28, pp. 75-104, 1977.
- Lee, J. H. S., "Dynamic Parameters of Gaseous Detonations," *Ann. Rev. Fluid Mech.*, 311-336, 1984.
- Miller, J. A. et al., "Towards a Comprehensive Chemical Kinetic Mechanism for the Oxidation of Acetylene," 19th International Symposium on Combustion, pp. 181-195, 1982.
- Mitrofanov, V. V. and R. I. Solouhkin, *Soviet Phys. Dokl.*, Vol. 9, p. 1055, 1965.
- Moen, I. O. et al., "Influence of Cellular Regularity on the Behavior of Gaseous Detonations," Progress in Astronautics and Aeronautics, 106, Dynamics of Explosion, pp. 220-243, 1986.

6. References

- Moen, I. O., S. B. Murray, D. Bjerketvedt, A. Rinnan, R. Knystautas, J. Lee, "Diffraction of Detonation From tubes into a Large Fuel-Air Explosive Cloud," 19th International Symposium on Combustion, p. 635, 1982.
- Oran, E. S. et al., "Numerical Simulation of Detonations in Hydrogen-Air and Methane-Air Mixtures," 18th International Symposium on Combustion, pp. 1641-1649, 1981.
- Reynolds, W. C., "The Element Potential Method for Chemical Equilibrium Analysis: Implementation in the Interactive Program STANJAN Version 3," Dept. Of Mechanical Engineering, Stanford University, Palo Alto, California, January 1986.
- Shchelkin, K. I. and Y. K. Troshin, Gas Dynamics of Detonations, Mono Book Corp., Baltimore, Maryland, 1965.
- Shepherd, J. E., I. O. Moen, S. B. Murray, and P. A. Thibault, "Analyses of the Cellular Structure of Detonations," Twenty-first Symposium (International) on Combustion, The Combustion Institute, 1988.
- Shepherd, J. E., "Chemical Kinetics of Hydrogen-Air-Diluent Detonations," Progress in Astronautics and Aeronautics, 106, Dynamics of Explosions, J. R. Bowen, et al., eds., 1986.
- Shepherd, J. E. and S. R. Tieszen, "Detonation Cellular Structure and Image Processing," Sandia National Laboratory Report SAND86-0033, 1986.
- Stamps, D. W. and S. R. Tieszen, "The Influence of Initial Pressure and Temperature on Hydrogen-Air-Diluent Detonations," Combustion and Flame, Vol. 83, pp. 353-364, 1991.
- Strehlow, R. A., "The Nature of Transverse Waves in Detonations," Acta Astronautica, Vol. 14, pp. 539-548, 1969.
- Thibault, P. A. et al., "Blast Waves Generated by Planar Waves," Proc. Of the 16th International Symposium on Shock Tubes and Waves, Aachen, West Germany, July 26-31, 1987.
- Tieszen, S. R., P. S. Martin, W. B. Bennedick, and M. Berman, "Detonability in Hydrogen-Air-Diluent Mixtures," NUREG/CR-4905, SAND85-1263, 1987.
- Toth, L. M., et al., Ed., "The Three-Mile Island Accident, Diagnosis and Prognosis," American Chemical Society Symposium Series, No. 293, 1985.
- Ul'yanitskii, V. Y., "Role of Flashing and Transverse-Wave Collisions in the Evolution of a Multifrontal Detonation-Wave Structure in Gases," Fiz. Goreniya Vzrya, Vol. 17, pp. 127-133, 1981.
- Westbrook, C. K. and P. A. Urtiev, "Chemical Kinetics Prediction of Critical Parameters in Gaseous Detonations," 19th Symposium on Combustion, 615-623, 1982.
- Yang, J. W., "High-Temperature Combustion in LWR Containments Under Severe Accident Conditions," Brookhaven National Laboratory, Technical Report L-1924 1/17/92, January 1992.

APPENDIX A

TABULATED DATA FROM HTCF

The following tables provide a summary of all the experiments performed in this test series. The data are grouped in terms of tests performed at common initial temperatures with, and without steam dilution. In all cases, the quoted initial temperature has an uncertainty of $\pm 14\text{K}$ which corresponds to the measured temperature uniformity from thermal calibration tests performed on the vessel. The hydrogen concentration, reported on a dry basis, is obtained from gas samples taken from the vessel prior to ignition and analyzed using a gas chromatograph. For each test, three gas samples were taken from the vessel covering the entire length of the vessel. For each sample bottle, typically three samples were run through the gas chromatograph. Shown in the table is the average and the standard deviation of these samples. The steam dilution reported is a nominal value obtained from the set venturi constituent flow rates, no direct measurement of the steam dilution was made. The partial pressure of the acetylene-oxygen driver gas used in each test is provided. Also given is the average detonation velocity measured in roughly the second half of the vessel, along with the standard deviation in the velocity measurements. The last column gives the average cell size measured from smoked foils. In those tests where a detonation with a double head spin (DH), or a single head spin (SH) was observed, no cell size is given.

TEST SERIES #1: Hydrogen-Air mixtures at 300K

Test#	Hydrogen Mole Fraction (%)		Driver Partial Pressure, psi (kPa)	Detonation Velocity (m/s)		Cell Size (cm)
	Average	Std. Deviation		Average	Std. Deviation	
23	51.36	0.12	0.7 (4.8)	2174	14	1.8
18	29.67	0.10	0.7 (4.8)	1976	5	0.8
21	24.11	0.15	0.7 (4.8)	1839	6	1.1
19	19.91	0.12	0.7 (4.8)	1700	9	2.7
22	17.29	0.23	0.7 (4.8)	1602	11	9.3
297	14.93	0.08	0.25 (1.7)	1498	25	18.7
298	14.89	0.10	0.5 (3.4)	1496	33	24.8
25	14.31	0.05	1.1 (7.5)	1429	47	DH
232	13.83	0.09	0.25 (1.7)	1449	25	DH
233	13.48	0.06	0.25 (1.7)	1423	21	DH

TEST SERIES #2: Hydrogen-Air at 500K

Test#	Hydrogen Mole Fraction (%)		Driver Partial Pressure, psi (kPa)	Detonation Velocity (m/s)		Cell Size (cm)
	Average	Std. Deviation		Average	Std. Deviation	
107	29.58	0.12	1.0 (6.8)	1935	9	0.6
108	14.61	0.13	1.1 (7.5)	1509	18	5.2
104	12.50	0.10	1.0 (6.8)	1413	14	9.8
109	11.16	0.06	1.1 (7.5)	1374	19	19.6
329	10.87	0.03	0.25 (1.7)	1344	19	42.9
110	9.90	0.18	1.15 (7.8)	1301	22	DH

TEST SERIES #3: Hydrogen-Air mixtures at 650K

Test#	Hydrogen Mole Fraction (%)		Driver Partial Pressure, psi (kPa)	Detonation Velocity (m/s)		Cell Size (cm)
	Average	Std. Deviation		Average	Std. Deviation	
119	14.28	0.22	1.3 (8.8)	1527	19	1.7
122	11.42	0.15	1.25 (8.5)	1415	19	3.0
249	9.58	0.02	0.2 (1.4)	1307	12	4.6
318	8.83	0.06	0.5 (3.4)	1280	14	7.4
254	8.77	0.02	0.3 (2.0)	1268	12	9.4
255	7.83	0.07	0.25 (1.7)	1214	23	21.3
256	7.51	0.07	0.2 (1.4)	1206	16	23.0
317	7.39	0.09	0.5 (3.4)	1214	26	SH
327	7.02	0.07	0.25 (1.7)	1172	31	DH
302	6.24	0.09	0.25 (1.7)	1143	32	SH

TEST SERIES #4: Hydrogen-Air-Steam mixtures

Test #	Dry Hydrogen (%)		Steam (%)	Temperature (K)	Driver psi (kPa)	Detonation Velocity (m/s)		Cell Size (cm)
	Average	Std. Deviation				Average	Std. Deviation	
300	29.46	0.03	30	650	0.2 (1.4)	1737	8	7.5
316	28.64	0.05	35	650	0.35 (2.4)	1708	8	17.5
301	29.43	0.05	40	650	0.2 (1.4)	1661	26	50.3
308	29.37	0.13	50	650	0.3 (2.0)	1578	22	SH (PT)
377	30.30	0.10	30	500	0.25 (1.7)	1761	13	28.6
382	30.23	0.12	25	400	0.25 (1.7)	1801	18	21.4
325	29.88	0.20	25	400	0.4 (2.7)	1828	10	16.2
388	30.00	--	40	400	0.25 (1.7)	Failed	--	--
328	17.55	0.06	10	650	0.3 (2.0)	1574	43	3.3
314	17.63	0.03	20	650	0.3 (2.0)	1532	6	9.1
315	18.06	0.05	25	650	0.25 (1.7)	1508	15	27.5
310	17.26	0.08	30	650	0.25 (1.7)	1457	44	DH (PT)
311	17.25	0.12	35	650	0.25 (1.7)	Failed	---	--
326	17.81	0.08	10	400	0.25 (1.7)	1572	16	30.5
385	18.21	--	20	400	0.25 (1.7)	1480	53	SH (PT)
381	18.00	--	25	400	0.25 (1.7)	Failed	--	--
392	9.85	0.08	7.5	650	0.35 (2.4)	1281	17	42.9
389	9.86	0.06	15	650	0.25 (1.7)	1260	46	SH (PT)

TEST SERIES #5: Hydrogen-Air-Steam at 650K and elevated pressure

Test#	Dry Hydrogen (%)		Steam (%)	Vessel Press. (kPa)	Driver Press. psi (kPa)	Detonation Velocity (m/s)		Cell Size (cm)
	Average	Std. Deviation				Average	Std. Deviation	
374	17.91	0.03	20	150	0.15 (1.0)	1526	8	10.3
370	17.78	0.09	20	200	0.25 (1.7)	1526	9	10.7
376	30.13	0.04	30	150	0.25 (1.7)	1766	6	4.5
375	30.22	0.05	30	200	0.25 (1.7)	1772	4	3.7
373	9.27	0.10	0	170	0.2 (1.4)	1289	5	0.2
358	9.30	0.05	0	240	0.5 (3.4)	1290	15	8.5

APPENDIX B

TABULATED CELL SIZE DATA FROM SSDA

The complete set of cell size data from the SSDA is given in Ciccarelli et al. (1994). a more detailed analysis of some of these smoked foils obtained from the SSDA was performed in order to obtain data on the uniformity of the cell size data. This was done by taking numerous cell size measurements per foil, for several foils, and calculating the average and the standard deviation (sdv) from these measurements. The results from this analysis are given in the following table.

Temperature (K)	Dry hydrogen (%)	Steam dilution (%)	Cell size (cm)	
			Average	Sdv
300	17.5	0	8.89	1.66
300	20	0	3.95	1.15
300	30	0	0.90	0.18
300	40	0	0.90	0.21
300	50	0	2.60	0.60
650	12	0	3.30	0.94
650	15	0	1.79	0.52
650	17.5	0	1.92	0.48
650	30	0	0.40	0.10
650	50	0	1.11	0.24
650	30	10	0.83	0.22
650	30	20	2.29	0.72
650	30	25	2.59	0.67
650	30	30	5.72	1.52

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11. ABSTRACT (200 words or less) <p>The High-Temperature Combustion Facility (HTCF) was designed and constructed with the objective of studying detonation phenomena in mixtures of hydrogen-air-steam at initially high temperatures. The central element of the HTCF is a 27-cm inner diameter and 21.3-m long cylindrical test vessel capable of being heated to $700K \pm 14K$. A unique feature of the HTCF is the "diaphragmless" acetylene-oxygen gas driver which is used to initiate the detonation in the test gas. Cell size measurements in hydrogen-air-steam mixtures have shown that increasing the initial mixture temperature, in the range of 300K to 650K, while maintaining the initial pressure of 0.1 MPa decreases the cell size and thus makes the mixture more detonable. Increasing the steam dilution increases the cell size, irrespective of initial temperature. It is also observed that the desensitizing effect of steam diminished with increased initial temperature. A one-dimensional, steady-state Zel'dovich, von Neumann, Doring model, with full chemical kinetics, has been used to predict cell size for hydrogen-air-steam mixtures at different initial conditions.</p>									
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